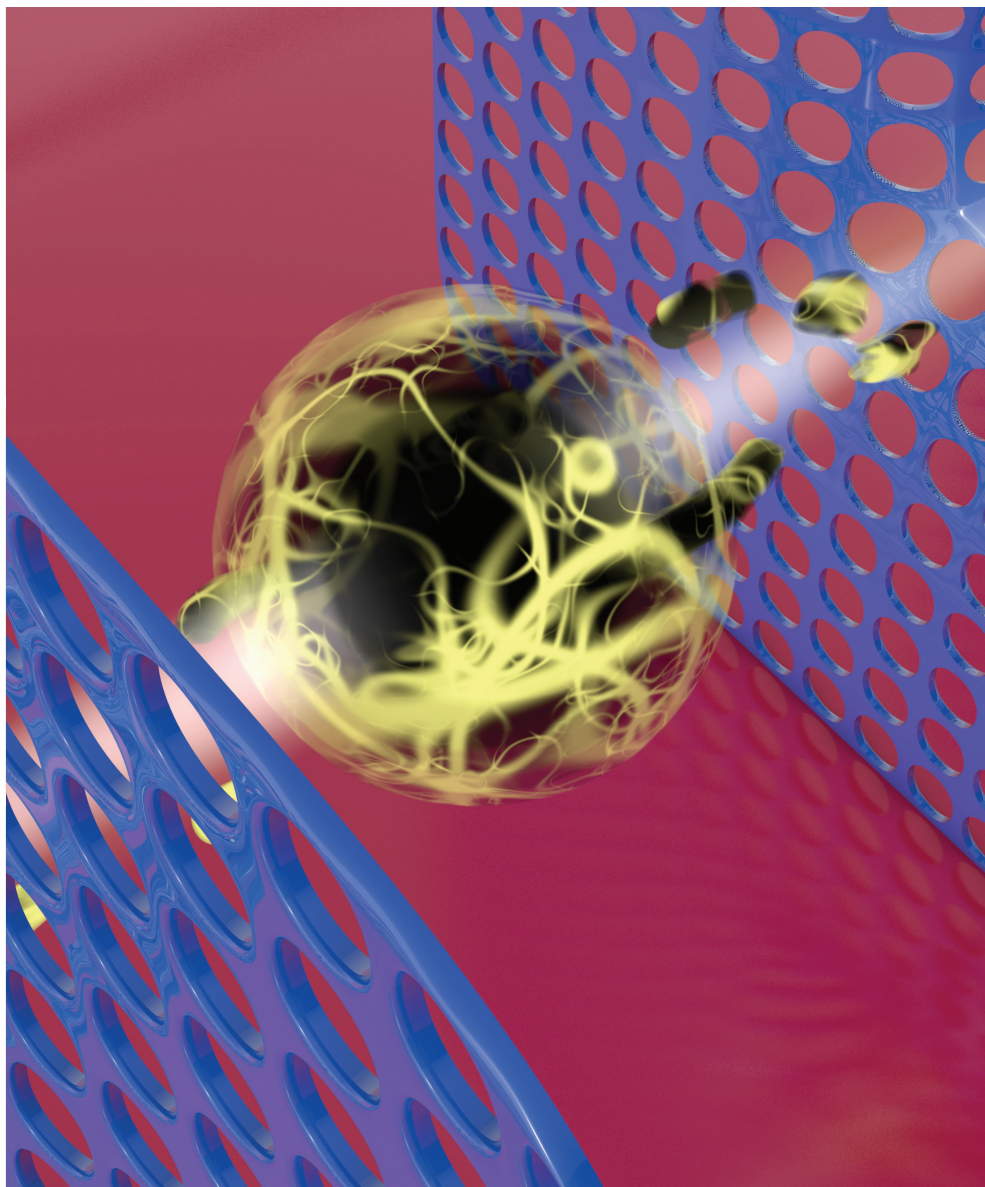
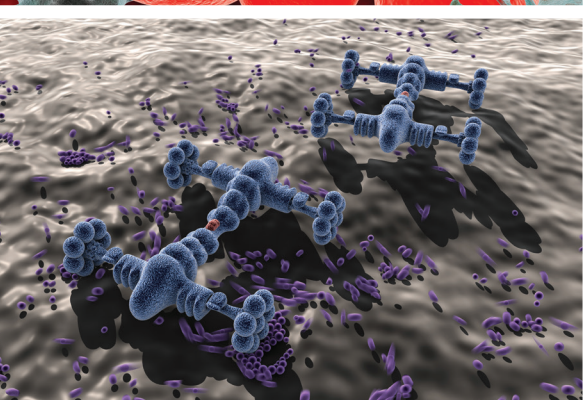
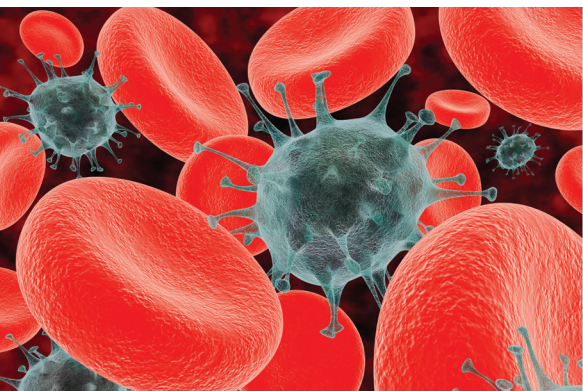


CRC Concise Encyclopedia of NANOTECHNOLOGY



Edited by

Boris Ildusovich Kharisov • Oxana Vasilievna Kharissova • Ubaldo Ortiz-Mendez



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Ubaldo Ortiz-Mendez



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To my grandfather Arsenii P. Chekalov and my grandmother Anna A. Chekalova

Boris Ildusovich Kharisov

To my mother Olga V. Chubur

Oxana Vasilievna Kharissova

To my wife, my daughters, and my son

Ubaldo Ortiz-Méndez

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Preface

This encyclopedia has been written by leading professionals in the field worldwide. The chapters are arranged alphabetically to simplify its use by readers. We expect that our book will be useful not only for specialists (professors, researchers, engineers), but also for undergraduate and graduate students. On the whole, the target audiences are as follows: students, scientists, college and university professors, research professionals, technology investors and developers, research enterprises, R&D and defense research laboratories, and academic and research libraries. These very broad spectra of specialists work in the fields of nanotechnology and nanoscience and have strong connections with materials science, electrical and electronic engineering, solid-state physics, surface science, catalysis, “greener” chemical processes, colloid science, ceramic and chemical engineering, coatings and adsorbents, drug delivery, polymer science and engineering, sol-gel science, supramolecular science, nanomedicine, metallurgy and powder technology, device and chip engineering, aerospace engineering, computer technology, information technology, environmental engineering, biomimetics, pharmacy, biotechnology, water splitting and remediation, etc.

Students can easily find any data on classic nanotechnology in this book and use them in classroom presentations. Professionals can use the book as a background for their research work, presentation in congresses, and lectures for graduate and postgraduate students in most universities worldwide. The book contains a host of illustrative material in black and white, and the accompanying e-book contains all of the figures/images in full color. You can access the e-book using the code provided on the inside cover of this book.

Placing specialists at the forefront of the nanoscience revolution, this book identifies current challenges and development paths sure to influence fields examining the design, application, and utilization of devices, techniques, and technologies critical to research at the atomic, molecular, and macromolecular levels ranging from 1 to 100 nm. We hope that this encyclopedia will be an invaluable reference source for the libraries of universities and industrial institutions, of government and independent institutes, and for individual research groups and scientists working in the fields of nanoscience and nanotechnology.

The editors are very grateful to the contributors for their hard work and patience.

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Antimicrobial Activity: Antibacterial Properties of Silver Nanomaterials

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HISTORY

Silver nanoparticles (Ag-NPs) have been used as powerful and wide-spectrum antimicrobial agents in the last decades. Their applications include wound dressings, coatings for medical devices, textiles for clothing, food storage containers, cosmetics, and refrigerator surfaces.

However, the biocidal properties of this metal have been known since the times of the Egyptians, Greeks, Romans, and Phoenicians. They used silver vessels to store water, but were unaware that the cause of disease was due to the presence of bacteria, viruses, and fungi and knew nothing of the effect that this metal had on these unknown microorganisms.¹

The story goes that the Persian kings drank boiled water from silver agons to prevent sickness, and they knew that it could be stored in them for years. This property was vital to keep fresh drinking water during military conflicts.

Aristotle suggested to Alexander the Great (335 BC) the transport of fresh water in silver containers during many campaigns, and the Macedonians indicated the use of silver plates to prevent infections in wounds (perhaps the first attempt to use this metal for medical applications).²

Hippocrates (460–370 BC), the Father of Medicine, prescribed the use of silver preparations to treat ulcers and to promote wound healing, and he even taught that the *flowers of silver alone, in the finest powder* would heal wound ulcerations.

The Romans used silver nitrate (AgNO₃) therapeutically. In 69 BC, it was described in the contemporary Roman pharmacopeia. Pliny the Elder, in his survey of world knowledge, Natural History (78 AD), states in his book that the slag of silver *...has healing properties as an ingredient in plasters, being extremely effective in causing wounds to close up...*

Paracelsus (1493–1541 AD), the alchemist, described among the virtues of silver its power as a healing substance. And the antibacterial qualities of silver were soon recognized when bacteria or microorganisms were discovered by Anton van Leeuwenhoek in 1674 and were recognized as disease-producing agents.

Another seminal contribution was made by Carl S. F. Crede, a German obstetrician, who introduced in 1884 the application of AgNO₃ solution diluted to 1% in the eyes of newborn children to prevent gonorrheal infection, and it became a standard practice in obstetrics.³

In 1899, Albert Barnes and Hermann Hille in Philadelphia invented Argyrol (a silver antimicrobial protein solution that avoids caustic effects in human tissues) as a local antiseptic, especially to prevent eye infections in newborn infants and to fight gonorrhea. This product was the basis for Barnes' personal fortune that he used to amass a notable French impressionist art collection.

Also early in the twentieth century, the surgeon William S. Halstead introduced the use of silver foil for wound dressings, which continued to be used until just after World War II, when antibiotics largely replaced silver in bacterial infection treatment. However, after the intensive use of antibiotics, many bacteria have developed resistance to them. This has led to a resurgence in the use of silver in antibacterial applications because all pathogenic organisms have failed to develop an immunity to this metal; thus, Ag is being used as a wide-spectrum antiseptic in several commercial areas.⁴

So in the face of increasing bacterial resistance against current antibiotics, and with the steady development of nanoscale science, research on silver has regained interest in the last decade.⁵

ANTIMICROBIAL MECHANISM

Although silver has been used as a biocide for hundreds of years and there is an extensive literature on it, the mechanism of the antimicrobial action of silver has not been fully elucidated.

However, a variety of processes may be involved in the activity of silver against microorganisms. Some of the commonly accepted mechanisms include silver–amino acid interaction^{6–9} (this may disturb many biological processes due to the affinity of the silver cation with sulfur, nitrogen, and oxygen), silver–DNA interaction,^{7,10,11} generation of reactive oxidative species (ROS),^{12–15} and direct cell membrane damage.^{7,16–19} Therefore, as there are various possibilities for silver to act in different biological processes, an overall statement about the origin of the toxic action of silver is not possible. In general, cells readily take up nanoparticles (mainly smaller than 20 nm).^{20–22} Eukaryotic, nonphagocytizing cells take up Ag-NPs by endocytosis and macropinocytosis,^{23,24} and electronic microscopy allows Ag-NPs to be visualized directly inside cells.²⁴

Nonetheless, Ag-NPs, metallic silver, salts, or even silver complexes release Ag(I) ions when they come in contact with water. These silver ions are the biologically active agents,^{25,26} but they can react with anions in the medium, such as chloride, sulfate, phosphate, among others, and precipitate. Silver ions also undergo complexation with proteins and other biomolecules in actual media like blood, cell cultures, or impure water with salts.²⁷

Recently, a study of the action of Ag-NPs against the bacterium *Escherichia coli* showed the specific effect of ion release on the bactericidal effect. Ag-NPs (5–11 nm) were tested under anaerobic conditions without presenting any biological effect (up to 200 mg/L), showing that the toxicity is clearly related to the amount of released silver ions and considered Ag-NPs as a silver ion reservoir or as a modern “Trojan horse.”^{28–30}

Using transmission electronic microscopy, silver ions have been shown to have direct influence on morphological changes of the cell wall, resulting in the detachment of

the plasma membrane and bacterial lysis.⁷ This effect also depends on the nature of the cell wall, showing a greater effect in the presence of Gram-negative (much thinner peptidoglycan membrane) than of Gram-positive strains. Similarly, Ag-NPs attach to the plasma membrane, changing its permeability, penetrate inside the cell (see Figure 1), unbalance the adenosine triphosphate pool and the proton motive force, and finally destroy the bacteria.^{16,17}

Another proposed mechanism for the penetration of Ag-NPs through the bacterial cell wall is the formation of pits. This would occur by interaction with peptidoglycan N-acetylglucosamine and N-acetylmuramic acid through the destruction of the β -1 $\rightarrow$ 4 glycosidic bonds.³¹ However, these different observations might be controlled by the bacterial strain, Ag-NPs concentration, functionalization, surface charge, size, shape, etc.

Another mechanism was proposed by several authors, who suggested the interaction of the released silver ions with the mitochondria of eukaryotic cells.^{32,33} With the possibility to penetrate inside the cells, silver species can interact with DNA and enzymes. In the case of DNA, it interacts with silver ions with a preference for guanine and adenine as binding sites,¹¹ producing a condensed product^{7,10} and thereby losing its ability to replicate (Figure 2).

At the same time and inside the cell, silver compounds interact with a number of enzymes by binding to amino acids and forming silver complexes, for instance, silver binding to the thiol groups of cysteine, and this affinity may be essential in the inactivation of the enzyme,^{8,9,34} even leading to replacement of the native metal ion in the active site of the metalloenzymes.³⁵

Other studies found inhibition of cell respiration by decreasing the respiratory chain dehydrogenase in the presence of Ag-NPs and by affecting the expression of some enzymes of *Staphylococcus aureus* and *E. coli*.^{10,33,36} Furthermore, interference of mitochondrial respiration has been observed by reduction in dehydrogenase activity in the presence of Ag-NPs.³³

One of the best-known examples of the interaction of Ag(I) with thiol groups (R-SH) in enzymes is reduced

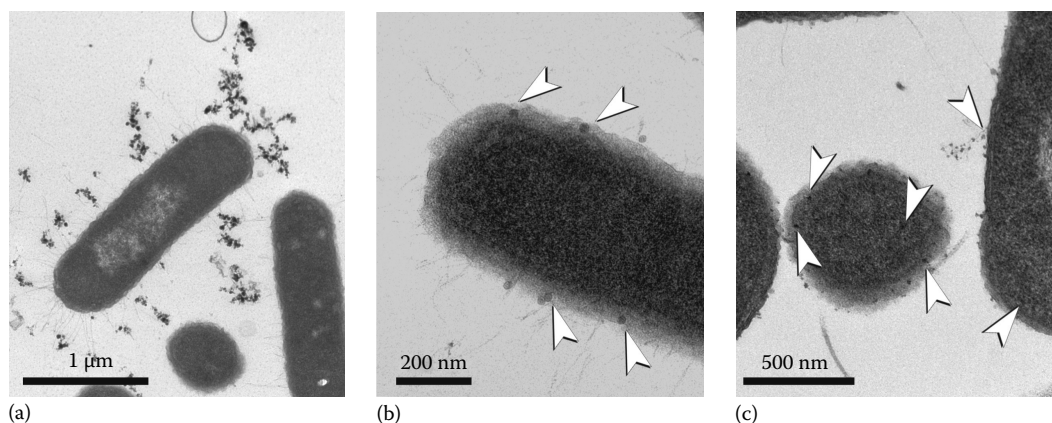


FIGURE 1 Interaction of Ag nanoparticles in the presence of *Escherichia coli*. (a) Agglomerated nanoparticles outside the bacteria and before penetration. (b) Ag nanoparticles interacting directly with the cell membrane. (c) Small nanoparticles inside the bacterial cells.

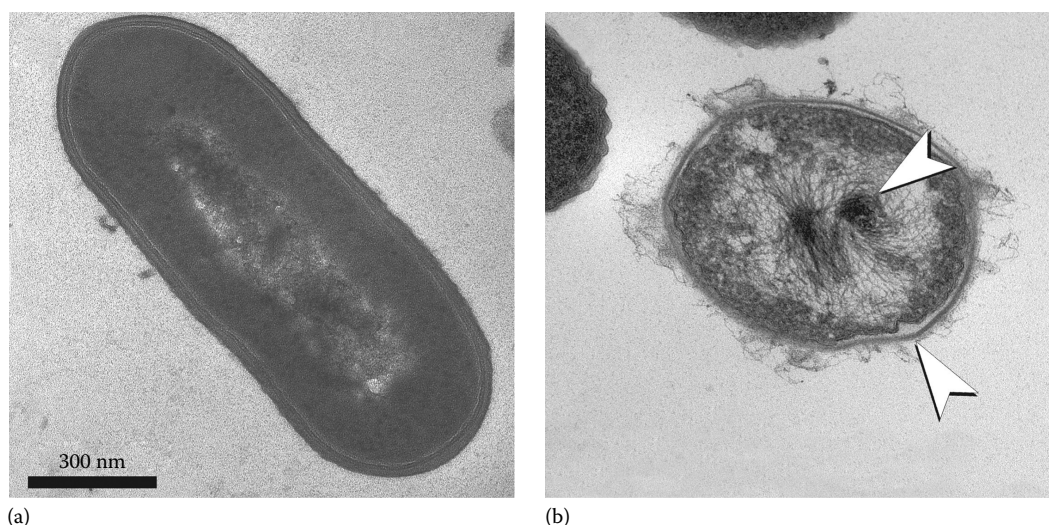


FIGURE 2 Internal structure of *Escherichia coli* cells. (a) Untreated *E. coli* cells. (b) Cytoplasm membrane detached from the cell wall and condensed form of DNA in the center of the electron-light region.

nicotinamide adenine dinucleotide (NADH) dehydrogenase, which impacts the respiratory chain.³⁷ This interaction between silver ions and NADH dehydrogenase leads to the production of ROS, which might explain the toxicity of this metal.^{12,38,39}

ROS are by-products of the respiration process: singlet oxygen, hydrogen peroxide, superoxide radical anion, and hydroxyl radical under aerobic conditions.^{14,40} At low level, they can be controlled by so-called *antioxidants*. However, excessive ROS production may generate free radicals that are extremely deleterious to cells and cause severe consequences in lipids, RNA, DNA, and proteins.¹⁴ Ag-NPs can kill bacteria directly by the catalytic generation of ROS without the presence of silver ions.^{13,40}

Some studies have also found that the production of ROS is a consequence of the interaction of silver ions with enzymes in the respiratory chain,^{12,41} but in some cases, ROS production is considered to have only a secondary role in the antibacterial activity and this mode of action is still being discussed.²⁶

In conclusion, silver can act in a multidirectional fashion whose complexity renders its study and understanding rather difficult because there are several factors involved in the antimicrobial activity.

Some of the commonly accepted mechanisms, not fully understood, include interaction with the bacterial cell wall, interaction with DNA, enzymes, and membrane proteins, and generation of ROS.

FACTORS THAT AFFECT BIOLOGICAL ACTIVITY: SIZE, SHAPE, ETC.

Silver has been well known for its toxicity toward a wide range of bacterial strains, including *S. aureus*, *Pseudomonas aeruginosa*, and *E. coli*.

To understand the factors that affect the ability of the antimicrobial Ag-NPs, it is necessary to characterize their

physicochemical properties and their structure. Some of the factors affect the size, shape, concentration, pH, and environment in which the experiments are performed.

Ag-NPs can be considered as silver ion depositories. However, it has been postulated that the antibacterial effect of Ag-NPs depends on their size. In general, larger nanoparticles (>20 nm) are less effective. This behavior has been related with the ability of the smaller nanoparticles to penetrate inside the cell (see Figure 1c).¹⁶ The antimicrobial activity is related to their specific surface area, and the larger specific surface area of the smaller nanoparticles generally results in a greater antimicrobial effect. Thus, smaller nanoparticles allow a higher silver ion release and also a direct interaction with the cell.^{42–44}

However, by increasing membrane permeability, Ag-NPs can penetrate with sizes up to 80 nm, as shown in the presence of *P. aeruginosa*.⁴⁵ The antimicrobial activity of Ag-NPs is also shape dependent. In some cases, triangular Ag-NPs are more effective than spherical nanoparticles.⁴⁶ Another important factor in antibacterial activity is related to the shape of the nanoparticles. A comparative study in the presence of ⁴⁶ *E. coli* showed shape-dependent activity. Truncated triangular silver nanoplates with a {111} lattice plane as the basal plane displayed the strongest biocidal action, compared with spherical and rod-shaped nanoparticles and with ionic silver.

On the other hand, studies with different types of bacteria and four shapes of Ag-NPs (spherical, cubic, wiry, and triangular) showed a crucial effect on microorganisms, and the result indicated that different bacteria respond in different ways to the nanoparticles. Perhaps the differences in the composition of the membrane are responsible for the different toxicity results.⁴⁷

Similarly, different nanosilver shapes (spheres, rods, and plates) were compared, and the antimicrobial effects indicate that the surface area of the nanoparticles is the key factor that controls the activity inside the cell. It was found that

silver nanoplates showed the best surface area and antimicrobial activity against the tested bacteria, so the antibacterial activity of nanosilver is dependent on the surface area of the nanoparticles.⁴⁸

On the other hand, antibacterial activity is also dependent on surface modifications. Different types of surfactants/polymers (sodium dodecyl sulfate [SDS] and polyoxyethylenesorbitan monooleate-Tween 80, polyvinylpyrrolidone-PVP 360) were tested, and the results showed differences in minimum inhibitory concentrations (MICs) depending on the bacterial strains and the surface modifications. Specifically, the antibacterial activity of Ag-NPs was significantly enhanced when modified by SDS, with MIC decreasing to below 1 µg/mL.^{49,50} In other studies, Ag-NPs were synthesized using fatty acids, especially oleic acid-stabilized Ag-NPs, and showed MICs against *E. coli* as low as 1 µg/mL.⁵¹

TOXIC EFFECTS

Ag-NPs and their applications are increasing steadily and are exploited in a wide range of applications such as cosmetics, medicine, and medical devices.^{52–54}

However, there is still a lack of information concerning the increase in human, animal, and ecological exposure to NPs, including Ag-NPs and the potential risks related to their short- and long-term toxicity.^{33,55}

The toxicity of Ag-NPs and their possible risk to mammalian cells has been studied more extensively in the last decade.^{30,39,56–59} In vitro test has been performed with human cells, mouse cells, and rat cells.^{38,60–63}

In the presence of mouse cells, Ag-NPs (15 nm), molybdenum (MoO₃ 30 nm), and aluminum (Al 30 nm)⁶⁴ were tested. A concentration-dependent toxicity was shown, but Ag-NPs were the most toxic (5–10 µg/mL), and the mechanism was associated with a reduction of mitochondrial function with increased membrane leakage. In addition,⁶⁰ in vitro experiments with rat-liver cell lines were evaluated, showing a significant decrease in mitochondrial function in comparison with other metal oxide nanoparticles (MoO₃, Al, Fe₃O₄, and TiO₂).

Other Ag-NPs in liver cells may be associated with oxidative stress due to LDH leakage at higher doses (100–250 µg/mL). The studies showed a significant depletion of reduced glutathione (GSH) levels, reduced mitochondrial membrane potential, and increased levels of ROS.⁶⁰

The size-dependent cellular interaction has also been investigated in the presence of Ag-NPs in a range between 15 and 55 nm,³⁸ and viability metrics showed a decreasing tendency with increasing dose. In this case, it is probably mediated through oxidative stress.⁵⁸ Moreover, the interaction of Ag-NPs with human fibrosarcoma and skin/carcinoma cells in vitro showed a safe concentration at doses of less than 6.25 µg/mL.⁶¹

In another study, it was suggested that although Ag-NPs seem to enter eukaryotic cells, cellular antioxidant mechanisms can protect the cells from possible oxidative damage.⁶² The genotoxic effect of Ag-NPs has been investigated in

mammalian cells, and the results have shown differences in DNA damage.³³ These differences were associated with functionalized (coated) and nonfunctionalized (uncoated) Ag-NPs surfaces in two types of mammalian cells: mouse embryonic stem cells and mouse embryonic fibroblasts. Coated Ag-NPs exhibited more severe damage than uncoated Ag-NPs.⁶³

Interestingly, in vitro toxicity of Ag-NPs at noncytotoxic doses to HepG2 human hepatoma cells showed that nanoparticles accelerate cells proliferation at low doses (<0.5 mg/L), even though they displayed significant cytotoxicity at higher doses (>1.0 mg/L) that induce abnormal cell morphology, cell shrinkage, and irregular shapes.⁵⁶ Moreover, Ag-NPs decreased the intracellular glutathione level, increased nitric oxide secretion, increased TNF-α in protein and gene levels, and increased the gene expression of matrix metalloproteinases. It was suggested that Ag-NPs ionized in the cells and caused cytotoxicity by a “Trojan-horse” type mechanism.³⁰

The effects of Ag-NPs (in a range of 9.8–48.8 nm) on skin have been studied on a human-derived keratinocyte HaCaT cell line. The results showed that on HaCaT keratinocytes a relatively short contact time with Ag-NPs causes a long-lasting inhibition of cell growth.⁶⁵

According to numerous investigations, cytotoxic mechanisms are based on the induction of ROS, DNA damage, apoptosis, and necrosis.^{66–68} In summary, the cytotoxicity and genotoxicity effects of Ag-NPs are influenced by size, concentration, and exposure time.

Generally, very few investigations on the in vivo toxicology of Ag-NPs are reported, and further studies are needed to evaluate the real impact of Ag-NPs in commercial products on humans and animals. Inhalation of Ag-NPs in rats did not show any significant changes.⁶⁹ Neither are there any significant changes in the hematology and blood biochemical values in rats.⁷⁰ However, potential neurotoxicity and immunotoxicity were detected in mice after 2 weeks. Oral toxicity of Ag-NPs did not cause any significant changes even after 28 days of exposure. But some significant dose-dependent changes were found in the alkaline phosphatase and cholesterol values in rats after 28 days of ingestion.⁷¹

Finally, smaller Ag-NPs exhibit higher toxicity due to their larger surface area and thus greater ion release, and they also cross biological barriers such as the blood or brain more easily.^{66,72,73}

CURRENT ANTIBACTERIAL APPLICATIONS

Ag-NPs are currently the most extensively marketed antimicrobial nanomaterial.⁷⁴ The applications include household antiseptic sprays,⁷⁵ wound dressings,⁷⁶ clothing,⁷⁷ coatings for implants,⁷⁸ dental materials,⁷⁹ water filters,⁸⁰ and food packaging.⁸¹

Ag-NPs have been incorporated into various food contact materials such as food containers, refrigerator surfaces, storage bags, and chopping boards.⁸² Clothing manufacturers have incorporated Ag-NPs into fabrics for socks to neutralize odor-forming bacteria. Water filters incorporate Ag nanowires for cleaning water polluted with bacteria.

The list that follows describes the main areas of application of Ag-NPs.

DENTAL MATERIALS

Bacterial biofilms are responsible for dental diseases, such as caries and parodontitis.⁸³ Ag-NPs have been used in dental materials with the aim of combating cariogenic bacterial colonization. The nanoparticles can be incorporated into orthodontic braces⁸⁴ or first dental resins,⁸⁵ fighting bacterial species such as *S. mutans* and *Lactobacillus* spp.⁸⁶ In vitro studies of the effects of a resin containing Ag-NPs have shown high antibacterial capacity without changing the color of the resin or their mechanical properties,⁸⁷ but in some cases, the incorporation of Ag-NPs in dental materials can cause cosmetic changes in tooth-colored materials when the concentration of nanoparticles is greater than 1%. In contrast, the dental adhesive with Ag-NPs inhibited *S. mutans*.⁸⁸

WOUND DRESSINGS

Damaged skin usually needs to be covered with a dressing immediately after the trauma. Ideally, a dressing should maintain moisture in the wound, enable the exchange of gases, remove excess fluids, and prevent the appearance of infections. Incorporation of Ag-NPs in the dressing can play a fundamental role in controlling the growth of microorganisms. For example, Ag-NPs supported within polyvinyl alcohol/cellulose acetate/gelatin composites were found to have antimicrobial activity against various fungi and bacteria.⁸⁹ Chitosan-based dressings and Ag-NPs have been proven effective in increasing the rate of healing.⁹⁰ A wound hydrogel dressing composed of 2-acrylamido-2-methylpropane sulfonic acid sodium salt with Ag-NPs has been developed and decreased bacterial viability by 94%–99% after 24 h exposure.⁹¹

There is a wide variety of wound dressings containing nanocrystalline silver offered commercially, such as Acticoat™, PolyMem Silver®, SILVRSTAT®, and ANSON.

COATINGS FOR ORTHOPEDIC IMPLANTS

The prevention of implant infections remains an important objective in orthopedic surgery. The antibacterial properties of silver as a coating for orthopedic implants have been studied in order to decrease the risk of perioperative implant infections.⁴¹ Ag-NPs incorporated into titanium oxide nanotubes possess the ability to kill all the bacteria in the culture medium during the first several days and the capability to prevent bacterial adhesion is maintained for 30 days.⁹² Ag-NPs-modified hydrogel coatings may have good potential for surface modification of titanium-based medical devices, with the result of being able to combine high antibacterial efficacy and low toxicity to eukaryotic cells.⁹³ Ag-NPs have also been deposited on stainless steel implants, composite orthopedic coatings containing chitosan, bioglass particles, and stainless steel 316, showing antibacterial efficiency up to 10 days.⁹⁴

FOOD PACKAGING

Antimicrobial packaging is a way to kill or inhibit the growth of microorganisms and thus extend the shelf life of perishable products and enhance the safety of packaged products.⁹⁵ Most commercial antimicrobial packaging systems consist of silver-containing active agents, either as salts, as zeolites, or as nanoparticles. Ag-NPs present some important advantages such as high-temperature stability and low volatility, making them perfect antibacterial agents for food-packaging applications.

Thus, the antibacterial action of Ag-NPs incorporated in packaging has been studied in various foods, and it has been found that Ag-NPs increased shelf life up to 10 days for some vegetables.⁹⁶ Low-density polyethylene films containing Ag-NPs were used to pack fresh orange juice at 4°C and were stored for 56 days. Results showed a significant decrease in mold and yeast population.^{97,98}

APPLICATIONS IN HOUSEHOLD DEVICES

Major consumer goods' manufacturers like LG™ and Samsung™ already produce household items that utilize the antibacterial properties of Ag-NPs. These products include nanosilver-lined refrigerators, air conditioners, and washing machines. Other current applications for Ag-NPs impregnated materials include baby toys, pacifiers, clothing, face masks, and laundry detergent.

Finally, it is important to note the importance of combating bacteria, which have become more and more resistant to antibiotics; therefore, silver compounds can be effective as an antibacterial solution universal in the future.

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Aquatic Species: Interaction of Nanoparticles with Aquatic Species

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INTRODUCTION

Nanotechnology is a multidisciplinary field of research that involves basic, engineering, and biomedical sciences. Materials at the nanoscale possess unique and enhanced properties compared to their bulk counterpart due to size/shape effect, high surface-to-volume ratio, and quantum confinement. The broad range of potential technological applications of nanomaterials (NMs) has attracted great attention from researchers as well as investors; thus, many companies have been established for the production of NMs, nanodevices, etc.

NP production has increased greatly in recent years, and the potential of their release to the environment has therefore increased. Their consequent effect on ecosystem health became an increasing concern that needs to be tackled. It became crucial to determine the fate and behavior of manufactured nonmaterial in the environment.

Nanoparticles (NPs) arrive on land have the possibility to contaminate soil, transferred into the surface and ground water, and interact with biota. Particles in solid wastes, wastewater effluents, direct discharges, or accidental spillages can be carried out to aquatic systems (Klaine et al., 2008; Matraga and Corsi, 2012; Smita et al., 2012).

SYNTHESIS OF NPs

It is well known and also reported in the literature that ZnO, TiO₂, and Fe₃O₄ have been extensively investigated as they present unique properties, which can be tuned by changing both shape and size via the synthesis route. Thus, the aforementioned nanostructured oxides offer promising

and potential wide range of applications including nano-electronics, cosmetics, nanomedicine, and photocatalysis. It is important to note that a certain number of oxides are already produced at large scale and used in various applications.

ZINC OXIDE (ZNO)

ZnO is a wide bandgap semiconductor material that crystallizes within two main structures: hexagonal wurtzite and cubic zinc blende. Various shapes of ZnO have been prepared by microwave hydrothermal method starting from zinc acetate dihydrate (ZAD), benzoic acid (BA), and sodium hydroxide (SH) (Gao et al., 2013). The Te on microwave digestion vessel was heated up to 120°C for 10 min. X-ray diffraction (XRD) analysis confirmed the formation of single pure ZnO phase and scanning electron microscopy (SEM) observations showed that both shape and size are dependent on alkali (A)/(ZAD) molar ratio (OH⁻ concentration) with the presence of BA: (1) flower bud shaped of 2 µm for 8:1, (2) for 10:1 and 12:1 bud shaped of 4–6 µm, and (3) a mixture of rod and flower shaped of about 20 µm for 14:1 and 16:1; see Figure 3a through c). Additionally, it was found that with the absence of BA and for A/ZAD molar ratio of 10:1 and 21:1, irregular aggregated microrods with some flower-shaped microstructures were obtained.

In another study, hydrothermal route was used to produce flowerlike ZnO nanostructures starting from zinc nitrate hexahydrate (ZNH) as precursor, tetramethylammonium hydroxide (TAMH) as mineralizer, and sodium citrate (SC) as modifier with distilled water as dissolvent and reaction medium solvent (Li et al., 2013). The sealed autoclave was heated at 100°C for 4 h.

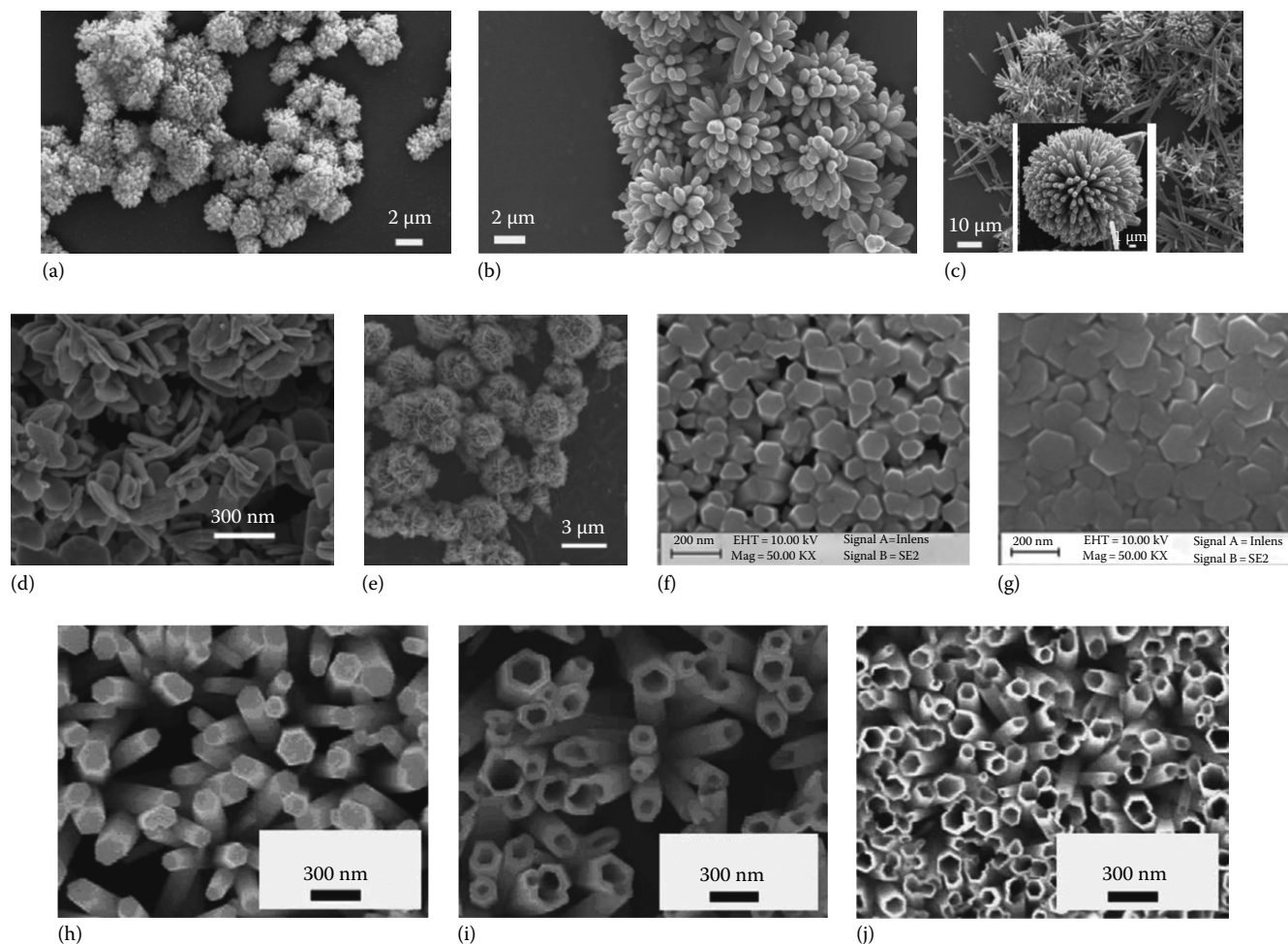


FIGURE 3 Scanning electron microscopy images of various ZnO nanostructures obtained under different conditions: (A)/(zinc acetate dihydrate) molar ratio, (a) 8:1, (b) 10:1, and (c) 14:1 (From Gao, X. et al., *Ceram. Int.*, 39, 8629, 2013.), (d) with tetra methyl ammonium hydroxide (TMAH) and (e) with TMAH and sodium citrate (From Li, F. et al., *J. Alloy Compd.*, 577, 663, 2013.), Si substrate precoated with a ZnO layer of thickness (f) of 20 nm and (g) 30 nm (From Gokarna, A. et al., *J. Luminescence*, 144, 234, 2013.), and (h) as-prepared nanorods and then converted into nanotubes by chemical etching for (i) 7 h and (j) 10 h. (From Yang, L. et al., *Physica E.*, 54, 53, 2013.)

SEM observations showed the formation of nanoplates with a thickness of ~50 nm and lateral size of 300 nm when using only TAMH whereas nanosheets with a thickness of ~10 nm self-assembled into flowerlike spheres of 1.5–3 μm when adding SC; see Figure 3d and e.

Gokarna et al. (2013) studied the effect of seed layer thickness (20, 30, and 50 nm) deposited on p-type Si substrate by radio frequency sputtering technique, on the growth (morphology, size, and density) of ZnO nanorods using hydrothermal process at 90°C for 1.5 h, starting from ZNH, hexamethylene-tetramine (HMN), and distilled water as solvent. SEM observations showed the formation of well-faceted hexagonal rods. It is noticed that as the seed layer thickness increases, (1) the diameter increases (80–150 nm), (2) the length increases from 190 up to 320 nm then decreases slightly to 270 nm, and (3) the density per unit area decreases; see Figure 3f and g.

Furthermore, ZnO nanorods previously grown on Si substrate by chemical bath deposition (CBD) were converted into nanotubes by chemical etching (the nanorods were suspended upside down in 100 mL of 5 M KCl aqueous

solution at 95°C) for various times (6, 7, 9, and 10 h). During the first stage, Si substrates were first coated with 5 mM of a solution of ZAD dissolved in ethanol; then, during CBD the precoated Si substrates were immersed into a solution of 0.1 M of ZNH and 0.1 M of aqueous solution of methenamine, followed by annealing at 93°C for 3 h with sealed beaker. SEM and TEM observations revealed that the as-grown ZnO nanorods of diameter 280 nm transform into nanotubes where the wall thickness decreases with increasing etching time: 80, 70, 40, and 25 nm for 6, 7, 9, and 10 h, respectively; see Figure 3h through j.

TITANIUM DIOXIDE (TiO₂)

TiO₂ crystallizes into three different phases: Anatase (A), Rutile (R), and Brookite (B). It has been reported that each phase is stable under different conditions and possesses different properties. Nanoellipsoid microstructure of A-TiO₂ phase has been synthesized by reflux at 100°C for 6 h using TiCl₄ and H₂O₂ aqueous solution with molar ratio [H₂O₂]/[Ti] = 20/1.

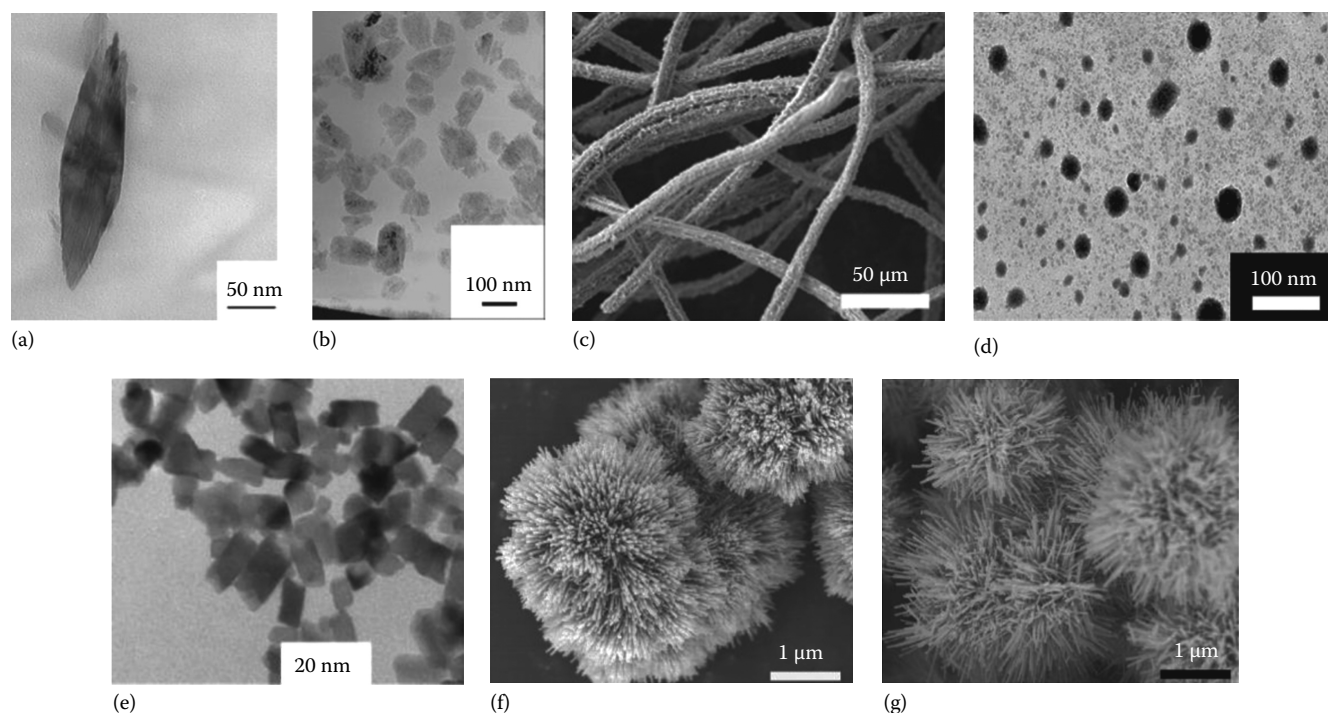


FIGURE 4 TEM/scanning electron microscopy (SEM) images of various TiO_2 nanostructures obtained under different conditions: with (a) 0.1 M TiCl_4 with H_2O_2 and (b) when H_2O_2 is replaced by HCl (From Zhang, Y. et al., *Mater. Chem. Phys.*, 121, 235, 2010.); (c) SEM image, bamboo-shaped microstructure calcined at 500°C and (d) its TEM image (From Lu, Y. et al., *J. Alloys Compd.*, 577, 569, 2013.); (e) TEM image, with molar ratio $[\text{H}_2\text{O}_2]/[\text{Ti (Ti isopropoxide)}] = 3.3$ (From Shen, P. et al., *J. Power Sources*, 247, 444, 2014.); and FE-SEM images for Ti isopropoxide/ethylene glycol (f) 1:2 and (g) 1:3 (From Bai, H. et al., *Water Res.*, 47, 4126, 2013.)

XRD analysis revealed the formation of (1) crystalline R phase for TiCl_4 concentration in the range of 0.1–0.0025 M whereas (2) A phase with low crystallinity for 0.1 M TiCl_4 without H_2O_2 and finally, (3) a mixture of R, A, and B phases when H_2O_2 is replaced by HCl. TEM images showed the formation of ellipsoid-shaped MPs growing along [110] direction having a smaller surface energy where the length-diameter ratio increases with increasing TiCl_4 concentration ($290 \text{ nm} \times 64 \text{ nm}$; $230 \text{ nm} \times 67 \text{ nm}$; $180 \text{ nm} \times 80 \text{ nm}$) and agglomerates of NPs for the remaining cases; see Figure 4a and b (Zhang et al., 2010). A detailed growth mechanism has been proposed.

Lu et al. (2013) studied the effect of calcination temperature (500°C – 900°C for 2 h) on phase stability (A/R) starting from TiCl_4 , deionized water, bamboo cellulose fiber as template, $(\text{NH}_4)_2\text{SO}_4$ (favors the formation of A phase and inhibits $\text{A} \rightarrow \text{R}$ phase transformation), and HCl with molar ratio $[\text{TiCl}_4]/[(\text{NH}_4)_2\text{SO}_4]/[\text{HCl}] = 1:2:10$. Then the reactants were refluxed in an oil bath at 98°C for 2 h followed by aging at room temperature for 24 h (Lu et al., 2013). XRD analysis confirmed the formation of A phase (100%) up to 600°C while R phase starts to appear at 700°C (in agreement with TG/DTA curves) where its amount increases with further increase in the calcination temperature (A/R = 0.78, 0.69, and 0.56 for 700°C , 800°C , and 900°C , respectively). SEM observations revealed the formation of straight and intertwined fluffy bamboo-shaped microstructure of A phase with an average diameter in the range of 8–10 μm ; see Figure 4c. TEM analysis of pulverized powder revealed the presence of

spherical NPs with an average diameter of 30 nm (in agreement with crystallite size determined by XRD); see Figure 4d. This means that the formed mm-long fibers are in fact NPs grown along the bamboo cellulose fiber direction. A detailed growth mechanism is also reported.

Shen et al. (2014) reported on the synthesis of TiO_2 A-phase NPs by solvothermal route using microwave-assisted heating (pressure = 300 psi, temperature = 220°C , time = 30 min) starting from titanium isopropoxide and deionized water with molar ratio $[\text{H}_2\text{O}_2]/[\text{Ti}] = 3.3$ (Shen et al., 2014). SEM and TEM observations showed the formation of nanocrystals with rectangular shape and size of $30 \text{ nm} \times 20 \text{ nm}$ with preferred crystal growth along [001] direction; see Figure 4e.

More recently, TiO_2 hierarchical 3D nanostructures have been synthesized by low-temperature hydrothermal route (Bai et al., 2013). A mixture of a solution A (Ti isopropoxide [TTIP] and HCl) with a solution B (cetyltrimethylammonium bromide [CTAB] and deionized water) and ethylene glycol (EG) was introduced into an autoclave and then heated at 150°C for 20 h. The influence of molar ratio [TTIP]:[EG] was investigated. XRD analysis confirmed the formation of R- TiO_2 phase in both 1:2 and 1:3 molar ratios, which was attributed to the acidic precursor reaction solution. SEM and TEM observations revealed the formation of (1) nanoribbon spheres with a diameter in the range of 2–3 μm (length $\times$ diameter of the ribbons 500 nm–1.5 $\mu\text{m} \times$ tens of nm, giving an aspect ratio larger than 10) for molar ratio 1:2 and (2) nanowire spheres with a diameter in the range of 1–1.5 μm (length $\times$ diameter

of the wires $1.0\text{--}1.5\text{ }\mu\text{m} \times$ less than 10 nm , giving an aspect ratio more than 100) for molar ratio 1:3. The excess of EG will induce slow hydrolysis rate of Ti^{4+} from TTIP thereby reducing the formation of TiO_2 .

MAGNETITE (Fe_3O_4)

Magnetite is a ferromagnetic material, which crystallizes within a spinel cubic structure. Fe_3O_4 nanobelts were prepared by surfactantless hydrothermal method starting from FeCl_2 and Na_2CO_3 with distilled water (Cheng et al., 2012a). The solution was placed into Te on-sealed autoclave followed by hydrothermal treatment at 180°C for 12 h. XRD analysis confirmed the pure nanocrystalline cubic Fe_3O_4 spinel phase. Both SEM and TEM images showed the formation of nanobelts with a width in the range of $80\text{--}120\text{ nm}$ and length in the range of $400\text{--}1500\text{ nm}$ (Figure 5a). Additionally, when FeCl_2 is replaced by FeSO_4 , TEM image revealed the formation of NPs (Figure 5b), where the size changes with FeSO_4 concentration.

However, Fe_3O_4 nano flowers were prepared by solvothermal technique starting from Fe pentacarbonyl ($\text{Fe}(\text{CO})_5$) and absolute ethanol (Cheng et al., 2012b). The solution was placed into Te on-sealed autoclave followed by solvothermal treatment at 180°C for 12 h. XRD analysis indicated the formation of pure cubic spinel phase. FE-SEM image showed the formation of uniform flowerlike microstructure with an average size of ca. 100 nm , consisting of irregular polyhedrons as building blocks (Figure 5c). When ethanol was replaced by EG, FE-SEM revealed the same morphology of flowerlike microstructure of size in the range of $1\text{--}2\text{ }\mu\text{m}$, composed of thin transparent nanosheets (Figure 5d).

Moreover, NPs with controllable size in the range of $90\text{--}100\text{ nm}$ were synthesized by coprecipitation method using $\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$, NaOH , and KNO_3 where the concentration of Fe^{3+} was varied (0%, 30%, and 200%) (Arun et al., 2013). XRD analysis revealed the formation of pure Fe_3O_4 phase where the crystallite size decreased from 45 to 10 nm with increasing Fe^{3+} concentration from 0% to 200%, respectively. TEM images indicated the formation of cubes at the nanoscale where the size decreased with increasing Fe^{3+} concentration in agreement with XRD results: (1) $90\text{--}55\text{ nm}$ for 0%, (2) $\sim 18\text{ nm}$ for 30%, and (3) $\sim 10\text{ nm}$ for 200%; see Figure 5e and f. This suggests that the presence of higher Fe^{3+} concentration promotes faster nucleation resulting in the reduction of the particle's size.

Additionally, monodispersed hollow Fe_3O_4 spheres were obtained by solvothermal process starting from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (precursor), PEG-2000 (serving as solvent and reducing agent as well as plays an important role in controlling uniformity of particle size and prevent agglomeration) and urea (providing basic medium) (Denga et al., 2012). The molar ratio $[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]/[\text{urea}]$ was fixed to 1:9. The solution was sealed in Te on-lined stainless steel autoclave and then heated at 200°C for various periods of time (5, 6, 12, 24, 48, and 72 h). XRD analysis indicated the formation of pure cubic spinel Fe_3O_4 phase for all periods of time except for 5 h, where $\alpha\text{-Fe}_2\text{O}_3$ phases were detected. The average crystallite size increases with increasing annealing time; 44 and 79 nm for 6 and 12 h and then higher than 100 nm for remaining times. SEM images revealed the formation of small spheres (5 h); smooth and compact sub- μm spheres formed by the aggregation of primary NPs (6 h); smaller sub- μm spheres with rough surfaces (12 h); monodispersed hollow spheres with larger

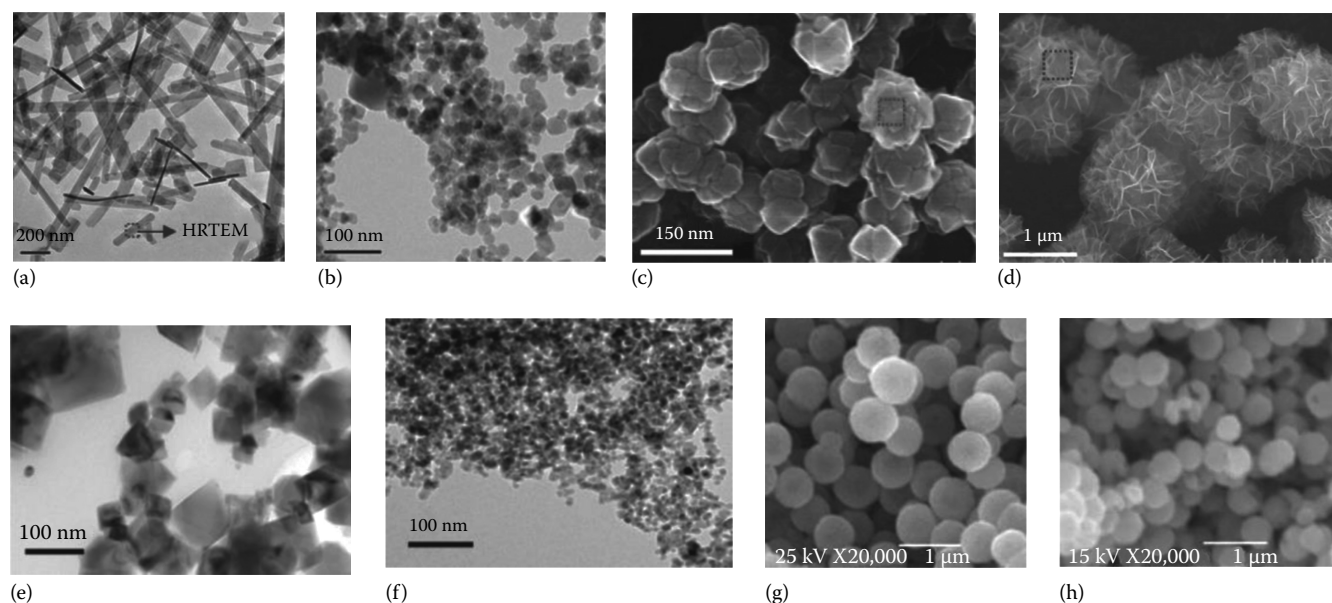


FIGURE 5 Scanning electron microscopy (SEM)/TEM images of various Fe_3O_4 nanostructures obtained under different conditions: TEM images for hydrothermal process using (a) FeCl_2 and Na_2CO_3 and (b) when FeCl_2 is replaced by 0.002 M FeSO_4 (From Cheng, Z. et al., *Mater. Lett.*, 75, 172, 2012a.), through thermal decomposition of $\text{Fe}(\text{CO})_5$ using (c) absolute ethanol (SEM) and (d) ethylene glycol (SEM) (From Cheng, Z. et al., *Mater. Lett.*, 76, 90, 2012b.), prepared with Fe^{3+} ion concentration of (e) 0% (TEM) and (f) 200% (TEM) (From Arun, T. et al., *J. Phys. Chem. Solids*, 74, 1761, 2013.), obtained at 200°C for (g) 12 h (SEM) and (h) 48 h (SEM). (From Denga, Y. et al., *Electrochim. Acta*, 76, 495, 2012.)

holes and internal voids become visible (24 h); smaller hollow spheres and internal voids become larger (48 h); some of sub- μm spheres are broken (72 h)

INTERACTION BETWEEN NPs AND AQUATIC ORGANISMS

FATE AND BEHAVIOR OF NPs IN MARINE ECOSYSTEMS

The behavior and toxicity of NPs in seawater are very different from those in freshwater (Matranga and Corsi, 2012). Here in this section, we will concentrate on the destiny and behavior of NPs in marine ecosystems. The marine system is more alkaline, with more ionic strength and has a variety of colloids and natural organic matter. Coastal runoff and deposition from the atmosphere can add more contamination to the marine environment (Klaine et al., 2008).

Klaine et al. (2008) outlined the fate of NPs in the marine environment and the organisms at risk of exposure in a diagram that can be summarized in the following points: In coastal areas, there are different types of organic matter according to the type of discharges. Oceans exhibit changes in physiochemical properties with depth that may lead to aggregation of NPs. NP aggregates will either sink very slowly to the ocean floor or be accumulated at the interface between cold and warm currents or even be recycled by organisms. In all cases, NPs may present a risk of exposure to different organisms at different depths. NPs at the surface microlayer of ocean may too present a way of aerosol exposure risk to marine mammals and birds and organisms living in the surface microlayer.

Abiotic factors such as pH, ionic strength, or the presence of organic ligands in water and how they influence ecotoxicology are poorly studied.

Agglomeration, aggregation, and precipitation of manufactured NPs in seawater may result in the deposition of NPs on sediment biolims, with subsequent accumulation in the sediment and exposure to sediment dwelling organisms. Additionally, marine bacteria and some organism are known to synthesize or accumulate NPs (Klaine et al., 2008).

CHARACTERISTICS OF NPs AND THEIR MOBILITY IN AQUATIC ECOSYSTEMS

The unique properties of NPs especially their surface area are very significant factors that lead to their stability and mobility as colloidal suspension or their aggregations into larger particles and deposition in aquatic systems. The efficient interactions between NPs and algae are due to the stable colloidal suspensions of NPs (Navarro et al., 2008a).

The metallic NPs are normally coated with inorganic or organic compounds (e.g., citrate, cysteine, carbonate, or surfactants such as sodium dodecyl sulfate). Therefore, the stability of the colloidal suspension is maintained (Mafune et al., 2000). At neutral pH, NPs become negatively charged largely due to the composition of their coatings, which lead to their stabilization in the aquatic systems (Mandal et al., 2001).

Other metal oxide NPs and nonmetallic NPs have different behaviors in the aquatic systems (Navarro et al., 2008a).

The surface properties of NPs also determine their deposition/aggregation processes. The surface properties are dependent mainly on factors such as temperature, ionic strength, pH, and particle concentration and size. Furthermore, NP association with natural organic matter or artificial organic compounds that are intended to improve the NP properties or solubility will increase the complexity of the interactions. In actual fact, the majority of natural organic matter has a biological basis including the organic matter released from algae (e.g., proteins, polysaccharides, nucleic acids, lipids) (Navarro et al., 2008a).

The bioavailability of NPs is a key factor for the hazard evaluation of NPs, which depends on (1) physicochemical properties of the NPs (aggregation, solubility), (2) target organism, and (3) NPs–organism contact environment (Kahru and Dubourguier, 2010).

EFFECTS OF NPs ON AQUATIC ORGANISMS

The exploration into the effect of NPs on the aquatic environment and therefore the aquatic organisms is of high interest, mainly because the water cycle eventually receives runoff and wastewater from domestic and industrial sources (Batley et al., 2013). Additionally, water remediation techniques based on the use of nanomaterial for wastewater treatments have increased (Farré et al., 2009). It is well known that most industrial discharges are to estuarine or marine environments. Additionally, coastal systems are more likely to be the direct sink for many NPs. It is quite important to determine the toxic effects of manufactured NPs on bacteria, diatoms, and sediment-dwelling organisms. It should be pointed here that most ecotoxicological tests were developed mostly for aquatic organisms and water-soluble chemical compounds (Kahru and Dubourguier, 2010).

The chemical composition and surface reactivity of NPs extremely determine the direct toxic effect of NPs on organisms. The great reactivity of NPs compared with the larger-sized particles of the same chemistry might lead to catalysis of redox reactions when they come in contact with organic molecules (Zhang, 2003) and affect photosynthetic or respiratory processes (Navarro et al., 2008a).

There are at least three distinct mechanisms for the toxic action of metal and metal oxide NPs (Brunner et al., 2006). First, particles can release toxic substances into the surrounding media; second, the surface interaction between NPs with media may produce toxic substances (e.g., chemical radicals or reactive oxygen species [ROS]). Third, NPs or their surfaces may interact directly with and disturb biological targets (Ma et al., 2013).

The indirect effects of NPs are caused mainly by the physical restraints or the release of toxic ions or the production of ROS. Furthermore, NPs themselves may serve as pollutant carriers, thus enhancing or reducing the bioavailability of other pollutants. An excellent example of physical restraint, the accumulation of NPs on the surface of photosynthetic

organisms may inhibit photosynthetic activity because of shading effects. NPs have the tendency to aggregate and combine with other organic materials; therefore, sorption of NPs to algal cells is to be expected. Adsorption of larger NP aggregates to cell wall of some organisms may alter the cellular acquisition of essential nutrients, through clogging of the walls or nutrient adsorption (Navarro et al., 2008a).

Additionally, NPs might produce ROS upon their contacts with organisms or with agents present in the environment (e.g., ultraviolet [UV] radiation). ROS production is particularly related in the case of NPs with photocatalytic properties such as TiO₂ (Kus et al., 2006). Simultaneously, the toxicity of NPs may be partly due to their release of toxicants (Navarro et al., 2008a).

On the contrary, some compounds may be excreted by organisms as a feedback response to change the NP toxicity (Navarro et al., 2008a). For example, substances that induce NP occlusion or metal ion chelation might be produced by some algae and thus reduce the bioavailability of NPs and metal ions they released (Soldo et al., 2005).

NPs may have good effects on organisms as well. For example, TiO₂ NPs were found to enhance the dry weight, chlorophyll synthesis, and metabolisms in photosynthetic organism. This could be due mainly to the fact that some NPs have antimicrobial properties, which can increase the strength and resistance of organisms to stress. At the same time, some NPs have high specific surface area, and they are able to sequester nutrients at their surfaces and therefore serve as nutrient stock to the organisms.

In extreme habitats, algae living in those areas were found to have the ability to accumulate mineral particles on their cell walls (Luetz-Meindl and Luetz, 2006). These mineral particles have been hypothesized to be important for the continued existence of these algae living in low-nutrient habitats. Thus, it is expected that NPs might be attached to the algae and enhance their growth by supplying them with the essential nutrients (Navarro et al., 2008a).

POTENTIAL MEANS OF BIOLOGICAL UPTAKE OF NPs AND ENTRY INTO ORGANISMS

NPs can be produced either intentionally or unintentionally, with the latter including natural sources such as aerosols from volcanic eruptions, forest fires, pollen fragments, and viruses as well as anthropogenic sources such as power plants, vehicles, coal combustion, frying, and welding, and include NPs such as soot, black, and elemental carbon (Navarro et al., 2008a). The physicochemical properties of NPs may be different according to their source. These properties affect the NP interactions with organisms, although their lethal effect has been found mainly due to size or surface area (Nel et al., 2006).

Unintentional interactions are more related to environmental impacts since these cannot be controlled, and they could greatly affect biota. The potential toxicity mechanisms may include disruption of membranes or membrane potential,

oxidation of proteins, genotoxicity, interruption of energy transduction, formation of ROS, and release of toxic constituents (Klaine et al., 2008).

The three major sources of engineered NPs discharged into marine ecosystems are (1) cosmetics and sunscreens as examples of personal care products. Sunscreens nowadays use inorganic UV filters, including ZnO and TiO₂ NPs; (2) for sewage treatment, the available information is limited on how nanomaterials may interact with the sewage treatment process or if NPs can be removed from wastewater sludge (Kim et al., 2010); (3) antifouling applications in paints that are designed to avoid the attachment and growth of aquatic organisms on vessel hulls (Dineshram et al., 2009; Chen et al., 2012; Matranga and Corsi, 2012).

The uptake of NPs by aquatic organisms is of a major concern. The most possible pathways include direct ingestion or entry across epithelial boundaries. At the cellular level, prokaryotes like bacteria are largely protected against the uptake of NPs, because they lack the mechanisms for bulk transport across cell wall. Nevertheless, with eukaryotes, the condition is different, since they have highly developed processes for the cellular internalization of nanoscale or microscale particles namely by endocytosis and phagocytosis, respectively (Na et al., 2003; Panyam et al., 2003; Moore, 2006; Nowack and Bucheli, 2007). NPs entering cells via endocytosis will end in either the endosomal or lysosomal compartments or via cell surface lipid raft-associated recognized as caveolae that avoid the degradative chance of material entering the endosomal/lysosomal system (Na et al., 2003; Panyam et al., 2003).

Figure 6 shows the potential endocytotic pathways for NP entry into cells.

Here in this chapter, we will focus on aquatic algae as a model organism present in aquatic systems. Microalgae represent key ecotoxicological models as they comprise the most important source of biomass production that supports all the other aquatic trophic levels (Melegari et al., 2013). It has been found that the toxicity of NPs to algae involves adsorption to cell surfaces and disruption to membrane transport (Batley et al., 2013). Algae possess cell walls that comprise a primary site for interaction and a barrier for the entrance of NPs into their cells. Cell walls in algae as in plants mainly consist of cellulose. In addition to that, algae have glycoprotein and polysaccharides in their cell walls. Nevertheless, diatom algae represent a special case, with cell wall composed of hydrated silicon dioxide. Cell walls of algae are selective and semipermeable (i.e., allowing the entry of small molecules while limiting the passage of larger molecules) with pores ranging from 5 to 20 nm (Harris, 2009 cited in Melegari et al., 2013). The pore size can change during the reproductive phase; they become more permeable and are large enough to allow NPs to penetrate to the interior of cells. These interaction can lead to the development of new pores that are usually higher than normal and allow the entry of NPs through the cell wall. After passing through the cell wall, NPs meet the plasma membrane (Navarro et al., 2008a). Here, NPs can pass to

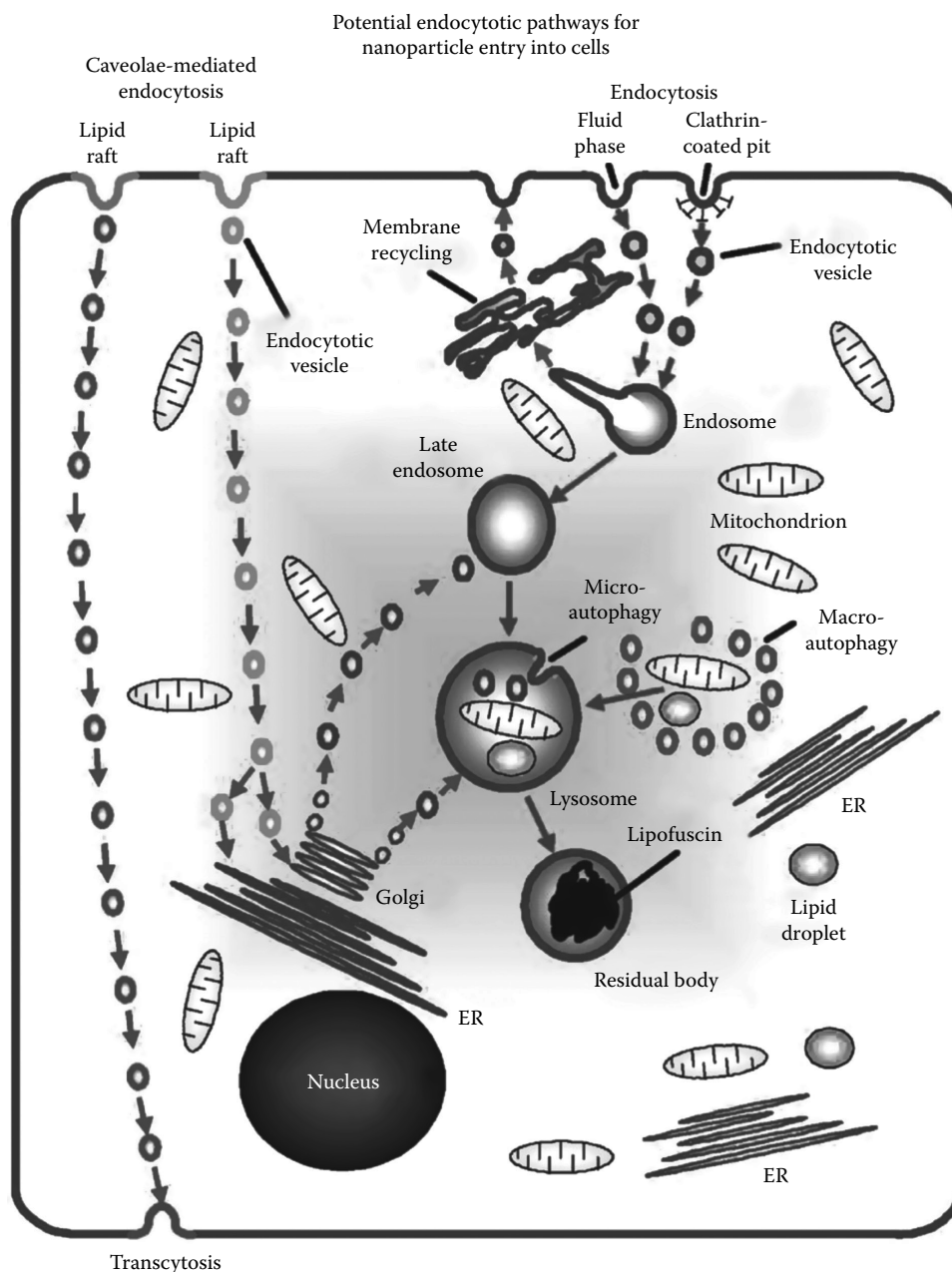


FIGURE 6 Pathways for endocytosis in the cell, which could be exploited by manufactured nanoparticles. Endocytosis via clathrin-coated pits (receptor mediated) or uncoated pits (fluid phase) transfers materials to the lysosomal degradative compartment, while caveolar endocytosis can result in translocation to the endoplasmic reticulum and Golgi body or through the cell by transcytosis. (From Moore, M.N., *Environ. Int.*, 32, 967, 2006.)

the interior parts of cells via cell membranes either by simple diffusion or through endocytosis and adhesion (Klaire et al., 2008) by carrier proteins or ion channels (Navarro et al., 2008a; Sahay et al., 2010). The uptake of NPs is size dependent (Chithrani et al., 2006). Moore (2006) has demonstrated that most internalization of NPs will occur by endocytosis. This endocytotic pathway into the cell can lead to either endosomal and lysosomal compartments or via cell surface lipid raft-associated domains known as caveolae that avoid the degradative fate of material entering

the endosomal/lysosomal system (Na et al., 2003; Panyam et al., 2003) cited in Moore (2006).

Inside the cells, NPs are more likely to be stored in certain locations (e.g., vesicles, mitochondria), and they are capable of exerting a toxic response (Nel et al., 2006; Nowack and Bucheli, 2007).

Manufactured NPs comprise seven main classes: carbonaceous nanomaterials, semiconductors, nanopolymers, nanoclays, emulsions, metals, and metal oxides (Batley et al., 2013). Table 1 shows the ecotoxicological effects of some representative of ve

TABLE 1

Summary of Ecotoxicological Data for Five Representative Metal-Based Nanoparticles Reported in Recent Years

NPs	Test Species	Exposure Conditions	Effects	Reference
ZnO (20–30 nm)	<i>Skeletonema marinoi</i> , <i>Thalassiosira pseudonana</i> , <i>Dunaliella tertiolecta</i> , <i>Isochrysis galbana</i>	1 mg/L	Growth rate was depressed by 50%–75%.	Miller et al. (2010)
ZnO (NPs, bulk)	<i>Pseudokirchneriella subcapitata</i>	72 h	EC ₅₀ = 0.04 mg/L.	Aruoja et al. (2009)
ZnO (NPs)	<i>Pseudokirchneriella subcapitata</i>	72 h	EC ₅₀ = 0.06 mg/L.	Franklin et al. (2007)
ZnO (20 nm)	<i>Thalassiosira pseudonana</i>			Miao et al. (2010)
ZnO (NPs)	<i>Anabaena flos-aquae</i> ; <i>Euglena gracilis</i>		Inhibit photosynthetic activity; cell death.	Brayner et al. (2010)
ZnO (NPs and bulk)	<i>Chlorella</i> sp.	6 days (1000 mg/L)	Growth inhibition.	Ji et al. (2011)
Fe ₃ O ₄ (<50 nm)	<i>Chlorella vulgaris</i>	50–1600 mg/L	Decrease in chlorophyll <i>a</i> content; CO ₂ absorption by <i>Chlorella</i> decreases as nano-Fe ₃ O ₄ increased; decrease in photosynthetic rate.	Chen et al. (2012)
TiO ₂ (bulk)	<i>Chlorella</i> sp.	6 days (1000 mg/L)	No toxic effect.	Ji et al. (2011)
TiO ₂ (NPs and bulk)	<i>Pseudokirchneriella subcapitata</i>	72 h	EC ₅₀ = 35.9 mg/L (bulk) and 5.83 mg/L (NPs).	Aruoja et al. (2009)
TiO ₂ (NPs and bulk)	<i>Chlorella</i> sp. and <i>Scenedesmus</i> sp.	72 h	NPs: EC ₅₀ = 16.12 (<i>Chlorella</i>); EC ₅₀ = 21.2 (<i>Scenedesmus</i>). Bulk: EC ₅₀ = 35.50 (<i>Chlorella</i>); EC ₅₀ = 44.4 (<i>Scenedesmus</i>).	Sadiq et al. (2011)
TiO ₂ (NPs)	10 freshwater microalgae	25 days (0–300 mg/L)	On average, increasing NP concentration had no significant effects on algal growth rates, but there was species-specific variation in responses.	Kulacki and Cardinale (2012)
TiO ₂ (NPs)	10 freshwater phytoplanktons	25 days	TiO ₂ has little effect on algal growth rates.	Kulacki and Cardinale (2012)
Ag (NPs) (10–200 nm)	<i>Chlamydomonas reinhardtii</i>	10–100,000 nM; 1–5 h exposure time	Reduction in photosynthetic yield: EC ₅₀ = 3300 ± 572 nM (after 1 h); EC ₅₀ = 1049 ± 396 nM (after 2 h).	Navarro et al. (2008b)
Ag (NPs 10–15 nm)	<i>Pithophora oedogonium</i> and <i>Chara vulgaris</i>	10 days	Significant reduction in total chlorophyll contents in both species.	Dash et al. (2012)
Au (12.5 nm)	<i>Scenedesmus subspicatus</i>	10 mg/L	No adverse effects.	García-Camero et al. (2013)
Amine-coated Au (10 nm)	<i>Scenedesmus subspicatus</i>	1.6 × 10 ² –1.6 × 10 ⁵ AuNP/cell	EC ₅₀ = 1.6 × 10 ⁵ AuNP/cell after 24 h.	Renault et al. (2008)

Source: Classification made by Blaise, C. et al., *Environ. Toxicol.*, 23, 591, 2008.

Notes: EC50 < 0.1 mg/L = extremely toxic to aquatic organisms; EC50 0.1–1 mg/L = very toxic to aquatic organisms; EC50 1–10 mg/L = toxic to aquatic organisms; EC50 10–100 mg/L = harmful to aquatic organisms; EC50 > 100 mg/L = nontoxic to aquatic organisms.

metal oxide-based NPs, namely, Fe₃O₄, ZnO, TiO₂, and the two metal-based NPs Ag and Au were chosen for comparison. The selected NPs are widely used in commercial nanoengineered materials as antibactericide coatings, catalysts, in biomedicine or for personal care products (Barrena et al., 2009). In addition to that, these NPs have received significant attention over their potential ecological impacts (Klaine et al., 2008).

In this chapter, we focused on the effects of these NPs on microalgae. This is due to the fact that algae have a key function in the aquatic ecosystem, not only producing biomass, but also contributing to the self-purification of polluted water. Consequently, algae are one of the normally used model organisms for the toxicity examination of toxicants and NPs as well (Ji et al., 2011).

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Arc Discharge: Arc Discharge Synthesis of Carbon Nanomaterials for Energy Device Application

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ARC DISCHARGES THAT SYNTHESIZE CARBON NANOMATERIALS

Since the discovery of fullerene in 1985, various kinds of carbon nanomaterials have appeared, and different applications have been proposed. Arc discharging has been commonly employed as a technique to produce carbon nanomaterials. In the conventional carbon arc discharge method, carbon nanotubes (CNTs) and nanocapsules are synthesized by the thermal arc plasma generated between two graphite electrodes under low pressure (10–100 kPa) [1,2]. In other words, it is a homoelectrode system arc. We tested the arc using a heteroelectrode system, namely, graphite and molybdenum (Mo) electrodes, and grew multiwalled CNTs (MWCNTs) [3]. MWCNTs are found at the cathode deposit that is formed from

the evaporated anode material. We found that MWCNTs grew only at the graphite cathode spot area [4], indicating that the graphite anode is not necessary for the synthesis of MWCNTs via the carbon arc cathode. This finding also suggests that an anode-free arc plasma may produce nanotubes. Since then, we have developed the apparatus for carbon nanomaterial synthesis using various kinds of arc plasma techniques, and we discuss this apparatus in this chapter.

In general, arc discharges are generated between electrodes when there is a current of ~100 A through them and a potential difference of ~20 V across them. Such a high current is obtained by the flow of many ionized particles in the discharge. The ion energy distribution of the vacuum arc obtained with a graphite cathode was measured in a cathodic arc deposition apparatus using a selected-mass

ion energy analyzer [5]. The experiment was carried out at an arc chamber pressure of 0.05 Pa without additional gas. The arc current was 50 A and was supplied by a DC power source in the constant-current mode. The arc voltage was approximately 24 V. The detected mass numbers per ionic mass number m/z were 6 and 12, which correspond to C^{++} and C^+ , respectively. The mass numbers m/z of 3 (C^{+++}) and 24 (C_2^+) were not detected. This result is in good agreement with the reports that the discovered majority ion in graphite cathodic arc plasma is C^+ [6]. The energy of C^+ ions varies widely from 10 to 50 eV and has a double peak composed of a strong peak at 20 eV and a weaker peak at approximately 40 eV. The energy of C^{++} was observed to vary widely from 10 to 50 eV without any specific peak, and the count was far lower than the C^+ count.

CARBON NANOMATERIALS DESCRIBED IN THIS CHAPTER

FULLERENE

Fullerene has a spherical shell structure containing several tens of carbon atoms, and its shell is composed of five-membered and six-membered rings of carbon atoms. In 1985, Kroto et al. synthesized a fullerene with 60 carbon atoms (C_{60}) by laser ablation, and this led to the discovery of fullerene [7]. Laser ablation is a phenomenon in which atoms and molecules near a solid target are explosively vaporized by irradiation with intense, pulsed laser light, and the vaporized particles form a plasma plume [8]. The particles in the plume are cooled by colliding with ambient gas molecules, and fullerenes and MWCNTs are synthesized in the gas ambient.

CNT

Fullerene was first synthesized by a laser ablation experiment and was then found to be synthesizable by an arc discharge. In 1991, Iijima discovered a rolled-up graphite sheet in which six-membered rings of sp^2 -bonded carbon atoms formed a 2D network [1]. This structure is called a *carbon nanotube* (CNT). The first-discovered CNT was an MWCNT in which several graphite sheets were nested and formed concentric cylinders. In 1993, the single-walled CNT (SWCNT) was discovered, also by Iijima and Ichihashi [9]. Figure 7 shows transmission electron microscopy (TEM) micrographs of SWCNTs and MWCNTs [10,11].

CNH

Carbon nanohorns (CNHs) were synthesized in 1999 as a new type of carbon particle produced by the carbon dioxide (CO_2) laser ablation of carbon at room temperature [12]. The product has a powdered form of graphitic particles with a uniform size of approximately 80 nm. Individual particles are composed of an aggregate of many horn-shaped sheaths of single-walled graphene sheets, which are named CNHs. Figure 8 shows a TEM micrograph of CNHs [13].

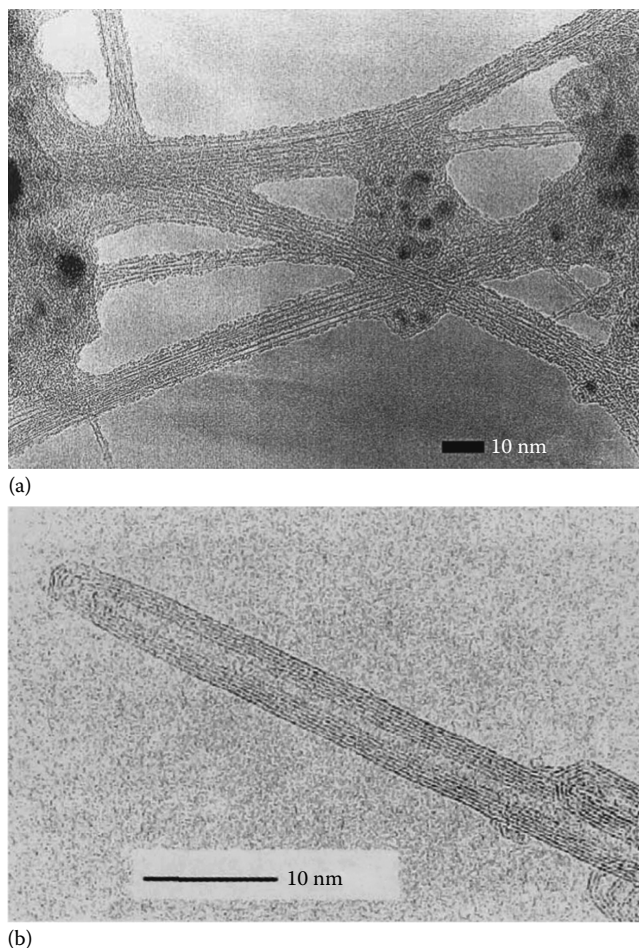


FIGURE 7 Transmission electron microscopy micrographs of (a) single-walled carbon nanotubes and (b) multiwalled carbon nanotubes. (From Takikawa, H. et al., *Mater. Sci. Eng. C*, 16, 11, 2001; Takikawa, H. et al., *Trans. Inst. Electric. Eng. Jpn.*, A-119, 1156, 1999.)

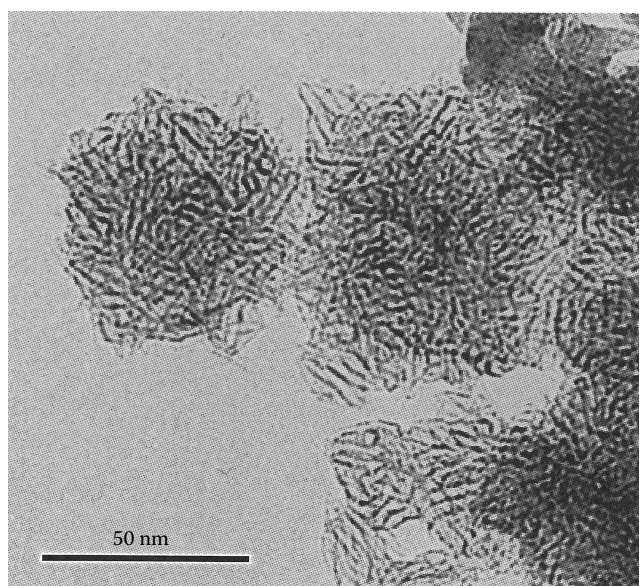


FIGURE 8 Transmission electron microscopy micrographs of carbon nanohorns. (From Ikeda, M. et al., *Jpn. J. Appl. Phys.*, 41, L852. Copyright 2002, The Japan Society of Applied Physics.)

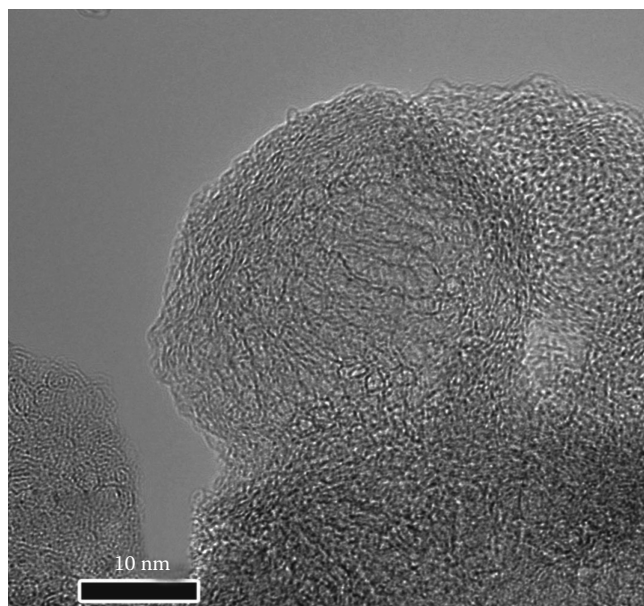


FIGURE 9 Transmission electron microscopy micrograph of arc blacks. (From Ikeda, T. et al., *Jpn. J. Appl. Phys.*, 50, 01AF13. Copyright 2011, The Japan Society of Applied Physics.)

AcB

Arc black (AcB) is a unique ball-like carbon material that exists both as individual spheres and as the aggregates of spheres and has an amorphous structure. The sizes of the spheres were measured to be approximately 35 nm with a standard deviation of 10 nm. When AcB is synthesized in the nitrogen (N_2) atmosphere using the twin-torch arc discharge apparatus [14,15], AcB contains a small amount of nitrogen. Figure 9 shows a TEM micrograph of AcBs [15].

CNB

After thermal treatment of AcB at more than 2400°C, a novel form of balloon-like carbon material with a diameter of 40 nm, a standard deviation of 15 nm, and a shell thickness of 10 nm was found. This new carbon material was called a *carbon nanoballoon* (CNB). Figure 10 shows a TEM micrograph of CNBs [15].

ARC DISCHARGE APPARATUSES AND EXPERIMENTAL PROCEDURES

In this section, we present the arc discharge apparatuses that were employed for synthesizing carbon nanomaterials. We commonly used carbon or catalyst metal-contained carbon as the electrode material. The arc discharge was operated at several tens to 100 A and 20–30 V for a discharge period of a few seconds. The arc discharges are classified by the operating gas pressures.

ARC DISCHARGE IN GASES

We developed the carbon arc apparatus for fullerene production [16]. A graphite anode and cathode with a diameter of

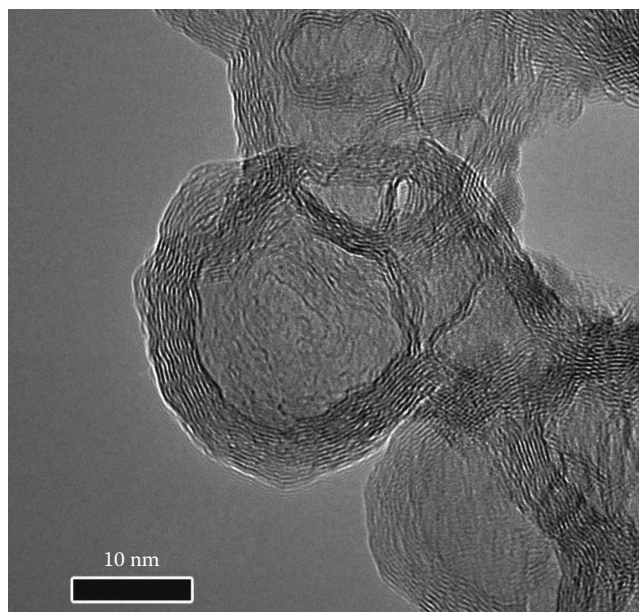


FIGURE 10 Transmission electron microscopy micrograph of carbon nanoballoons. (From Ikeda, T. et al., *Jpn. J. Appl. Phys.*, 50, 01AF13. Copyright 2011, The Japan Society of Applied Physics.)

10 mm were horizontally arranged in a cylindrical vacuum chamber made of SUS304, and they were evacuated by a rotary pump. A water-cooled inner jacket (130 mm in diameter and 200 mm long) made of SUS304 surrounded the electrodes and efficiently reduced the heat generated by the arc plasma. During the arc burning process, the surface positions of the electrodes varied because of evaporation from the anode and deposition to the cathode. Therefore, the electrode gap length was kept constant during the arc burning.

After the production of the apparatus for fullerene synthesis, we developed the other carbon arc apparatus for AcB synthesis, which is operated at close to atmospheric gas pressure [14]. Figure 11 shows a new twin-torch arc apparatus with two arc torch electrodes placed at an angle of 80° in order to prevent materials from being deposited on the cathode. An AC arc discharge was generated between the electrodes. For long-term operation, both electrodes of the arc torches were continuously supplied. In the apparatus, a constant-rate gas flow was introduced from the torches and was evacuated by the pump. The pressure in the chamber was constantly controlled by a conductance valve, balancing the gas supply and the exhaust. Synthesized materials were deposited on the chamber walls, a cold trap chilled by liquid nitrogen, and a paper filter.

LOW-PRESSURE ARC

The apparatus of a running arc in vacuum (cathodic running arc) is depicted in Figure 12. The term “running arc” implies that the cathode spot is driven by a magnetic field and that the cathode spot creates a continuous crater on the cathode surface [17]. The graphite cathode was placed in a cylindrical vacuum chamber. The chamber acted as the anode. Two permanent magnet plates were placed on both

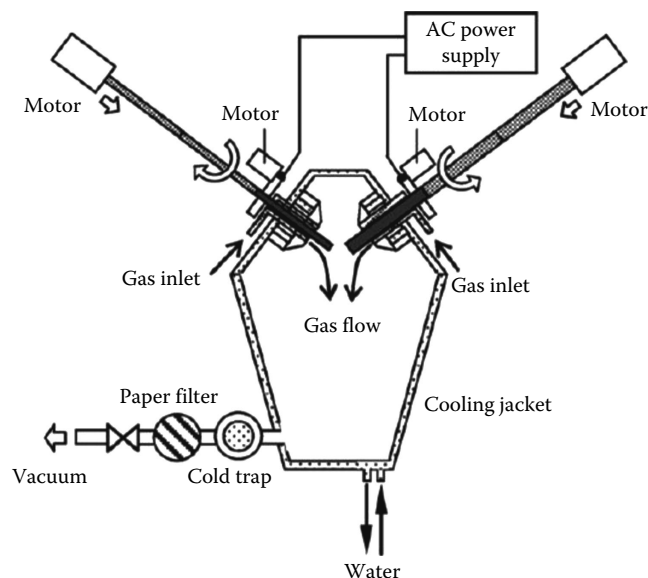


FIGURE 11 A new twin-torch arc apparatus for arc discharge. (From Oke, S. et al., *Chem. Eng. J.*, 143, 225, 2008.)

sides of the cathode in order to apply a parallel magnetic field to the cathode surface. The arc was ignited by a mechanical triggering system with a Mo trigger electrode. When the trigger electrode was brought into contact with the cathode and then withdrawn, an electric spark was ignited between the cathode and the trigger electrode. This spark induced the cathodic arc between the cathode and anode. After the desired discharge period, the arc was extinguished by switching off the power supply.

ATMOSPHERIC PRESSURE ARC

A conventional torch for tungsten-electrode inert gas (TIG) metal welding was used to generate the arc discharge. The experimental setup for the synthesis of CNTs is depicted in Figure 13. The torch electrode was changed from tungsten (W) to graphite in order to prevent the contamination

of W vapor and macrodroplets. A plate target (2 mm thick, 10 mm wide) made of graphite containing metal catalysts (Ni and Y) (C-Ni/Y) was fixed on the sidewall of a water-cooled, steel base electrode. The edge of the C-Ni/Y target was located approximately 20 mm above the surface of the substrate. The torch arc was generated in open air and was aimed at the edge of the target. The target was a counter electrode of the torch arc. When the arc was operated in DC mode, the arc spot (anode spot) was created on the target by blasting the target material, and the arc jet was formed beyond the target. The blasted material passed through the arc jet plasma, and the soot was deposited on the collecting substrate [18].

Various modified types of the open-air arc method have been tested; however, we have discovered a new method for selectively fabricating CNH aggregates with comparably high yields [13]. Figure 14 depicts the experimental setup. Two graphite plate electrodes (3 mm thick) were arranged such that they sandwich a larger thin polytetrafluoroethylene (PTFE) sheet (0.5 mm thick) with a V-shaped cut (typically with a 5 mm base side and a height of 7.5 mm) in open air. The electrodes and the notched PTFE sheet formed a thin cavity. The electric power was supplied to the electrodes using a welding power supply with an radio frequency (RF) trigger starter. Then, an electric arc discharge was generated between the thin-gap electrodes. Because a considerable amount of the graphite anode had evaporated, the evaporated gas overflowed from the notched exit in the form of a plasma jet, which we call a cavity arc jet (CAJ) [13]. The CAJ was quickly cooled on a collection plate made of stainless steel placed 15 mm from the cavity exit. The carbon soot was deposited on the collection plate.

GROWTH MECHANISM OF CARBON NANOMATERIALS

The experimental conditions used in the various apparatuses are listed in Table 2. Each of the conditions is shown to have an important role in the synthesis of carbon nanomaterials with a desired structure and property.

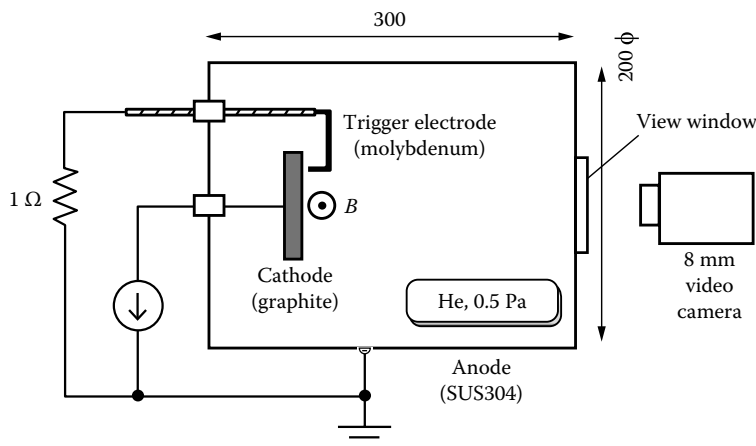


FIGURE 12 Schematic diagrams of arcs under applied magnetic field. The cathodic vacuum arc is composed of a graphite cathode and an inert anode. B denotes the magnetic flux density. (From Takikawa, H. et al., *Jpn. J. Appl. Phys.*, 40, 3414. Copyright 2001, The Japan Society of Applied Physics.)

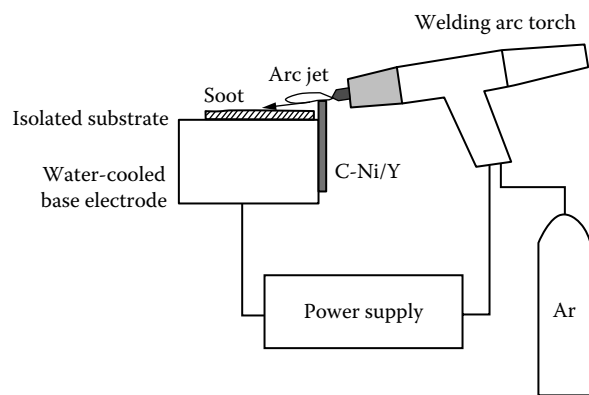


FIGURE 13 Experimental setup of the torch arc method used for preparing single-walled carbon nanotubes. (From Takikawa, H. et al., *Phys. B*, 323, 277, 2002.)

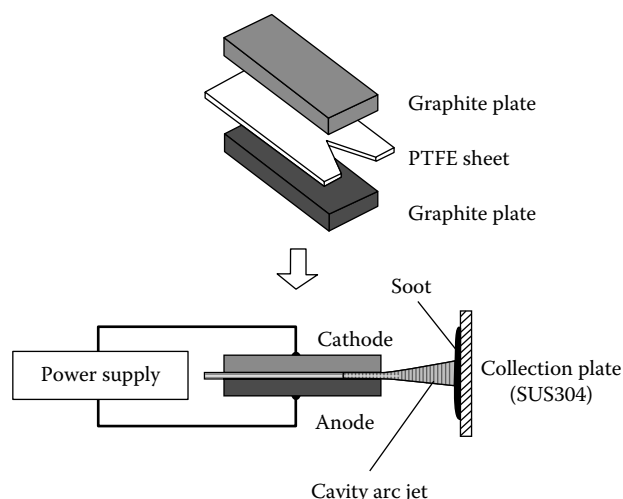


FIGURE 14 Schematic diagram of the structure of the arcing cavity formed with two graphite electrodes and an insulating sheet (polytetra fluoroethylene) and the experimental setup. (From Ikeda, M. et al., *Jpn. J. Appl. Phys.*, 41, L852. Copyright 2002, The Japan Society of Applied Physics.)

FULLERENE PRODUCTION AND INFLUENCE OF AIR LEAKAGE

When fullerene was produced in different ambient gases of He, Ne, Ar, Kr, H₂, O₂, CO₂ and CH₄, the following results were obtained. Maximum fullerene productivity was obtained with the He ambient, that is, a fullerene yield of 16 wt.% and a fullerene production rate of 33 mg/min. However, for O₂, the fullerene yield and production rate were only 6.5 wt.% and 16 mg/min, respectively, and for N₂, they were 0.7 wt.% and 2.5 mg/min, respectively. Then, we investigated the fullerene productivity using the carbon arc discharge method when air was deliberately introduced into the He-filled arc apparatus. The values of the fullerene yield and production rate did not vary until the air leakage rate, which is defined as the increase in the ratio of the air partial pressure relative to He pressure, was 0.2%/min. The fullerene productivity drastically decreased when the air leakage increased above 0.2%/min [16].

CNT PRODUCTION AND ROLE OF EACH ELECTRODE

In a low-pressure arc apparatus, a DC arc discharge was generated between graphite and Mo electrodes at 25 kPa of He gas ambient for a period of about 1 s in order to verify the relation between the CNT growth and the arc discharge phenomena. The electrode surface was observed with a scanning electron microscope (SEM) and a high-resolution (HR) SEM.

We observed the entire surface of the graphite cathode (Mo was the anode) using SEM. Several consecutive craters, which were explosively created by randomly moving the cathode spot, were seen at the center of the electrode. The remainder of the outer part was still the original graphite surface. As observed by SEM, very dense CNTs and carbon nanocapsules were formed throughout the crater surface [4]. The CNT diameters were typically 5–10 nm, and the lengths had increased to 10 μm (typically 3–4 μm) [11]. The CNTs and fiber-like products decreased with increasing distance from the crater. On the Mo anode, a small amount of soot was deposited, although no CNTs were found. This finding suggests that an anode-free arc plasma may produce CNTs. Thus, we employed a cathodic vacuum arc, which has an inert anode, and found that MWCNTs existed at the traces of the cathode spot. MWCNTs are considered to grow at the ex-cathode spot during the quenching period after the cathode has moved to a new position [3].

Then, we tried various catalyst metals including Ni, Y, Fe, and Ni/Y [3], and found that the CNTs were observed both at the cathode spot at which the arc was forcibly extinguished and at the anode spot when the C-Ni/Y was used for the electrode. A large amount of CNTs was observed at the anode spot, as shown in Figure 15 [10]. Figure 7 shows the HR-TEM image of the typical SWCNTs in the weblike soot bridged between the electrodes, which were generated by the arc with a graphite cathode and C-Ni/Y anode. The presence of the CNTs may be summarized, as shown in Table 3.

After performing the aforementioned experimental study of the synthesis of CNTs, Takikawa et al. provided a new and simple method for preparing CNTs using a welding arc torch operated in an open-air environment [19]. SWCNTs and CNHs were fabricated using the torch arc method in open air and were found in the deposit that collected on the substrate [18]. Many CNTs were obtained on the C-Ni/Y substrate with a DC arc and on the graphite and C-Ni/Y substrates with an AC arc. However, few were located on the graphite substrate with a DC arc. The largest number of CNTs was obtained on the C-Ni/Y substrate with a DC arc [19].

CNH SYNTHESIS IN OPEN AIR

CNHs were prepared by a new CAJ method under open-air conditions, as shown in Figure 14. When the CAJ was successfully formed, the arc voltage was low (25–30 V) and stable; the graphite anode surface was uniformly evaporated. The soot grown in this technique is composed of round particles ranging in size from 30 to 150 nm and is typically less than 100 nm in size, as shown in Figure 8. This TEM

TABLE 2
Experimental Conditions Used in the Various Apparatuses and Arc Plasma

Cathode Material	Arc Current (Density)	Atmosphere and Operating Pressure	Magnetic Flux Density	Materials Synthesized	Reference
Graphite (99.998%)	DC 150 A	He, Ne, Ar, Kr, H ₂ , O ₂ , CO ₂ , and CH ₄ , 7.7 kPa	—	Fullerene	[16]
Graphite (99.998%)	DC 50–150 A	He, H ₂ , N ₂ , O ₂ , C ₂ H ₂ , and CO ₂ , 3–100 kPa	—	MWCNTs	[5]
Graphite (99.998%) Mo	DC 60 A	He, 25 kPa	—	MWCNTs	[4]
Graphite (99.998%)	DC 100 A	He, 0.5 Pa	—	MWCNTs	[11]
C-Ni (3.2 wt.%) C-Y (0.82 wt.%) C-Fe (3 wt.%) C-Ni/Y (14.6/4.9 wt.%)					
Graphite (99.998%)	DC 100 A	He and H ₂ , 0.5 Pa	—	MWCNTs	[3]
C-Ni (3.2 wt.%) C-Y (0.82 wt.%) C-Fe (3 wt.%) C-Ni/Y (14.6/4.9 wt.%)					
Graphite (99.998%)	DC 50 A	He, 0.5 Pa (running arc in vacuum) He, 25 kPa (low-pressure running arc)	4 mT (running arc in vacuum) 15 mT (low-pressure running arc)	MWCNTs	[17]
Graphite C-Ni/Y (14.6 and 4.9 wt.%) Mo	DC 50 A	He, 25 kPa	15 mT	MWCNTs	[10]
C-Ni/Y (3.6 and 0.8 atm%)	DC 100 A	Open air and shielding Ar gas that was own at 1 L/min	—	SWCNTs and CNHs	[18]
Graphite plate	DC 150 A	Open air		CNHs	[13]
Graphite	7.1 A/mm ²	N ₂ , 80 kPa		AcB	[14]

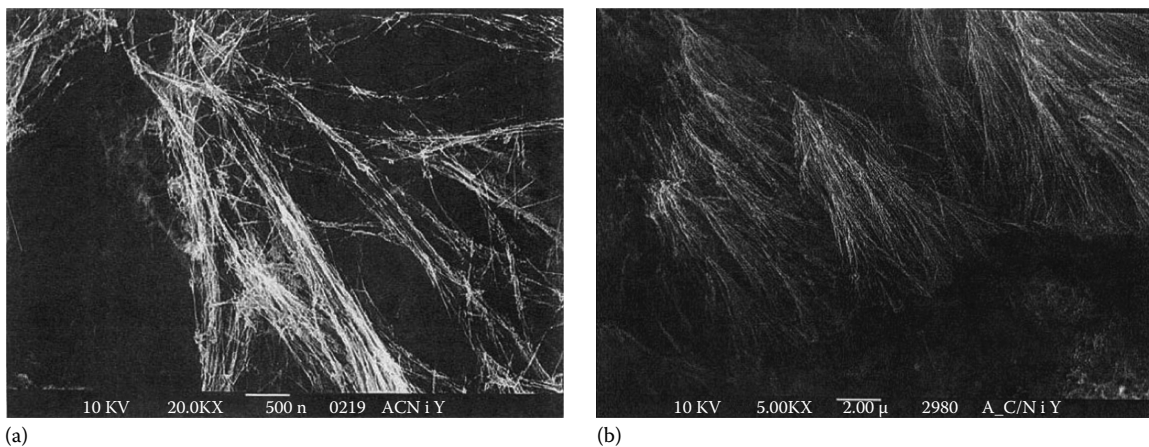


FIGURE 15 (a) High-resolution scanning electron microscope (HR-SEM) micrograph of crater surface of C-Ni/Y anode spot in stationary arc (Mo cathode). (b) Lower-magnification HR-SEM of (a). (From Takikawa, H. et al., *Mater. Sci. Eng. C*, 16, 11, 2001.)

micrograph shows that the particles were CNH aggregates, and they account for more than 30% of the soot particles. The remainder consisted of graphite balls, aggregates of shorter single-walled graphene tubules, and particles consisting of polymerized fullerene-like cages. MWCNTs were rarely observed [13].

EFFECT OF MAGNETIC FIELD ON CNT GROWTH

In an experiment of the cathodic running arc in vacuum, upon applying the magnetic field, the cathode spot of the cathodic arc moved downward. The direction of this motion was opposite to that indicated by the Lorentzian rule. This reverse motion of the cathode spot under a magnetic field is

TABLE 3
Presence of Multiwalled Carbon Nanotubes on
Electrode Surfaces in Various Experimental Conditions
(the Arc Was Forcibly Extinguished after 1–3 s)

Arc Mode	Electrodes		CNTs	
	Cathode	Anode	Cathode	Anode
Stationary	C	Mo	Yes	No
	Mo	C	No	No
	C-Ni/Y	Mo	Yes	No
	Mo	C-Ni/Y	No	Yes: bunch like
Running	C	Mo	Yes: at the end	No
	Mo	C	No	No
	C-Ni/Y	Mo	Yes: at the end	No
	Mo	C-Ni/Y	No	Yes: wide area, bunch like

well known in low-current cathodic vacuum arcs [20]. The mechanism responsible for the reverse motion is believed to be due to the effect of the motion of ions being diffused from the ion cloud in the cathode spot to the anode under a magnetic field [17].

On the contrary, in the low-pressure arc experiment at a He gas pressure of 25 kPa, the cathode spot moved in the direction following the Lorentzian rule. It is known that when the arc is operated at more than 1 kPa (viz., in low-pressure and high-pressure arcs), upon applying a magnetic field, the arc column is driven in the Lorentzian direction and the cathode spot is dragged by the column and moves in the same direction. Figure 16 shows an SEM micrograph of the cathode spot crater. Numerous CNTs were observed at the center of the crater. These CNTs are longer and more curved compared with the CNTs in the cathodic vacuum arc. Figure 16b shows the surface of the position 2 mm away from the position in Figure 16a, which corresponds to the boundary between the

forcibly extinguished crater and the previous cathode spot crater. A few CNTs can be observed, as indicated by arrows, but numerous spherical particles chained together are dominant. The CNTs that were observed were found to bridge the spherical particles.

The result in the low-pressure arc is entirely consistent with the CNTs observed at the forcibly extinguished positions of the cathodic running arc and the random-walk arc [21]. The random-walk arc is operated without a magnetic field, and indicates that the CNTs are not only formed by the cathode spot, but also destroyed by the cathode spot after their formation, even in the low-pressure arc.

Regardless of the ambient pressure and the presence of the magnetic field, based on the results obtained in [17] as well as the previous results involving a random-walk cathodic arc [21], the process required for CNT formation and deformation in an arc discharge may be considered as follows (refer to the illustration in Figure 17). The site on the cathode surface at which the next cathode spot will be created is heated, as shown in Figure 17a, and may be ion bombardment in a cathodic vacuum arc, thermal conduction from the previous cathode spot, or contact with a hot arc column in a low-pressure thermal arc. CNTs are considered to have excellent field-emission capabilities [22]. Thus, the heated cathode spot surface self-forms CNTs (Figure 17b) because the mobility of the atoms and/or molecules is high due to the considerable heat. After CNT formation on the cathode surface, the CNTs may be destroyed by Joule heating and/or by the emission of the carbon clusters as well as electrons, as shown in Figure 17c. Once CNTs are formed during the development of the cathode spot, they are consumed and destroyed during the most active period of the cathode spot. As the CNTs become fully consumed, the arc seeks a new cathode spot because it is no longer possible for an adequate number of electrons to be supplied at the current spot. If the arc cannot find an appropriate electron emission site, it will self-extinguish.

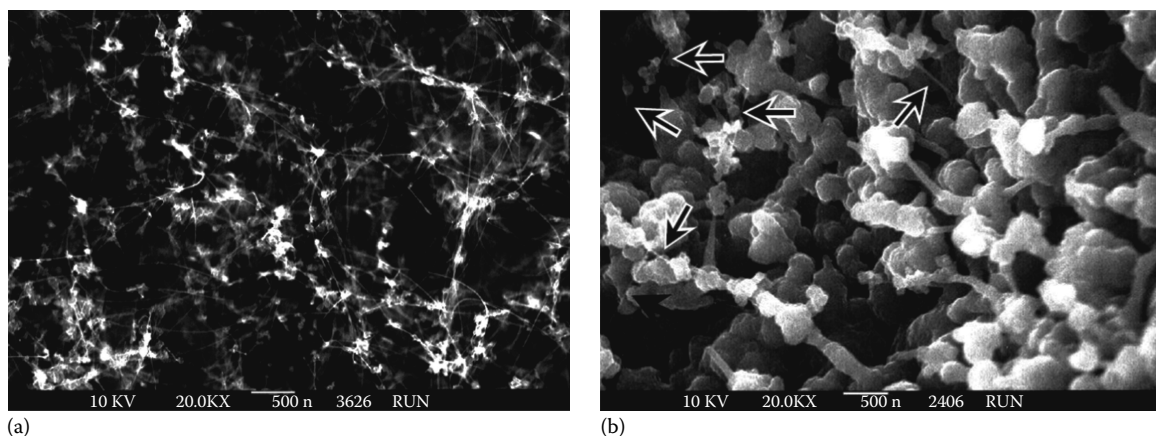


FIGURE 16 Scanning electron microscope micrographs of the crater surface taken at (a) the center of the crater and (b) about 2 mm away from (a). (From Takikawa, H. et al., *Jpn. J. Appl. Phys.*, 40, 3414. Copyright 2001, The Japan Society of Applied Physics.)

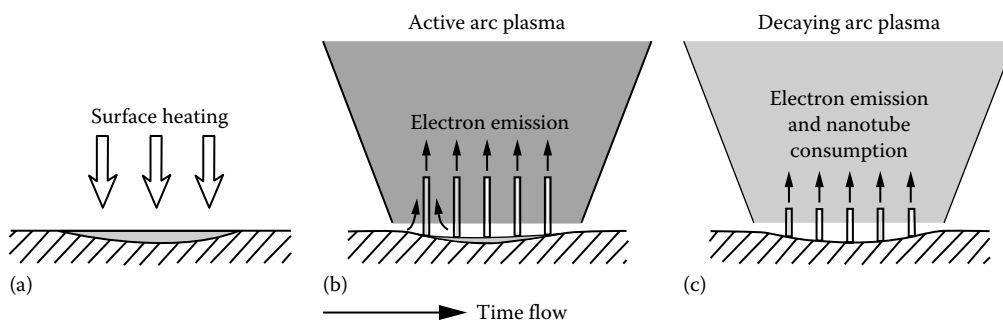


FIGURE 17 Illustrative diagram of carbon nanotube formation and consumption following the development and decay of the cathode spot activity. (From Takikawa, H. et al., *Jpn. J. Appl. Phys.*, 40, 3414. Copyright 2001, The Japan Society of Applied Physics.)

CNB FORMATION BY HEAT TREATMENT

A novel form of balloon-like carbon material, CNB, with a diameter of 40 ± 15 nm and a shell thickness of 10 nm, was found after thermal treatment of AcB at more than 2400°C.

When these ball-like materials were observed by TEM, they appeared to be in several forms such as graphite spheres

with horned surfaces, graphite spheres with smooth surfaces, amorphous spheres, and some nonspherical structures. All of these forms appeared at relatively low densities. Figure 18 shows TEM images of AcB annealed in Ar atmosphere for 30 min at different temperatures. The graphitic shells were formed from the outside of AcB, and the thickness of the shells

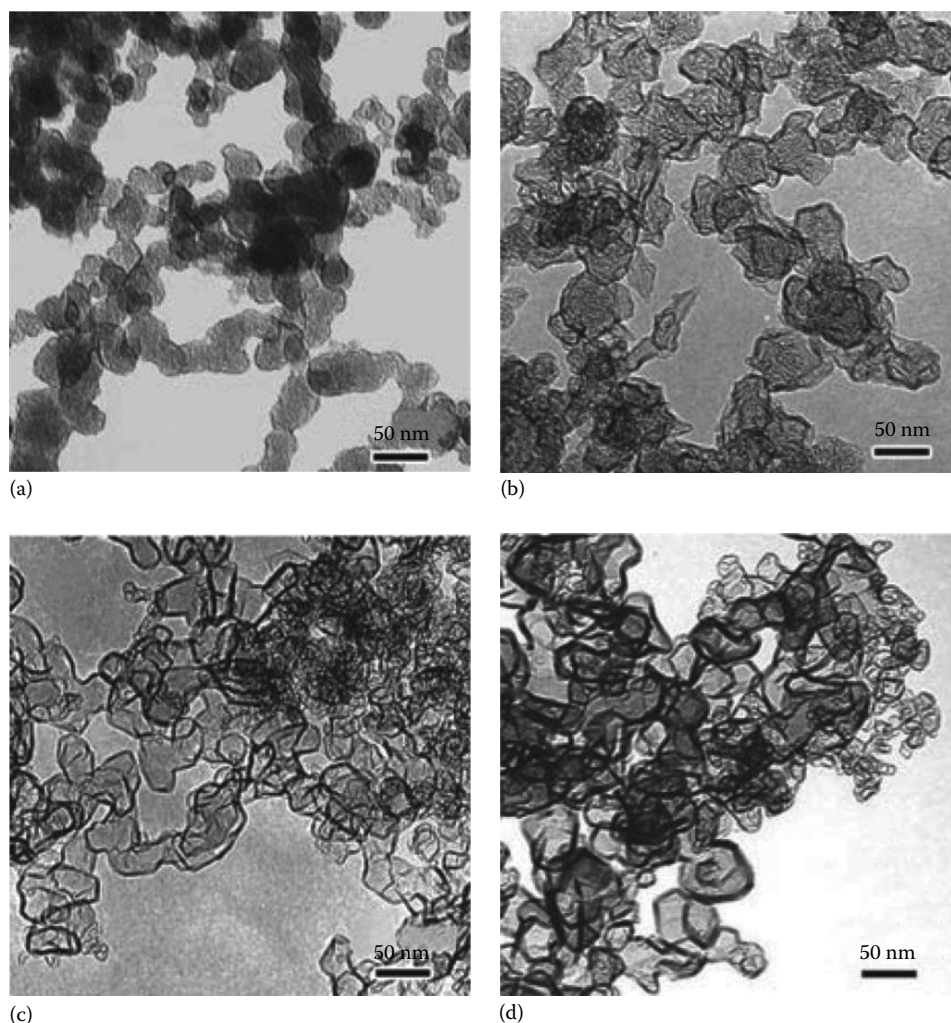


FIGURE 18 Transmission electron microscope images of AcB heated in Ar for 30 min at (a) 1600, (b) 2000, (c) 2400, and (d) 2800°C. (From Xu, G. et al., *New Diamond Frontier Carbon Technol.*, 15, 73, 2005.)

increased gradually with treatment temperature. Because there were no obvious size changes in the spherical structure of AcB, we deduce that the carbon supply for the growth of the shells originated from the migration of carbon inside the shells.

APPLICATIONS OF CARBON NANOMATERIALS

FIELD-EMISSION MATERIALS

CNT is considered one possible candidate for cathode materials of field emitters [22]. In order to provide a practical method of manufacturing field emitters of CNTs, a welding arc torch was employed to produce a nanotube surface on graphite and catalyst-contained graphite substrates.

We used a general welding arc torch for TIG welding, although the W electrode of the torch was replaced with a pure graphite one of diameter 3 mm in order to prevent the contamination of W vapor or macrodroplets. The substrates (2 mm thick) were pure graphite (C) and graphite containing metal catalysts (Ni and Y) (C-Ni/Y). The arc was operated in open air (1.01×10^5 Pa) in either the DC or AC (60 Hz) mode at an arc current of 100 A. Shielding Ar gas flowed through the welding torch with a flow rate of 1.8 L/min. The gap length between the torch electrode and the substrate was approximately 2 mm. The arcing period was approximately 1 s. Hereafter, DC-cat, AC-C, and AC-cat denote the cases of the C-Ni/Y substrate processed in the DC mode, the C substrate processed in the AC mode, and the C-Ni/Y substrate processed in the AC mode, respectively. For DC-cat, many CNTs were observed on the surface. Using TEM, the CNTs that were observed were confirmed to be MWCNTs.

We examined the electron emission from the arc spot surface in a diode system with a cathode–anode gap of 100 μm and an anode diameter of 2 mm at 2×10^{-5} Pa [24]. Figure 19 shows current–voltage characteristics of as-prepared nanotube surfaces. We found that the emission current increased in the order of DC-cat, AC-C, and dc-cat. This order is observed

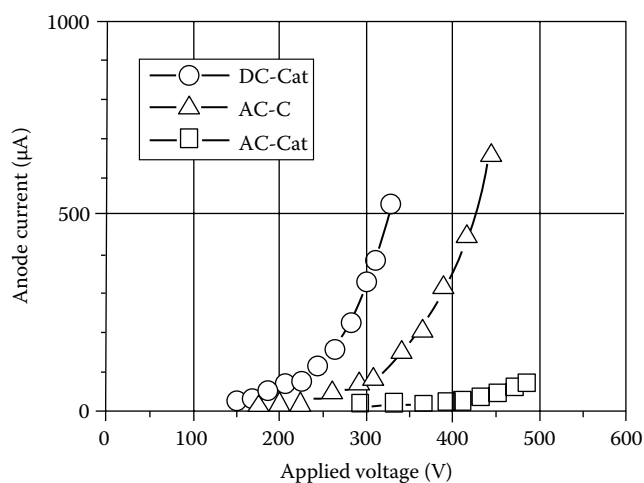


FIGURE 19 Field-emission characteristics of as-prepared, nanotube surface, measured in diode system. (From Takikawa, H. et al., *Trans. Inst. Electric. Eng. Jpn.*, A-121, 495, 2001.)

to be the same as the increase in the CNT number density and the decrease in the coexisting nanoparticle density.

HYDROGEN STORAGE MATERIALS

According to Chahine and Benard [25], a hydrogen density of 6.5 wt.% is required for an electric vehicle powered by a hydrogen fuel cell to achieve a range of 500 km. Orimo et al. reported that the hydrogen concentration in mechanically prepared nanostructured graphite reached 7.4 wt.% after milling for 80 h under a hydrogen atmosphere [26]. If reversible dehydrogenation and rehydrogenation are possible, a new type of hydrogen storage system could be constructed. We plan to measure isotherms for SWCNTs at room temperature under pressures near or below 100 kPa.

SWCNTs were fabricated using the torch arc method in open air [18]. N_2 adsorption and H_2 sorption were conducted using a common Sieverts-type apparatus equipped with two pressure gauges, which had full ranges of 13.3 and 133 kPa. The sample cell was made of quartz, and its dead volume was 10 mL when it was empty. The quantity of the samples used was 10 mg for SWCNT and 100 mg for the raw material, and these were chosen such that the actual surface areas of the samples totaled at least 5 m^2 in order to obtain reproducible data. First, the sample was degassed at 393 K for 15 h using a rotary vacuum pump with a cold trap cooled to 77 K. Then, an isotherm of N_2 adsorption was recorded at 77 K, and isotherms of H_2 sorption were measured at 295 and 77 K without exposing the sample to air. Prior to each measurement, the sample was subjected to evacuation at 393 K for 15 h. In most cases, it took approximately 2 h to obtain one equilibrium point for hydrogen sorption.

Figure 20 shows N_2 adsorption isotherms for SWCNTs and the raw graphitic material. On SWCNTs, the adsorbed amount exceeded that on the raw material by a factor of 10. It is

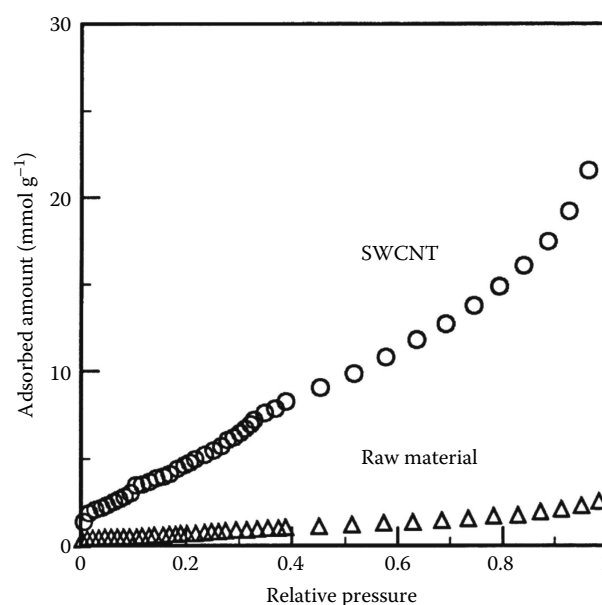


FIGURE 20 N_2 adsorption isotherms at 77 K. (From Nishimiya, N. et al., *J. Alloys Comp.*, 339, 275, 2002.)

noteworthy that the surface area of SWCNTs was 8.4 times as large as that of the raw material. The maximum H_2 concentrations in SWCNTs produced using the torch arc method in open air reached 0.932 wt.% at 295 K under 106.7 kPa and 2.37 wt.% at 77 K under 107.9 kPa, with the H_2 uptakes not yet saturated.

FUEL CELLS

Catalyst Loading

The direct methanol fuel cell (DMFC) is a polymer electrolyte fuel cell and is applicable to portable electric power supplies because the liquid fuel has a high energy density [28]. As fuel cells employ precious metals including platinum (Pt) and ruthenium (Ru) for the oxidation of fuel and reduction of oxygen, these catalyst metals need to be used effectively. Carbon nanomaterials are effective for supporting nanometer-sized metal catalysts and have been used as a catalyst support in energy devices. We supported PtRu catalysts on AcB and evaluated their catalytic activity by electrochemical characterization [15,29].

PtRu catalysts were loaded by the reduction method using sodium boron hydride ($NaBH_4$) [29]. Hydrogen hexachloroplatinate (IV) hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) and ruthenium trichloride ($RuCl_3$) were used as precursors of Pt and Ru, respectively. The carbon nanomaterial was dispersed in deionized water by sonication for 20 min. The metal precursor solution was then added to the carbon nanomaterial solution. The $NaBH_4$ solution with a 30-fold mole of the metal precursors was added to the metal precursor solution and stirred for 2 h. The solution was filtered by a membrane and washed repeatedly with deionized water, and the catalyst was obtained after drying. An energy-dispersive x-ray analyzer equipped with TEM revealed that the nanoparticles that were loaded consisted of Pt and Ru. The average diameter of the catalyst nanoparticles loaded on AcB was ~ 2 nm.

The cyclic voltammograms (CVs) of PtRu-loaded AcB (PtRu/AcB) were obtained in Ar-purged 0.5 mol/L H_2SO_4 solution. The electrochemically active surface area (ECSA) of PtRu/AcB was obtained by integrating the total charge corresponding to the desorption peak of hydrogen and normalizing with a scan rate, Pt loading, and the charge value of $210 \mu C/cm^2$ for Pt surface. Based on the results obtained, the ECSA of PtRu/AcB was $8.14 m^2/g$.

Fuel Cell Performance

PtRu-supported AcB and Pt-supported AcB were used as the anode and cathode catalysts, respectively, and a CNB was used as an additive in the catalyst layers in order to improve the electric conductivity. These catalysts were prepared by the colloidal process [14,15,30]. The catalyst and additive were thoroughly mixed and evenly laid on a carbon paper. The CNB content was 10%. After dropping 5% $NaOH$ solution, which is an electrolyte, onto the catalyst/additive layer, this layer and $NaOH$ on 115 were jointly hot-pressed at 2 MPa at $120^\circ C$. The membrane electrode assembly (MEA) was built into a DMFC standard cell (Japan Automobile Research Institute). Methanol–water solution was introduced into the anode, and dry air was

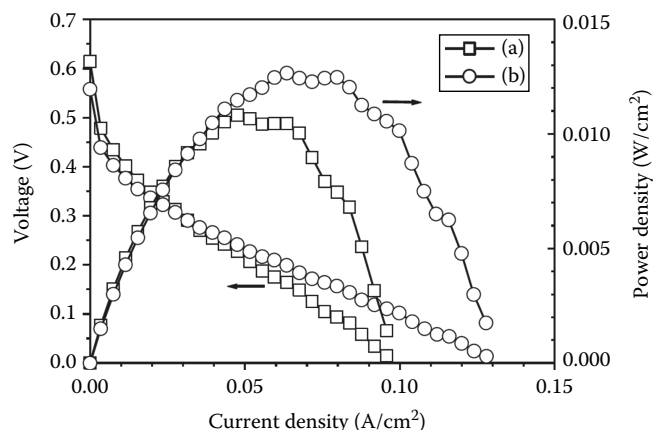


FIGURE 21 I – V polarization curves of membrane electrode assemblies: (a) with and (b) without CNB. (From Ikeda, T. et al., *Jpn. J. Appl. Phys.*, 50, 01AF13. Copyright 2011, The Japan Society of Applied Physics.)

introduced into the cathode. The polarization property was measured with a fuel cell impedance meter.

Figure 21 shows the I – V polarization curves of the DMFCs with and without the CNB. The current density was evaluated by the surface area of the MEA, and the I – P curves are also shown. The figure clearly shows that the DMFC performance was enhanced by adding the CNB. The resistivity of the CNB ($= 0.56 \Omega \cdot cm$) was much lower than that of the AcB ($= 31.8 \Omega \cdot cm$). The CNB material effectively improves the electric conductivity. The DMFC performance per catalyst weight was enhanced by about 15%, by adding the CNB into the electrodes in an MEA.

ELECTRIC DOUBLE-LAYER CAPACITORS

Electric double-layer capacitors (EDLCs) perform charge and discharge operations by the electric double layer that arises from the interface of an electrode and the electrolysis solution [31,32]. However, no oxidation–reduction reaction is formed from the charge and discharge process. Therefore, EDLCs are considered safe and robust. However, the energy density of EDLCs is 1/10 or less than that of the existing Li-ion battery [33]. Because the discharge amount of EDLCs depends on the electron transport between electrodes, the conductivity of electrodes is strongly related to the charge and discharge capability of EDLCs.

AcB was prepared using a twin-torch arc discharge apparatus [14,15,34]. CNB was obtained by heating AcB in a Tammann oven in Ar gas at $2400^\circ C$ for 2 h. In this study, we used a two-electrode cell with two coin-type electrodes for the electrochemical measurement of the EDLC [35]. First, 160 mg of AcB, 160 mg of CNB, and 40 mg of the conductive improvement agent (EC-600JD) were kneaded for 10 min using an automatic mortar, for use as the main material. Then, $45 \mu L$ of PTFE dispersion liquid was dropped into the main material and mixed for 15 min. Finally, 200 mg of the mixed material was placed into a jig (inside diameter: 20 mm). The jig was pressed at a pressure of 14 MPa for 30 min at room

TABLE 4
Summary of Characteristics of Arc Black and Carbon Nanotube

Material	Diameter (nm)	Specific Surface Area (m ² /g)	Conductivity (S/cm)	Differential Thermal Analysis Peak (°C)	G/D Ratio in Raman Spectrum	Structure
AC	1,000–20,000	2165	0.4	—	0.9	Micropore
AcB	20–50	153	0.2	620	0.9	Amorphous
CNB	20–50	35	1.8	760	1.3	Graphite shell

Source: Okabe, Y. et al., *Jpn. J. Appl. Phys.*, 52, 11NM05, 2013.

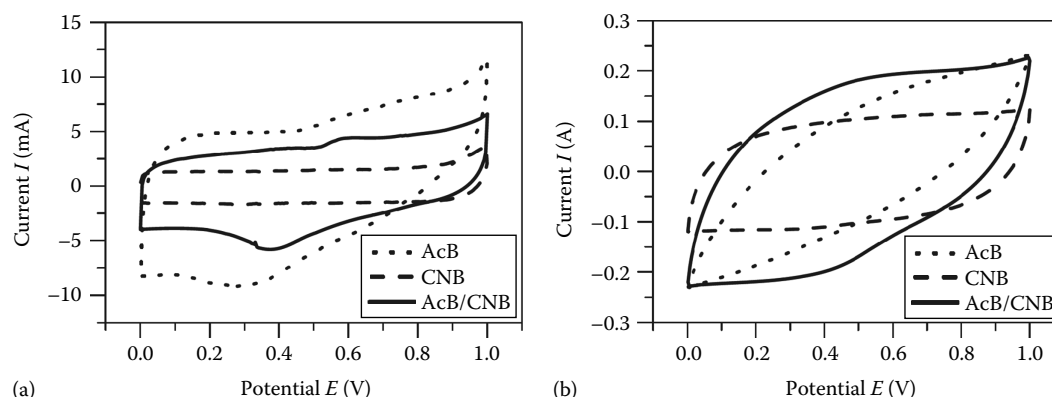


FIGURE 22 Cyclic voltammetry at (a) 1 and (b) 100 mV/s. (Okabe, Y. et al., *Jpn. J. Appl. Phys.*, 52, 11NM05. Copyright 2013, The Japan Society of Applied Physics.)

temperature. For comparison, four types of main material were prepared as follows: (1) 320 mg of AcB, (2) 320 mg of CNB, (3) a mixture of 213 mg of AcB and 107 mg of CNB, and (4) a mixture of 107 mg of AcB and 213 mg of CNB. Furthermore, for comparison with the activated carbon (AC), we prepared an electrode using 320 mg of AC as the main material [36]. The materials were placed into the cell in the following order: collector electrode, prepared electrode, separator, prepared electrode, and collector electrode. The cell was clamped at 100 N·m. The inside of the cell was filled with 1 M H₂SO₄ solution and left to stand for 60 min to enable the solution to penetrate the electrodes and separator. From CV, we calculated the specific capacitance, power density, and energy density [37].

The characteristics of AcB, CNB, and AC are summarized in Table 4. We observe that there is little difference between the sizes of AcB and CNB. The specific surface area of AcB calculated by the BET method was 152 m²/g. On the other hand, the specific surface area of CNB was 35 m²/g. The number of CNB micropores decreased because the surface of AcB was graphitized by heating.

Figure 22 shows the CV of EDLCs. At a scan rate of 1 mV/s, we observe that AcB shows a larger curve than CNB. However, at 100 mV/s, the curve of CNB is rectangular. The specific capacitances were calculated from the CV waveform at each scan rate. Compared with that of CNB, the specific surface area of AcB was large, and at a low scan rate, we obtained a specific capacitance that was larger than that of CNB. However, when the scan rate was increased, the specific

capacitances of AcB and CNB decreased. In particular, the specific capacitance of AcB decreased more rapidly than that of CNB. As a result, the specific capacitance of AcB became lower than that of CNB at scan rates of over 100 mV/s. The AcB/CNB weight ratio of 1:1 showed the highest specific capacitance when compared with those of 1:2 and 2:1. Figure 23 shows the electric power and energy densities of AcB/CNB compared with those of AC. AcB/CNB showed a higher electric power density than AC.

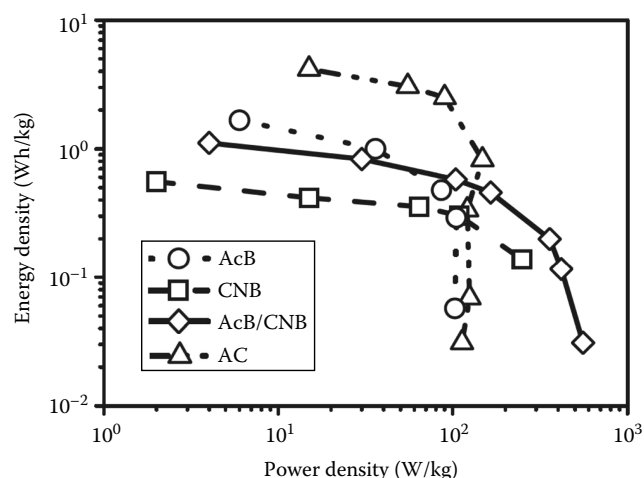


FIGURE 23 Ragone plots of electric double-layer capacitors compared with activated carbon. (Okabe, Y. et al., *Jpn. J. Appl. Phys.*, 52, 11NM05. Copyright 2013, The Japan Society of Applied Physics.)

CONCLUSIONS

We introduced various types of arc discharge apparatuses for the processing of carbon nanomaterials. Because of their unique properties, carbon nanomaterials can be applied to fuel cells, electric double-layer capacitors, field emitters, and hydrogen storage material.

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Battery: Nanobattery by Atom Trapping and Bottom-Up Technique

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INTRODUCTION

Nanobatteries have been widely studied and investigated by researchers in many areas [1–4], where the most important aspects of the required device are small size, long life, and high efficiency. To date, many types of thin-film battery (nanobattery) have been investigated and reported [5–8]. Many researchers have reported characteristics and applications of thin-film [9–12]. From the previous reasons, the major aspects of the expected device are small size with long-life operation and ease to use. Here, the optical thin-film battery is recommended to be a good candidate for such requirements [5]. However, a problem of the required nanobattery is the construction technique, which requires more reliable technique, where recently, Suwanpayak et al. [13] have reported the use of a PANDA ring for drug trapping and delivery applications, in which photons/atoms/molecules can be trapped and moved within an optical router.

Atom bottom-up technique is recognized as the great method that can be used to fulfill the scientific need. The platform of new materials and techniques is required to improve the device function and efficiency, especially, when the device dimension is decreasing to reach the nanoscale regime. To date, there are various techniques of atom bottom-up that have been reported [14–17], whereas the search for the appropriate method still remains. Therefore, in this work, we present the use of a trapping tool for moving atoms/molecules to form the atom delivery [18] and assemble within the desired position, where finally, the wavelength-selected tweezers are formed and the atom assembly within the proposed device (a thin-film grating) by using a PANDA microring resonator can be realized. The thin-film grating design is derived and the design device (nanobattery) discussed.

THEORETICAL BACKGROUND

By using the optical trapping tool generated by a PANDA ring resonator, which is well described by the authors in Refs. [13,19,20], in which the specified trapping tools (tweezers) can be generated and controlled, where in this work, atoms/molecules can be moved and embedded to the specified grating layers.

To start this concept, the proposed system consists of an add/drop filter and double nanoring resonators as shown in Figure 24a. To perform the trapping, dark and bright solitons are input into the add/drop optical filter system, whereas the input optical field (E_{in}) and the control port optical field (E_{con}) of the dark–bright solitons pulses are given by

$$E_{in}(t) = A \tanh\left[\frac{T}{T_0}\right] \exp\left[\left(\frac{z}{2L_D}\right) - i\phi(t)\right], \quad (1)$$

$$E_{con}(t) = A \operatorname{sech}\left[\frac{T}{T_0}\right] \exp\left[\left(\frac{z}{2L_D}\right) - i\phi(t)\right]. \quad (2)$$

where A and z are the optical field amplitude and propagation distance, respectively.

$\phi(t) = \phi_0 + \phi_{NL} = \phi_0 + \frac{2\pi n_2 L}{A_{eff} \lambda} |E_0(t)|^2$ is the random phase term related to the temporal coherence function of the input light, where ϕ_0 is the linear phase shift, ϕ_{NL} is the nonlinear phase shift, and n_2 is the nonlinear refractive index of *InGaAsP/InP* waveguide. The effective mode core area of the device is given by $A_{eff} L = 2\pi R_{ad}$, where R_{ad} is the radius of device, λ is the input wavelength light field, and $E_0(t)$ is the circulated field within the nanoring coupled to the right and left add/drop optical filter system as shown in Figure 24. T is a soliton pulse

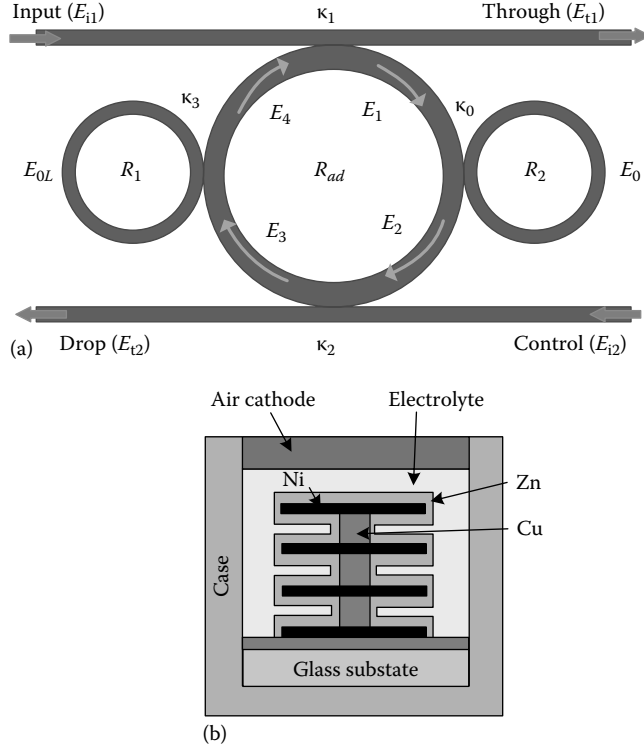


FIGURE 24 Schematic diagram of atom bottom-up assembly: (a) a PANDA microring resonator, which is pumped and controlled by light [21], and (b) bottom-up multilayer assembly P and N types design for nanobattery.

propagation time in a frame moving at the group velocity, $T = t - \beta_1 z$, where β_1 and β_2 are the coefficients of the linear and second-order terms of Taylor expansion of the propagation constant. $L_D = T_0^2 / |\beta_2|$ is the dispersion length of the soliton pulse. T_0 in equation is a soliton pulse propagation time at initial input (or soliton pulse width), where t is the soliton phase shift time and the angular frequency shift of the soliton is ω_0 . This solution describes a pulse that keeps its temporal width invariance as it propagates, and thus is called a *temporal soliton*. When a soliton peak intensity ($|\beta_2 / \Gamma T_0^2|$) is given, then T_0 is known. For the soliton pulse in the microring device, a balance should be achieved between the dispersion length (L_D) and the nonlinear length ($L_{NL} = 1 / \Gamma \phi_{NL}$), where $\Gamma = n_2 k_n$ is the length scale over which dispersive or nonlinear effects makes the beam become wider or narrower. For a soliton pulse, there is a balance between dispersion and nonlinear lengths, hence $L_D = L_{NL}$.

When light propagates within the nonlinear medium, the refractive index (n) of light within the medium is given by

$$n = n_0 + n_2 I = n_0 + \frac{n_2}{A_{eff}} P. \quad (3)$$

where

n_0 and n_2 is the linear and nonlinear refractive indexes, respectively

I and P are the optical intensity and the power, respectively

The effective mode core area of the device is given by A_{eff} . For the add/drop optical filter design, the effective mode core areas range from 0.10 to 0.50 μm^2 , in which the parameters are obtained by using the related practical material parameters *InGaAsP/InP*. When a dark soliton pulse is inputted and propagated within an add/drop optical filter as shown in Figure 24, the resonant output is formed. The resonator output field, E_{t1} and E_1 , consists of the transmitted and circulated components within the add/drop optical multiplexing system, which can perform the driven force to photon/molecule/atom.

When the input light pulse passes through the first coupling device of the add/drop optical multiplexing system, the transmitted and circulated components can be written as

$$E_{t1} = \sqrt{1 - \gamma_1} [\sqrt{1 - \kappa_1} E_{i1} + j\sqrt{\kappa_1} E_4], \quad (4)$$

$$E_1 = \sqrt{1 - \gamma_1} [\sqrt{1 - \kappa_1} E_4 + j\sqrt{\kappa_1} E_{i1}], \quad (5)$$

and

$$E_2 = E_0 E_1 \exp \left[-\frac{\alpha}{2} \frac{L}{2} - jk_n \frac{L}{2} \right]. \quad (6)$$

where

κ_1 is the intensity coupling coefficient

γ_1 is the fractional coupler intensity loss

α is the attenuation coefficient

$k_n = 2\pi/\lambda$ is the wave propagation number

λ is the input wavelength light field

$L = 2\pi R_{ad}$

R_{ad} is the radius of add/drop device

For the second coupler of the add/drop optical multiplexing system,

$$E_{i2} = \sqrt{1 - \gamma_2} [\sqrt{1 - \kappa_2} E_{i2} + j\sqrt{\kappa_2} E_2], \quad (7)$$

$$E_3 = \sqrt{1 - \gamma_2} [\sqrt{1 - \kappa_2} E_2 + j\sqrt{\kappa_2} E_{i2}], \quad (8)$$

and

$$E_4 = E_0 E_3 \exp \left[-\frac{\alpha}{2} \frac{L}{2} - jk_n \frac{L}{2} \right]. \quad (9)$$

where

κ_2 is the intensity coupling coefficient

γ_2 is the fractional coupler intensity loss

The circulated light fields, E_0 and E_{0L} , are the light field circulated components of the nanoring radii, R_r and R_L , which coupled into the right and left sides of the add/drop optical multiplexing system, respectively. The light field

transmitted and circulated components in the right nanoring, R_r , are given by

$$E_2 = \sqrt{1-\gamma} \left[\sqrt{1-\kappa_0} E_1 + j\sqrt{\kappa_0} E_{r2} \right], \quad (10)$$

$$E_{r1} = \sqrt{1-\gamma} \left[\sqrt{1-\kappa_0} E_{r2} + j\sqrt{\kappa_0} E_1 \right], \quad (11)$$

and

$$E_{r2} = E_{r1} \exp \left[-\frac{\alpha}{2} L_1 - jk_n L_1 \right]. \quad (12)$$

where

- κ_0 is the intensity coupling coefficient
- γ is the fractional coupler intensity loss
- α is the attenuation coefficient
- $k_n = 2\pi/\lambda$ is the wave propagation number
- λ is the input wavelength light field
- $L_1 = 2\pi R_r$
- R_r is the radius of right nanoring

The structure of zinc–air is formed by the multilayer zinc (anode)/air(cathode)/zinc(anode)/structure. Te on Im or insulator layer is used as “case” of nanobattery as shown in Figure 24b. A bottom-up multilayer is constructed by using P and N types, which is a Ni/Cu/Zn structure in this work, and the electrical current is biased on the surface; the zinc–air nanobattery is depicted schematically in Figure 24b. The anode structure, surrounded by an epoxy case that contains the electrolyte, is assembled with a commercially available air cathode (E4A with separator, electric fuel) consisting of three major layers. The top blocking layer comprises a laminated porous Te on Im that allows oxygen to diffuse in and prevent the battery from leaking electrolyte. The median layer contains the active cathode material, which is manganese-based catalyzed carbon supported by a woven Ni mesh. To complete the circuit in the testing stage, a copper wire is soldered to the edge of this Ni mesh after cleaning off the carbon. The bottom layer facing the electrolyte serves as a separator layer composed of a laminate of a polypropylene microporous Im with a thin polypropylene nonwoven that is made hydrophilic with a surfactant. This layer acts as an insulator between the anode and the cathode while allowing flow of ions in the electrolyte. Once the soldering is completed, the cut edges of the air cathode are sealed with epoxy. The cathode area is important in the sense that it regulates the oxygen transfer to the electrolyte. For the sake of consistency, air cathodes with the same surface area are utilized for both thin- Im and multilayer batteries. A 7M aqueous KOH solution to be used as the electrolyte was injected into the assembled nanobattery following a vacuum treatment. The vacuum treatment ensures the removal of the air trapped deep in between the laminated layers and thus provides a perfect contact between the electrolyte and the whole Zn anode surface.

As already noted, the strong isotope effect as well as the strong effect of potential P_{Zn} and thickness on the conductivity is consistent with a proton-tunneling mechanism for the transport of protons on the wall surfaces of nanobattery. The tunneling distance is of the order of the proton wavelength, which is again of the order of 0.2×10^{-10} m for proton energies of the order of 1 eV. The proton-tunneling probability, which determines the current density, depends on the local environment of the proton in its Poisson-Boltzmann (PB) cloud, which is practically unaffected by the field strength $\Delta U/L$. In fact, it can be shown that the tunneling current density is given by

$$i = \frac{k_b T}{h} C_{H^+} F \ell_T^* P_T \Theta_{H^+} (1 - \Theta_{H^+}), \quad (13)$$

where

- Θ_{H^+} is the fraction of sulfonate groups with a proton counterion, that is, with a proton localized in their Debye-Huckel (DH) cloud
- k_b is the Boltzmann constant
- T is the thermal effect (K)
- ℓ_T^* the average distance between two adjacent sulfonate groups (connected with the main polymer chain via exible ether bonds and the tunneling probability)
- P_T is given by the Gamow equation [21]

$$P_T = e^{-(\pi^2/\hbar)r_T[2m(E^0-E)]^{1/2}}. \quad (14)$$

Both the tunneling distance r_T and the energy barrier $E^0 - E$ can be computed using the Debye–Huckel theory [22]:

$$r_T = \kappa^{-1} v^{1/2}, \quad (15)$$

$$E^0 - E = e_0 \left[\Phi v^{1/2} e^{-v^{1/2}} + \Phi v \right]. \quad (16)$$

Here, the potential Φ is given by

$$\Phi = \frac{me_0^3}{\epsilon^2 \hbar^2}, \quad (17)$$

and m is the proton mass. The dimensionless proton potential v is defined from

$$v = \frac{-U_p}{\Phi}. \quad (18)$$

Since i does not vary linearly with the field $\Delta U/L$, it follows that σ will be proportional to L :

$$\sigma = \frac{k_b T}{h} C_{H^+}^0 F \ell_T^* P_T \frac{L}{U} \Theta_{H^+} (1 - \Theta_{H^+}), \quad (19)$$

where U equals the open-circuit potential U_{rev} for fuel cell operation and the applied potential ΔU for symmetric multilayer nanobattery.

ATOM BOTTOM-UP MANIPULATION

By using the proposed design, atoms/molecules can be trapped and transported via the optical waveguide [13,19,20]. In this work, a thin-film nanobattery as shown in Figure 24 can be constructed by using the atom bottom-up assembly. Simulation results of the atom-trapping manipulation within the PANDA ring are as shown in Figure 25. In this case, the Gaussian-modulated CW is input into the control port. The parameters of a PANDA microring are $R_{ad} = 10 \mu\text{m}$, $R_1 = 4 \mu\text{m}$, and $R_2 = 4 \mu\text{m}$, in which the evidence of the practical device was reported by the authors in Ref. [23].

In this case, the dynamic light pulses (tweezers) can be in the form of Gaussian pulses as shown in Figure 25; the dynamic pulse is generated at a center wavelength of $1.55 \mu\text{m}$, which can be used to trap the required atom. The transported pulses are as shown in Figure 25.

In operation, the trapped P-type and N-type atoms are required to embed within the specified thin-film grating. By using the through port signal for trapping as shown in Figure 25, the bottom-up two-cell assembly P and N types of thin-film nanobattery design can be constructed. The selected tweezers and atoms can be used to allocate the required thin-film layers. The atom trapping and embedding

can be used to assemble atoms within the thin-film grating, where in the case of many atoms, trapping and assembly can also be available as shown in Figure 26. In Figure 26a, the atom manipulation output is generated by the output port (through) of a PANDA ring resonator as a function of wavelength that is used as light source pump in the nanobattery. When the light source is pumped into the nanobattery, the dynamic of atom bottom-up manipulation outputs is detected at the P type, and N type of nanobattery decreased because the atom absorption is made by the nanobattery as shown in Figure 26b and c. In Figure 27, the selected wavelength tweezers for trapping and controlling the single-atom bottom-up assembly controlled by light are shown, where (a) is the selected wavelength at $1.5800 \mu\text{m}$. In this proposal, the single atom is trapped and controlled within thin-film nanobattery by the selected wavelength at $1.5811 \mu\text{m}$ and $1.6524 \mu\text{m}$ for the P-type and N-type, respectively. In application, the trapped P-type and N-type atoms can be embedded within the thin-film grating layers by using the transporter, and the thin-film battery is formed.

The discharge data are also used to calculate the areal energy density E of the battery, which is determined to be in $2 \mu\text{A}/\text{cm}^2$ as shown in Figure 28. To determine the areal

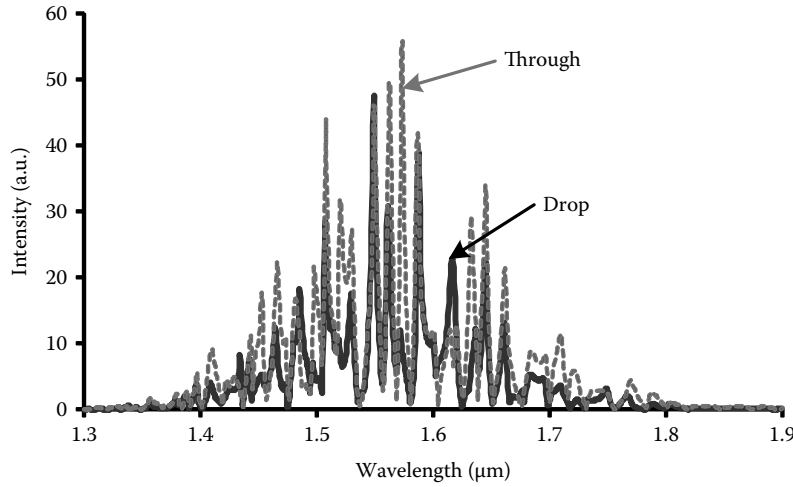


FIGURE 25 Simulation results of the optical trapping tool using a PANDA microring resonator in both through port and drop port signals.

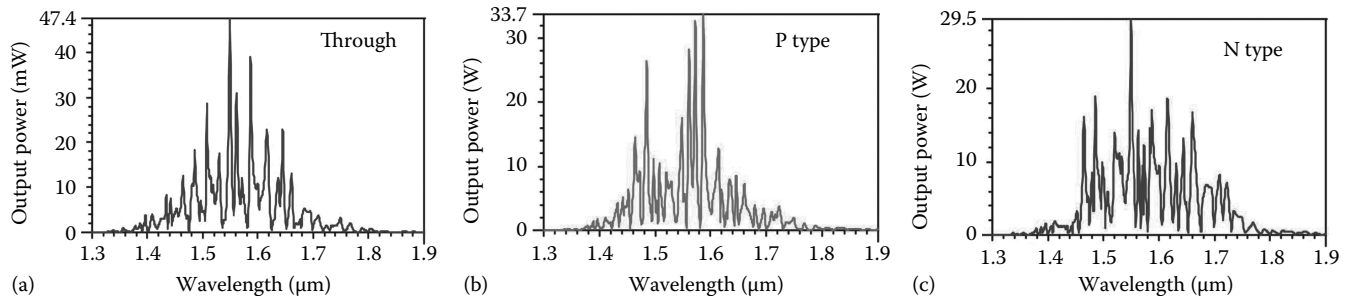


FIGURE 26 Dynamic results of atom bottom-up assembly controlled by light: (a) output at through port, (b) output at P type, and (c) output at N type.

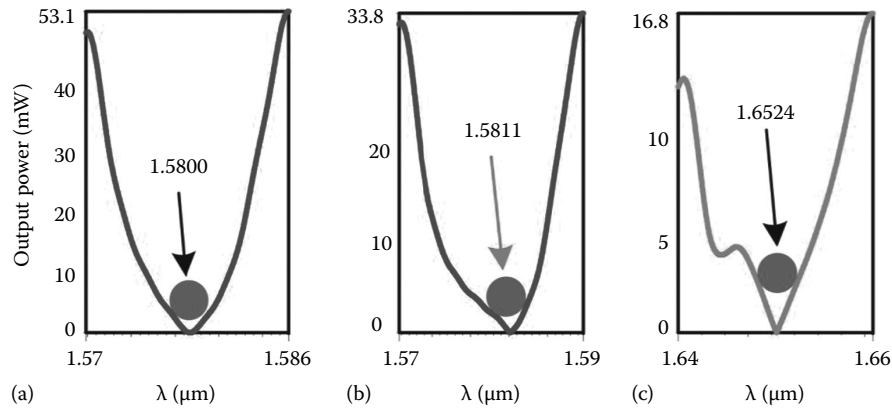


FIGURE 27 Simulation results of atom bottom-up assembly controlled by light: (a) through port pump signal at 1.5800 μm , (b) single-atom trapping at 1.5811 μm for P type, and (c) single-atom trapping at 1.6524 μm for N type.

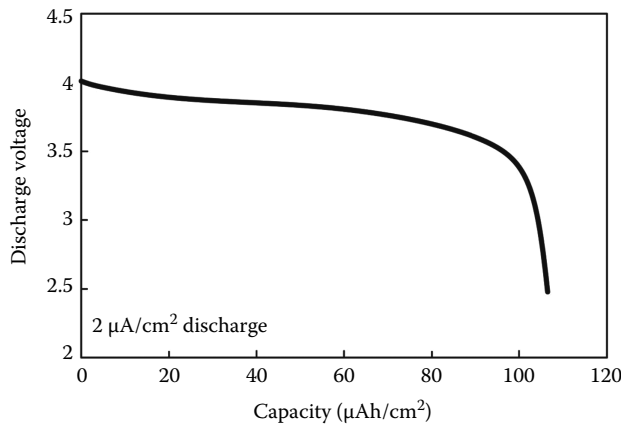


FIGURE 28 The capacity data for discharge nanobattery.

energy density of the zinc–air battery, first, its capacity Q in milliampere-hours is calculated by taking the integral of the discharge current I_d over time t . The capacity is then multiplied by the average discharge voltage V_{av} and divided by the footprint area A to give the areal energy density [24]:

$$Q = \int I_d dt, \quad (20)$$

$$E = \frac{QV_{av}}{A}. \quad (21)$$

The calculated areal energy densities for a sample with 10 layers and $1.5 \times 1.5 \text{ mm}^2$ footprint area, as well as with 50 layers and $3.7 \times 1.8 \text{ mm}^2$ footprint area, are used. A discharge characteristic of the zinc–air microbatteries under electrical capacity is illustrated in Figure 29. The discharge curves maintain relatively flat voltage profiles over time, with a small voltage decrease right after the start-up and a sharp voltage decrease near total discharge.

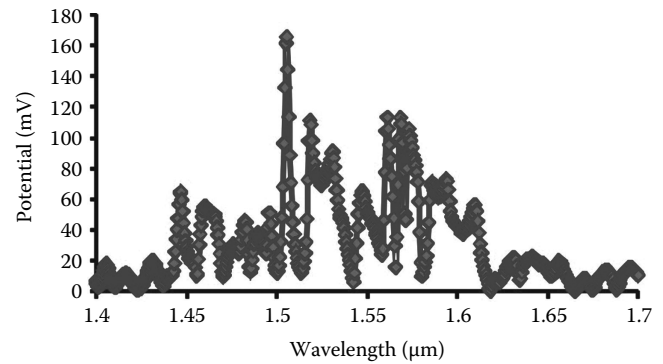


FIGURE 29 Typical charge/discharge cycles for an individual nanobattery. The batteries were charged at a constant current 20 μA and discharged at a constant current of 2 μA .

CONCLUSION

In this chapter, we have proposed the use of a trapping tool for atom trapping, delivery, and embedding, which can be later trapped within a thin-film grating. The selected atoms/molecules can be trapped and moved and then filtered and embedded within the required thin-film grating layers, where finally, the nanobattery operation can be realized. In principle, required atoms (P or N type) can be trapped and confined within the required region (layers). The Fabry–Perot multilayer cavity is used to explain the confinement and storage energy of the zinc–air nanobattery. The materials such as lead, cobalt, platinum, silver, and metamaterial can be used as anode or cathode. Finally, the nanobattery construction based on thin-film grating using a PANDA microring resonator that is pumped and controlled by light can be realized.

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Biomimetics: Biomimetics in Nanotechnology

Ille C. Gebeshuber and Manfred Drack

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INTRODUCTION

This chapter deals with the biomimetic method in nanoscience and nanotechnology. Predictability on the basis of scientific understanding is a precondition for technology. The aims of science are to *explain* and *understand* and to *organize knowledge*. With a solid scientific basis, it shall be possible to *make predictions*, for example, about the movement of planets or asteroids, molecules, water flow around pillars, or emergent properties such as bird flocking patterns and swarm intelligence in ants. To achieve this, various techniques and methods are applied.

Nanoscience and nanotechnology tools and techniques have rapidly developed since the 1980s. Current tools and techniques for characterization, manipulation, and fabrication of matter at the nanoscale are manifold. The four major groups of nanoscale probing tools are scanning probe microscopy, (including scanning tunneling microscopy, atomic force microscopy (AFM), and scanning near-field optical microscopy), as well as electron microscopy, x-ray methods, and optical techniques (Bhushan 2010). The core tool, the AFM, was invented in 1986 (Binnig et al. 1986). This lenseless microscope has subnanometer resolution, can be used for imaging as well as *manipulation* down to the single atom level, and works in various environments such as vacuum, air, water, buffer solutions, and oil (Haugstad 2012). This makes it so interesting for applications regarding the investigation of biological samples (Parot et al. 2007). Even live cells (Henderson 1994) or protein–protein interactions on the single protein level can be imaged with this device in real time at unprecedented resolution (Viani et al. 2000).

Nanotechnological *products and processes* can be developed on the grounds of nanofabrication (lab scale), molecular manufacturing (manufacture of complex nanoscale structures by means of nonbiological mechanosynthesis and subsequent assembly), and nanomanufacturing (industrial scale) (Bhushan 2010). In such products and processes, nanotechnology can be embedded in numerous aspects of the manufacturing processes. While the physics itself is the same across all length scales, materials and structures have unique size-dependent properties (that may be very different from the properties of bulk material). Also, the smaller the size, the more relevant the structure of the material becomes. Single atoms, molecules and nanostructures exhibit unusual physical, chemical, and biological properties when compared to the bulk material. Gold, for example, has golden coloration at the macroscale and is known as a highly inert material; nanogold colloids, however, exhibit different colors at different sizes and concentrations, and they are not bio-inert (Brown et al. 2008).

The ideas for new nanotechnological products and processes are often rooted in physics or inorganic chemistry. There is, however, also a considerable and expanding body of knowledge at the nanoscale in biology. Such knowledge about materials, structures and functions in living nature can be applied in different ways. One possibility is to use macromolecules or organisms directly, like in biotechnology. Another way is to strive for the understanding of principles behind particular phenomena and to apply them in distinct areas, like in biomimetics. The following focuses on biomimetics.

What we describe here is perhaps a small but probably significant method for nanotechnology, because the role models

that can be found in living nature have been tested in evolution since billions of years.

COMMON GROUND OF BIOMIMETICS AND NANOTECHNOLOGY

Most often biology and engineering do not touch on each other (Figure 30). There is, however, an intersection of both elds. Different disciplines are found in this intersection, such as the two distinct elds of biotechnology and biomimetics. Biotechnology is not our concern here; we only deal with biomimetics. The intersection itself can be sliced into pieces according to their scale. By doing so, the eld discussed in this chapter can be illustrated like in Figure 30.

In the following, the elds of biomimetics and nanotechnology are characterized in order to investigate how the former can contribute to the latter.

WHAT IS BIOMIMETICS?

Biomimetics is about transferring principles from biology to engineering to enhance and bring up new products and processes for human needs. Although the name and the scientific eld were only established in the last decades, the method is an old one. Leonardo da Vinci and his studies of bird flight, for example, eventually have led to airplanes. At the end of the twentieth century, the eld of biomimetics became established both methodically and institutionally, leading to an ever-increasing number of applications.

In this recent definition, the main aspects are covered: “Biomimetics combines the disciplines of biology and technology with the goal of solving technical problems through the abstraction, transfer, and application of knowledge gained from biological models” (VDI 6220 2012).

At the core, biomimetics is about understanding functional or operational principles that are at work in biology and results in the abstractions of them in order to find out if they might also work in engineering. This procedure is different from biotechnology, which is not necessarily about transferring principles.

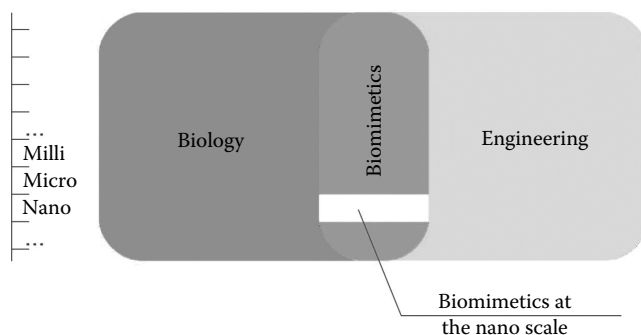


FIGURE 30 Biomimetics and biotechnology are some of the few areas at the intersection of engineering and biology. Biomimetics at the nanoscale is a small but probably significant method in nanotechnology.

Biomimetics works because biological and engineering entities are part of the same world and therefore underlie the same natural laws. Hence, principles in living organisms can also work in technical applications. Nevertheless, there are large differences between entities from the respective elds. One difference is the development throughout which a fertilized egg turns into an embryo and eventually into a mature organism. This is completely different from production devices or machines in engineering. Another difference is that every machine has its engineer who builds it, whereas organisms do not. But this paradigm is slowly changing, with the development of engineered self-replicating machines (see, e.g., Griffith et al. 2005).

Basically, two ways of working in biomimetics can be distinguished. They are referred to as technology pull (also called top-down biomimetics and biomimetics by analogy) and biology push (also called bottom-up biomimetics and biomimetics by induction) (see, e.g., Gebeshuber and Drack 2008).

Technology pull biomimetics is problem based: it starts with a problem in engineering. The next step is to see if similar “problems” occur in living nature. Drag reduction, for instance, is a problem for ship builders and similarly for fish. After such equal problems are found, the biological role models are investigated with the tools and methods of engineering. The term “technical biology” (*Technische Biologie*) was introduced by Nachtigall to name this methodical part of biomimetics (cf. Nachtigall 1998). In the drag reduction case, for example, the engineer would measure relevant parameters of the fish and look at the surface, shape, and so on. In doing so, the researcher might find interesting features, so far not thought about in engineering. The process of finding out more about the principles starts with the potential result of an abstraction that can be transferred and applied in human-built devices or machines.

Biology push biomimetics starts with basic research in biology, without having an application in mind. During or after such work, it might turn out that the found results are also useful for engineering (solution-based biomimetics). The found principles are then transferred and applied.

Technology pull, in general, has a large potential for finding within a short time principles that are useful for particular problems. Utilization of such principles is usually restricted to a small area of application. In contrast, biology push biomimetics has a lower potential for immediate applications, but the chance for finding revolutionary or generic principles is much higher.

Whether a product or technology is the result of biomimetics or not follows from the description of the method. Three necessary conditions have to be fulfilled (i.e., answered with yes) to legitimately speak about biomimetics (Frey et al. 2011, VDI 6220 2012):

1. *Role model from biology*: Did the inspiration come from living nature (biology)?
2. *Abstraction from biological role model*: Was there an abstraction (of a principle) of the natural role

model? Was the biological knowledge analyzed and abstracted step by step (with an understanding of the principle)?

3. *Transfer to technical application:* Was the principle applied in engineering?

The scope of biomimetics is broad. Most of the established knowledge transfer was done in the field of constructions. However, processes in living nature are also of interest, for example, photosynthesis. Furthermore, information processing like in neuronal networks or optimization with genetic algorithms can be referred to as biomimetics (Gruber et al. 2011).

As we have seen, research in biomimetics can lead to applications in engineering. Additionally, the process of doing biomimetics can also reveal new insights for biology, besides those accomplished with technical biology. This can be termed as reverse biomimetics (cf. Masselter et al. 2012, p. 380). One example is the evolutionary strategy of Rechenberg (1994). He introduced algorithms for optimization in engineering based on the concepts of mutation, selection, and recombination from evolutionary biology and achieved good results in engineering. Analyzing those algorithms in turn was of interest for evolutionary biology (cf. Wagner and Altenberg 1996).

WHAT IS NANOTECHNOLOGY?

According to ISO definition ISO/TS 80004-1:2010, nanotechnology is the “application of scientific knowledge to manipulate and control matter in the nanoscale [...] in order to make use of size- and structure-dependent properties and phenomena, as distinct from those associated with individual atoms or molecules or with bulk materials.” In a note to this entry, ISO states that manipulation and control includes material synthesis. Nanotechnology has functional parts in the range of nanometers to some hundreds of nanometers. The rise of nanotechnology began when we were able not just to image but also to manipulate matter on the nanometer scale. These possibilities were greatly enhanced with the increasing availability of scanning probe microscopes for the scientific community (Meyer et al. 2004/2012). One of the early examples of nanotechnological manipulation is the spelling of the company name IBM by Don Eigler and coworkers from IBM Almaden with just 35 xenon atoms on a single-crystal nickel surface (Eigler and Schweizer 1990). The group thereby demonstrated tailored manipulation of single atoms.

The two major approaches for obtaining nanotechnological products and processes are termed *top down* and *bottom up* (not to be confused with the terms as used in biomimetics).

In top-down approaches, nanoobjects are constructed from larger entities without atomic-level control. Top-down approaches comprise lithography, deposition, and etching. In bottom-up approaches, materials and devices are built from

molecular components that assemble themselves chemically by principles of molecular recognition. Bottom-up methods include (self-)assembly of atomic and molecular building blocks to form nanostructures. This method is widely used in sol-gel and chemical vapor deposition. In nature, self-assembly has existed for billions of years, from simple biomolecules to complete organisms.

Gebeshuber et al. (2010)

The history of nanomaterials can be dated back to pre-Columbian times: The first permanent organic blue pigment, Maya Blue, is a result of ancient “nanotechnology” (Chiari et al. 2008). Further examples of historical nanomaterials are the Lycurgus Cup in the British Museum, dating back to the late Roman Empire, and stained glasses in Medieval Europe (Francis 2010). Properties of nanomaterials are responsible for the respective effects described in this paragraph. It remains to be discussed if it is justified to call such ancient approaches “nanotechnology,” since the people back then did not know the reason for the respective material properties.

In general, nanoscience deals with research on materials, structures, and processes on the nanometer scale, and nanotechnology deals with the development of materials, structures, and processes where the functional units are in the nanometer range (generally from a few nanometers to some hundreds of nanometers). Nanoscience and nanotechnology can rather be associated with tools, techniques, and methods than with established research fields. Most research in these fields is rather interdisciplinary and touches upon pure and applied mathematics, physics, chemistry, materials science, engineering, and life sciences. The methods, concepts, and goals of the respective fields converge. This inherent interdisciplinaryity of nanotechnology poses a challenge and offers an enormous potential for fruitful cross-fertilization among specialist areas. The properties of many materials change when they exist as nanosized particles. Besides the chemistry, surface physics becomes increasingly important, and not just the material itself but also its structure is of relevance for its mechanical, electrical, catalytic, optical, and toxic properties. Furthermore, quantum effects such as the tunneling effect, confinement properties, spin effects, and quantum coherence are important.

The scope of nanotechnology is to individually address, control, and modify structures, materials, and devices with nanometer precision and to synthesize such structures into systems of micro- and macroscopic dimensions such as microelectromechanical systems-based devices. For this, we need to establish a thorough understanding of the fundamental physics, chemistry, biology, toxicology and technology of nanoscale objects (nanomaterials, nanoparticles, nanostructures), the respective fabrication, diagnostics and analytics and of how such objects can be used in areas such as computation, cosmetics, engineering, medicine, nanobiotechnology, nanostructured materials, optics, resource sustainability, science, sensors, textiles, and many more.

FIELDS OF COMMON POTENTIAL

Phenomena of life occur on different hierarchical levels, down to the nanoscale. The micro- and nanoscale are of special importance in living systems. Single molecules, their interactions, and emergent properties on larger length scales are the very constituents of life. The complexity of a single cell in the human body by far exceeds any current engineered device. A cell's activities such as sensing, actuation, energy conversion, or information storage are carried out with the contribution of biomolecules, such as proteins. Protein sizes range from about 1 to about 20 nm; there are millions of different proteins. Biological materials are amazing: there are tough materials, "smart" materials, adaptive materials, functional materials, materials with molecular precision, hierarchical materials, and multifunctional materials. Many functionalities on the macroscale are based on functionalities on the nanoscale. The more we understand and abstract deep principles of biology on these length scales, the more successful can the biomimetic method transfer knowledge from materials, structures, and processes in living nature to engineering, for independent technological applications and devices.

With increasingly powerful microscopes, researchers have started to see amazing order, structure, and functionalities of biological materials, down to very small scales. Biomolecular "machines" such as the ribosome, built with atomic precision (Yusupov et al. 2001), powerful composites such as the Abalone shell (Smith et al. 1999) or the crystal eyes of brittle stars (Aizenberg et al. 2001), biomineralized beautifully structured little gems such as diatoms (Gebeshuber and Crawford 2006, Round et al. 1990/2007), optimized biotribological properties, for example, decreasing the friction coefficient to numbers so low that lubrication engineers are amazed (Gebeshuber 2007) and functional surfaces with nanoscale properties responsible for exciting tricks such as increased antireflective properties (Stavenga et al. 2006) or iridescent coloration in plants and microorganisms based on nanostructures (Gebeshuber and Lee 2012) are just some examples for the properties of organisms that are also interesting for engineering.

Currently, merging of nanoscience and nanotechnology with the life sciences, especially biology, biotechnology, biomimetics, nanomedicine, genetic engineering, and synthetic biology, can be recognized (see, e.g., Bainbridge 2007, Chen and Ho 2006, Ulvick 2010). This new and emerging field with enormous creative potential is called nanobioconvergence.

Andreas Lymberis from the European Commission, Information Society and Media Directorate-General, describes converging micro- and nanobiotechnologies toward integrated biomedical systems as

research and development at the convergence of microelectronics, nano-materials, biochemistry, measurement technology and information technology that is leading to a new class of biomedical systems and applications, e.g., molecular imaging, point of care testing, gene therapy and bionics (including on and inside the body sensors and other miniaturised smart systems) which are expected to revolutionise the healthcare provision and quality of life. In particular they are expected

to identify diseases at the earliest possible stage, intervene before symptomatic disease becomes apparent and monitor both the progress of the diseases and the effect of intervention and therapeutic procedures.

Lymberis (2008)

Nanobioconvergence is an emerging field, and no rigid definition has been established yet. One potential definition is the following: "Nanobioconvergence denotes the merging of life sciences, especially biology and biotechnology, with nanoscience and nanotechnology, focusing on the technical output from the connections of these particular fields as well as on the unified opportunities and challenges they present to human nature and our values" (Gebeshuber et al. 2013). Biotechnology (genetic engineering, engineering of proteins, etc.), bionanoscience (focusing on molecular building blocks of living cells), and biomimetics form important constituents of nanobioconvergence. Biomimetics can be done on many length scales, but because of the hierarchical organization of organisms, with many properties based on functionalities originating from the nanoscale, biomimetics is especially rewarding when taking into account nanoscale properties of life.

Since all these fields are currently emerging, there is still a lot of defining and categorizing going on. What one set of researchers would place in biotechnology, others categorize as biomimetics. Research toward producing spider silk is a case in point. The categories can also change with time. Sarikaya and coworkers, for example, wrote in their 2003 paper "Molecular biomimetics: nanotechnology through biology" (Sarikaya et al. 2003): "Molecular biomimetics is an emerging field in which hybrid technologies are developed by using the tools of molecular biology and nanotechnology. Taking lessons from biology, polypeptides can now be genetically engineered to specifically bind to selected inorganic compounds for applications in nano- and biotechnology." Eight years later, the group reports the fabrication of hierarchical hybrid structures using bioenabled layer-by-layer self-assembly, functional hybrid nanomaterials with well-defined hierarchical and spatial organization (Hnilova et al. 2012)—something one would nowadays rather call biotechnology than biomimetics.

Biomimetic techniques applied to nanotechnology comprise technology pull and biology push. Examples for biomimetics in nanotechnology are principles of self-assembly (Valéry et al. 2003), self-repairing materials (dynamic breaking and repair of "sacrificial" bonds) (Fantner et al. 2005), bioinspired sensors (Barth et al. 2012), mass production of nanostructures (Guozhong and Ying 2011), and artificial photosynthesis (Razeghifard 2013).

On a more abstract level, Werner Nachtigall, the doyen of biomimetics in Germany, identified 10 general principles of biomimetics that can be applied by everybody working in the field, even by people who are not (or who do not want to be) involved in biology at all (Nachtigall 2009). These principles are as follows:

1. Integration instead of additive construction
2. Optimization of the whole instead of maximization of a single component feature

3. Multifunctionality instead of monofunctionality
4. Fine-tuning regarding the environment
5. Energy efficiency
6. Direct and indirect usage of solar energy
7. Limitation in time instead of unnecessary durability
8. Full recycling instead of piling waste
9. Interconnectedness as opposed to linearity
10. Development via trial-and-error processes

Nachtigall's general principles are of high relevance for biomimetics that draws its inspiration from nanoscale properties of living matter. One example for "fine-tuning regarding the environment" is navigation in honeybees. These animals orient themselves with the help of the polarization of the skylight. Abstraction of the deep principles of polarized skylight-based navigation leads to the development of technical navigation systems (produced with micro- and nanofabrication techniques) that are completely independent from the normally used GPS systems (reviewed in Karman et al. 2012).

Biomimetics at the nanoscale has as integral parts abstraction of the principles of the investigated nanomaterials, nanostructures, and nanoprocesses, followed by principle transfer to nanotechnology. In the remainder of this section, we illustrate in two examples the technology pull and biology push methods of biomimetic nanotechnology.

TECHNOLOGY PULL

The Carinthia University of Applied Sciences in Austria offers the MSc course "Biomimetics in Energy Systems." One of the authors of this chapter (ICG) supervised the MSc thesis "Biomimetic potential of sponge spicules" by Ehret (2012). The work performed in this thesis shall now serve as an example for "technology pull." Bioinspired improvement of daylight-guidance systems in buildings was the problem in engineering on which the thesis is based. Glass sponges (animals) were selected as model organisms with similar "problems" in living nature. The silica spicules of glass sponges serve as light guides, providing light to the photosynthesizing microorganisms and algae that live in close association with the "glass fiber" in the interior from the sponge. Detailed description of investigations of the biological role model, the glass sponges, with tools and methods from engineering, including dynamical mechanical analysis, light transmission studies, and the propagation of ultra short laser pulses, lead to the following abstractions that can subsequently be transferred to engineering: self-assembly of metal oxides on functionalized surfaces, the manufacturing of layered organic-inorganic composites with enhanced mechanical properties, and the tuning of optical and mechanical properties by means of nanostructuring and hierarchical architecture. Application of these abstractions in construction of daylight-guidance systems shall yield more conveniently illuminated workspaces in offices proof (Figure 31).

BIOLOGY PUSH

One example for successful "biology push" is nanoscale structures on moth eyes (Figure 32). The eyes of certain moths are covered with nipple-like arrays, which basic biological research revealed to be antireflective (Vukusic and Sambles 2003). The nipple array gradually matches the optical impedance of one medium with that of its neighbor across the interface. Such a property is of paramount interest in engineering applications, for example, for lens surfaces of camera and photographic equipment. Principle transfer to engineering is straightforward, since the property in question is dependent on the structure rather than on the material. Man-made similar nanofabricated structures (Reonexite™) yield amazing antireflective properties in a wide bandwidth, from 400 to 700 nm (Boden and Bagnall 2006, Figure 32).

REVERSE BIOMIMETICS

Prominent examples for reverse biomimetics at the nanoscale remain to be seen. Nevertheless, there is a considerable potential for such examples. Though not in the realm of reverse biomimetics, the discovery of the mechanism of ATP production in mitochondria can serve as an illustration. ATP is a universal carrier molecule of energy in organisms. Peter D. Mitchell proposed the chemiosmotic theory to explain how ATP production could work, for which he received the Nobel Prize. For the production of ATP, an electrochemical (proton) gradient across the membrane of the mitochondrion was proposed. Experiments to support this theory were performed by Racker and Stoeckenius (1974). They artificially "built" vesicles that contained ATPase (the enzyme that catalyzes the decomposition of ATP into ADP and a free phosphate ion) in their membranes and through some other means they provided for a proton gradient. The arrangement of these components turned out to be causally sufficient to explain the processes in the organism (Weber 2005). Similarly, one can think of future examples where, by building of biomimetic nanoproducts, knowledge can be gained in biology.

METASCIENTIFIC CONSIDERATIONS

In this section, we deal with further considerations that are deemed important when describing biomimetics in nanotechnology: the goal and future of nanotechnology, ethical, legal, and social issues (leading to governance and risk research) and educational as well as accessibility issues in an age of converging technologies.

According to the Foresight Institute (Palo Alto, California), the goal of nanotechnology is "to improve our control over how we build things, so that our products can be of the highest quality [...] while causing the lowest environmental impact." (Foresight Institute 2015). However, it needs to be ensured that nanotechnology that is intended to cause the lowest environmental impact is not only upfront "green" with negative side effects on ourselves, further organisms, and the environment. Some human actions and technological developments might

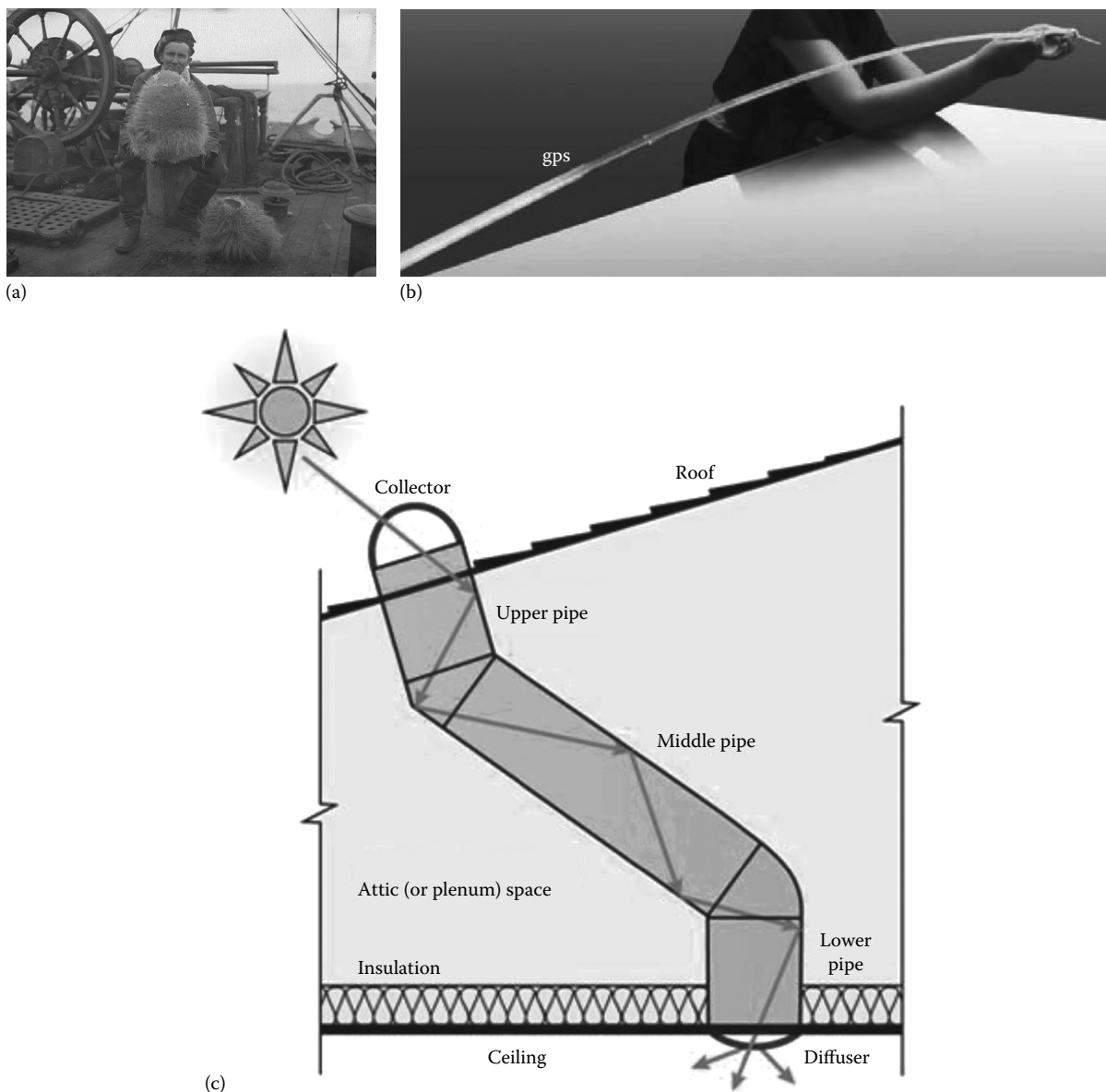


FIGURE 31 (a) A member of the 1910–1913 British Arctic expedition with a glass sponge. Some glass sponges have hydrated silica spicules that are 3 m long. Based on functionalities on the nanoscale, such spicules can be very effective fracture-resistant light guides. (Copyright Ponting Collection, Scott Polar Research Institute, Cambridge, U.K., <http://www.spri.cam.ac.uk/>.) (b) The largest biosilica structure on Earth: the giant basal spicule from the deep-sea glass sponge *Monorhaphis chuni*. (Reproduced from Wang, X. et al., *Evid. Based Compl. Altern. Med.*, 540987, 14, Copyright 2011. With permission.) (c) Principle of daylight guiding in buildings. (Copyright Dr. Aziz Laouadi, National Research Council Canada, Ottawa, Ontario, Canada.)

have short-term benefits on the environment, but come with unforeseeable long-term effects that are hard and impossible to predict for the complex system we are all embedded in.

The progress of nanoscience and nanotechnology is accompanied by important ethical, health, environmental, and social issues. Because of the huge envisaged impact of science and technology on society, increasingly also social scientists and technology assessment specialists deal with nanoscience and nanotechnology. Prospects, problems, and potential risks require focused consideration by third parties such as parliaments, NGOs, sociologists, philosophers, insurance companies, law enforcement agencies, or scientific researchers from other fields.

Technological, environmental, societal, health, and safety issues must be addressed in research, societal studies, regulatory measures, and government policies (Holsapple et al. 2005, Holsapple and Lehman-McKeeman 2005, Huber 2010, Powers et al. 2006, Thomas and Sayre 2005, Thomas et al. 2006a,b, Tsuji et al. 2006).

Societal implications of nanoscience and nanotechnology should be judged using a balanced approach between the potential achievements (leading to envisioned societal benefits) and potential hazardous consequences (which could be a combination of unexpected benefits and risks) (Roco 2003).

“Futures” in terms of visions, expectations, scenarios, fears, and hopes increasingly dominate science outreach and the

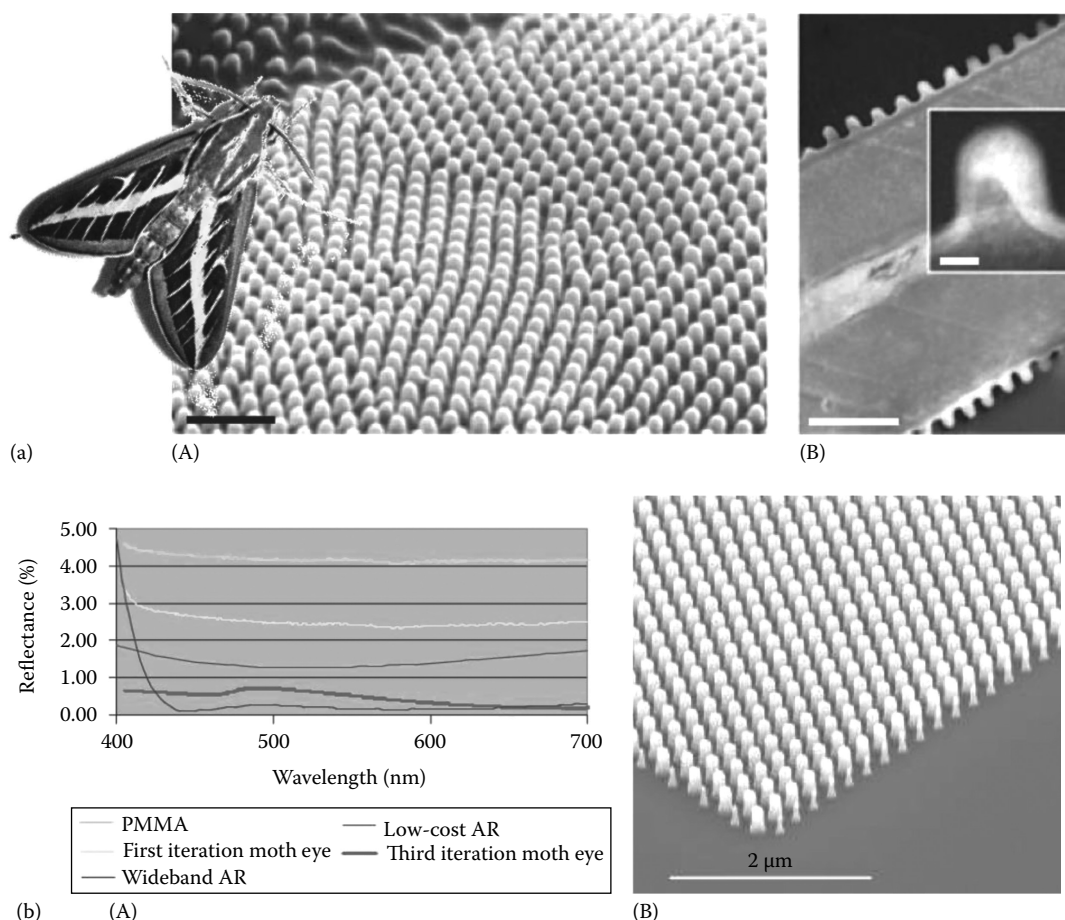


FIGURE 32 Antireflective surfaces on moth eyes (a) and the respective engineered biomimetic antireflective structures (b). (a): (A) SEM of a moth eye, showing nipple-like structures. *Inset*: Moth. Scale bar, 1 μm . (B) Similar structures on transparent wings of hawkmoths. Scale bar, 1 μm . *Inset*: Single nipple. Scale bar, 100 nm. (b): (A) Reflectance measurements on engineered antireflective surface structures. For the surface called “third iteration moth eye,” reflectance is below 1% for the whole spectrum that is visible to humans. (B) Biomimetic structure, machined in silico. Scale bar, 2 μm . (a): Reproduced by permission from Macmillan Publishers Ltd. *Nature*, Vukusic, P. and Sambles, J.R., Photonic structures in biology, 424, 852–855, Corrigendum in *Nature*, 429, 680, Copyright 2003; b: Boden, S.A. and Bagnall, D.M., Biomimetic subwavelength surfaces for near-zero reflection sunrise to sunset, *Proceedings of the Fourth IEEE World Conference on Photovoltaic Energy Conversion*, Waikoloa, HI, pp. 1358–1361, 2006 © IEEE.)

drive and motivation of scientists (Grunwald 2007). Futures are socially constructed. Especially concerning nanoscience and nanotechnologies, the ongoing debate is very much a debate about futures. The visions for the future of nanotechnology have a wide bandwidth, ranging from “expectations of salvation and anticipations of paradise” (Grunwald 2010) to the announcement of the “ultimate catastrophe” (Grunwald 2010)—both extremes being based on the same futuristic technical ground.

The high degree of interdisciplinarity in nanoscience and nanotechnology poses a grand challenge as well as provides great opportunities to today’s mainly specialist scientists.

To fully exploit the potential of biomimetics in the age of nanotechnology, scientists and engineers will have to substantially change their ways of thinking, especially on the level of fundamental research and education (Casert and Deboelpaep 2006, Gebeshuber and Majlis 2010, Roco 2002). Still, many researchers use for their research on a specific field in nanotechnology just the instruments they or their close collaborators have at their disposal, which are not always the best-suited ones. We

have to move from tool-based nanotechnology to understanding-based nanotechnology. Martin Rees from Trinity College in Cambridge describes in his foreword to James Lovelock’s 2010 book the current way of doing science as “the specialized quasi-industrial style in which most research is conducted” (Rees 2009). In such a way, true interdisciplinarity cannot be obtained. Interdisciplinary scientific principles and concepts that allow specialist scientists to understand complex phenomena need to be developed toward a unification of science (Roco and Bainbridge 2002). To allow for proper, accessible organization of knowledge, the specialist results that currently appear in increasingly specialist journals need to be rearranged and connected across fields (Gebeshuber and Majlis 2010).

CONCLUSIONS AND OUTLOOK

One of the paramount advantages of the biomimetic method as opposed to other innovation methods in nanotechnology is that we have biological “best practice” examples and know that they

work. However, due to the integrated multifunctionality of biological materials, structures, and processes, it might sometimes be hard to identify the respective principles responsible for one single technological aspect that we want to transfer to research and development. In the biomimetic method applied to nanoscience and nanotechnology, we have the option to go along two roads: either to take the typical Western science approach and try to dissect the best practice models in living nature to various single, unrelated properties, some of which may be highly intriguing and successful for immediate application in common products, but that might come with unintended long-term effects, or to take a more holistic approach and appreciate the best practice models as a whole, trying to develop a deep understanding why life as we know it has developed the way we currently experience it and to develop a kind of engineering and way of *managing* resources that is closer to the way nature does it—biomimetic nanotechnology with the strive for sustainability.

Organisms show us, for example, a completely different way of resource “management” as opposed to the one we currently have in engineering and construction. They predominantly use water-based chemistry, are subject to limits and boundaries, and are in a state of dynamic nonequilibrium. They are locally attuned and responsive (they harvest locally, use common materials, etc.), integrate cyclic processes via feedback loops, cross-pollinate and mutate, and are resilient (diverse, decentralized and distributed, redundant) (Biomimicry 3.8 2014).

Biomimetics is perhaps a small but probably significant method, because the role models that can be found in living nature have been tested in evolution since billions of years and promise great nanoscience and nanotechnology-based innovations. To sum up, biomimetics in nanotechnology has great potential for exciting nanoscience and nanotechnology-based innovations.

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Bone Repair: Nanohydroxyapatite as a Bone Repair Material

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Over the past decades, autologous and allogeneic bones have been used as implants to repair bone defects. However, those approaches have limitations that cannot be ignored. Currently, a lot of artificial materials have been prepared for bone repair, one of which is nanosized hydroxyapatite (nHA), which is the major inorganic component of natural bone with good biocompatibility and osteoconductivity. From the point of biomimic, nHA should be a kind of good bone repair material. However, its clinical applications are restricted because of its inherent brittleness and poor shape ability. Fortunately, introduction of some kind of polymers can bring satisfactory mechanical properties and make the materials keep stable shapes. Furthermore, porous structures can be made for the cells to grow in so as to accelerate new bone formation. Therefore, nHA/polymer composites are very promising bone repair materials.

This chapter mainly introduces the physical and chemical properties of nHA, the main methods to prepare nHA, the polymers used in nHA/polymer composites, as well as the main methods to prepare nHA/polymer composites. Moreover, some new findings about the techniques of both preparation and in vitro or in vivo evaluation for nHA-based bone repair materials are included.

PHYSICAL AND CHEMICAL PROPERTIES OF nHA

Bone is a natural organic–inorganic ceramic composite consisting of collagen fibrils containing embedded, well-arrayed, nanocrystalline, rodlike inorganic materials 25–50 nm in length. The main bone mineral calcium phosphate is the

carbonate-substituted hydroxyapatite (HA) containing between 2.3 and 8 wt.% of carbonate.

The HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, which belongs to the group of calcium phosphates, has a chemical composition similar to the natural bone mineral in composition, structure, and size. The HA crystallizes into hexagonal rhombic prisms and has unit cell dimensions of $a = 0.9432 \text{ nm}$ and $c = 0.6881 \text{ nm}$. Polycrystalline HA has a high elastic modulus (40–117 GPa). The ideal Ca/P ratio of HA is 10:6 and the calculated density is 3.219 g/cm^3 . Electron micrographs show that the HA of bone has a platelet shape with a very small size, about $(1.5\text{--}3.5 \text{ nm}) \times (5.0\text{--}10.0 \text{ nm}) \times (40.0\text{--}50.0 \text{ nm})$ [1].

The HA is stable, biocompatible, biodegradable, and osteoconductive and is widely applied as bone graft material [2]. Through osteoconductive mechanism, HA forms chemical bonds with living bone tissue. Chemical bonding with the host tissue offers HA a greater advantage in clinical applications compared to most other bone substitutes such as allografts or metallic implants. The pure HA bioceramic, which could not degrade in the human body, is only suitable to the repair of non-load-bearing bones because of its fragility, low mechanical strength, easy rupture, and weak fatigue resistance in the humoral surrounding.

Compared to micron-size particles, nHA possesses improved mechanical properties and superior bioactivity for promoting bone growth and regeneration due to greater surface area, which may improve fracture toughness, as well as other mechanical properties. According to researches about nHA, the nHA can enhance the formation of new bone tissue by increasing osteoblast adhesion, osteointegration, and

deposition of calcium-containing minerals on its surface [3]. nHA has been used to fill a wide range of bony defects in orthopedic and maxillofacial surgeries and dentistry. It has also been widely used as a coating for metallic prostheses to improve their biological properties [4].

METHODS TO FABRICATE nHA

HA ($\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$) nano- and microcrystals with multi-form morphologies including separated nanowires, nanorods, microspheres, micro flowers, and microsheets have been successfully synthesized by the wet chemical method and the dry chemical method, including sol-gel synthesis, hydrothermal synthesis, solid-state reactions, precipitation, microemulsion syntheses, chemical vapor deposition, and microemulsion techniques. Among these methods, the sol-gel synthesis, hydrothermal synthesis, and solid-state reaction are used widely.

Sol-gel synthesis can be defined as a method to prepare mineral in solution at slow temperature. The sol-gel process comprises solution, gelation, drying, and densification. Sol-gel chemical processes at first disperse the raw material in solvent, and then the reactive monomers synthesize under the effect of hydrolysis. The reactive monomers polymerize, start to become a sol, and then generate gel with spatial structure. By drying and heat treating, nanoparticles were prepared.

Hydrothermal synthesis can be defined as a method of synthesis of single crystals, which depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called autoclave, in which a nutrient is supplied along with water. A gradient of temperature is maintained at the opposite ends of the growth chamber so that the hotter end dissolves the nutrient and the cooler end causes seeds to take additional growth. The advantage of the proposed technique is the simple but precise control of the HA crystal morphology, which is achieved by employing an intensive, stepwise, and slow thermal decomposition of urea as well as varying initial concentrations of starting reagents.

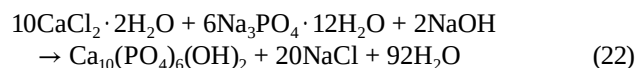
The solid-state reaction route is the most widely used method for the preparation of polycrystalline solids from a mixture of solid starting materials. Solids do not react together at room temperature over normal timescales and it is necessary to heat them to much higher temperatures, often to 1000°C – 1500°C in order for the reaction to occur at an appreciable rate.

Some other novel methods that have been developed synthesize nHA efficiently besides the aforementioned methods. Ultrasound-assisted wet precipitation method, dispersant-aided precipitation method, and 3D printing will be described in the following sections.

When fabricated by an ultrasound-assisted method, at first, HA is synthesized by adding ammonia aliquot of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution under ultrasound irradiation. The pH value is checked and maintained. While under ultrasound irradiation, KH_2PO_4 solution is slowly added dropwise. A white

precipitate was formed, and the mixture is continuously irradiated with ultrasound power. The Ca/P ratio should be kept at 1.67. The solution is filtered by centrifugation and after filtration the white precipitate is proportioned into a number of samples. These samples are then transferred into ceramic boats and placed in an electric tube furnace for thermal treatment at temperatures varying for a fixed time period. The duration of heat treatment time for the white precipitate and the duration of heat treatment time for the white precipitate at temperatures are different. The duration of heat treatment time for the white precipitate at lower temperature is longer, while the duration of heat treatment time for the white precipitate at higher temperature is shorter. The longer heat reaction time for the lower-temperature samples is necessary so as to produce crystalline and harder samples as initial work indicated mixed crystalline and amorphous soft end product [5].

The reactants were prepared to achieve a resultant stoichiometric Ca/P ratio of 1.67 to ensure the formation of HA using dispersant-aided precipitation method. The aqueous solutions of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ were prepared using double-distilled H_2O . NaOH was added to the PO_4 precursor to control the pH. These were mixed using drop feeding at a constant rate and adding the Ca precursor to the PO_4 precursor. The precipitation reaction occurred immediately under stirring, according to Equation 22. The solution was then centrifuged and washed to remove the NaCl by-product. The precipitate was resuspended using sonication to yield a nonaggregated nHA suspension or freeze-dried to generate a fine powder [6].



POLYMER USED IN THE nHA-BASED COMPOSITE SCAFFOLD AND THE FABRICATION OF POROUS COMPOSITE SCAFFOLD

HA ceramics have been widely used as artificial bone substitutes because of their high biocompatibility, bioactivity, and osteoconductibility [7]. However, the induction of bone growth into HA blocks is unsatisfactory, because it is quite slowly replaced by host bone after implantation. For this reason, porous bodies and granules of HA ceramics have been developed and have been widely used in clinical settings. Due to the closed structure of conventional porous HA, which has nonuniform pore geometry and low inter-pore connections, it is very difficult for implant pores to become completely filled with newly formed host bone. A high porosity with a high interconnectivity between the pores is necessary to allow ingrowth of cells, vascularization, and diffusion of nutrients and wastes. Thus, porous HA ceramics with highly interconnecting structures have been developed, and osteoconduction can occur deep inside such ceramics [8].

Scaffolds for bone tissue engineering must have sufficient mechanical strength to support bone tissue regeneration at the site of implantation [9,10]. A key requirement for these

scaffolds is to match the mechanical properties of the injured. The main limitation for the use of HA ceramics is their inherent brittleness; it cannot be used as load-bearing bone replacements. Hence, to combine the osteoconductivity of nHA and good mechanical property of polymer and fabricate polymer/nHA or nHA/polymer, composite scaffolds have been developed for bone tissue engineering.

Several methods of fabricating porous composite scaffolds including thermally induced phase separation (TIPS) [11,12], freeze-drying technique, and solvent casting/particle leaching [13] have been presented in the following:

Thermally induced phase separation: TIPS is used to fabricate porous materials widely. TIPS includes the following procedure. nHA powder was dispersed in solution (such as dioxane), which has high boiling point and low volatility, and then polymer is dissolved in the HA suspension. The nHA and polymer turn to be a homogeneous mixture. The solution was then ultrasonicated and rapidly transferred into a freezer to solidify and induce solid-liquid-phase separation. Remove the previous solution and then a porous material forms.

Freeze-drying: Freeze-drying is a method that utilizes the phase transition of water. The polymer is added into a nHA slurry with stirring until the powders were thoroughly dispersed in the slurry. Some acid can be added into the slurry. Stirring should be continued until the slurry mixture solidified. The mixture is then allowed to freeze. Finally, the solid is transferred into a freeze-drying vessel to get a porous scaffold. The scaffold was immersed in alkaline solution to neutralize the residue acid, which was washed with deionized water.

Solvent casting/particle leaching: The polymer and nHA are mixed and stirred to obtain a homogeneous mixture. Particle such as NaCl is added into the mixture. The mixture is loaded and heated to make the mixture solid. Then, samples are immersed in deionized water under room temperature to leach the salt particulates out. Finally, the porous materials are fabricated.

A bone tissue engineering scaffold should be biocompatible and biodegradable to nontoxic products during the application time besides good mechanical property. The addition of HA in the polymer/HA composites could improve the activity and viability of cells cultured on them or improve both the mechanical and cell-attachment properties of the alginate scaffolds [14]. Composites of HA with polymers such as poly(L-lactic acid) (PLLA), poly(lactic acid), poly(glycolic acid) (PGA) and their copolymers (poly(lactide-co-glycolide) acid [PLGA]), polysaccharides, poly(3-hydroxybutyrate) (PHB) polymethyl methacrylate, poly(3-hydroxybutyrate-co-3-hydroxyvalerate), polyamide (PA), polyurethane (PU), and polyacrylic acid have been widely used to develop porous 3D scaffolds using various

fabrication techniques, which show improved mechanical properties and good biocompatibility, as well as bioactivity. Degradable and nondegradable polymers are used in tissue engineering.

To better mimic the mineral component and the microstructure of natural bone, novel nHA/polymer composite scaffolds with high porosity and well-controlled pore architectures were prepared using TIPS techniques [15]. The high porosity (90% and above) was easily achieved, and the pore size was adjusted by varying phase separation parameters. The nHA particles were dispersed in the pore walls of the scaffolds and bound to the polymer very well. nHA/polymer scaffolds prepared using pure solvent system had a regular anisotropic but open 3D pore structure similar to plain polymer scaffolds, while micro-sized HA (mHA)/polymer scaffolds had a random irregular pore structure. The introduction of HA greatly increased the mechanical properties and improved the protein adsorption capacity.

PLLA

PLLA satisfies most of these requirements due to good mechanical properties, low toxicity, and predictable biodegradation kinetics. However, it does not provide a favorable surface for cell attachment and proliferation due to its lack of specific cell-recognizable signals [16].

nHA and mHA particles are used to fabricate HA-filled PLLA (HA/PLLA) composite scaffolds using TIPS method. The porosity of scaffolds was up to 85.06% and their average macropore diameter was in the range of 64–175 μm . Some molecular interactions and chemical linkages between HA particles and PLLA matrix are observed. The compressive strength of nanocomposite scaffolds could be elevated up to 14.9 MPa, while those of pure PLLA and microcomposite scaffolds were 1.79 and 13.68 MPa, respectively. The cell affinity and biocompatibility of the nanocomposite scaffold were found to be higher than those of pure PLLA and microcomposite scaffolds.

Therefore the incorporation of synthesized nHA instead of mHA reinforcement enabled the nanocomposite scaffold to possess higher mechanical strength, better cytocompatibility, and more regular microarchitecture due to its more interfacial area, surface reactivity, and ultrafine structure. The nHA/PLLA composite scaffold can be a suitable bone substitute for bone tissue engineering applications.

Poly-L-lactic acid (PLLA)/HA composite has become an important representative of these materials, which is widely used in bone tissue engineering, since they combined the bone conduction and bone bonding ability of HA with the resorbability and the processing ease of the PLLA [17,18].

NATURAL POLYSACCHARIDES

Some natural polysaccharides (chitosan [CS], pectin, alginate, etc.) and proteins (collagen and gelatin) have been investigated because of the similarity of their structures and biocompatibility [19,20].

CS, which is generally obtained by deacetylation of chitin, is a natural cationic polysaccharide. Due to its good biocompatibility and biodegradability, it has been widely used in the biomedical field, and it has been reported that it can promote adhesion and functional expression of osteoblasts because of its similarity to glycosaminoglycan in structure.

The addition of HA in the CS could improve the activity and viability of cells cultured on them or improve both the mechanical and cell-attachment properties of the alginate scaffolds. With increasing nHA content in the composite, the quantity of the apatite formed on the scaffolds increases. Compared with pure CS, the composite with nHA could form apatite more readily during the biomimetic process, which suggests that the composite possessed better mineralization activity. Furthermore, preosteoblast cells cultured on the apatite-coated scaffolds show different behaviors. On the apatite-coated composite scaffolds, cells present better proliferation than on apatite-coated CS scaffolds. In addition, alkaline phosphatase (ALP) activities of cells cultured on the scaffolds in conditioned medium were assessed. The cells on composite scaffolds show a higher ALP activity that suggested a higher differentiation level. The results indicated that the addition of nHA improved the bioactivity of CS/nHA composite scaffolds [21].

Carboxymethyl cellulose (CMC) obtained from natural cellulose by chemical modification is a water-soluble cellulose ether derivative and is very similar to CS in structure. What is more important is that it has opposite electric charge to CS, so CMC can react strongly with CS and act as an ionic cross-linking agent at the appropriate pH.

The nHA/CS/CMC scaffolds can be fabricated by freeze-drying. Strong chemical interactions were formed between the three phases in the nHA/CS/CMC. The highest compressive strength is 3.54 MPa. The SBF soaking experiment shows that the scaffold of 30 wt.% CMC had an acceptable degradation rate and good bioactivity in vitro. The nHA/CS/CMC composite scaffolds have a potential to be bone tissue engineering materials [22].

Pectin is a plant polysaccharide primarily obtained from edible plants, which is enriched in galacturonic acid and galacturonic acid methyl ester units. The carboxyl groups of pectin play important roles in the process of mineralization, which have a catalytic effect for heterogeneous apatite nucleation. Pectin can provide mechanical strength for cell walls of higher plants as well as play important roles in various cellulars. Pectin has also been investigated for possible applications in bone tissue engineering.

Gelatin is a partially denatured derivative of collagen, which has the potential to support the growth of osteoblasts and promote bone regeneration in defective areas. The morphology and structure of the nHA crystals could be modulated by these natural polymers if the nHA crystals were formed in situ in these polymer solutions.

The multicomponent polysaccharide/nHA composites (nHCP/CG) are prepared via freeze-drying. The nHCP/CG scaffolds exhibited high porosity, interconnectivity, water absorption ability, controllable degradation behaviors, and

good mechanical strength. Furthermore, the nHCP/CG scaffolds also showed excellent mechanical stability and biocompatibility. This significantly improves biological responses of preosteoblast (MC 3T3-E1) to nHCP/CG that included improved cell attachment and proliferation [23].

POLYAMIDE

PA has already been proved to possess good biocompatibility with various human cells and tissues probably owing to its similarity to collagen protein in chemical structure and active groups and widely used in biomaterial application. Especially, PA also exhibits excellent mechanical properties resulting from the strong hydrogen bonds between the amide group in PA macromolecules. As a polar polymer with high polarity, PA has a relatively high affinity and may form hydrogen bonds with nanosized apatite.

The nHA/PA composite scaffolds that are prepared by TIPS exhibit good biocompatibility and extensive osteoconductivity with host bone. Moreover, the introduction of MSCs to the scaffolds dramatically enhanced the efficiency of new bone formation, especially at the initial stage after implantation. The scaffolds fulfill the basic requirements of bone tissue engineering scaffold and have the potential to be applied in orthopedic, reconstructive, and maxillofacial surgery [24].

POLYURETHANE

PU is widely employed for numerous biomedical applications due to its excellent mechanical property, good biocompatibility, and high flexural endurance. In spite of its wide recognition and application in biomedical field, PU is still paid more attention to its degradation.

nHA/PU scaffold was prepared by a foaming method. First, castor oil and nHA were mixed together under an inert atmosphere of nitrogen; then, TDI was added to form the viscous, milky liquid. After 1,4-butanediol was dropped by stirring, the reacting mixture was immediately poured into a plate and put into an oven; thus, nHA/PU porous scaffold can be obtained and stored.

The interconnected porous structure and high porosity of the scaffold provide good microenvironment for cell seeding and proliferation and for the growth of tissues. The compressive strength and degradation property are suitable in tissue engineering for the cartilage repair. The scaffold has good cytocompatibility in vitro and good biocompatibility in vivo. The degradation of the nHA/PU scaffold mainly comes from hydrolysis and macrophage enzymolysis. The nHA/PU scaffold has the potential to be applied in repair and substitute of human menisci of the knee joint and articular cartilage [25].

POLY(VINYL ALCOHOL)

Poly(vinyl alcohol) (PVA) hydrogel is an excellent articular cartilage repair material due to its biocompatibility and biotribological properties. It possesses high porous

structure and high content of free water, similar to that of natural articular cartilage. PVA hydrogel has increasingly attracted interest in application as an articular repairing material. However, it has limited durability and does not adhere well to tissue.

nHA-reinforced PVA gel (nHA/PVA gel) composite has been proposed as a promising biomaterial, especially used as an articular cartilage repair biomaterial. nHA/PVA gel composites were prepared from mixing nano-HA particles modified by silicon coupling agent, with physiological saline solution of PVA by freeze-drying method.

The tensile strength and tensile modulus of the composites improved correspondingly with the increase in freeze-drying times and concentration of PVA solution. The more the concentration of PVA solution, the higher influence the degree of concentration on the tensile strength of composites. The tensile strength and tensile modulus of nano-HA/PVA hydrogel composites increased first and then decreased with the rising nano-HA content of the composites. The tensile modulus of the composites improved remarkably with the increase in elongation ratio. The mechanical behavior of nano-HA/PVA composites is similar to that of natural articular cartilage. The composite is an excellent articular cartilage repair material [26].

POLY(3-HYDROXYBUTYRATE)

PHB/nHA composite scaffolds were fabricated via powder mixing, compression molding, and particle leaching technique. The scaffolds had high porosity with interconnected porous architecture, a favorable structure for cell attachment, and new bone tissue ingrowth. A homogeneous dispersion and a uniform distribution of HA nanoparticles in the polymer matrix were obtained. The scaffolds exhibited improved compressive modulus and compressive strength, which were all in the range of compressive modulus and compressive strength of cancellous bone. In addition, the use of toxic organic solvents was eliminated. Thus, the fabricated PHB/nHA composite scaffolds tend to be promising for application in bone tissue engineering [27].

OTHER POLYMERS AND METHODS USED TO FABRICATE nHA-BASED COMPOSITES

Finally, we present an effective and novel technique in obtaining nHA in cognate with native apatite on electrospun nanofibers within minutes without any pretreatment [28]. Using an alternate calcium and phosphate (Ca-P) solution-dipping method, nHA is formed on PLGA and blended PLGA/Col nanofibers. The presence of the functional groups of collagen significantly hastened nHA deposition closed to ninefold. The quantity of nHA impinged upon the specific surface area, whereby mineralized PLGA/Col has a greater surface area than nonmineralized PLGA/Col, whereas nHA did not significantly improve the specific surface area of mineralized PLGA compared to pure PLGA. The novelty of the process is that nHA on PLGA had a

positive modulation on early osteoblast capture (within minutes) compared to pure PLGA. Contrary, cell capture on mineralized PLGA/Col was comparable to pure PLGA/Col. Interestingly, although nHA impeded proliferation during the culture period, the cell functionality such as ALP and protein expressions were ameliorated on mineralized nanofibers. The amount of nHA appeared to have a greater effect on the early stages of osteoblast behavior (cell attachment and proliferation) rather than the immediate/late stages (proliferation and differentiation).

A metal that has good bioactivity and good mechanical property such as titania can also be used in bone tissue engineering except nHA mentioned in this chapter. Titania can be combined with nHA in the application of bone graft. Titania can be used to reinforce nHA/gelatin composites. Bioinert titania as a reinforcing phase and gelatin as protein that mimic the natural bone exhibiting improved biomechanical features. The composites of nHA/TiO₂/gelatin in different weight percentages were prepared by phase separation technique. The compressive strength of titania-reinforced nanocomposite scaffolds could be elevated up to 10.15 MPa, while that of nHA/gelatin was 4.87 MPa. nHA/TiO₂/gelatin composites may be superior for bone tissue engineering [29].

Electrospinning has been used in the fabrication of porous nHA-based composites except for the aforementioned method. Besides, 3D printing has been studied for their application in bone repair. It is promising to combine this newly developed technology with nHA.

EVALUATION FOR nHA-BASED BONE REPAIR MATERIALS IN VITRO OR IN VIVO

Optical images of the scaffolds were obtained using optical microscope. The ultrastructure and physicochemical properties of the scaffolds are studied using scanning electron microscopy (SEM) and spectroscopic techniques. For ultrastructural analysis, circular scaffold samples are sputter coated with carbon and viewed and digitally photographed in a field emission SEM (FESEM) equipment. Porosity is studied by using SEM or liquid displacement method.

An FESEM equipped with an energy-dispersive x-ray spectroscopy system was used to assess calcium and phosphorous contents and the crystallinity of the materials. In order to elucidate chemical interaction between the different phases, IR spectroscopy measurements are taken. The stretching frequencies of samples can be examined by FTIR and spectrum GX spectrometer.

The mechanical properties of the scaffolds are tested using the Instron Table Mounted Materials Testing System. The compressive strength can be determined from the maximum load recorded. The compressive modulus can be evaluated from the slope of the initial linear region of the stress-strain curve. The stress-strain characteristics, tensile strength of the composites, and tensile modulus can be obtained in the mechanical property test.

The degradation of composite scaffolds was investigated by using phosphate buffer solution. The initial weight of the scaffold and its final weight after being freeze-dried were noted and used to calculate the degradation.

To evaluate the morphology of cells growing on the scaffolds, samples are fixed and serially dehydrated in ethanol and hexamethyldisilazane. The samples are left to air-dry in a chemical fume hood overnight at room temperature, sputter coated with carbon, and observed under SEM.

Cell viability and proliferation can be continually monitored using the continual AlamarBlue™ assay. The cytotoxicity test of composite scaffolds was done according to ISO 10993-5. By treating with MG63, Vero, NIH3T3, and HDF cells, the cell viability of the composite scaffolds can be analyzed.

The proliferation of BMSCs on scaffold was determined using the MTT 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide assay. The bioactivity of the composite scaffolds was studied by examining the apatite formed on the scaffolds by incubating in simulated body fluid and the activity of preosteoblasts cultured on them. The apatite layer was assessed using scanning electronic microscope (SEM), XRD, FTIR, and weight measurement.

Proliferation and differentiation of MSCs into osteoblastic phenotype were determined using MTT assay [30,31], ALP activity, and collagen type I (COL I) immunohistochemical staining and scanning electronic microscopy (SEM).

Healthy SD mice, New Zealand rabbits, or other animals were anesthetized with pentobarbital sodium. One centimeter parallel lengthwise incision was made on the back of the mice. Porous nHA-based scaffold was inserted into unilateral experiment animal of the spinal column or radius bone of a unilateral experiment animal and stabilized using suture. Animals were sacrificed at different periods after implantation. The scaffolds with surrounding tissue were excised, fixed in 10% neutral buffered formalin, decalcified and embedded in paraffin, sectioned at 5 mm in thickness, and stained with hematoxylin and eosin (H&E), and the degradation was observed by light microscope.

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Boron Nanostructures: All-Boron Nanostructures

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INTRODUCTION

Boron (B) belongs to the group of least abundant chemical elements: Earth crust contains only around 0.001 wt.% B. As for the role of boron in the formation of the various structural phases, it is incommensurably great. Understanding the diversity of boron structures reduces to the electronic structure of an isolated boron atom. In multiatomic networks, by adding an electron, the valence shell configuration peculiar to the free B atom $2s^2 2p$ transforms at first in the energetically more favorable configuration $2s^2 2p^2$, which then tends to most stable one $2s 2p^3$. Thus, boron is a distinct electron acceptor and, consequently, all-boron structures have to be electron deficient. This is the reason why all modifications of boron exhibit complex, clustered structures. For them, the icosahedron B_{12} with 12 boron atoms at vertices serves as a main structural motif.

Since carbon nanosystems were discovered, it has triggered interest in other materials, including bare boron, which may also exhibit nanostructures. Due to its rich chemistry, boron is a natural choice for constructing nanosystems like clusters, nanotubes, and nanowires. Relatively recently, they were actually synthesized.

A boron atom of the given icosahedron is bonded with five neighboring atoms and, usually, is linked with an atom of the neighboring icosahedron. It explains why the average coordination number of atomic sites in all the solid-state forms of boron is almost six. But a free regular icosahedron B_{12} still remains electron deficient: it needs two extra electrons to saturate all the B–B bonds. In boron crystals and amorphous boron, electron deficiency is compensated by the presence of intrinsic point defects (vacancies in the form of partially occupied boron sites and self-interstitials) and/or certain impurity atoms in very high concentrations.

In addition to solid-state modifications, constructed from full and fused icosahedra, elemental boron forms diboron molecule B_2 and molecular clusters B_n , $n > 2$. At relatively

low n , these clusters are (quasi)planar, but at sufficiently high n , they can take polyhedral, nearly spherical, cage-like shapes and, in particular, icosahedral shape if dangling bonds at boron atoms are saturated by hydrogen or other foreign atoms. Thus, most boron atoms should be surrounded by six nearest neighbors, that is, five intra-plus one intericosahedral bonds. Alternatively, this circumstance leads to the possibility of synthesizing the fragments of (quasi)planar nanosheets in the form of surfaces with triangular six-coordinated 2D lattices, which can be wrapped into nanotubes. There is known number of other nanostructured forms of boron as well: nanowires, nanobelts, nanoribbons, quasicrystals, etc. They reveal many interesting features in addition to the complex of useful properties of the bulk boron. Strong B–B bonds make all these high-temperature materials resistive against harsh environments and cause their unusual semiconducting properties.

This chapter might be considered as an overview of the last two decades' achievements in the field of nanostructured boron shortly summarizing the available data on methods of fabrication, structural forms, and main physical properties of these species. Let us emphasize that here we are concern only for all-boron nanosystems, not huge data available on boranes and other boron-rich nanocompounds.

CLUSTERS

As it is known, clusters as systems of a finite number of bound atoms are physical objects occupying an intermediate position between atomic particles (atoms and molecules) and macroscopic atomic systems (solids and liquids). One of the most interesting features of elemental boron is the occurrence of highly symmetric icosahedral clusters. However, the fivefold symmetry does not lend B_{12} clusters to construct ideal 3D periodic frameworks, and various degrees of compromise in the pattern of icosahedral linkage give rise to the observed proliferation of boron polymorphs. Then, in bare boron

structures, most of the atoms usually are members of almost regular atomic triangles. This circumstance leads to the possibility of the boron-based nanomaterials in the form of (quasi) planar or convex boron surfaces with triangular 2D lattices. The rich chemistry of boron is also dominated by 3D cage structures. Consequently, it is important to gain deep insight into boron clusters—*building blocks* of nanostructured boron.

According to the mass-spectrometric analysis [1] of the boron cluster ions from the high-purity (99.99995% B) target source in the process of growing amorphous boron films, there are some peaks corresponding to the interval from B_2^+ to B_8^+ .

Let us start with diboron molecule B_2 , the simplest boron cluster. The Douglas–Herzberg transition, observed [2] in the optical absorption spectrum of B_2 , indicated that its ground electronic state is of Σ -type. On the other hand, the molecule B_2 was not observed via electron spin resonance, what was interpreted as support for the $^3\Sigma_g^-$ ground state rather than $^5\Sigma_u^-$ favored by *ab initio* calculations. Further, more accurate configuration interaction (CI) calculation established [3] that the ground electronic state of B_2 indeed is of $^3\Sigma_g^-$ symmetry, and Douglas–Herzberg emission system is due to the transitions from the second $^3\Sigma_u^-$ state to the $X^3\Sigma_g^-$. Hyperfine coupling constants for the ground electronic state $^3\Sigma_g^-$ of the B_2 molecule were computed [4] using correlation procedures based on spin-unrestricted wave functions. As for the potential curves, transition energies, and spectroscopic constants of several low-lying electronic states of the molecular ion, B_2^+ and part of doubly excited states of B_2 were given in [5]. At the first time, a theoretical study of the ionization potentials (IPs) of the B_2 molecule was performed in [6]. An *ab initio* molecular orbital (MO) study [7] of B_2 and B_2^+ determined the dissociation energy of the $^3\Sigma_g^-$ ground state of B_2 as 2.71 eV and the adiabatic IPs to states $^2\Sigma_g^+$ and $^2\Pi_u$ of B_2^+ as 8.99 and 9.27 eV, respectively. The singlet, triplet, and quintet states of B_2 in the succeeding text about $45,000\text{ cm}^{-1}$ were studied at the multireference CI level of the theory in an atomic natural orbital basis set [8]. The dissociation energy for the $X^3\Sigma_g^-$ state was computed to be 2.78 eV and estimated as 2.85 eV in the complete CI limit. Calculations of excitation energies utilizing the standard coupled cluster hierarchy were presented [9] up to the quadruple excitation level for the open-shell B_2 molecule using an excited closed-shell state as a reference one.

Optimum geometries and harmonic spectra were obtained theoretically [10] for a number of different states of B_3 cluster. B_3 is found to be an equilateral triangle in its $2A_1'$ ground state. Estimated dissociation energy is 197.9 kcal/mol. From a statistical thermodynamical analysis, B_3 should be stable against dissociation to B_2 and B up to very high temperatures. *Ab initio* electronic structure calculations on several low-lying valence states of B_3 were also carried out using correlation-consistent polarized valence basis sets and self-consistent field (SCF) treatments [11]. Stable triangular structures, linear structures, and Jahn–Teller unstable structures were all observed. The ground state of B_3 was predicted to have an equilateral triangular structure and to be of $^2A_1'$ symmetry in the D_{3h} point group. By carrying out a systematic basis set and electron

correlation investigation, the isotropic and anisotropic parts of the hyperfine coupling tensor of the B_3 molecule using the multi-CI SCF restricted–unrestricted method were determined accurately [12]. The spin polarization of the $1s$ orbital on each B atom was found to be very small. This implies that in B_3 , the isotropic hyperfine coupling is dominated by valence orbital contributions rather than by $1s$ orbital contributions.

The potential energy surface (PES) of B_4 cluster was *ab initio* studied using extended basis sets and coupled cluster methods [13]. The ground-state $^1A_{1g}$ is the singlet square that undergoes pseudo Jahn–Teller distortion to a rhombic structure 1A_g , but the energy gain is too small. Total atomization energies of B_2 , B_3 , and B_4 clusters were computed as 62.2, 189.1–192.6, and 312.2 kcal/mol, respectively. The two small boron clusters B_3 and B_4 in their neutral and anionic forms were studied by photoelectron spectroscopy and *ab initio* calculations [14]. Vibrationally resolved photoelectron spectra were observed for B_3^- at 355, 266, and 193 nm, and the electron affinity (EA) of B_3 was measured to be 2.82 eV. An unusually intense peak due to two-electron transitions was observed in the 193 nm spectrum of B_3^- at 4.55 eV. It was confirmed that both B_3^- and B_3 are of D_{3h} symmetry. The photoelectron spectra of B_4^- were also obtained at the three photon energies, but much broader spectra were observed. The B_3^- anion was found to have the lowest electron detachment energy, 1.6 eV, among all-boron clusters with more than three atoms, consistent with its extremely weak mass signals. The neutral B_4 cluster was found to have a D_{2h} rhombus structure, which is only slightly distorted from a perfect square. For B_4^- , two low-lying isomers $^2B_{1u}$ and 2A_g , were identified computationally both of D_{2h} symmetry, with the slightly more stable $^2B_{1u}$ state.

The electronic structure and chemical bonding of boron clusters B_5 and B_5^- were investigated [15] using anion photoelectron spectroscopy and *ab initio* calculations. Extensive searches were carried out for global minimum of B_5^- , which was found to have a planar structure with a closed-shell ground state. Excellent agreement was observed between *ab initio* detachment energies and the experimental spectra. A bonding orbital was found to be completely delocalized over all five atoms in the B_5^- . Such bonding makes B_5^- more rigid toward butterfly out-of-plane distortions. The structure and stability of B_5 , B_5^+ , and B_5^- clusters were also investigated theoretically in [16]. Eight B_5 , seven B_5^+ , and seven B_5^- isomers were identified. The planar five-membered ring structures, B_5 and B_5^+ , were found to be the most stable on the neutral and cationic PES, respectively. The most stable B_5^- isomer has an arrangement of atoms similar to the neutral. Natural bond orbital analysis suggests that there are three-centered bonds in both the neutral and anionic structures, as well as the multicentered centripetal bond in the cationic structure.

The electronic structure and chemical bonding of B_6 and B_6^- clusters were investigated using anion photoelectron spectroscopy and *ab initio* calculation [17]. The global minimum of B_6^- has a doublet ground state. The corresponding ground-state structure of B_6^- is planar. The chemical bonding

in B_6^- can be interpreted in terms of linear combinations of MOs of two B_3^- fragments. The antiaromatic nature of chemical bonding was established for both B_6^- and B_6^{2-} .

Probes of bonding in small boron clusters B_{2-8}^+ performed by the measurements of threshold energies and fragmentation patterns for collision-induced dissociation [18] showed that primary fragmentation channel has a loss of B^+ in all cases and B_5^+ is a particularly abundant cluster in the distribution produced. The stabilities of B_n clusters with $4 \leq n \leq 8$ based on the vibrational analysis were investigated by *ab initio* MO calculations in [19]. It was found that there exist two types of stable clusters: a low-symmetry, structurally “soft,” species with lower frequencies and lower geometrical change barriers and a high-symmetry, structurally “hard,” species with higher frequencies. By means of *ab initio* techniques, the equilibrium geometries, total, binding, and fragmentation energies of clusters B_n , with $n = 2-8$, were calculated in both the neutral and cationic states in [20].

The experimental and theoretical evidence that eight- and nine-atom boron clusters are perfectly planar molecular wheels, with a hepta- or octa-coordinated central boron atom, respectively, was reported in [21].

Density functional theory (DFT) calculations using a plane wave (PW) basis set and a pseudopotential (PP) were employed [22] to investigate the structure, vibrational characteristics, and energetics of small (up to 10 atoms) boron clusters. A comparison with other studies revealed a great deal of consensus about the most stable structures for B_2 , B_3 , B_4 , B_7 , and B_8 and maybe B_5 as well. Additionally, all studies agree about the existence of two stable B_6 isomers.

Geometries, electronic structures, and energies of the neutral and cationic clusters B_{2-12} and B_{2-12}^+ were investigated by the *ab initio* MO method [23]. The geometries of boron cluster cations B_{3-12}^+ are essentially the same as those of the neutral clusters—the (pseudo)planar cyclic structures. Clusters of 8–11 atoms characteristically have the most stable structure of a cyclic form with 1 atom in the middle. The capped pentagonal B_6 , B_7 , and B_7^+ and the trigonal bipyramidal B_{12} and B_{12}^+ seem to be the exceptions. The electronic and geometric structures, total and binding energies, harmonic frequencies, point symmetries, and highest occupied MO–lowest unoccupied MO (HOMO–LUMO) gaps of small neutral boron B_n clusters ($n = 2-12$) were investigated in [24] using DFT. Linear, (quasi)planar, and open- and 3D cage structures were found. None of the lowest-energy structures and their isomers has an inner atom. Within the size range, the (quasi)planar, that is, convex, structures have the lowest energies.

It is expedient to consider boron icosahedron B_{12} separately from other boron clusters. For the first time, the electron structure of a regular icosahedron of boron atoms was investigated [25] theoretically by the method of MOs. It was found that 30 bonding orbitals are available for holding the icosahedron together, besides the 12 outward-pointed equivalent orbitals of the separated atoms. In [26], the energy spectrum of a real boron icosahedron—unit cell of the α -rhombohedral boron crystal—was studied using MO–linear combination of atomic orbitals method. It is an electron-deficient structure.

Besides, in distorted crystalline icosahedron, the bond lengths are different and now there is no fivefold symmetry axis. It was found that molecular levels placed at -9.35 eV should be half filled, while all lower energy levels should be filled. Using a PW expansion, [27] the *ab initio* calculations of the energy bands, equilibrium structural parameters, atomic positions, and cohesive energy of boron icosahedron B_{12} were performed. As for the calculated charge-density contour plots, they revealed strong intraicosahedral bonding. Based on the group properties of a regular icosahedron, its normal vibrational modes were pictured [28]. There are eight distinct frequencies for the 30 normal modes with one-, three-, four-, and fivefold degeneracies. Icosahedral oscillations can be pictured in terms of three equilibrium descriptions: the first involves two parallel regular pentagons and two polar atoms, the second has two polar triangles and one equatorial puckered hexagon, while the third consists of six pairs of atoms on opposite faces of a cube. It was shown [29] that by the interaction between electron and pair of phonons, which are the slightly modified two breathing modes of the isolated icosahedron B_{12} , an electron trapping level generates icosahedral boron-rich solids. The polar vibrations for the B_{12} icosahedron were demonstrated [30] within the harmonic approximation by using the shell model. The tensor nature of dynamical effective charges was emphasized. It was shown that the effective charge of the regular B_{12} is very small ($\approx 0.01 e$), while that of α -rhombohedral boron unit cell is enhanced by the deformation. The covalent-to-metallic bonding conversion in boron icosahedral cluster solids was discussed [31] in relation to the occupation by an atom, the center of this cluster. The corresponding change in the electron localization was quantitatively estimated by using electron localization indicator (ELI). Namely, the distributions of the ELI were compared for the pair of clusters B_{12}^+ and B_{13}^- . This comparison revealed that the bonding conversion from covalent to metallic one involves a decrease in both the electron density and ELI between boron atoms.

Bonding of small boron cluster cations from B_2^+ to B_{13}^+ was examined [32,33] by the measurement of appearance potentials and fragmentation patterns for collision-induced dissociation. Cluster stabilities were generally found to increase with increasing size. The lowest-energy fragmentation channel for all size cluster ions has the loss of a single B atom. Clusters, smaller than six atoms, preferentially lose B^+ ion, while for larger clusters, the charge remains on the B_{n-1}^+ fragment. Electronic and geometric isomers of B_{13} clusters were calculated within the local density approximation [34]. The filled icosahedral structure was found unstable, while heating and slow cooling lead to a considerably more stable (by 0.68 eV) structure with high symmetry (C_{3v}) and coordination. The remarkable stability of this isomer may explain the measured high survival of B_{13}^+ clusters on collision and its relatively low reactivity. Analogous problem was considered [35] for the neutral and cationic clusters B_{12} and B_{13} . Several planar and nonplanar stationary structures were optimized for neutrals and cations of each cluster size. A characteristic cyclic form with one atom in the middle was found to be stable for

each cluster, while the icosahedral B_{12}^+ was found to be the most stable. The triplet icosahedral state was found to be stable, but energetically unfavorable than the cyclic B_{12} . The structures and energies of B_{13}^+ , observed experimentally to be an unusually abundant species among cationic boron clusters, were studied systematically with DFT in [36]. The most thermodynamically stable B_{12}^+ and B_{13}^+ clusters are confirmed to have (quasi)planar rather than globular structures. However, the computed dissociation energies of the 3D B_{13}^+ clusters are much closer to the experimental values than those of the (quasi)planar structures. Hence, planar and 3D B_{13}^+ may both exist. The curiously stable cationic B_{13}^+ cluster and its neutral and anionic counterparts were examined in [37] through the use of DFT. While no minima that corresponded to the

lled icosahedron could be found for the cluster, an intriguing atom-in-cage structure was found, that is, a local minimum on the cationic, neutral, and anionic surfaces. In the structure found for the B_{13}^- anionic cluster, the 12 external boron atoms are arranged as three of six-membered rings back-to-back. The (quasi)planar structures are seen to be more stable than 3D isomers, but their ordering by stability changes depending on the charge state. It was found that planar structures benefit from π -delocalization, and in the case of the global minimum of the B_{13}^+ cationic cluster, this delocalization is reminiscent of aromaticity. As it was postulated, the lowest-energy B_{13}^+ isomer proved to be highly aromatic. The topological resonance energy of this cationic boron cluster is positive in sign and very large in magnitude. This constitutes the definitive reason why B_{13}^+ is kinetically stable and (quasi)planar in geometry [38]. The electron-deficient and multivalent character of boron is responsible for the high aromaticity of this cluster. In addition, its minimum bond resonance energy is not too small. Some of thermochemical parameters of a set of small-sized neutral B_n and anionic B_n^- boron clusters, with $n = 5-13$, were determined using coupled cluster theory calculations [39]. Enthalpies of formation and adiabatic electron EAs were evaluated in good agreement with experiments (values are given in eV): B_5 (2.29–2.48 and 2.33), B_6 (2.59–3.23 and 3.01), B_7 (2.62–2.67 and 2.55), B_8 (3.02–3.11 and 3.02), B_9 (3.03 and 3.39), B_{10} (2.85 and 2.88), B_{11} (3.48 and 3.43), B_{12} (2.33 and 2.21), and B_{13} (3.62 and 3.78). The calculated adiabatic detachment energies to the excited states of B_6 , which have geometries similar to the state of B_6^- , are 2.93 and 3.06 eV, in excellent agreement with the experiment. Based on the *ab initio* quantum chemical (QC) methods, fragmentation channels, IPs, and the Coulomb explosion of multicharged boron clusters B_n ($n = 2-13$), where n is the cluster size, were determined [40]. The electron-deficient boron clusters sustain more stability and hardly fragment when they are negatively charged. The stability of boron clusters decreases with increasing ionization. Only by the first ionization the odd-size clusters are more stable than the even-size clusters. Further ionizations cause the repulsive Coulomb force between the constituent atoms to get stronger and lead first to metastable states and then to the Coulomb explosion of clusters. None of the cationic boron clusters studied remains stable after six times ionization. The critical charge for metastability was estimated as $Q_m \leq n/2$

for even-size clusters and $Q_m \leq (n-1)/2$ for odd-size clusters. In addition, the critical charge for the Coulomb explosion is found to be $Q_c = n/2 = 1 \rightarrow Q_c = n/2 + 1$, respectively. Several dissociation channels of B_n^+ and B_{13}^Q isomers with the lowest fragmentation energies were presented. All of the vibrational frequencies were found positive indicating that no transition state is possible for the clusters studied.

The geometrical structures and properties of small cationic boron clusters B_n^+ ($n = 2-14$) were determined [43] using local-spin-density (LSD) formalism. Most of the final structures of the cationic boron clusters prefer (quasi)planar arrangements and can be considered as fragments of a planar surface or as segments of a sphere. The calculated adiabatic IPs of B_n exhibit features similar to those of measured IPs. Most of the calculated normal modes of the cationic clusters have frequencies around 1000 cm^{-1} and strong IR intensities. Most of the calculated normal vibrational modes of the cationic clusters have frequencies that are around 1000 cm^{-1} and have strong infrared (IR) intensities. The structures of B_{14} and B_{14}^{2-} in octahedral symmetry were investigated by *ab initio* calculations [42]. The geometrical structures and properties of small cationic boron clusters B_n^+ ($n = 2-14$) were determined [43] using the LSD formalism. Most of the final structures of the cationic boron clusters prefer (quasi)planar arrangements and can be considered as fragments of a planar surface or as segments of a sphere. The calculated adiabatic IPs of B_n exhibit features similar to those of measured IPs. Most of the calculated normal modes of the cationic clusters have frequencies around 1000 cm^{-1} and strong IR intensities. A linear search for minima on PESs based on analytical gradient methods and the determination of binding energies of small boron clusters B_n ($n = 2-14$) were conducted using the *ab initio* Hartree–Fock (HF) and SCF CI and QC methods, as well as by means of DFT at the levels of LSD and nonlocal corrections to the exchange–correlation functional [43]. The final optimized HF topologies of the neutral boron clusters are identical with those derived with the LSD approximation. The most stable boron clusters have convex or (quasi)planar structures and the convex clusters seem to be segments of the surface of a sphere. The geometries of B_n^+ clusters for $n \leq 14$ were optimized in [44] applying DFT. The calculation suggested that the experimental results for the $B_n^+ \rightarrow B^+ + B_{n-1}$ fragmentation energies are too small, while experimental $B_n^+ \rightarrow B + B_{n-1}^+$ fragmentation energies for B_4^+ , B_5^+ , and B_{13}^+ are too large. Then, the fragmentation energies were calibrated based on coupling cluster theory. Overall corrected fragmentation energies are found to be in reasonable agreement with experiment. The most stable structure for each cluster was found to be (quasi)planar. The larger clusters are derived from fusing six- and/or seven-membered atomic rings, which share four atoms for the six–six and six–seven rings and five atoms for the seven–seven rings. Based on *ab initio* QC methods, accurate calculations on small boron clusters B_n ($n = 2-14$) were carried out in [45] to determine their electronic and geometric structures. Most of these final structures with $n > 9$ are composed of two fundamental units: either of hexagonal or of pentagonal pyramids. Using the “Aufbau principle,” one

can easily construct various highly stable boron species. The resulting (quasi)planar and convex structures can be considered as fragments of planar surfaces and segments of nanotubes or hollow spheres, respectively.

Above a certain size, boron clusters prefer a cylindrical arrangement over a planar one. Experimental determination of the collision cross section combined with DFT calculations showed [46] that the transition to cylindrical structures takes place at B_{16}^+ . The structure and chemical bonding of B_{16}^- were studied [47] using *ab initio* calculations and photoelectron spectroscopy. Its global minimum is found to be a (quasi)planar and elongated C_{2h} structure. Addition of an electron to B_{16}^- resulted in a perfectly planar and closed-shell B_{16}^{2-} (D_{2h}).

Photoelectron spectroscopy reveals a relatively simple spectrum for B_{19}^- , with a high electron binding energy [48]. Theoretical calculations show that the global minimum of B_{19}^- is a nearly circular planar structure with a central B_6 pentagonal unit bonded to an outer B_{13} ring.

Experimental studies and computational simulations revealed [49] that boron clusters, which favor 2D structures up to 18 atoms, prefer 3D structures beginning at 20 atoms. Using global optimization methods, it was found that the B_{20} neutral cluster has a double-ring tubular structure with diameter of ~ 5.2 Å. For the B_{20}^- anion, the tubular structure is shown to be isoenergetic to 2D structures, which were observed and confirmed by photoelectron spectroscopy. The 2D-to-3D structural transition observed at B_{20} suggests that it may be considered as the embryo of the thinnest single-walled boron nanotubes. B_n^- cluster anions were produced by laser vaporization of a target made of enriched ^{10}B isotope in the presence of the He carrier gas and analyzed with time-of-flight (TOF) mass spectrometer. High-level *ab initio* MO methods were employed [50] to determine the relative stability among four neutral and anionic B_{20} isomers, particularly, the double-ring tubular isomer versus three low-lying planar isomers. They also suggest that the planar-to-tubular structural transition starts at B_{20} for neutral clusters but should occur beyond the size of B_{20}^- for the anion clusters. In order to elaborate a direct experimental method available for structural determination of boron clusters, photoelectron spectroscopy of size-selected cluster anions was combined with quantum calculations to probe the atomic and electronic structures and chemical bonding of small boron clusters up to 20 atoms [51]. Based on this method, the experimental and theoretical evidences were presented showing that small boron clusters prefer planar structures and exhibit aromaticity and antiaromaticity according to the Hückel rules. Aromatic boron clusters possess more circular shapes, whereas antiaromatic ones are elongated. It was found that for neutral boron clusters, the planar-to-3D structural transition occurs at B_{20} , which possesses a double-ring structure, even though the B_{20}^- anion remains planar.

The equilibrium geometries and the systematics of bonding in various isomers of a 24-atom boron cluster using Born–Oppenheimer molecular dynamics (MD) within the framework of DFT were investigated [52]. The B_{24} isomers studied were the rings, convex and (quasi)planar structures,

the tubes, and closed structures. A staggered double ring is found to be the most stable structure among these isomers.

Using *ab initio* QC methods, different structures of B_{32} clusters were investigated in [53]. The most stable isomers have (quasi)planar or tubular structures often containing dove-tailed hexagonal pyramids. In contrast, hollow spheres are less stable. Their stability can be understood as a competition between a curvature strain (favoring [quasi]planar clusters) and an elimination of dangling bonds (favoring tubular and cage structures).

Recently, it was detected [54] experimentally boron quasiplanar cluster B_{36} of hexagonal symmetry with hexagonal hole at the center, which can serve as building block for boron sheets. The boron clusters B_n , $n = 2$ –52, formed by laser ablation of hexagonal boron nitride were discovered with a TOF mass spectrometer [55].

Using *ab initio* QC and DFT methods, the structural transition from planar 2D boron clusters into 3D double-ring system and then into triple-ring system [56] was investigated. The first structural transition occurs at B_{19} and B_{20} clusters, while the second transition occurs between B_{52} and B_{54} clusters. The effect of the repulsive Coulomb forces in boron clusters when they are multi-ionized was also studied.

A mass-spectrometric study of boron cluster anions B_n^- , $n = 7$ –55, produced by laser vaporization from two different types of boron-containing sample rods, YB_{66} and pure boron, was reported in [57]. In mass spectra recorded from the YB_{66} sample, a repeating intensity pattern of boron cluster anions having local maxima at $(B_{13}^-)(B_{12})_{0,2,3}$ as well as at B_{26}^- was observed. Similar phenomena were not observed with a pure boron sample. These facts were attributed to the structural differences between the two materials, in particular, $(B_{12})(B_{12})_{12}$ supericosahedral structure of crystalline YB_{66} .

And finally, let us refer to some studies considering the issue of boron clusters. Some symmetrical clusters of boron, and carbon as well, were discussed [58] by introducing the concept of conjugate polyhedra. It was concluded that if a polyhedron of carbon is given, its conjugate polyhedron of boron can be obtained and the conjugate polyhedron should be of the same symmetry. Based on *ab initio* QC and HF approximations and DFT and linear muffin-tin orbital methods (LMTO) within the atomic sphere approximation (ASA) in [59], the geometric and electronic structures of some atomic-scaled boron clusters were determined. In [60], there were reported experimental and theoretical evidences that small boron clusters prefer planar structures and exhibit aromaticity and antiaromaticity according to the Hückel rules. The planarity of the species was further elucidated on the basis of multiple aromaticity and antiaromaticity and conflicting aromaticity. The major aims of the current research in the field of boron clusters, which are developing, simulating, modeling, and predicting new boron structures to build preselected, uniform nanostructural materials with specific properties, for example, superhardness, superconductivity, superlightness, and propellance, were formulated in the review [61]. According to these and other results obtained by Boustani and coworkers, one can conclude that most structures of boron clusters can be classified into

four groups: (quasi)planar, tubular, convex, and spherical clusters. The transition of the (quasi)planar surfaces into tubules may be pictured by rolling the surfaces and forming cylinders. The closure of boron (quasi)planar surfaces into tubules goes through an energy barrier path. Small boron clusters as individual species in the gas phase were reviewed in [62]. Free boron clusters were characterized using photoelectron spectroscopy and *ab initio* calculations, which have established the (quasi)planar shapes of small boron clusters for the first time.

SHEETS

There are a number of theoretical studies and only few experiments, respectively, predicting and showing the stability of the boron sheets' fragments—planar or quasi-planar boron clusters.

Based on the investigation [41] of geometrical structures and properties of small cationic boron clusters B_n^+ ($n = 2-14$) and using LSD formalism with a nonlocal correction, it was found that a part of the final structures of the cationic boron clusters prefers planar atomic arrangements and can be considered as fragments of a planar surface. The geometry optimization performed in [44] using DFT for B_n^+ clusters with $n \leq 14$ also suggested that the most stable structure for each boron cluster should be planar or quasi-planar. Accurate calculations carried out on small boron clusters B_n ($n = 2-14$) based on *ab initio* QC methods determined [45] that part of the final structures of the boron clusters, namely, with indexes $n > 9$, results in quasi-planar structures and fragments of 2D surfaces.

Very stable quasi-planar clusters of bare boron were found [63] by systematic *ab initio* DFT and QC methods. These quasi-planars are fragments of quasi-planar surfaces, which can be easily obtained and constructed from a basic unit of hexagonal pyramids. An interpretation on double layers of boron quasi-planar surfaces showed an increase in the stability of the system, which can be related to the overlap of π -orbitals between the layers. Therefore, the existence of a series of parallel boron layers was predicted. Based on *ab initio* QC and HF approximations and DFT and LMTO (within the ASA) methods, Boustani and Quandt determined the geometric and electronic structures of atomic-scaled boron surfaces [59]. In contrast to semiconducting boron crystals, the boron sheets showed a metallic behavior. Using *ab initio* QC methods, different structures of B_{32} clusters were investigated in [53]. The part of the most stable isomers was found to have a quasi-planar structure often containing dove-tailed hexagonal pyramids. A curvature strain was found to favor their stability. Among curiously stable cationic B_{13}^+ cluster and its neutral and anionic counterpart isomers examined in [37] through the use of DFT, the (quasi)planar structures were seen to be more stable than 3D isomers. But the ordering by the stability of the (quasi)planar structures changes depending on the cluster charge state. In particular, planar structures of boron benefit from π -delocalization.

The structures of B_7 , B_{10} , and B_{13} boron clusters were studied [64] using the full-potential LMTO MD method. Seven stable structures for B_7 and 15 for B_{10} were obtained. The most stable structures for B_7 , B_{10} , and B_{13} clusters are 2D (quasi)

planar clusters, rather than the 3D ones. Generally speaking, these clusters obey the "Aufbau principle." As for the clusters B_5 and B_5^- , their electronic structure and chemical bonding were investigated [15] using anion photoelectron spectroscopy and *ab initio* calculations. Global minimum of B_5^- was found to have a planar structure with a closed-shell ground state. The geometric structures and total energies of small boron clusters B_n ($n = 2-12$) were investigated using DFT [24]. Within this size range, (quasi)planar structures were found to have the lowest energies. In order to elaborate a direct experimental method available for structural determination of boron clusters, Wang combined [51] photoelectron spectroscopy of size-selected cluster anions with quantum calculations to probe the atomic and electronic structures and chemical bonding of small boron clusters up to 20 atoms. It was found that for neutral boron clusters that the planar-to-3D structural transition occurs at B_{20} , which possesses a double-ring structure.

Zhai et al. reported [60] more experimental and theoretical evidences that small boron clusters prefer planar structures. Small boron clusters as individual species in the gas phase were reviewed by Alexandrova et al. [62]. Free boron clusters were characterized using photoelectron spectroscopy and *ab initio* calculations, which established the (quasi)planar shapes of small boron clusters.

In [65], the results of *ab initio* calculations showing that boron can form a wide variety of metastable planar forms with unusual electronic and mechanical properties were suggested. The preferred planar structure is a buckled triangular lattice that breaks the twofold ground-state degeneracy of a flat triangular plane. Special DFT calculations were carried out [66] to obtain the geometric and electronic structures of boron sheets. The buckled boron sheet formed by alternating up and down rows of B atoms, with a buckling height of 0.85 Å, is found to be about 0.20 eV/atom more stable in energy than the corresponding atomically flat sheet. Two different B–B bond lengths characterize the buckled geometry: 1.63 Å between the atoms in row and 1.81 Å between the atoms in adjacent rows. The flat and buckled sheets have different geometric and bonding characteristics, but both are metallic. The structural and electronic properties of sheets of boron were also investigated using DFT in [67]. Calculations predict the stability of a reconstructed {1221} sheet over the "idealized" triangular {1212} sheet. Analysis of the charge density reveals a mixed metallic and covalent type of bonding in the reconstructed {1221} sheet, in contrast to metallic-type bonding in the idealized {1212} sheet.

Based on a numerical *ab initio* study, in [68], a structure model for a broad boron sheet was discussed. The sheet has linear chains of *sp*-hybridized σ -bonds lying only along its armchair direction of high stiffness and anisotropic bonds properties. The puckering of the sheet was explained as a mechanism to stabilize the *sp* σ -bonds. The anisotropic bond properties of the boron sheet lead to a 2D reference lattice structure, which is rectangular rather than triangular. As a consequence, the chiral angles of related boron nanotubes range from 0° to 90°. *Ab initio* calculations based on generalized-gradient approximation (GGA) to DFT were

performed [69] to study structural and electronic properties of the 2D sheets consisting of the elemental boron. The results found that the boron sheet can be stable and can possess metallic or semiconducting character depending on its atomistic configuration.

In [70], a comparative theoretical study of the structural, electronic, and optical properties of boron sheets by *ab initio* PP calculations was presented. The results indicated that purported 2D boron sheets are metastable. The unusual bond properties of the boron sheets lead to different 2D lattice configurations. In addition to electronic properties of anisotropic bonds, calculated electronic band structures revealed that all proposed boron sheets are metallic.

Based on *ab initio* calculations, the properties of single- and double-layered boron sheets [71] were presented. Single-layered boron sheets, made of hexagons and triangles, have buckled ground-state geometries if the ratio of triangles to hexagons is large and stay flat otherwise. The double-layered boron sheets can form strong interlayer bonds between two layers only if the precursor single-layered sheet itself prefers a buckled ground-state structure. The optimal double-layered boron sheet is semiconducting and more stable than any single-layered sheets.

In [72], a new class of boron sheets, composed of both triangular and hexagonal motifs, which are more stable than structures considered earlier, was presented. The importance of three-center bonding and its competition with two-center bonding was highlighted. These findings called for reconsideration of some earlier data on boron sheets. Using *ab initio* calculations, the work [73] predicted a novel stable boron sheet, which shows different electronic properties. Such sheet is flat and has the structure that the two centers of each three hexagons in the hexagonal lattice are filled with additional atoms, which preserves the symmetry of the triangular lattice. This boron sheet is metal, and there are bands similar to the π -bands near the Fermi level. In [74], the configurations, stability, and electronic structures of a new class of boron sheets were predicted within the framework of DFT at the GGA level. They should be sparser than other proposals. Theoretical results showed that such kind stable boron sheet remains flat and is metallic. There are bands similar to the π -bands near the Fermi level.

Boron sheets of various types were investigated using *ab initio* QC and DFT methods [75]. It was confirmed that the noninteracting free-standing triangular buckled sheet is more stable than the γ -sheet, assembled in the cited work, and than the α -sheet, proposed previously. In contrast, however, when these sheets are considered as infinite periodic systems, the α -sheet remains the most stable one.

A different class of electronically stable boron nanostructure in the form of planar boron sheet can be designed [76], which like the α -boron sheet consists of triangular and hexagonal motifs and has symmetrically arranged hexagonal holes. The binding energy of the proposed new boron sheet is only 0.02 eV/atom lower than that of α -sheet.

The results of a study of the high-pressure phase diagram of elemental boron, using full-potential DFT calculations were

presented in [77]. At sufficiently high pressures (>100 GPa), boron crystallizes in quasi-layered bulk phases, characterized by in-plane multicenter bonds and out-of-plane unidimensional σ -bonds. These structures are all metallic, in contrast to the low-pressure icosahedral ones that are semiconducting. The structure and bonding of layered bulk phases can be easily described in terms of single puckered boron sheets. These results bridge the gap between boron nanostructures and bulk phases. The structural stability and diversity of elemental boron layers were evaluated [78] by treating them as pseudo-alloy $B_{1-x}\Diamond_x$, where $\Diamond$ is a vacancy in the close-packed triangular B lattice. This approach allows for an elegant use of the cluster expansion method in combination with DFT calculations, leading to a thorough exploration of the configurational space. A finite range of composition x was found where the ground-state energy is essentially independent of x , uncovering a variety of stable B-layer phases (all metallic) and suggesting polymorphism.

Due to their metallicity, the boron sheets can serve as a good protective material against the electromagnetic radiation accompanying neutron capture in boron-rich neutron shields [79].

NANOTUBES

There are known number of theoretical and experimental studies on the stability and electronic structure of boron nanotubes.

Based on *ab initio* QC methods, accurate calculations on small boron clusters B_n ($n = 2-12$) were carried out to determine their electronic and geometric structures [45]. Part of the final structures of the boron clusters, with $n > 9$, results in convex structures, which can be considered as segments of nanotubes. Then, using *ab initio* QC and DFT methods, the structures of bare boron clusters were determined [80]. These highly stable nanotubular structures are composed of hexagonal pyramids only and can be considered as segments of extended pips. Applying the "Aufbau principle," one can easily construct stable boron structures besides the nanotubular clusters. Thus, it should help in illuminating the chemical and physical nature of boron materials based on boron nanotubules. The stability of boron tubules defined through binding energy per atom is comparable to that of the most stable quasi-planar clusters, and nanotubular structures were also found inside the boron quasicrystals. Based on *ab initio* QC and HF approximations and DFT and LMTO (within the ASA) methods, the geometric and electronic structures of atomic-scaled boron nanotubes were determined in [59]. Then, using same *ab initio* QC methods, Boustani et al. investigated different structures of B_{32} clusters [53]. The part of the most stable isomers had a tubular structure often containing dove-tailed hexagonal pyramids. The elimination of dangling bonds was found to favor the tubular structures' stability. The results of *ab initio* simulations of bundled single-wall zigzag boron nanotubes-ropes in [81] were presented. Besides the known smooth and puckered modifications, there were different forms found that are radially constricted and seem to be energetically superior. Based on the survey of novel classes

of boron nanotubular materials presented in [82], pure boron nanotubes were shown to be a consequence of a general “Aufbau principle.”

Experimental studies and computational simulations revealed [60] that boron clusters, which favor 2D structures up to 18 atoms, prefer 3D structures beginning at 20 atoms. Using global optimization methods, it was found that the B_{20} neutral cluster has a double-ring tubular structure with a diameter of 5.2 Å. For the B_{20}^- anion, the tubular structure is shown to be isoenergetical to 2D structures, which were observed and confirmed by photoelectron spectroscopy. The 2D-to-3D structural transition observed at B_{20} suggests that it may be considered as the embryo of the thinnest single-walled boron nanotubes.

Evans et al. also reported [65] the results of *ab initio* calculations showing that boron can form a wide variety of metastable planar and nanotubular forms with unusual electronic and mechanical properties. When the plane is rolled into a tube, the twofold ground-state degeneracy of the triangular plane leads to a strong chirality dependence of the binding energy and elastic response. The achiral $(n,0)$ tubes derive their structure from the triangular plane. The achiral (n,n) tubes arise from the buckled plane and have large cohesive energies. The (n,n) boron nanotubes have an internal relaxation mechanism that results in very low Poisson ratio.

DFT calculations were carried out [66] to obtain the geometric and electronic structures of boron nanotubes. Boron nanotubes formed by rolling a buckled B-sheet also exhibit buckled surface when their helicity allows for the formation of alternating up and down B rows in the surface. In all other cases, boron nanotubes exhibit only flat surfaces. Hence, all the $(n,0)$ boron nanotubes have buckled geometry, while not all $(n,0)$ boron nanotubes. The flat and buckled nanotubes have different geometric and bonding characteristics, but both are metallic. The structural and electronic properties of nanotubes of boron were investigated again using DFT in [67]. Nanotubes formed by wrapping the half-metallic reconstructed {1221} sheet show a curvature-induced transition in their electronic properties. An analysis of the charge density reveals a mixed metallic and covalent type of bonding in the {1221} nanotubes, in contrast to metallic-type bonding in the idealized {1212} nanotubes.

Ciuparu et al. reported the first synthesis of pure boron single-wall nanotubes by reaction between BCl_3 and H_2 with Mg-based catalyst over parallel cylindrical pores with uniform diameter of ~36 Å in pure siliceous template [83]. The boron nanotubes produced were approximately 3 nm in diameter, comparable to that of the template pore. The initial length of a tube outside the pore was determined at 16 nm. In order to elaborate a direct experimental method available for structural determination of boron clusters, photoelectron spectroscopy of size-selected cluster anions was combined [51] with quantum calculations to probe the atomic and electronic structures and chemical bonding of small boron clusters up to 20 atoms. In particular, it was found that for neutral boron clusters, the planar-to-3D structural transition occurs at B_{20} , which possesses a double-ring structure, even though the B_{20}^- anion remains planar. The stability of the double-ring

structure suggests the existence of all-boron nanotubes. Real properties of boron nanotubes have been not fully understood because they are hard to synthesize. Fortunately, in [84], a large quantity of boron nanotubes, which may provide a way to master their electric and field emission properties, were successfully fabricated.

Based on DFT calculations, in [85], stable structures of free-standing double-walled boron nanotubes in the form of two single-walled boron nanotubes inside one another were proposed. Puckering of the boron sheets allows the inner atoms of the outer wall and outer atoms of the inner wall to be matched giving *sp*-type hybrids bonding between the walls. The structural stability, in the case of double-walled tubes, increases as the bond interaction between the walls strengthens. All the optimized structures reported are electronically conducting in good agreement with the metallic behavior of the experimentally observed nanotubes.

The structures of a family of multiwalled boron nanotubes, which are built from hexagonal pyramids, were proposed by Mukhopadhyay et al. for the first time in [86].

In [87], the properties of nanotubes obtained from newly described boron α -sheet using DFT were investigated. Computations confirmed their high stability. The frequency of the Raman breathing mode was identified as 210 cm^{-1} . Careful relaxation revealed the curvature-induced buckling of certain atoms off the original plane. This distortion changes the overlap of the orbitals near the Fermi level and opens up the gap in narrow tubes, rendering them semiconducting. However, wider tubes with the diameter $d > 1.7$ nm retain original metallic character of the α -sheet. The configurations, stability, and electronic structures of this class of boron nanotubes were predicted within the framework of DFT at the GGA level as well [74]. Only thin [8,0] nanotube was found to be semiconducting with a bandgap of 0.44 eV, while all the other thick boron nanotubes should be metallic independent of their chirality.

The electronic structure and transport properties of large-diameter boron nanotubes of different structures and chiralities were theoretically studied. [88] The structural and electronic properties of the boron nanotubes by means of dispersion-corrected DFT calculations were investigated. They yield nonpuckered boron nanotube conformations and an associated metallic state for zigzag tubes. The electronic structure and transport properties of boron nanotubes were investigated theoretically in [89]. In particular, for comparison with transport measurements, the intrinsic conductance of ideal nanotubes with large diameters ($D \approx 10$ nm) was determined. All considered nanotubes were found to be highly conductive, irrespective of their structures and chiralities. The value of work function for the nanotubes obtained from the α -sheet agrees well with the experiment. The α -nanotubes with diameters >2 nm are the most stable ones. However, for diameters <0.5 nm, the most stable structures are zigzag nanotubes of the buckled triangular sheet. For structures related to the distorted hexagonal sheet, the most stable nanotube is discovered to have a diameter of 0.4 nm.

For the analysis of the boron nanotubular structures and future purposeful designing the devices based on nanotubular

boron, it is important to be able to predict reliably the sizes of nanotubes with given indices. At the first time, such model was proposed in [90].

We have solved this task with equal B–B bond lengths for the mostly regular forms, which exhibit rolled flat surfaces. Within the frames of the model proposed, the explicit expressions in terms of B–B bond length for atomic sites coordinates and intersite distances in boron nanotubes of regular geometry were obtained [91–95].

If $d_{(n,0)}$ is the B–B bond length in a zigzag $(n,0)$ nanotube, the tube radius $r_{(n,0)}$ is expressed as (Figure 33)

$$r_{(n,0)} = \frac{\sqrt{3}d_{(n,0)}}{4 \sin \pi/2n}$$

Let $d_{(n,n)}$ and $r_{(n,n)}$, respectively, denote the B–B bond length and radius in an armchair (n,n) nanotube (Figure 34), then

$$r_{(n,n)} = \frac{d_{(n,n)}}{2 \sin \pi/n}$$

Here, nanotube index $n = 1, 2, 3, \dots$ determines the number of atoms because the boron nanotube's 1D unit cell consists of $2n$ atoms.

At $n = 1$, zigzag nanotube degenerates into the zigzag atomic chain, while armchair nanotube degenerates into the straight atomic chain. Correspondingly, the formula obtained for $r_{(n,n)}$ in general case does not work; instead, it should be assumed as $r_{(1,1)} = 0$. Degenerated geometries of boron nanotubes were specially considered in [96,97].

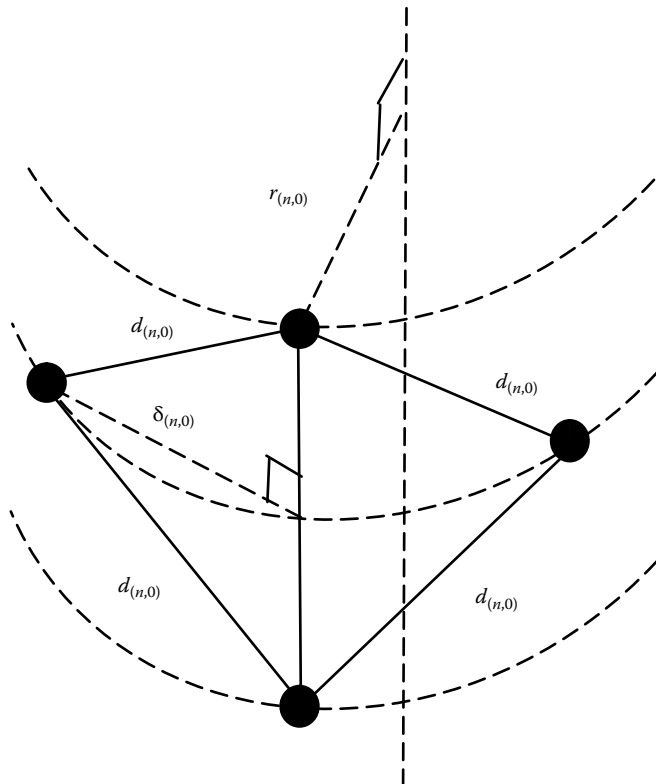


FIGURE 33 For the calculation of boron zigzag nanotube radius. (From Chkhartishvili, L., *J. Phys. Conf. Ser.*, 176, 012013, 2009.)

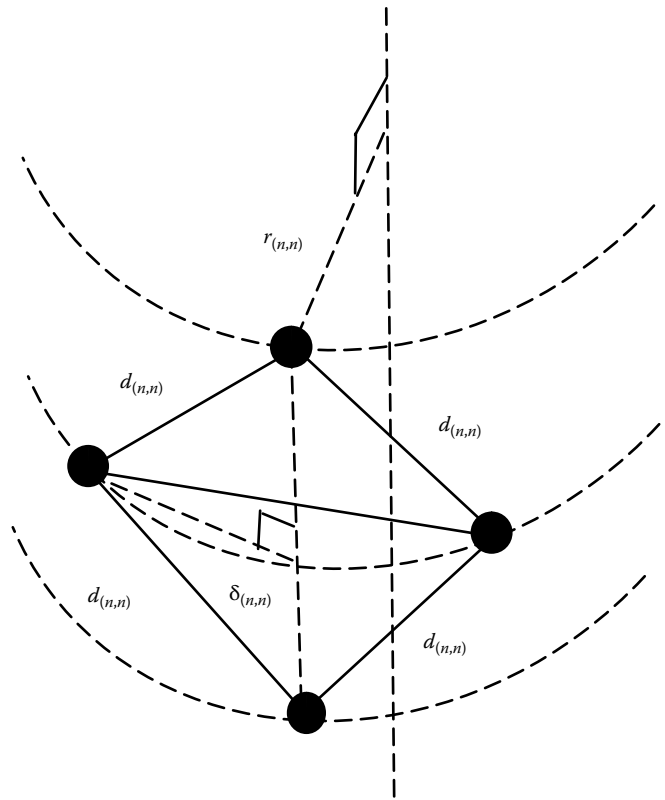


FIGURE 34 For the calculation of boron armchair nanotube radius. (From Chkhartishvili, L., *J. Phys. Conf. Ser.*, 176, 012013, 2009.)

Now, let's consider the detailed regular geometries of the zigzag and armchair boron nanotubes, which one can describe using cylindrical coordinates $\vec{r}(\rho, \phi, z)$.

Constant of the zigzag $(n,0)$ nanotube 1D lattice equals to $d_{(n,0)}$ (Figure 35). Its unit cell consists of two equidistant atomic rings in parallel planes perpendicular to the axis, each with n boron atoms.

Evidently, cylindrical coordinate ρ for all atomic sites equals to tube radius

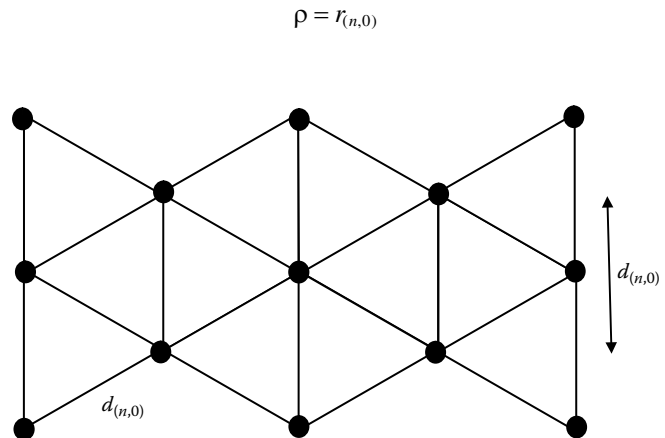


FIGURE 35 For the calculation of lattice constant of boron zigzag nanotube. (From Chkhartishvili, L., *J. Phys. Conf. Ser.*, 176, 012013, 2009.)

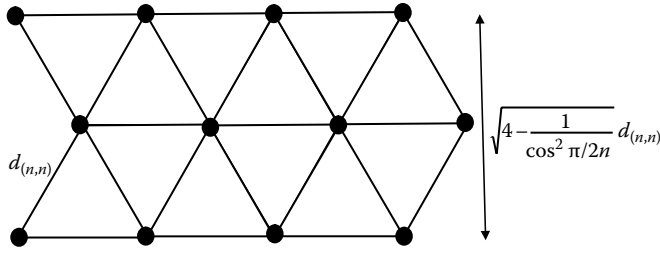


FIGURE 36 For the calculation of lattice constant of boron armchair nanotube. (From Chkhartishvili, L., *J. Phys. Conf. Ser.*, 176, 012013, 2009.)

As for the coordinates ϕ and z , they equal to

$$\phi = \frac{(4k - 3 - (-1)^l)\pi}{2n}$$

and

$$z = \frac{ld_{(n,0)}}{2}$$

Here

$$k = 1, 2, 3, \dots, n$$

$l = 0, \pm 1, \pm 2, \dots$ are the number atomic sites in given and atomic planes, respectively

If $d_{(n,n)}$ is the B–B bond length in an armchair (n,n) nanotube, then its 1D lattice constant equals to $\sqrt{4 - 1/\cos^2 \pi/2n} d_{(n,n)}$ (Figure 36).

The unit cell also consists of two atomic rings in parallel planes perpendicular to the tube axis and, from its part, each ring consists of n boron atoms. Coordinate ρ for all atomic sites again equals to tube radius

$$\rho = r_{(n,n)}$$

while the rest of the cylindrical coordinates equal to

$$\phi = \frac{(4k - 3 - (-1)^l)\pi}{2n}$$

$$z = \sqrt{1 - \frac{1}{4\cos^2 \pi/2n}} ld_{(n,n)}$$

where again $k = 1, 2, 3, \dots, n$ and $l = 0, \pm 1, \pm 2, \dots$

On the basis of the aforementioned obtained relations, the squared distances between an arbitrary atomic site $\vec{r}(\rho, \phi, z)$ and site $\vec{r}_0(\rho, 0, 0)$ of the so-called central atom with $l = 0$ and $k = 1$, that is, with $\phi = 0$ and $z = 0$, in zigzag

$$\frac{\left(\binom{kl}{(n,0)} \text{B} - \binom{00}{(n,0)} \text{B} \right)^2}{d_{(n,0)}^2} = \frac{3\sin^2(4k - 3 - (-1)^l)\pi/4n}{4\sin^2 \pi/2n} + \frac{l^2}{4}$$

and armchair tubes

$$\frac{\left(\binom{kl}{(n,n)} \text{B} - \binom{00}{(n,n)} \text{B} \right)^2}{d_{(n,n)}^2} = \frac{\sin^2(4k - 3 - (-1)^l)\pi/4n}{\sin^2 \pi/n} + \left(1 - \frac{1}{4\cos^2 \pi/2n} \right) l^2$$

were found.

Sizes of the small single-walled B-nanotubes were estimated [93] assuming bond lengths as $d_0 \approx 1.78 \text{ \AA}$, that is, the equilibrium interatomic distance value according to the quasiclassical B–B pair potential [98]. Actually, $d_{(n,0)}$ and $d_{(n,n)}$ depend on n , and their exact values cannot be determined geometrically. In general, this task requires solving of the physical problem of the binding energy maximization for given nanotubular structure with respect to the B–B bond length. But these dependences have to be too weak. Similarly, one can estimate molar binding energy of a boron nanotube: 8.40 eV/atom [92].

Based on the aforementioned geometrical model—so-called *analytical* model—all-boron nanotubular bundles were evaluated [99–101] as the best neutron-shield material, that is, material with highest possible concentration of ^{10}B -atoms.

Independently, the so-called *idealized* polyhedral model was formulated to describe the geometry of single-walled boron nanotubes in [102]. The boron nanotubes were assumed to be formed by sp^2 -hybridization and adopt a at equilateral triangle pattern. Beginning from the fundamental postulates that all bond lengths are equal and all atoms are equidistant from the common cylindrical axis, exact formulas were derived for the geometric parameters of the nanotube—radius, bond angle, and unit cell length—and presented asymptotic expansions for these quantities to the first two orders of magnitude. The fundamental variable of this model is the subtend semi-angle from which all the other parameters are derived and given as a root of a transcendental equation and, therefore, cannot be written as an explicit analytical function of tube indices. Further, authors surveyed [103] a number of existing nanotubular boron structures proposed by themselves as possible exact geometric models for boron nanotubes, taking into account that conventional rolled-up model of nanotubes completely ignores any curvature effect.

It is evident that the success of future nanotechnologies will strongly depend on the ability to control the structure of materials on the atomic scale. For usual carbon nanotubes, it turns out that one of the key structural parameters, the chirality, may not be controlled during synthesis. It was shown that boron nanotubes, which are related to sheets with anisotropic in-plane mechanical properties, could actually overcome these problems [104].

Based on the first-principle calculations, the properties of single- and double-walled boron nanotubes were presented [71]. The curvature energies, buckling behavior, and soliton structural fluctuations for single-walled boron nanotubes and the implications for the electronic properties of

these nanotubes were discussed. The semiconducting nature of small-diameter single-walled nanotubes is robust under various perturbations and fluctuations. Due to strong bonds forming between walls, the optimal double-walled boron nanotubes have different wall structures from single-walled ones. Such double-walled nanotubes are always more stable than any single-walled nanotube and are furthermore metallic.

FULLERENES

An interesting feature of elemental boron and boron-rich compounds in solid state is the occurrence of highly symmetric icosahedral clusters. The rich chemistry of boron is also dominated by other 3D cage structures.

The electronic and geometric structures, total and binding energies, harmonic frequencies, point symmetries, and HOMO–LUMO gaps of small neutral boron B_n ($n = 2$ –12) clusters have been investigated [24] using DFT. Convex and 3D cage and open-cage structures were found along with other structures. None of the lowest-energy structures and their isomers has an inner atom, that is, all the atoms are positioned at the surface.

The curiously stable B_{13}^+ cationic cluster and its neutral and anionic counterparts were examined [37] through the DFT. An intriguing atom-in-cage structure was found to be a local minimum on the cationic, neutral, and anionic surfaces. A structure was found for the B_{13}^- anionic cluster, and the 12 external boron atoms were determined to be arranged as three of six-membered rings back-to-back.

Part of the final structures of the cationic boron clusters B_n^+ ($n = 2$ –14) obtained [41] by the linear search for minima on the LSD PES prefers such quasi-planar atomic arrangements that can be considered as segments of a sphere. The structure and stability of small neutral boron clusters B_n ($n = 2$ –14) was investigated [105] employing DFT. The search for minima was performed using gradient methods at the LSD. Using *ab initio* QC methods, accurate calculations on small boron clusters B_n ($n = 2$ –14) were carried out [45] to determine their electronic and geometric structures. The geometry optimization with a linear search to local minima on the PES was performed using analytical gradients in the framework of the restricted HF SCF approach. Most of the final structures of the boron clusters with $n > 9$ result in convex structures, the segments of hollow spheres.

Calculations using Born–Oppenheimer MD within the framework of DFT revealed [52] that a B_{24} cluster does form closed 3D structures. The fusion between two icosahedra occurs when the distance is less than a critical distance of about 6.5 a.u.

Applying *ab initio* QC methods, different structures of B_{32} cluster were investigated [53]. However, hollow spheres were found to be less stable than quasi-planar and tubular isomers.

Based on a systematic *ab initio* HF SCF and direct CI methods, Boustani suggested [106] that stable convex and spherical structures of bare boron clusters can easily be obtained with the help of the “Aufbau principle.” It should be

emphasized that introduced convex and small spherical clusters differ from the “classical” forms known for boron crystals. Convex surfaces simulate boron surfaces, which can be considered as segments of open or closed spheres. Two convex clusters B_{16} and B_{46} are relatively stable and can be considered to act as a calibration mark. The closed spherical clusters B_{12} , B_{22} , B_{32} , and B_{42} are found to be less stable.

Recently, it was detected [107] experimentally boron anionic fullerene B_{40}^- . A new class of electronically stable boron nanostructures in the form of $60n^2$ boron fullerene family can be designed [76]. The $60n^2$ boron fullerenes are chiral and the initial icosahedral symmetry of the fullerenes is lowered due to Jahn–Teller distortion.

Among the boron cages, B_{80} is of special interest. The geometry, electronic, and structural properties of an unusually stable boron cage made of 80 boron atoms were studied using *ab initio* calculations [108,109]. In the B_{80} case, there is an atom in the center of each hexagon. The resulting cage has HOMO–LUMO energy gap of ~ 1 eV and, most importantly, is energetically more stable than boron double rings, which were detected in experiments and considered as building blocks of boron nanotubes. This seems to be the most stable boron cage. Using *ab initio* calculations, the work [110] analyzed electronic structure and vibrational modes of the boron fullerene B_{80} . There exist several isomers, lying close in structure and energy, with total energy difference within 30 meV. Calculated radial breathing mode frequency turns out to be 474 cm^{-1} , which can be a characteristic of B_{80} in Raman spectroscopy. Since the B_{80} structure is made of interwoven double-ring clusters, double rings with various diameters were also investigated, presented their structure and HOMO–LUMO dependence on the diameter, and found out that the gap alternates for different sizes and closes its value for infinite double ring. According to [111], the boron buckyball avoids the high-symmetry icosahedral cage structure. The previously reported I_h symmetric structure is not an energy minimum in the PES and exhibits a spontaneous symmetry breaking to yield a puckered cage with a rare T_h symmetry. The HOMO–LUMO gap amounts to 1.94 eV. A symmetry analysis of the valence shell in the boron buckyball B_{80} shows [112] that the cap atoms participate in the bonding by 30 orbitals, which transform as the σ -bonds along the 6–6 edges. The symmetry of the boron buckyball and a related boron nanotube was investigated in [113]. Using large-scale *ab initio* calculations up to second-order Møller–Plesset perturbation theory, the equilibrium geometry/symmetry of two structurally related boron clusters was determined unambiguously: the B_{80} fullerene and the finite-length (5,0) boron nanotube. The structural and electronic properties of the B_{80} buckyball by means of dispersion-corrected DFT calculations were investigated [114]. Analysis reveals the vibrational stability for the icosahedral B_{80} , in contrast to the instability to a tetrahedral B_{80} with puckered capping atoms. It was shown in [115] by means of *ab initio* calculations that in boron nanostructures a large variety of 2D structures can be obtained, all with similar energetic properties and some of them are even more stable than the B_{80} fullerene. Disordered configurations

are energetically comparable with ordered ones. Cage-like structures that are not ordered are thus comparable in energy to the more ordered original B_{80} fullerene. This result opens a new pathway for the synthesis of the B_{80} fullerene as an endohedral fullerene. The isocentric method at the coupled HF level was used for the calculation of magnetically induced ring currents in the boron buckyball B_{80} , for both I_h and distorted T_h geometries [116]. Paratropic currents on the pentagons are predominant in the boron buckyball. The observations support the conclusion that B_{80} should be considered (weakly) antiaromatic. The largest orbital contributions to the ring currents in the molecule were identified and related to specific excitations in the frontier orbital region.

The general constructing schemes for a large family of stable hollow boron fullerenes with $80 + 8n$ ($n = 0, 2, 3, \dots$) atoms were revisited [117]. In contrast to the hollow pentagon boron fullerenes with 12 hollow pentagons, the stable boron fullerenes constitute 12 filled pentagons and 12 additional hollow hexagons, which are more stable than the empty pentagon boron fullerenes including the “magic” B_{80} buckyball. On the basis of results from DFT calculations, an empirical rule for filled pentagons is proposed along with a revised electron-counting scheme to account for the improved stability and the associated electronic bonding feature.

From the curvature and size of the convex clusters, it was predicted in [105] that a spherical boron cluster should consist of 90 boron atoms, and there may exist a group of elemental spherical boron clusters. The frequency analysis was carried out for the most stable convex and quasi-planar clusters only. Most of the calculated IR vibration frequencies lie in the interval $200\text{--}1400\text{ cm}^{-1}$. In addition to the main conclusion that most of the neutral and cationic boron clusters have similar topologies, one can deduce that the evolution of most of the structures with increasing cluster size exhibits some regularities including the tendencies of convex clusters to converge to a definite spherical cluster consisting of about 90 boron atoms and 3D structures to close the open spheres with a small number of atoms.

In [118], the performance of the DFT methods in the energetics of boron clusters and confirmed that the core-shell construction (stuffed fullerene) is thermodynamically the most favorable structural pattern for B_{80} was carefully evaluated. The global minimum search showed that both B_{101} and B_{103} also prefer a core-shell structure and that B_{103} can reach the complete core-shell configuration.

Ab initio electronic structure calculations showed that boron clusters B_{98} , B_{99} , B_{100} , B_{101} , and B_{102} based on icosahedral- B_{12} stuffed fullerenes are more stable than the fullerene-like boron clusters [119]. These structures are envisaged as an icosahedral B_{12} each vertex of which is connected to the apex of a pentagonal pyramid B_6 via radial σ -bonds. B_n ($n = 84\text{--}116$) clusters are generated around the resulting structure $B_{84} = B_{12}@B_{12}@B_{60}$. The possibility of producing such B_{12} -based giant clusters was also considered.

Boron nanostructures in the form of spheres and multirings beside a ring consisting of icosahedral B_{12} units were investigated using *ab initio* QC and DFT methods [75]. The structure

of the B_{100} fullerene exhibits unusual stability among all non-interacting free-standing clusters and is more stable than the B_{120} cluster fragment of the γ - B_{28} solid. The stability of the multirings was compared and the structural transition from double-ring to triple-ring systems was reported. This structural transition occurs between B_{52} and B_{54} clusters.

Based on *ab initio* QC and DFT methods, the work [86] determined the geometric, electronic, and structural properties of boron cluster families, including spheres, up to a cluster size of 122 atoms. The most stable structure is the B_{100} sphere showing similar shape but more stability than the B_{80} cage. The structures of a family of nearly round boron cages, which are built from hexagonal pyramids, had been proposed for the first time.

Some highly spherical shells of boron atoms including “supericosahedron” B_{156} , which can exist in boron-rich solids, were considered by Perkins et al. [120].

QUASICRYSTALS, NANOBELTS, NANORIBBONS, NANOWIRES

Quasicrystals are intermediate species between periodical crystals and amorphous solids: on the one hand, they possess a symmetry materialized in the corresponding structural element, but, on the other hand, they are not periodic. This issue takes on special significance in connection with boron because icosahedral cluster structures are characteristic of all-boron crystalline modifications.

Quasicrystals in an oblate rhombohedral unit cell of α -rhombohedral boron crystal were constructed, and the transition of two icosahedra lying at the ends of its short body diagonal was simulated in [121]. By applying HF SCF methods, different configurations of two icosahedra were investigated. The obtained structure B_{24} exhibits a closed tubular form of two coalesced interpenetrating icosahedra. A model based on a B_{21} cluster, composed of two icosahedra with mutual three interfacing atoms, was also investigated. Based on a series of *ab initio* studies, the remarkable structural stability of nanotubular and quasi-planar boron clusters was pointed out and postulated the existence of novel layered, tubular, and quasicrystalline boron solids built from elemental subunits [122]. Then, the unit cell of hypothetical α -B quasicrystals by applying accurate *ab initio* QC methods was considered [123]. As it is known, atomic decoration of the α -rhombohedral boron unit cell is based on a suitable arrangement of eight boron icosahedra, and thus, the mechanism of their cohesion is stimulated by relaxing a B_{96} supercluster composed of icosahedral boron clusters located at the vertices of the rhombohedral unit cell. Total energies showed that segments of nanotubes and quasi-planar sheets turn out to be more stable than the unit cell of α -B quasicrystal. The surface energies of α - and β -rhombohedral and tetragonal boron were *ab initio* calculated [124] to investigate their role in nanoscale crystal growth. Equilibrium shapes of boron crystals were obtained using Wulff’s theorem. Although the existence of pure α -tetragonal boron had long been denied, it was recently prepared in the form of

a nanowire. Results of calculations showed that nano- α -tetragonal boron, despite its low cohesive energy, is more stable than the other structures as a result of its low surface energy when the number of atoms is less than about 216. The surface energy of β -tetragonal boron was found to be higher than that of α -tetragonal boron and lower than that of α - and β -rhombohedral boron. Nevertheless, β -tetragonal boron has the lowest total energy of all-boron polymorphs in a region with a number of atoms 216–512.

In addition to the 3D quasicrystals, boron can exist in quasi-2D and quasi-1D nanocrystalline forms such as nanobelts, nanoribbons, and nanowires.

Wang et al. have successfully fabricated single-crystalline tetragonal boron nanobelts by laser ablation method in a furnace at the temperature range of 700°C–1000°C under the 25 Pa of argon [125]. The obtained boron nanobelts were rectangular in cross-sectional shape with a width-to-thickness ratio of about 5, several tens to about 150 nm in width, and several μm to the order of mm in length. The interior was well crystallized in tetragonal and amorphous structures of 2–4 nm thick. Kirihaara et al. studied [126] electrical transport in single-crystalline boron nanobelts. These nanobelts were synthesized using pulse laser ablation. Thickness and lengths were approximately 25 and 100 nm, respectively. From the temperature dependence of electrical conductance, the material was found to be a semiconductor. The electrical conductivity was of order of $10^{-3} \text{ Ohm}^{-1} \cdot \text{cm}^{-1}$ at room temperature. Fitting results to variable-range hopping conduction revealed a high density of localized states at the Fermi level. The Mg-doped boron nanobelts had the almost same α -tetragonal crystalline structure as the pristine nanobelts [127]. The pure boron nanobelt was a p-type semiconductor, and its electrical conductivity and carrier mobility at room temperature were estimated to be on the order of $10^{-3} \text{ Ohm}^{-1} \cdot \text{cm}^{-1}$ and $10^{-3} \text{ cm}^2/\text{V} \cdot \text{s}$, respectively, with activation energy of $\sim 0.19 \text{ eV}$. After Mg-vapor diffusion, the nanobelts were still semiconductor, while the electrical conductance increased by a factor of 100–500. Single-crystalline boron nanobelts were catalyst free synthesized using pulse laser ablation in [128]. Temperature coefficients of electrical conductance and carrier mobility revealed a hopping conduction. On the other hand, doping of Mg atoms into the boron nanobelt increased the conductance by a factor of more than ~ 100 at room temperature. In vacuum, a photoresistivity effect consisting of the continuous decrease of conductance under blue light illumination was observed. The convergent-beam electron diffraction at room temperature was applied [129] to the boron nanobelt structural analysis. All obtained reflections can be indexed with tetragonal unit cell. The pattern showed two mirror symmetries, which are consistent with space group of the α -tetragonal boron structure. The crystal structural parameters and electron density were determined. The electron energy loss spectroscopy and soft x-ray emission spectroscopy were used [130] to investigate the electron structure of boron nanobelts with 40 and 130 nm width. The energy position of top of valence band was found to be almost the same as in β -rhombohedral boron. At the same time, boron nanobelt spectrum shows some different structures, from

which it is expected to be a semiconductor with a narrow bandgap of $\sim 0.2 \text{ eV}$. Boron nanobelts are either a semimetal or a narrow-gap semiconductor. Hyodo et al. attempted Li and Mg doping into boron nanobelts [131], whose crystalline structure was of α -tetragonal boron and discussed the possibility of metal transition and superconductivity. As it is known, the thermal neutron transmutation of ^{10}B isotope of boron is a method of carrier doping into boron structures because the neutron capture reaction $^{10}\text{B}(n, \alpha)^7\text{Li}$. After healing-induced radiation damages, Li atoms can modify their transport property. The effects of this neutron capture reaction on the structure and electrical transport of ^{10}B -enriched single-crystalline boron nanobelts were reported in [132]. The corresponding drastic change in the conductance was discussed [133] based on the distribution of localized states in forbidden band of the crystalline α -tetragonal boron.

Catalyst-free growth of boron nanoribbons was observed [134] by pyrolysis of diborane at 630°C–750°C and $\sim 200 \text{ mTorr}$ in quartz tube furnace. Nanodiffraction, TEM, and SEM analysis indicated that the nanoribbon is single-crystalline α -tetragonal boron covered by a 1–2 nm thick amorphous layer. Low-pressure chemical vapor deposition (CVD) was used [135] to synthesize crystalline boron nanoribbons of 16 nm thickness by pyrolysis of diborane at relatively low temperature of 925°C. Obtained nanoribbons were with α -tetragonal structure, however, with significant amounts of impurities presented at surface, ~ 14 , 14, and 2% of O, C, and N, respectively.

Using *ab initio* QC and DFT methods to determine stable structures of bare boron, in addition to other forms, the existence of the boron scroll-type filaments arising from coaxial closed layers of tubular surfaces can be predicted [80]. *Ab initio* QC methods were used to study ground-state energies and geometrical configurations of boron chains [136]. Vertically aligned boron nanowires in self-assembled large-scale arrays with excellent uniformity and high density were fabricated [137] using radio frequency (RF) magnetron sputtering of boron and B_2O_3 powder onto various substrates. The produced nanowires were several tens of μm long and 20–80 nm wide, with typically platform-shaped tips. The ground-state energies of the boron chain were found to be comparable with those of boron clusters. The structure of chains can be obtained by unfolding the two rings of boron nanotubes. Well-aligned amorphous boron nanowires were prepared using magnetron sputtering also in [138]. One type is straight without any branch, and the other type is feather like in morphology. It was revealed that both the straight and feather-like boron nanowires possess the microstructure of the outer oxidized cover layer and inner pure boron. Well-aligned boron nanowire arrays were grown vertically on silicon substrates over areas up to several tens of square centimeters using RF magnetron sputtering of highly pure boron [139]. During the growth and self-assembly of boron nanowire arrays, no template or catalyst was needed. The thickness of the outer oxidized cover layer was about 1–2 nm. Actually, crystalline boron nanowires with tetragonal structure were synthesized based on laser ablation of a B/NiCo target in [140]; the nanowires were sometimes single crystals and had a droplet at one end; the droplet contained all

the target elements, which indicates that the vapor–liquid–solid (VLS) mechanism may play a key role in the growth. Highly ordered boron nanowire multiple nanojunctions with unilateral feather-like morphology were created via a magnetron sputtering method [141]. In [142], the growth of the boron nanowires by CVD process was reported. The nanowires had diameters in the range of 20–200 nm (mean value ~ 60 nm), lengths of several μm . These nanowires are semiconducting and exhibit electrical properties consistent with those of elemental boron. The nanowires are whisker crystals rather than nanotubes. However, lattice parameters $a = 9.4$, $b = 7.1$, and $c = 5.4$ Å of the orthorhombic unit cell did not match those of any known boron polymorph. High density of arrays of self-oriented boron nanowires grown on silicon substrates was synthesized by RF magnetron sputtering with a target of highly pure boron and boron oxide mixture using argon as the sputtering atmosphere [143]. The vapor–cluster–solid mechanism was proposed for the well-aligned growth of the amorphous boron nanowires. Crystalline boron nanowires were also produced [144] through annealing of the synthesized amorphous boron. Selected-area electron diffraction studies showed that the crystalline boron nanowires belong to the β -rhombohedral structure. In [145], the large-scale synthesis of well-ordered boron nanowires and their structural stability at high pressure was reported. These boron nanowires with uniform diameter and length grown vertically on silicon substrates were synthesized by RF magnetron sputtering with a target of pure boron using argon as the sputtering atmosphere without involvement of templates and catalysts. Detailed characterization indicated that the boron nanowires are amorphous. No crystallization was observed up to a pressure of 103.5 GPa, suggesting that the amorphous structure of boron nanowires is stable under high pressure at ambient temperature. Large-scale arrays of feather-like boron nanowires were successfully prepared using magnetron sputtering with a target of highly pure boron and boron oxide mixture in [146]. It was revealed that the feather-like boron nanowires possess the microstructure of outer oxidized coating layer and inner pure boron. The thickness of the outer oxidized layer is about 1–2 nm. Electrical transport in crystalline boron nanowires was studied [147] using electrodes made on individual nanowires. Measurements demonstrated p-type semiconductor behavior with estimated carrier mobility of $10^{-3} \text{ cm}^2/\text{V}\cdot\text{cm}$. This behavior was attributed to electric-field-induced impact ionization. These T- and Y-type nanojunctions stand freely in line to form uniform and well-oriented arrays on the substrate surface over areas of up to several tens of square centimeters. Boron nanowires were synthesized by laser ablation at high temperature [148]. The boron nanowires have lengths of several tens of μm long and diameters of 30–60 nm. Boron nanowires with different morphologies and diameters were fabricated by laser ablation in [149]. The systematic analyses show that the VLS model may play an important role in their growth. As it was demonstrated [150], boron nanowire Y-junctions can be synthesized in a self-assembled manner by fusing two individual boron nanowires grown inclined toward each other. Using DFT approach [24], the linear structures have been found along with other boron structures.

APPLICATIONS

All-boron nanostructures are considered as a class of materials perspective in various fields of technical and technological applications.

Although mostly observed in gas phase, pure boron clusters are promising molecules for coordination chemistry as potential new ligands and for materials science as new building blocks. Polyhedral boron clusters are also interesting for creating medicines for boron neutron capture therapy.

Multilayered boron sheets and bundles of boron nanotubes have to be effective shielding materials against neutron beams and accompanying electromagnetic radiation.

Boron sheets, nanotubular, and fullerene surfaces are the promising structures for hydrogen storage in nanoreservoirs. In particular, boron nanoribbons, which do not roll up to multiwall tubular forms, possess the dangling bonds at their surfaces that may be available for bonding other elements, including hydrogen.

Boron nanotubes are predicted to have high metallic conductivities. Consequently, boron-related (quasi-) 1D nanostructures might be good candidates for applications as nanoscale interconnects. Any 1D structure of boron could be useful in various functional nanoscale devices (such as nanoprobe with high strength, nanowire chemical sensors with high sensitivity, thermoelectric nanoconverters, and solid-state neutron sensor) because of their thermal stability and mechanical strength. The 1D structure of boron has also attracted much attention as a building block for microelectromechanical systems. Additionally, the electronic properties and diameters of B-based nanowires are amenable to synthetic control. Thus, both the conducting and semiconducting components necessary to build devices of nanoelectronics can be obtained from B-based nanowires. The structure of the boron nanowires Y-junctions' arrays may allow construction of three- or multiple-terminal nanowire devices directly on readout circuits through controlled nanowire growth.

Furthermore, it was shown that the strain energy of boron nanotubes depends on their radii as well as chiral angles. This is a rather unique property among nanotubular systems, and it could be the basis of a different type of structure control within nanotechnology.

The study of adsorbents on boron nanoparticle surfaces, in particular boron nanotubes, has become of interest in surface science because of its importance of catalytic and gas sensors for industrial applications.

Recently, a large quantity of boron nanotubes, which may provide a way to master their electric and field emission properties, have been successfully fabricated.

Boron icosahedral cluster solids have the high density of electron states due to the high symmetry of the B_{12} cluster. On the other hand, the high phonon frequency and large electron–phonon coupling constant are also characteristic for boron-rich solids. These features give an advantage for high- T_c superconductivity. If one can dope metallic element into boron icosahedral cluster solid, in particular, in boron nanobelts, to adjust the Fermi energy to the position of the high density of states, then high- T_c superconductivity can be expected.

Boron nanomaterials enriched in ^{10}B isotope can serve as lightweight neutron protective armor and neutron absorber in fusion reactors or as very high-temperature semiconductors. Recently, the large-scale single-crystalline ultrathin boron nanosheets have been fabricated via thermal decomposition of diborane [151]. The strong combination performances of low turn on field of field-emission, favorable electron transport characteristics, high sensitivity and fast response time to illumination reveal that the nanosheets have high potential applications in field-emitters, interconnects, integrated circuits, and optoelectronic devices.

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Boron Nanostructures: Boron Nitride Nanostructures

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INTRODUCTION

For the first time, a modified neglect of diatomic overlap (MNDO) study of boron nitride analogs of carbon fullerenes was presented in [1], and $B_{30}N_{30}$ cage molecule was predicted to be stable and, consequently, possible to be synthesized. Based upon the similarity of structures of BN-layered crystals with graphite, the stable BN nanotubes and hexagonal BN layered into cylinders were assumed. Actually, by means of arc discharge, BN nanosystems had been obtained both from carbon templates [3] and in carbon-free media [4].

Classification scheme of the 3D nanostructures based on crystallite and grain boundary forms and chemical composition, in particular, useful for boron nitride was suggested in Ref. [5]. According to the extended classification [6], 1D, 2D, and 3D structures may serve as building blocks for any kD structure if $k \geq l, m, n$ ($k, l, m, n = 0, 1, 2, 3$) are dimensions of the nanostructures. At present, there are available several reviews on boron nitride nanostructures (see, e.g., Ref. [7–11]).

MOLECULES

It is expedient to start with characterizing the molecular boron nitride and, especially, diatomic molecule BN because it can be considered as the main building block of all the boron nitride nanostructures with the stoichiometry B/N = 1:1.

BOND LENGTH

Boron nitride diatomic molecule can be considered as an isolated B–N bond (Figure 37). The experimental value of its length d (at the isotopic composition of the molecule $^{11}B^{14}N$), according to the handbook [12], is 1.281 Å.

As for the available theoretical estimates of the distance between the centers of atoms B and N in the diatomic molecule, they are the following. From the boron–nitrogen interatomic interaction potential graph (a discrete points plot) [13], at equilibrium, one gets $d = 1.307$ Å. The closely comparable theoretical result, 1.320 Å, was reported in Ref. [14]. Parameterization of short-range interaction in the diatomic

molecule BN by the Morse potential (based on not only the *ab initio* calculations but also experimental data) carried out in Ref. [15], for the length of a single B–N bond, gave the value 1.32523 Å. Using quasi-classical analysis of the potential curve obtained in the so-called “potential–density” parameterization scheme, we have obtained the overestimated value of 1.58 Å [16,17]. Later, similar calculations were carried out in the scheme of “density–potential,” leading to the estimate $d = 1.55$ Å [18]. Thus, the semiempirical and theoretical values of the single B–N bond length giving the right order of magnitude overestimate its real value. A possible explanation is that the triplet ground state of the diatomic BN is too close in energy with singlet excited state with a longer bond.

As for the quasi-classical estimates, 1.55 and 1.58 Å, they are closer to the lengths of B–N bonds realized in structures of boron nitride: 1.45 Å for intralayer bonds in h-BN, 1.57 Å for equivalent bonds in cubic (c-BN), and 1.57 and 1.59 Å for two types of bonds in wurtzite-like (w-BN) structures. The bond length in the layers of h-BN, where each atom has three neighbors, is the most deviated from these quasi-classical estimates, by about 6.5%, while the bond length in the tetrahedrally coordinated crystal c-BN falls between the two quasi-classical estimates. Bond lengths in the w-BN, for which the coordination number is also equal to 4, differ no more than by 0.6% from the quasi-classical estimates. Thus, there is a tendency that the accuracy of the quasi-classical approach improves with an increase in the coordination of the structure. The reason for the lower accuracy at low coordination number (in a diatomic molecule, it is equal to 1) should be associated with the used parameterization schemes that are based on the assumption of spherical symmetry of the constituent atoms.

BOND POLARITY

In the BN molecule, as well as in any other (nano)structural modification of boron nitride, the chemical bond is mainly covalent with a relatively small ionicity caused by the redistribution of the valence electronic charge between the B and N atoms when bonding.

The calculation of a quasi-molecular minimum unit cell of h-BN in the 2D approximation, that is, essentially of B_1N_1 , leads to the following populations of the valence levels: $s(B) = 0.88$, $p_{xy}(B) = 0.23$, $p_z(B) = 0.69$, $s(N) = 1.12$, $p_{xy}(N) = 0.77$, and $p_z(N) = 1.31$ [19]. For the effective deficit of valence electrons in B and N atoms in the molecule relative to their numbers of isolated atoms, we obtain, respectively, $3 - (0.88 + 0.23 + 0.69) = +1.20$ and $3 - (1.12 + 1.77 + 1.31) = -1.20$, which means the configuration $B^{+1.20}N^{-1.20}$. Thus, an electron charge transfer

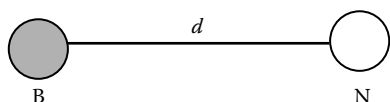


FIGURE 37 Isolated B–N bond of diatomic boron nitride.

from boron to nitrogen is predicted, which is as it should be based on the electronegativities of these chemical elements. However, the magnitude of the ionic charge of ± 1.20 seems too overestimated. One should pay attention to the fact that the distance between neighboring atoms within the layers of h-BN, for which these calculations were carried out, differs from that of the isolated molecule BN.

Studies [20,21] reported the *ab initio* calculation of BN diatomic system using molecular wave functions, which leads to a configuration $B^{+0.47}N^{-0.47}$. So, at this time, a physically reasonable value of the transferred charge ± 0.47 was obtained.

DISSOCIATION ENERGY

Earlier, as an experimental value of the dissociation energy D of BN molecule, the value of (4.0 ± 0.5) eV was recommended [22]. Now, a number of semiempirical and theoretical estimates of the energetic characteristics of this molecule have been reported.

By using a self-consistent field (SCF) molecular orbital (MO) method [23], for the total energy of the lowest state of BN molecule, 2141.6 eV was obtained, whereas the experimental value is lower at 2161.7 eV. For the binding energy, calculated as the difference between the sum of total energies of boron and nitrogen atoms in the isolated states (respectively, 671.0 and 1486.1 eV) and the energy of their diatomic molecule, a meaningful value of $D = 4.6$ eV was obtained.

The potential energy of interaction between atoms B and N was calculated using an original SCF [13] for some discrete values of the interatomic distance: 0.748, 1.175, 1.281, 1.387, and 3.500 Å. The estimate according to spectroscopic parameters of the corresponding B–N interatomic potential curve, for the dissociation energy, yields 5.05 eV.

Theoretical potential curves of the BN molecule were referred [24] in the supplement to the handbook [12]. Using a Monte Carlo-type method within the quantum chemical model involving the Coulomb and electron contributions, the energy of interaction in the B–N system was calculated [25] to obtain some thermodynamic properties of multiboron-based molecules.

We have constructed the binding energy curve of the molecule BN within the initial quasi-classical approximation using the parameterization schemes “potential–density” (Figure 38) [16,17,26] and the “density–potential” [18]. This curve exhibits behavior typical of pair interatomic potentials. In particular, $E(0) = -\infty$ and $E(d) \equiv 0$ if d is equal to or greater than the sum of the atomic radii, $d \geq r(B) + r(N)$, while in the region $0 < d < r(B) + r(N)$, it oscillates. Among several peaks that stand out of the curve part with $E = E(d) \equiv 0$, only one is attainable kinetically, and it corresponds to the equilibrium state—the figure shows the range in its vicinity. The quasi-classical binding energy of BN molecule within “potential–density” and “density–potential” schemes was evaluated as 4.79 and 4.51 eV, respectively.

In relation to the molecular dynamical (MD) investigation [27] of the BN fullerene structures, it was noted that

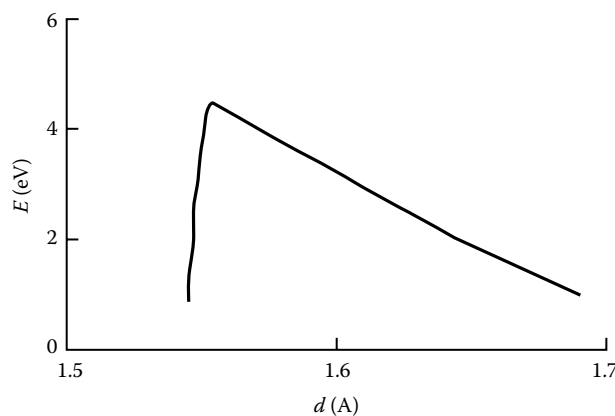


FIGURE 38 Dependence of the binding energy of molecule BN on the distance between the centers of B and N atoms calculated quasi-classically within the “potential–density” scheme. (From Chkhartishvili, L. et al., *Trans. AMIAG*, 1, 295, 1999.)

the standard forms—Morse, Mie–Grüneisen, Buckingham, etc.—of the interatomic potential decay very slowly and therefore require the cutoff at large distances. But this procedure causes nonphysical spikes in the radial dependences of potential and force of the interatomic interaction. Authors, using the embedded atom method, had constructed B–N potential, with $D = 4.00$ eV, which has a cutoff point where the potential itself and its derivative, that is, the force, become zero. Interestingly, the same conditions of the “smooth end” are automatically satisfied by the quasi-classical potential at the distance equal to the sum of quasi-classical radii of interacting atoms, B and N in the case under the consideration.

As is noted earlier, the interaction between B and N results in a structure with partially covalent and partially ionic bonds. But long-range Coulomb attraction and short-range Pauli repulsion are spatially anisotropic, and such bonding always includes angular corrections. For this reason, the corresponding classical force field, in general, should be described in terms of three-particle interactions. Only approximately that field can be represented by the sum of only two-particle interactions. For these reasons, on the basis of experimental and *ab initio* calculated data for BN diatomic molecule and some solid-state modifications of boron nitride, an accurate model short-range potential of the classical force field can be constructed [15]. And if the Morse formula is implemented, the dissociation energy of BN molecule is 5.0007 eV.

As can be seen from the previously stated results, the spread of the theoretical values of the binding energy of BN molecule overlaps with the experimentally recommended range. As for the values calculated quasi-classically, they are close to its upper limit.

A density functional theory (DFT) method proposed in Ref. [28] was proven to be sufficiently accurate and transferable to all scale BN structures from molecules and small clusters to crystalline solids and solid surfaces. The calculation of tight-binding B–N potential is straightforward and allows an application of the method to MD simulations of structure formation in complex BN systems.

VIBRATION FREQUENCY

According to Ref. [12], the vibrational quantum $\hbar\omega$ of the diatomic molecule in the isotopic composition of $^{11}\text{B}^{14}\text{N}$ is 1514.6 cm^{-1} . The almost the same value, $(1519.0 \pm 0.2)\text{ cm}^{-1}$ [29], was established by Fourier analysis of the absorption spectra and laser-induced fluorescence of the BN molecule.

At the conversion of the molecule in the positive ion BN^+ , the cyclic frequency of relative vibrations of the atoms increases to 1740 cm^{-1} [30]. The theoretical value of $\hbar\omega = 1446\text{ cm}^{-1}$ was obtained in Ref. [13] based on the calculations of the several discrete points of the B–N potential curve. Reference 14 reported another theoretical result 1750 cm^{-1} , which however is closer to the value measured for the ionized molecule.

By fitting the quasi-classical potential curve of B–N in the vicinity of the minimum to a parabola, we had found $\hbar\omega = 1435\text{ cm}^{-1}$ [16,17,26,31]. This value corresponds to the “potential–density” scheme. For an alternative form of parameterization, that is, “density–potential” scheme, the curve becomes quite asymmetric making it difficult to fit a parabola. It should be noted that one of the previously known theoretical results agrees well with that defined quasi-classically.

OTHER MOLECULAR STRUCTURES

Studies on the more complex molecular clusters of B and N are of interest for deeper insight into the defect formation processes in boron nitride nanosystems.

High-temperature Knudsen cell mass spectrometry was used to study the equilibrium involving the B_2N molecule [32], and room temperature atomization and formation enthalpies were determined as 10.84 and 5.71 eV, respectively.

Mixed clusters of B and N atoms— B_2N , BN_2 , B_3N , B_4N , B_2N_2 , and B_3N_2 —can be produced by sputtering of a solid-state BN [33]. Atom ordering in assumed linear species had been derived from the measurement of the mass distribution of products from the fragmentation of the anionic clusters in a gas target. The neutral configurations were calculated as $\text{B}^{+0.28}\text{B}^{-0.11}\text{N}^{-0.17}$, $\text{N}^{+0.03}\text{B}^{-0.06}\text{N}^{+0.03}$, $\text{B}^{+0.08}\text{B}^{+0.14}\text{B}^{-0.03}\text{N}^{-0.19}$, $\text{B}^{-0.04}\text{B}^{+0.07}\text{B}^{+0.05}\text{B}^{+0.03}\text{N}^{-0.11}$, and $\text{B}^{-0.07}\text{B}^{+0.02}\text{N}^{+0.02}\text{N}^{+0.03}$. There is a tendency that the structure with the most number of B–N bonds is most stable in both neutral and anionic species.

Ab initio calculations of the ground state of infinite 1D chain of alternating B and N atoms were performed [34] using the restricted Hartree–Fock (HF) approach, while the many-body effects were taken into account by second-order perturbation theory and coupled-cluster model. At both the HF and the correlated levels, boron–nitrogen chain exhibits equidistant bonds.

For all the group III–V binary compounds, including BN, structural properties of atomic chains were studied [35] using the *ab initio* plane-wave (PW) pseudopotential (PP) method.

APPLICATIONS

Diatomic molecule of boron nitride is formed at high temperatures and can exist only at extreme environments. This is

the reason why the BN molecule is mainly of theoretical interest, as one representative of the class of diatomic molecules. The problem of diatomic molecules in the electron theory of matter is addressed separately. Because of their structure and, consequently, electronic properties, they are intermediaries between atoms and polyatomic systems. The knowledge of characteristics of BN molecule is important for the reason that it is the basic “building block” [29] of mainly covalently bonded structural modifications of boron nitride.

As for the area of industrial applications of boron nitride chains, it was proposed [36] that BN polymers, with the same structure as organic polymers, will allow the idea to be a cheap alternative to inorganic semiconductors for the designing of the nanoelectronic devices and demonstrated some other innovations, including the bandgap tuning.

SHEETS

One of the characteristic features of boron nitride is the possibility of the existence in several allotropic layered structures. The layers are built of monocyclic rings with alternatively located B and N atoms. Most often, the layers, which form these structures, are grids constructed of regular hexagons. In this case, each atom has three nearest neighbors within a given layer. This is a strong binding—mainly of covalent type with some contribution of ionicity due to the partial displacement of the electronic charge from boron atoms to nitrogen atoms.

An isolated infinite hexagonal planar layer—so-called BN sheet—apparently has the minimal molar energy among the 2D structures of boron nitride and, therefore, should be stable.

But, virtually only finite pieces of such a sheet can be grown with end atoms having free bonds. For this reason, these fragments cannot remain plain: the tendency to minimize molar energy forces them to twist and form structures with saturated bonds. The simplest of these are single-walled boron nitride nanotubes—a closed surface built of hexagons, which is inscribed in a cylinder. Alternative structures are boron nitride fullerene molecules in the form of a cage—a closed surface built of $2n$ polygons (not only hexagons), which is inscribed in a sphere. A variety of more complicated combinations of fragments of BN sheets have been observed as well. For example, the single-walled BN nanotubes were produced [37], which ended with fullerene-like structures in the form of knots or twists. Also the conical nanoscale BN particles were found [38]. It can be argued that their structure is consistent with the ordered packing without cracks if the packaging model is realized, which implies the presence of the B–N bonds. However, through the different technologies, the 2D boron nitride nanostructures in different forms of isolated clusters have been produced [39], which can contain not only four- and six- but also five- and seven-membered atomic rings, that is, not only B–N but also B–B and N–N bonds.

Alternatively, pieces of boron nitride layers are able to coalesce into the systems of collinear surfaces. The interlayer coupling is much weaker because it is caused not by covalent/ionic but by van der Waals polarization forces. Accordingly,

interlayer bonds are more than two times longer than intralayer ones. In boron nitride ground-state modification of h-BN, at layers with six-membered rings are stacked on each other in the way that the B atoms are located directly above the N atoms and vice versa (this leads to a distorted wurtzite-like structure). From such a structure, one would have thought that even in the interlayer bonding, there is some part of ionicity. But in fact, such an electrostatic component is negligible due to too large distance between the adjacent layers. The same is also indicated by the existence of layered BN crystals with graphite-like packing, r-BN, in which each successive layer is rotated relative to the previous by an angle $\pi/3$, as well as the existence of planar stacking defects in real h-BN crystals. One can also synthesize turbostratic boron nitride (t-BN) structures. As it has been noted [27], it should be clear that the interatomic interaction in BN nanotubes, cage molecules, and similar structures is almost the same as in 3D layered modifications.

Two-dimensional functions with wallpaper group symmetry can be written as Fourier series displaying both translational and point-group symmetry. The symmetry-adapted Fourier series were elaborated [40] for each of the 17 wallpaper groups, and explicit expressions were given for the Fourier series, readily applicable to the description of boron nitride sheet. A general structural characterization of the BN sheet was given in microreview [41] on analogs of graphene.

GEOMETRY

The 2D crystal structure of a flat layer of boron nitride consists of six-membered rings with vertices alternately occupied by unlike atoms (Figure 39). In each unit cell, there are single B and N atoms. The corresponding basis vectors are $(a/2, a\sqrt{3}/2)$ and $(-a/2, a\sqrt{3}/2)$, where a is the shortest distance between unlike atoms, that is, the length of the B–N or

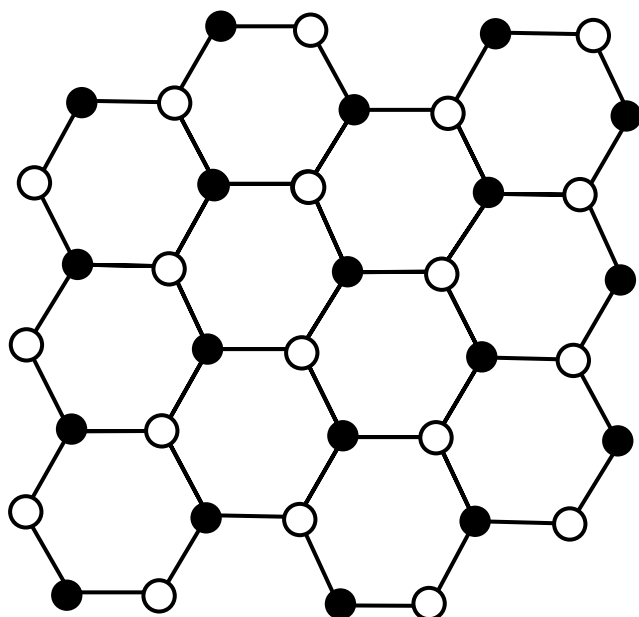


FIGURE 39 Structure of BN sheet.

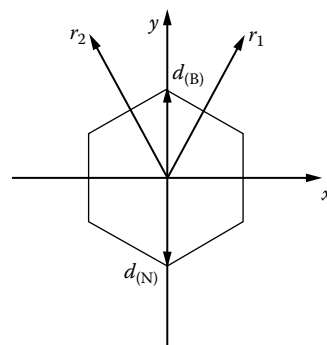


FIGURE 40 Unit cell of BN sheet.

N–N bonds (Figure 40). The length of B–N bonds, that is, the distance between the nearest neighbors is $d = a/\sqrt{3}$. B and N atoms of a unit cell are located at the points $(0, a/\sqrt{3})$ and $(0, -a/\sqrt{3})$.

As it was previously noted, such an infinite structure is experimentally unobservable. For this reason, on the values of the lattice parameter a and the bond length d , one can be judged only from the results of calculations. Molecular calculations performed [42] within the standard and iterative Hückel methods and also with the periodic small cluster model [43] gave 1.480, 1.500, and 1.441 Å for the bond length, respectively.

In Ref. [44], the three-coordinated $B_{12}N_{12}$ network of six-membered atomic rings was examined theoretically. Namely, the total energy of boron nitride nanosystems, calculated using HF approach and DFT in local and gradient-corrected approximations, was minimized with respect to B–N bond length. But “graphitic” isomer $B_{12}N_{12}$ is only a fragment of the BN sheet, and its geometry appears to be somewhat distorted because of finite sizes. As should be expected, the smallest deviations of the bond angles from the ideal value of 120° were observed for the bonds of atoms forming the central hexagon: $-(2.52 - 2.65)^\circ$ for B atoms and $+(2.52 - 2.65)^\circ$ for N atoms. A number of unequal bond lengths were also obtained as follows: 1.266 – 1.283, 1.371 – 1.378, 1.427 – 1.442, 1.434 – 1.444, 1.520 – 1.536, and 1.553 – 1.576 Å.

In Ref. [45], the total energy of h-BN crystal as a function of unit cell volume V had been calculated using the orthogonalized linear combinations of atomic orbitals (LCAO) method within local-density approximation (LDA) of the DFT. The equilibrium was found at $V/V_{\text{exp}} \approx 0.998$, where V_{exp} is the experimental value of V . Such result corresponds to the intralayer B–N distance of 1.438 Å. The calculations of Ref. [46] were also based on DFT within LDA, but PW expansion was used for both PP and wave function. Computed total energies and, consequently, the intralayer bond lengths in h-BN and r-BN were nearly the same: 1.441 and 1.439 Å, respectively. The short-ranged classical force field modeling of boron nitrides leads to exactly the same intralayer B–N bond lengths in both layered structures: 1.454 Å [15].

The finiteness of the quasi-classical atomic radii allowed us to obtain the B–N bond length for infinite BN sheet within the initial quasi-classical approximation [47]. The calculated

dependence of the molar binding energy on the lattice constant exhibits the maximum at 2.64 Å, which should correspond to the equilibrium state for an isolated hexagonal layer. The so-called analytical optimization [48] using the binding energy calculated in quasi-classical approximation, which is possible only by neglecting the vibration energy, yields the slightly different value: 2.66 Å. The lattice constant of 2.64 Å means B–N bond length of 1.52 Å.

On the other hand, summarizing all the theoretical and semiempirical results concerning intralayer bond lengths in h-BN and also r-BN layered crystals, one can state that they are in agreement with the experimental value of 1.446 Å [49].

The quasi-classical bond length of 1.52 Å in isolated BN sheet is in reasonable agreement (with deviation of 4.6%) with the bond length of ~1.45 Å observed in layers of real layered crystals. At first glance, the surprising thing is that the theoretical result for the isolated layer is in better agreement (with deviations of 2.6%–3.8%) with the bond lengths in tetrahedrally coordinated modifications c-BN (1.57 Å) and w-BN (1.56 and 1.58 Å). However, it is worth noting that in some respects, 2D boron nitride looks like 3D crystals c-BN and w-BN: these three structures do not contain weak interlayer bonds, which occur in h-BN- and r-BN-layered modifications. The aforementioned lengths of 1.52–1.54 and 1.55–1.58 Å obtained [44] for the bonds of atoms forming the central (almost undistorted) hexagon in $B_{12}N_{12}$ plane fragment are also in good agreement with the quasi-classical result found for an idealized infinite BN sheet. As for another approach using alternative scheme of the quasi-classical parameterization employed [50] for hexagonal layers in h-BN, it somewhat underestimates the intralayer bond length. The reason may be that the equilibrium configuration was selected by maximizing the static binding energy with respect only to the intralayer lattice parameter, while the interlayer distance was fixed.

BOND POLARITY

Within the semiempirical tight-binding model [43], total atomic charges in an h-BN layer are found to be ± 0.3 .

Electronic structures of boron nitrides calculated [19] within the atom model cluster approximation for the quasi-molecular unit cells $B_{12}N_{12}$ and $B_{16}N_{16}$ are virtually indistinguishable from each other, and they are assigned the following populations of valence states in B and N atoms: $s(B) = 0.69$, $p_{xy}(B) = 0.55$, $p_z(B) = 0.32$, $s(N) = 1.25$, $p_{xy}(N) = 1.48$, and $p_z(N) = 1.68$. Hence, for the charges of these atoms, one has the following values, respectively: $3 - (0.69 + 0.55 + 0.32) = +1.44$ and $3 - (1.25 + 1.48 + 1.68) = -1.41$. The electron charge deficiency of -0.03 has to be distributed in the interatomic space—but in this case, the compound would have to be regarded as a semimetal like the graphite—or it goes to pseudo-atoms that in these calculations are located on the boundary of a cluster.

Signs of the obtained atomic charges, $B^{+1.44}N^{-1.41}$, are consistent with that suggested by chemical intuition. However, their (high) absolute values should be viewed with suspicion.

BINDING ENERGY

Within different versions of HF and DFT methods, the energy of a $B_{12}N_{12}$ fragment of a flat layer was calculated [44] relative to the level of an isomer in the form of a ring. The HF method gave the values +1.98, +2.46, and +2.53 eV; the DFT in the LDA –2.18, –1.61, and –1.51 eV; and the DFT with gradient corrections +1.40, +2.02, and +2.07 eV. The differences in values and even signs of the obtained energies indicate the absence of the definitive evidences for the stability of such a fragment. *Ab initio* calculations [51] of elasticity of nanoshells of various shapes agree to the conclusion that among 2D lattices of boron nitride, relative minimum energy is actually achieved for a flat sheet. The numerical values of the total molar energy of such a structure estimated by the HF and DFT methods, respectively, are –2130.5 and –2141.5 eV/mol [52].

The quasi-classically calculated [47] (see also Ref. [48]) dependence of the molar binding energy of infinite BN sheet on the lattice constant (Figure 41) exhibits a maximum of 23.0 eV/mol, which should correspond to the equilibrium state for an isolated hexagonal layer.

Since this structure is hypothetical, the predictive power of a method used should be analyzed based on comparisons with results obtained for similar, but realizable BN structures. As what follows from standard thermochemical data [53], the binding energy of h-BN equals to 13.0 eV/mol. The binding energies of 14.5, 16.0, and 14.4 eV/mol were determined from semiempirical calculations performed using two variants of the semiempirical LCAO method and an approach based on a periodic small-sized cluster [42,43]. Within a classical force field potential model, the semiempirical estimate of 11.5 eV/mol was obtained [15]. In the framework of DFT, optimization

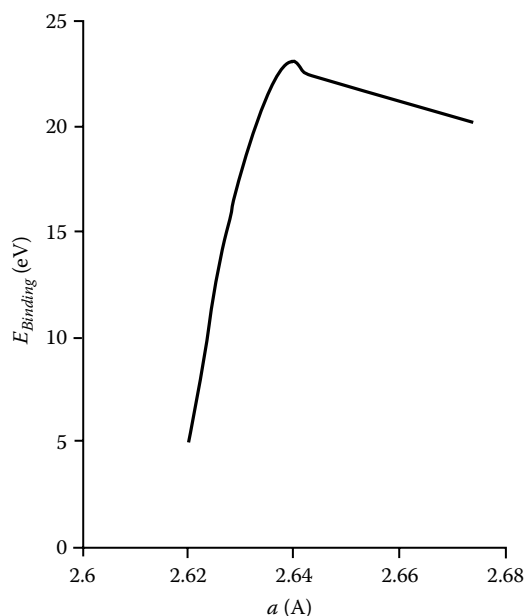


FIGURE 41 Molar binding energy of the boron nitride layer depending on the lattice constant, calculated quasi-classically within the parameterization scheme “density–potential.” (From Chkhartishvili, L.S., *Phys. Solid State.*, 46, 2126, 2004.)

of the structural parameters led to the theoretical binding energy of 12.5 eV/mol [46]. Therefore, it should be expected that the molar binding energy for h-BN-layered crystal lies in the range from 11.5 to 16.0 eV/mol, which is placed much lower than the quasi-classical value. But comparing these two values, one should take into account the extreme weakness of interlayer bonds relative to intralayer ones and the fact that in BN-layered structures, each atom participates in five bonds, from which only three are intralayer. Therefore, if one neglects the energy of interlayer coupling, the molar energy of such modifications can be calculated approximately as $3/5$ of the molar energy of an isolated layer. The use of the quasi-classical value gives $3.0 \text{ eV/mol} \times 3/5 = 13.8 \text{ eV/mol}$, which actually is located near the center of the aforementioned energy range.

ZERO-POINT VIBRATION ENERGY

The quasi-classically calculated [31,47] dependence of the molar binding energy of infinite BN sheet on the lattice constant exhibits the correction introduced by zero-point vibrations estimated as 0.242 eV/mol (note that the so-called analytical optimization [48] of the lattice parameter using the binding energy calculated in quasi-classical approximation is possible only by neglecting the vibration energy).

In spite of the molar binding energies, the molar vibration energies of the isolated layer and layered crystals can be directly compared because the atoms of the 2D system can execute vibrations in three independent directions in physical space. Quasi-classical result of 0.242 for 2D BN agrees well with that of analogous calculations of 0.266 [31] and semiempirical estimate of 0.225 for zero-point vibration energy in h-BN [15] and coincides in the order of magnitude with the estimate of 0.350 eV/mol derived [46] from the theoretical phonon spectrum of h-BN.

Investigation [54] of the lattice dynamics of low-frequency rigid-plane modes in insulating hexagonal BN multilayers shows that the frequencies of shearing and compression (stretching) modes depend on the layer number, and only the (van der Waals and Coulomb) interactions between nearest-neighbor planes are effective, while the interactions between more distant planes are screened.

DEFECTS

Electron energy loss spectroscopy (EELS) profiles not only clearly discriminate [55] the chemical species of single atoms but also show different delocalization of the B and N *K*-edges. A monovacancy at the boron site is unambiguously identified.

According to the MD study [56] of the structural properties of BN sheet, the Tersoff bond order potential gives a thermally stable hexagonal single layer. The lowest energy point defect in single-layer hexagonal BN involves an out-of-plane displacement of a N atom to form a tetrahedron with three B atoms in the plane.

Boron nitride nanosheets prepared by an exfoliation technique were observed [57] by aberration-corrected transmission

electron microscopy (TEM). Single B and N atoms in a monolayer region were imaged with different image contrasts: a boron atom gave less intensity reduction than a nitrogen atom. A double BN sheet was found to have a boron vacancy layer, and a triple BN layer has also a boron-deficient layer. Using methods of model PP and expanded unit cell, N vacancies in BN sheet, as well as di- and trivacancy clusters including two or three neighboring defects in BN layer characterized by small binding energies, were found [58]. In Ref. [59], the results of *ab initio* MD simulations of nitrogen vacancy complexes in monolayer h-BN were presented. Activated nitrogen dynamics triggers the annihilation of defects in the layer through the formation of Stone–Wales-type structures. By the *ab initio* calculations performed for 20 structures of $B_xC_yN_z$ derived from a hexagonal BN layer by placing B, N, or C atoms on each site, their relative stabilities were investigated [60].

From the *ab initio* calculations [61], two types, zigzag and armchair oriented, of grain boundaries are expected in the real structure of BN sheets. Simulation results reveal that the zigzag-oriented grain boundaries are more stable than the armchair-oriented ones. Dislocations and grain boundaries in 2D boron nitride were described in Ref. [62].

OTHER SHEET STRUCTURES

Classification and consideration of the BN haeckelite sheet structures consisting of not only hexagonal atomic rings but also other even-membered rings can be found in Ref. [63]. The geometries of the haeckelite BN sheets were constructed by the DFT [64], and it was found that their molar energy of cohesion is higher (by $\sim 0.6 \text{ eV/mol}$) than that of the regular one.

APPLICATIONS

A strong chemical bonding of atoms in layers along with a weak interlayer interaction points to the possibility of intercalation in layered structures of BN, that is, the introduction of various atoms or molecules between layers by physical or chemical means to functionalize the material.

A resonant tunneling diode based on a double-barrier graphene/boron nitride heterostructure was proposed [65] as a device suitable to take advantage of the elaboration of atomic sheets containing different domains of BN and C phases within a hexagonal lattice. Planar graphene/h-BN heterostructures can be formed by growing graphene in lithographically patterned BN atomic layers [66]. The technique can be used to fabricate 2D devices, such as a split closed-loop resonator that works as a band-pass filter. The silver nanoparticle-decorated BN nanosheets could be useful for reusable, thermal oxidation-resistant surface-enhanced Raman spectroscopy devices [67]. Few-atomic-layer boron nitride films could serve for various semiconductor diodes [68], as well as a dielectric layer for graphene devices [69].

The results obtained in Ref. [70] enabled a convenient growth of pure BN nanosheet coatings with controllable levels

of water repellency, ranging from partial hydrophilicity to superhydrophobicity with contact angles exceeding 150° . The nonwetting tendency of the ultrathin BN films was explained [71] based on the interactions of the dipole moments of polar water molecules and BN nanosheets.

Ab initio simulations on the interaction of molecular hydrogen H_2 with the native and substitutional defects of a single hexagonal BN sheet were performed in Ref. [72]. The adsorption of H_2 on structures was found to be endothermic with respect to dissociation. In planar sheets, vacancies reduce the barriers for H_2 dissociation. So, BN sheets grown on various substrates are prospective structures for hydrogen fuel nanoreservoirs.

The large-scale production of 2D nanosheets of BN based on the increased yield and reduced cost of BN nanosheets should promote their wide practical applications. A facile, efficient, and scalable method for the fabrication of monolayer and few-layer BN, using combined low-energy ball milling and sonication, was reported [73]. Boron nitride nanosheets were also synthesized [74] at 350°C using a pulsed-laser plasma deposition technique by irradiating a pyrolytic h-BN target. An improved chemical-blowing route presuming atmospheric pressure pretreatment and moderate heating rate of designated precursors was developed [75] to synthesize ultrathin boron nitride nanosheets with large lateral dimensions. The yield reached as high as 40 wt.% with respect to raw materials. Atomically thin hexagonal boron nitride films were grown [76] on both the top and bottom surfaces of a polycrystalline Co or Ni film by annealing a Co(Ni)/amorphous boron nitride/ SiO_2 structure in vacuum. This method of growing hexagonal boron nitride sheet is much simpler than other methods, such as thermal chemical vapor deposition (CVD).

Recently, hexagonal BN has received a great deal of attention as a substrate material for high-performance graphene electronics because it has an atomically smooth surface, lattice constant similar to that of graphene, large optical phonon modes, and a large electrical bandgap. So, it is too important to develop the large-scale synthesis methods of high-quality BN nanosheets. In Ref. [77], a CVD-type process was proposed by controlling the surface morphologies of the copper (Cu) catalysts.

NANOTUBES

The types and structures of the noncarbon, in particular, BN nanotubes were overviewed in Ref. [78–80]. Symmetry operators of armchair, zigzag, and chiral BN nanotubes have been identified in Ref. [81]. Each type belongs to different families of the nonsymmorphic rod groups; armchair tubes with even indices n are found to be centrosymmetric. Using these symmetry properties, the numbers of Raman and infrared (IR) active vibrations in single-walled BN nanotubes were determined. In contrast to the regular C nanotubes, zigzag BN tubes possess almost twice the number of vibrations as armchair ones.

For *ab initio* simulations on hexagonal single-walled BN nanotubes, the formalism of line symmetry groups describing

one-periodic nanostructures with rotohelical symmetry was applied [82]. These nanotubes can be formed by rolling up the stoichiometric nanosheets of a (0001) monolayer of BN hexagonal phase.

An extensive *ab initio* study of the phonons in BN nanotubes using perturbation DFT in the LDA was performed in Ref. [83]: based on the nonsymmorphic rod group symmetry of the tubes, the Raman and IR active modes at the point of the 1D Brillouin zone were evaluated. For zigzag and chiral nanotubes, the set of IR active modes was found to be a subset of the Raman active modes. In particular, the radial breathing mode is not only Raman but also IR active. However, for armchair tubes, the sets of IR and Raman active modes are disjointed. The frequencies of the active modes of zigzag, chiral, and armchair tubes were presented as a function of the tube diameter and compared with the frequencies obtained by the so-called zone-folding method. Except for the high-frequency tangential modes, the zone-folding results are in very good agreement with the *ab initio* calculations. The radial breathing mode frequency can be derived by folding a sheet of finite width. Finally, the effects of bundling on the phonon frequencies are shown to be small. *Ab initio* calculations of the nonresonant Raman spectra of zigzag and armchair BN nanotubes were presented, and a generalized bond-polarizability model, where the parameters are extracted from *ab initio* calculations of the polarizability tensor of a BN sheet, was implemented in Ref. [84]. For light polarization along the tube axis, the agreement between model and *ab initio* spectra is almost perfect, but for perpendicular polarization, depolarization effects have to be included in the model in order to reproduce Raman intensities.

GEOMETRY

Elementary form for a single-walled BN nanotube is a wrapped closed hexagonal surface inscribed in a cylinder. Such BN nanotubes can be found in achiral (regular), that is, zigzag $(n,0)$ or armchair (n,n) , and also in chiral (n,m) forms. Here, $n = 1,2,3,\dots$ and $m = 0,1,2,\dots,n$ are the tube indices (Figure 42).

EELS of chemically pure boron nitride nanotubes showed [4] that the ratio of B/N is approximately equal to 1. This result is consistent with the theoretical predictions about the stable stoichiometry of such structures. The analysis of a number of nanotube models [85] leads to the conclusion that the $B_{36}N_{36}$ nanotube cluster must be stable and also enables to explain the microstructure of BN nanotubes [86].

In Ref. [63] within frames of DFT in generalized gradient approximation (GGA) by the searching of equilibrium values of B–N bond length and radii, the geometry of the tubular supercell consisting of 32 atoms was optimized. For $(8,0)$, $(10,0)$, and $(4,4)$ tubes, it has been found that $d \approx 1.46 \text{ \AA}$ and for $(5,5)$ tube $d \approx 1.45 \text{ \AA}$.

Conventional model of geometry of carbon nanotubes was expanded [2] for BN nanotubes as well. However, the conventional rolled-up model of nanotubes does not apply to the

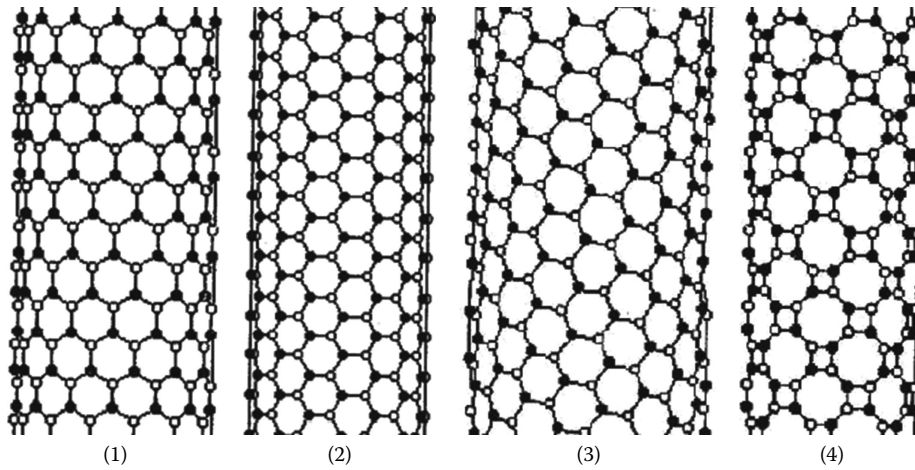


FIGURE 42 Structures of hexagonal zigzag (1), armchair (2), chiral (3), and haeckelite (4) boron nitride nanotubes.

very small radii tubes, for which curvature effects become significant. Instead, the polyhedral geometric model was proposed [87] (see also Review [88]), which accommodates this deficiency being based on the exact polyhedral cylindrical structure and extended to a nanotube structure involving two species of atoms, B and N, in equal proportion. This generalization allows the principle features to be included as the fundamental assumptions of the model, such as equal bond length but distinct bond angles and radii between the two species. Working from five simple geometric assumptions, expressions were derived for the various structural parameters such as radii and bond angles for the two species for specific values of the chiral vector numbers. However, structural parameters can be found only as numerical solutions of transcendental equations.

For purposeful designing devices based on nanotubular BN, it is important to be able to predict reliably the sizes of the nanotubes with given indices. This task was solved for the most stable forms analytically. Namely, the formulas determining $(n,0)$ and (n,n) BN nanotubes radii $r_{(n,0)}$ and $r_{(n,n)}$, and lattice parameters $l_{(n,0)}$ and $l_{(n,n)}$, have been derived in terms of B–N bond lengths $d_{(n,0)}$ and $d_{(n,n)}$ in Ref. [89–94]:

$$r_{(n,0)} = \frac{\sqrt{3}d_{(n,0)}}{4 \sin \pi/2n},$$

$$r_{(n,n)} = \frac{\sqrt{5 + 4 \cos \pi/2n} d_{(n,n)}}{4 \sin \pi/2n},$$

and

$$l_{(n,0)} = 3d_{(n,0)},$$

$$l_{(n,n)} = 2\sqrt{3}d_{(n,0)}.$$

Nanotube index n determines the number of atoms as nanotube unit cell consists of $2n$ formula units of BN.

Based on this model for achiral nanotubes, the interpolation formula of chiral nanotube radius can be constructed [94–96]. Analysis of asymptotic behavior at high index, $n \gg 1$, of formulas for chiral and achiral BN nanotubes radii has shown [94] that they are almost proportional to n .

Later, it was also demonstrated how the analytical model for BN nanotubular geometries is appropriate in refinement of structural data obtained for C nanotubes: namely, indices were specified for nanotubes with given diameters [97,98].

At the detailed analysis of the single-walled geometry of BN nanotubes, it is necessary to take into account that basically there is a question of the average radii, as the detailed research [99] performed by a generalized tight-binding MD method revealed that dynamic relaxation (similar to the reconstruction at atomically clean surfaces of groups III–V crystalline semiconductors) results in a wavelike or “rippled” surface, in which B atoms rotate inward and N atoms more outward. A general feature of BN nanotubular systems is that the stronger surface potentials are associated with regions of higher curvature [100].

The detailed regular geometries of the zigzag and armchair BN nanotubes were described [90,91,101,102] using cylindrical coordinates (ρ, ϕ, z) .

The unit cell of the zigzag $(n,0)$ nanotubes consists of four atomic rings in parallel planes perpendicular to the axis. There are two pairs of rings and each consists of two planes with n boron or n nitrogen atoms. Evidently, coordinate ρ for all the atomic sites equals to tube radius:

$$\rho_B = \rho_N = r_{(n,0)} = \frac{\sqrt{3}d_{(n,0)}}{4 \sin \pi/2n}.$$

As for the coordinates ϕ and z in the first and second pairs of atomic rings, they, respectively, equal to

$$\phi_B = \phi_N = \frac{2l\pi}{n},$$

$$z_B = \frac{(6m+1)d_{(n,0)}}{2},$$

$$z_N = \frac{(6m-1)d_{(n,0)}}{2},$$

and

$$\phi_B = \phi_N = \frac{(2l+1)\pi}{n},$$

$$z_B = (3m-1)d_{(n,0)},$$

$$z_N = (3m+1)d_{(n,0)}.$$

Here

$$l = 0, 1, 2, \dots, n-1$$

$m = 0, \pm 1, \pm 2, \dots$ are the number of atomic pairs in a given pair of the atomic rings and these rings themselves, respectively

The unit cell of the armchair (n,n) -nanotubes consists of two atomic rings in parallel planes perpendicular to the tube axis. From its part, each ring consists of n boron and n nitrogen atoms. Coordinate ρ for all atomic sites equals to tube radius:

$$\rho_B = \rho_N = r_{(n,n)} = \frac{\sqrt{5+4\cos\pi/2n}d_{(n,n)}}{4\sin\pi/2n},$$

while the rest of the cylindrical coordinates in the first and second atomic rings equal to

$$\phi_B = \phi_1 + \frac{2l\pi}{n},$$

$$\phi_N = -\phi_1 + \frac{2l\pi}{n},$$

$$z_B = z_N = \sqrt{3}md_{(n,n)},$$

and

$$\phi_B = -\phi_1 - 2\phi_2 + \frac{2l\pi}{n},$$

$$\phi_N = \phi_1 + 2\phi_2 + \frac{2l\pi}{n},$$

$$z_B = z_N = \sqrt{3}\left(m + \frac{1}{2}\right)d_{(n,n)},$$

respectively.

Here,

$$\sin\phi_1 = \frac{2\sin\pi/2n}{\sqrt{5+4\cos\pi/2n}},$$

$$\sin\phi_2 = \frac{\sin\pi/2n}{\sqrt{5+4\cos\pi/2n}},$$

$$l = 0, 1, 2, \dots, n-1$$

$m = 0, \pm 1, \pm 2, \dots$ are the number of B or N atoms in atomic rings and these rings themselves

Based on this, the distances between a given atomic site and sites in the so-called central atomic pairs in zigzag were found ($l = m = 0$: $\phi_B = \phi_N = 0$, $z = d_{(n,0)}/2$, and $z = -d_{(n,0)}/2$):

$$\frac{\left(\begin{smallmatrix} lm \\ (n,0) \end{smallmatrix} B1 - \begin{smallmatrix} 00 \\ (n,0) \end{smallmatrix} B1\right)^2}{d_{(n,0)}^2} = \frac{3\sin^2 l\pi/n}{4\sin^2 \pi/2n} + 9m^2,$$

$$\frac{\left(\begin{smallmatrix} lm \\ (n,0) \end{smallmatrix} B2 - \begin{smallmatrix} 00 \\ (n,0) \end{smallmatrix} B1\right)^2}{d_{(n,0)}^2} = \frac{3\sin^2(2l+1)\pi/2n}{4\sin^2 \pi/2n} + \frac{9(2m-1)^2}{4},$$

$$\frac{\left(\begin{smallmatrix} lm \\ (n,0) \end{smallmatrix} N1 - \begin{smallmatrix} 00 \\ (n,0) \end{smallmatrix} B1\right)^2}{d_{(n,0)}^2} = \frac{3\sin^2 l\pi/n}{4\sin^2 \pi/2n} + (3m-1)^2,$$

$$\frac{\left(\begin{smallmatrix} lm \\ (n,0) \end{smallmatrix} N2 - \begin{smallmatrix} 00 \\ (n,0) \end{smallmatrix} B1\right)^2}{d_{(n,0)}^2} = \frac{3\sin^2(2l+1)\pi/2n}{4\sin^2 \pi/2n} + \frac{(6m+1)^2}{4},$$

$$\frac{\left(\begin{smallmatrix} lm \\ (n,0) \end{smallmatrix} B1 - \begin{smallmatrix} 00 \\ (n,0) \end{smallmatrix} N1\right)^2}{d_{(n,0)}^2} = \frac{3\sin^2 l\pi/n}{4\sin^2 \pi/2n} + (3m+1)^2,$$

$$\frac{\left(\begin{smallmatrix} lm \\ (n,0) \end{smallmatrix} B2 - \begin{smallmatrix} 00 \\ (n,0) \end{smallmatrix} N1\right)^2}{d_{(n,0)}^2} = \frac{3\sin^2(2l+1)\pi/2n}{4\sin^2 \pi/2n} + \frac{(6m-1)^2}{4},$$

$$\frac{\left(\begin{smallmatrix} lm \\ (n,0) \end{smallmatrix} N1 - \begin{smallmatrix} 00 \\ (n,0) \end{smallmatrix} N1\right)^2}{d_{(n,0)}^2} = \frac{3\sin^2 l\pi/n}{4\sin^2 \pi/2n} + 9m^2,$$

$$\frac{\left(\begin{smallmatrix} lm \\ (n,0) \end{smallmatrix} N2 - \begin{smallmatrix} 00 \\ (n,0) \end{smallmatrix} N1\right)^2}{d_{(n,0)}^2} = \frac{2\sin^2(2l+1)\pi/2n}{4\sin^2 \pi/2n} + \frac{9(2m+1)^2}{4},$$

and the central atomic pairs in armchair ($l = m = 0$: $\phi_B = \phi_1$, $\phi_N = -\phi_1$, and $z_B = z_N = 0$) nanotubes:

$$\frac{\left(\begin{smallmatrix} lm \\ (n,n) \end{smallmatrix} B1 - \begin{smallmatrix} 00 \\ (n,n) \end{smallmatrix} B1\right)^2}{d_{(n,n)}^2} = \frac{(5+4\cos\pi/2n)\sin^2 l\pi/n}{4\sin^2 \pi/2n} + 3m^2,$$

$$\begin{aligned}
\frac{\left(\begin{smallmatrix} lm \\ (n,n) \end{smallmatrix} B2 - \begin{smallmatrix} 00 \\ (n,n) \end{smallmatrix} B1 \right)^2}{d_{(n,n)}^2} &= \frac{(5 + 4 \cos \pi/2n) \sin^2(2l-1)\pi/2n}{4 \sin^2 \pi/2n} \\
&\quad + \frac{3(2m+1)^2}{4}, \\
\frac{\left(\begin{smallmatrix} lm \\ (n,n) \end{smallmatrix} N1 - \begin{smallmatrix} 00 \\ (n,n) \end{smallmatrix} B1 \right)^2}{d_{(n,n)}^2} &= \frac{(2 \sin(2l-1)\pi/2n + \sin l\pi/n)^2}{4 \sin^2 \pi/2n} + 3m^2, \\
\frac{\left(\begin{smallmatrix} lm \\ (n,n) \end{smallmatrix} N2 - \begin{smallmatrix} 00 \\ (n,n) \end{smallmatrix} B1 \right)^2}{d_{(n,n)}^2} &= \frac{(\sin(2l+1)\pi/2n + 2 \sin l\pi/n)^2}{4 \sin^2 \pi/2n} \\
&\quad + \frac{3(2m+1)^2}{4}, \\
\frac{\left(\begin{smallmatrix} lm \\ (n,n) \end{smallmatrix} B1 - \begin{smallmatrix} 00 \\ (n,n) \end{smallmatrix} N1 \right)^2}{d_{(n,n)}^2} &= \frac{(2 \sin(2l+1)\pi/2n + \sin l\pi/n)^2}{4 \sin^2 \pi/2n} + 3m^2, \\
\frac{\left(\begin{smallmatrix} lm \\ (n,n) \end{smallmatrix} B2 - \begin{smallmatrix} 00 \\ (n,n) \end{smallmatrix} N1 \right)^2}{d_{(n,n)}^2} &= \frac{(\sin(2l-1)\pi/2n + 2 \sin l\pi/n)^2}{4 \sin^2 \pi/2n} \\
&\quad + \frac{3(2m+1)^2}{4}, \\
\frac{\left(\begin{smallmatrix} lm \\ (n,n) \end{smallmatrix} N1 - \begin{smallmatrix} 00 \\ (n,n) \end{smallmatrix} N1 \right)^2}{d_{(n,n)}^2} &= \frac{(5 + 4 \cos \pi/2n) \sin^2 l\pi/n}{4 \sin^2 \pi/2n} + 3m^2, \\
\frac{\left(\begin{smallmatrix} lm \\ (n,n) \end{smallmatrix} N2 - \begin{smallmatrix} 00 \\ (n,n) \end{smallmatrix} N1 \right)^2}{d_{(n,n)}^2} &= \frac{(5 + 4 \cos \pi/2n) \sin^2(2l+1)\pi/2n}{4 \sin^2 \pi/2n} \\
&\quad + \frac{3(2m+1)^2}{4}.
\end{aligned}$$

BOND POLARITY

The deal of ionicity of binding in boron nitride structures is important in explaining the electronic differences between BN tubes and similar C tubes [2].

On the basis of the review of the vibrational and other physical characteristics of BN nanotubes [103], it was concluded that a certain charge transfer and, therefore, piezoelectric properties must be characteristic for them. Within frames of semiempirical MNDO approach, the nanotubular piezoelectric characteristics were calculated in Ref. [104].

To help understand and predict nanotube interactions, the electrostatic potentials on both the outer and the inner surfaces of single-walled model systems were computed [100] at the HF level. The surface potentials were characterized in terms of both site-specific and global properties: positive and negative extremes and average values, average deviation, positive

and negative variances, and electrostatic balance. The boron nitride tubes have strong and variable surface potentials; there are characteristic patterns of positive and negative sites on the outer lateral surfaces, while the inner ones are markedly positive. A general feature of all of the systems studied is that the stronger potentials are associated with regions of higher curvature. Later, similar results were obtained [105] based on a DFT study.

BINDING ENERGY

Stabilities of the boron nitride nanotubular structures were studied by means of nonorthogonal tight-binding formalism [106].

Semiempirical values of the binding energy per unit length of a boron nitride nanotube, for armchair, chiral, zigzag, and twisted zigzag structures, were found [27] (with diameters in parentheses), respectively, as 17.1 (1.10), 10.7 (1.253), 13.5 (1.116), and 8.9 eV/nm (1.257 nm). In Ref. [63], the binding energy of the regular BN nanotubes had been calculated using DFT in GGA. Within frames of semiempirical MNDO calculations of the nanotubular piezoelectric characteristics [104], energies in dependence on bond length were calculated for the molecular fragments containing three or four elementary layers.

The binding in small-radius single-walled BN nanotubes in Ref. [107] was studied based on DFT using LDA. The results show that the chirality preference observed in experiments may be explained from the relative stability of the corresponding BN strips: the zigzag strips have larger binding energies and thus may be more easily formed. The smallest stable BN nanotube was found to be the (5,0) zigzag nanotube. The dependence of the tube deformation energy on its radius R was approximated by the formula ΔE [eV/mol] = $5.82/(R [\text{\AA}])^{2.09}$. The geometries of the BN nanotubes were also constructed using DFT [64]. Molar energy of cohesion is higher (by ~ 0.6 eV/mol) than for sheet. A similar relation for deformation energy dependence on tube radius $\sim C/R\alpha$ with different C for different structures and $\alpha \approx 2$ was found.

BN nanotubes with zigzag- and armchair-type structures were investigated [108] using high-resolution electron microscopy (HREM), image processing, image simulation, and molecular mechanics calculations. Total energies of BN nanotubes with a zigzag-type structure were lower than those of armchair-type structure, and these results agreed well with the experimental data of disordered tubular structure.

Based on the analytically described nanotubular geometries, binding energies (including both electrostatic and zero-point vibration terms) per mole of the ultrasmall-radius BN nanotubes (1,0), (1,1), (2,0), (3,0), (2,2), (4,0), (5,0), and (3,3) were calculated using the quasi-classical approach [101]. The molar binding energy oscillatory dependence on the tube radius (Figure 43) was found. According to obtained values, the formation probabilities for BN tubes with indices (5,0) and (3,3) and higher are almost the same that for the layered BN crystals. Ultrasmall-radius BN nanotubes (1,1), (2,0), (2,2), and (4,0) seem to be metastable as their molar binding energies are positive, but less than that for layered BN crystals,

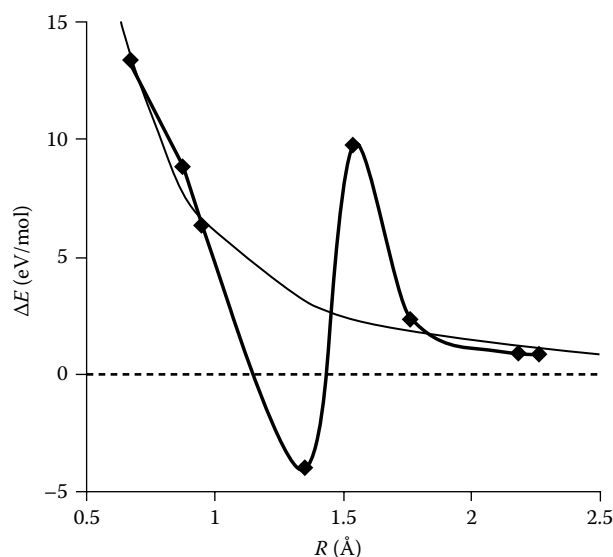


FIGURE 43 Energy difference between in nite- (dashed line) and ultrasmall-radius BN nanotubes calculated by quasi-classical method [101] (heavy solid line) and by the extrapolating formula [107] (regular solid line). (From Chkhartishvili, L.S., *Mater. Sci. Nanostruct.*, 1, 33, 2009.)

while the smallest (1,0) tube structure degenerated in zigzag atomic strip should be unstable (with negative binding energy). Exception is the (3,0) tube, formation of which was predicted energetically preferable than layered crystal growth.

Later, analogous calculations of molar binding energies (see Figures 44 and 45) were performed for wide intervals of nanotubular indices ($n,0$) and (n,n) and structural parameter a near the equilibrium [96,109–113].

Nanotubes (1,1), (3,0), and (4,0) were predicted to be more stable species among single-walled BN nanotubes (Figure 46). The obtained binding energies of single-walled BN nanotubes corrected with zero-point vibration energies lie within the interval (12.01–29.39) eV/mol. In particular, molar binding energy of the ultra-large-radius tube is determined as 22.95 eV/mol. The binding energy peak located at 2.691 Å corresponds to the equilibrium structural parameter of all realized stable BN nanotubular structures.

The effects of defect complexes on the stability and structural properties of single-walled boron nitride nanotubes were investigated [114] using the *ab initio* PP DFT method.

ZERO-POINT VIBRATIONS

The vibrations in small-radius single-walled BN nanotubes in Ref. [107] were studied by means of DFT using LDA. The phonon dispersions of BN nanotubes were calculated, and the frequency of the radial breathing mode was found to be inversely proportional to the nanotube radius.

According to the quasi-classical calculations [96,109–113] performed for wide intervals of nanotubular indices ($n,0$) and (n,n) and structural parameter a near the equilibrium, the spread of the molar zero-point vibration energy of BN nanotubes is 0.25–0.33 eV/mol, and its limit for ultra-large-radius tubes is estimated as 0.31 eV/mol.

Using the spectral moment's method, the IR spectra of single-walled boron nitride nanotubes were calculated [115]. The dependence of these modes was found as a function of the nanotube chirality, diameter (from 0.7 to 5 nm), and length. These predictions are useful for understanding the experimental IR spectra of real boron nitride nanotubes. Raman spectra

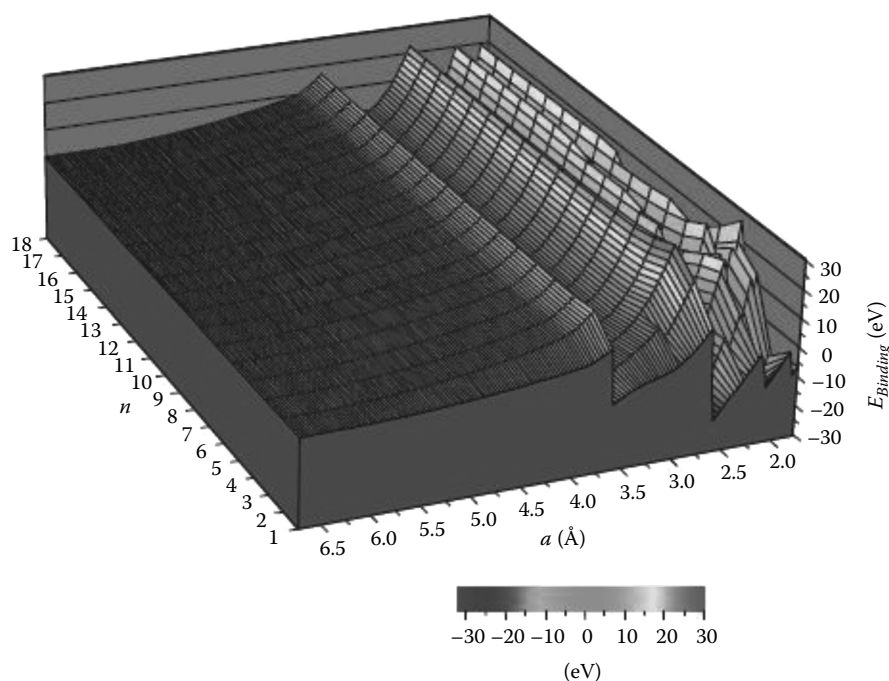


FIGURE 44 Surface plot of the molar binding energy of a zigzag BN nanotube as a function of the structural parameter and nanotube index. (From Chkhartishvili, L. and Murusidze, I., *Mater. Sci. Appl.*, 1, 223, 2010.)

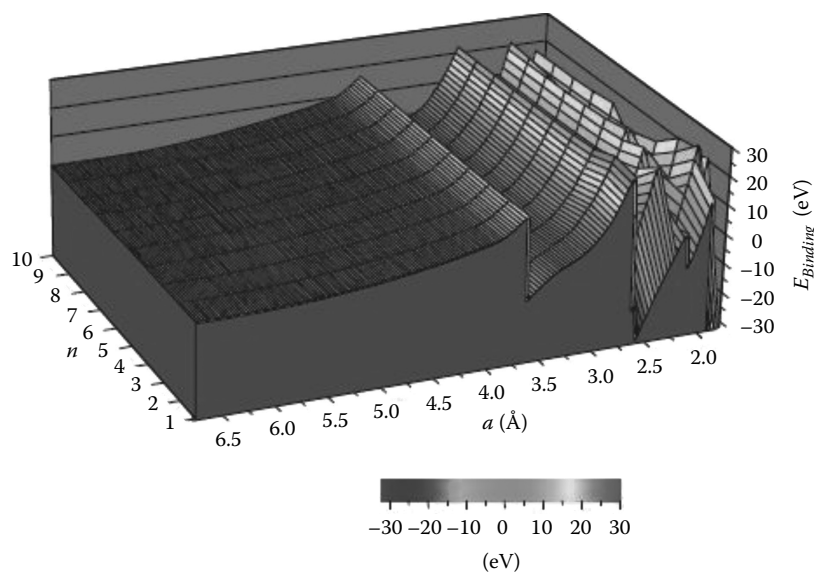


FIGURE 45 Surface plot of the molar binding energy of an armchair BN nanotube as a function of the structural parameter and nanotube index. (From Chkhartishvili, L. and Murusidze, I., *Mater. Sci. Appl.*, 1, 223, 2010.)

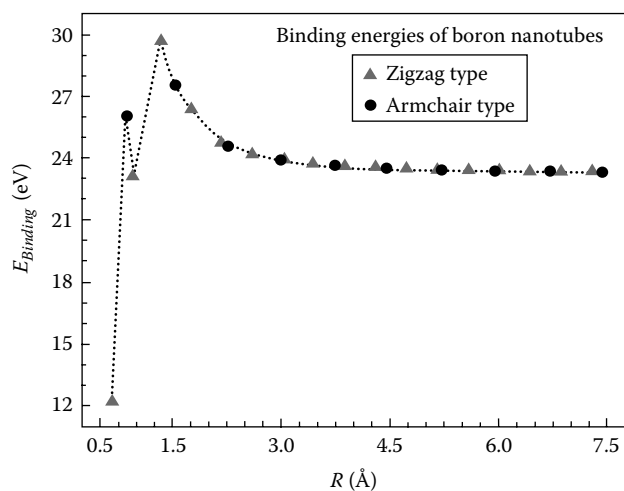


FIGURE 46 Molar binding energy of a chiral BN nanotube vs. radius. (From Chkhartishvili, L. and Murusidze, I., *Solid State Sci.*, 14, 1664, 2012.)

of single-walled boron nitride nanotubes were calculated [116] using the *ab initio* HF methods. Calibration procedure was proposed to fit the calculated spectra to experimental frequency peculiar to h-BN that allows to interpret unambiguously the experimental spectra of BN nanotubes. The most intensive and high-frequency whispering mode was shown to be peculiar to armchair nanotubes. IR and nonresonance Raman spectra of the zigzag single-walled and double-walled boron nitride nanotubes were calculated in Ref. [117]. In the low-frequency range, radial breathing modes are strongly diameter dependent and, in addition, in the double-walled nanotubes are blue shifted.

By the application of group theory with the state of projection operators, a systematic method for getting the vibration

model of molecule of a zigzag single-walled boron nitride nanotube was proposed [118].

A uni ed macroscopic continuum model was constructed [119] to calculate the long-wavelength optical phonons of single-walled boron nitride nanotubes.

MULTIWALLED NANOTUBES

In real multiwalled boron nitride nanotubes with the right stoichiometric composition, the interlayer distances according to Ref. [4] are at ~ 3.3 Å. This value agrees well with the length of the interlayer bonds in the structure of a bulk layered h-BN crystal.

Real nanotubular structures are not infinite in length: they are definitely truncated. Multiwalled BN nanotubes obtained by carbothermal reduction showed [120,121] that for large tubes the factor of form depends on radius. In the process of chemical substitution in carbon nanotubes, BN nanotubes with two to six walls were obtained [122], in which graphite-like surfaces turned out to be ordered in the so-called nonhelical zigzag.

Interwall interaction of BN nanotubes differs from bonding in 3D layered crystals. However, most likely, the distinctions are weak enough to change essentially the equilibrium interlayer distances, which are observed in h-BN and r-BN crystals. The given conclusion is also argued by the results of an experimental study of the multiwalled nanotubes applying HREM [123]. In these structures, like the 3D layered BN crystals, hexagonal and rhombohedral stacking sequences in nanotube wall assembly can freely coexist. There are also possible some different cross-sectional attenuing, as well as ordering of layers in nonspiral zigzag. According to *ab initio* total-energy calculations [124], the most favorable double-walled BN nanotubes are structures in which the interwall distances are about 3 Å, that is, as interlayer distances in

layered BN crystals. So, because of the weakness of the interlayer van der Waals forces, various types of multiwalled BN nanotubes can exist. Then, there is more probable formation of such multiwalled boron nitride nanotubes, which consists of tubes with difference in radii close to interlayer distance in layered h-BN crystal, that is, to half of the height of the hexagonal unit cell $c = 6.6612 \text{ \AA}$ [125].

On the basis of expressions derived previously, the sizes of the small single-walled BN nanotubes (1,0), (1,1), (2,0), (3,0), ..., (17,0), and (10,10) were estimated and also their most stable aggregates in the form of double-walled nanotubes predicted (assuming $d = 1.4457 \text{ \AA}$ what is the experimental value of the B–N bond length in h-BN layers): (1,0)@(9,0), (1,0)@(10,0), (1,1)@(10,0), (1,1)@(6,6), ..., (8,0)@(17,0), (5,5)@(17,0), and (5,5)@(10,10) [89–91,93]. Therefore, the estimations of radii of the single-walled BN nanotubes, from its part, can be used for a prediction of their most probable combinations in multiwalled structures. The remaining small divergences in sizes of the neighboring regular nanotubes can be compensated by defects and small chiral distortions. Such transformations of the zigzag and armchair nanotubes into chiral one will be accompanied, respectively, by the increase and decrease in their radii. Hence, if the difference in radii between regular nanotubes is more (less) than $c/2$, the realization of the structure in which the internal wall will be zigzag (armchair) and external armchair (zigzag) is more probable.

Thus, based on estimations of sizes of the single-walled BN nanotubes, it is possible to predict successfully the most stable double-walled forms. But how will it be solved in the same problem for multiwalled nanotubes? In this case, it will be necessary to calculate radii of nanotubes with high indices to choose sequences of single-walled nanotubes, whose radii are close to terms of arithmetical progression with arithmetic ratio of $c/2$. However, now only geometrical consideration will be insufficient. The matter is that unlike double-walled nanotubes in multiwalled ones, there are also medial layers. For this reason, the choice of the most stable structure should be made on the basis of comparison of reduction in energy caused by deviation from the equilibrium interlayer distance with its gain caused by the chiral distortions.

The line symmetry groups for one-periodic nanostructures with rotohelical symmetry were applied [126] for symmetry analysis of double-walled boron nitride nanotubes formed by rolling up the stoichiometric two-periodic slabs of hexagonal structure with the same or opposite orientation of translation and chiral vectors. To establish the equilibrium interwall distances corresponding to the minima of energy, the chiral indices were varied. The inversely stacked structure of zigzag-type nanotubes, characterized by the arrangement of positively and negatively charged rings in each atomic cross section (consisting of either B or N atoms, respectively), was found to be energetically more preferable as compared to the straightly stacked structure containing nanotube rings consisting of the same type of atoms in cross sections. The two sets of commensurate double-walled boron nitride hexagonally structured nanotubes possessing either armchair- or zigzag-type chiralities were considered in Ref. [127] as well.

The calculation of the IR spectrum of double-walled boron nitride nanotubes was performed [128] in the framework of the force constants model, using the spectral moment's method. The calculation of the IR active modes as a function of the diameter and chirality of the inner and outer tubes allows us to derive the diameter dependence of the wave number of the breathing-like modes, intermediate-like modes, and tangential-like modes in a large diameter range.

BUNDLES OF NANOTUBES

IR active modes were computed [129], for homogeneous bundles of single-walled BN nanotubes, using the so-called spectral moment's method. The dependence of the wave number on these modes in terms of diameters, lengths, and numbers of tubes was investigated. For a finite homogeneous bundle, additional modes appear as a specific signature.

In Ref. [130], a set of new nanophases in the form of porous crystal zeolite-like structures with elements of nanotubes in skeletons on the basis of refractory compounds, including BN, was simulated. The structure of the boron nitride E phase was resolved on the basis of modeling nanotubular crystals of zeolite. The phase transition processes of aligned crystalline BN nanotube bundles under transverse pressure were simulated [131] to investigate the phase transition mechanism and transition conditions. The antiparallel polar bonds rule, associated with the interaction between the tubes, was demonstrated to be crucial to such phase transitions. And the curvature of the tubes can greatly affect the phase transition behavior.

DEFECTS

A systematic study of vacancies in single-walled BN nanotubes was carried out in Ref. [132]. *Ab initio* calculations within the framework of DFT were used to optimize fully the geometries of the systems. For the BN nanotube, it was found that the vacancies on the nitrogen and boron site, namely, V_N , and V_B , are, respectively, the more stable vacancies in the B- and N-rich environments.

On the basis of calculations [133] also using the DFT, it was shown that BN nanotubes synthesis could produce tubes deprived of one (B1 hole) or two (B2 hole) boron atoms under the condition where nitrogen atoms exist in excess. The relative populations of various isomers of defective tubes will depend on the chirality of the tube. Interestingly, calculations show that B2 holes are much more favored than B1 holes, particularly, in armchair tubes.

The effect of divacancies on the stability and structural properties of boron nitride nanotubes was studied [134] using the *ab initio* DFT method. The defect $V_B V_N$ is more stable in the boron-rich and less stable in the nitrogen-rich growth conditions, and $V_N N_B$ is more stable in the nitrogen-rich than in the boron-rich conditions.

Native defects in BN nanotubes—antisites, carbon substitutionals, and vacancy defects—were investigated [135] theoretically by *ab initio* total-energy calculations, based on

a density functional spin-polarized method. All these defects introduce localized energy levels inside the bandgap.

A combination of electron microscopy and theoretical calculations has provided [136] insights into point defects and vacancy lines (dislocations) in single-walled BN nanotubes. Due to the partially ionic character of the BN bonding, divacancies behave like an associated Schottky pair. Clustering of multiple vacancies is energetically favorable and leads to extended defects that locally change the nanotube diameter and chirality.

The possible dislocation dipoles as defect nuclei under tension in BN nanotubes were identified by dislocation theory and MD simulations [137]. Formation energies of the dipoles evaluated through gradient-corrected DFT are high and remain positive at large strains, thus suggesting great yield resistance of BN nanotubes. The dipole appears to be more favorable in spite of its homoelemental B–B and N–N bonds.

The resonant photoabsorption and vibration spectroscopy combined with scanning tunneling microscopy unambiguously identify the presence of Stone–Wales defects in BN nanotubes [138]. The geometries and formation energies of Stone–Wales defects in single-walled boron nitride nanotubes were investigated [139] by means of DFT computations. Stone–Wales defects deform BN nanotubes severely and result in local curvature changes at defect sites. The energies of defect formation increase with increasing tube diameters and are orientation dependent.

Intrinsic defects in zigzag BN nanotubes, including single vacancy, divacancy, and Stone–Wales defects, were systematically investigated using DFT calculation in Ref. [140]. It was found that the structural configurations and formation energies of the topological defects are dependent on the tube diameter. The results demonstrate that such properties are originated from the strong curvature effect in BN nanotubes.

The defected BN tubes with C substitutions were considered in Ref. [104]. Using DFT, the physical properties of boron nitride nanotubes with the substitutional carbon pair defect were studied [141], in particular, considering the Stone–Wales rearrangement of the C–C pair defect. The activation energies have shown that the Stone–Wales defect in the C-doped BN nanotubes may be observed with a higher probability than in the undoped ones.

Defective single-walled BN nanotubes of armchair- and zigzag-type chiralities with uniform diameter can be simulated using a total geometry optimization for the one-periodic model. From the calculations of BN nanotubes containing N vacancies as well as C and O substitutes of N atoms, it was found [142] that single N vacancy and C and O substitutes of N atom cause an appearance of the energy levels inside the bandgap accompanied by relaxation of the nearest atomic spheres closest to the point defect and electronic charge redistribution around it.

NANOTUBULAR ENDS

The real nanotube structures of boron nitride have not been the infinite length, but are truncated in a certain way.

For example, in the arc discharge, there were formed [143] single- or double-walled chemically pure BN nanotubes with the structure close to stoichiometric, most of which were with ends closed by α layers perpendicular to the tube axis. A closure by a triangular facet, resulting from three 120° disclinations, was proposed to account for this specific shape.

In the process of carbothermal reduction, boron nitride nanotubes are formed, which are fragmentary or are terminated with plane, cone, or amorphous domain [120,121]. Besides, with the help of ballistic atomic displacements caused by high-energy electrons in the h-BN structure, it is possible to form the so-called nanoarches—fullerene structures containing half the nanotube, which is closed at the edges by α layers [144,145].

It is important to note that [146] three different morphologies of the tube cap— α , tapered, and amorphous, which are observable in experiments—were shown [99] to be directly attributed to the characteristics (mainly, chirality) of a given tube.

Hemi- $B_{16}N_{16}$ and hemi- $B_{36}N_{36}$ capped zigzag boron nitride nanotube was introduced [147], and its so-called Kekule count was studied; recurrence formulas were established. Numerical results reveal that the Kekule counts increase exponentially with respect to the number of layers in the nanotubes concerned.

The morphology of the tips of multiwalled BN nanotubes formed in arc suggested [145,148] the presence of pentagons and heptagons, which are energetically less favorable compared with squares.

OTHER NANOTUBULAR STRUCTURES

In addition to BN hexagonal nanotubes, the haeckelite nanotubular structure can exist (Figure 42). Concerning the haeckelite structures of BN tubes, a variety of chiral angles, including zigzag and armchair types, were observed. Based on DFT calculations [63], it was found that energies of haeckelite BN nanotubes exceed by ~ 0.6 eV/mol that for corresponding hexagonal nanotubes. They are less stable in comparison with corresponding haeckelite sheets as well, but they are stable and can be synthesized. Energy of deformation (i.e., energy needed to wrap nanotube from its sheet prototype) for large haeckelite BN tubes is extrapolated by the formula $\sim 1/R^2$ where R is the tube radius.

Depending on the structure formation kinetics characteristic for given technology, BN nanotubes quite often take the bamboo-like morphology and forms of a nanoarch, that is, half tube at the ends closed by planes. Bamboo-type BN nanotubes with cup-stacked structures were produced [149] by annealing Fe_4N and boron particles in nitrogen atmosphere. Atomic structure models and the formation mechanism were proposed from the results of HREM, image simulations, and molecular mechanics calculations. The nanotube structures would be stabilized by stacking the BN cup layer. Nanotube and nanobamboo structures of boron nitride were synthesized [150] by heating a mixture of boron and iron oxide in flowing ammonia gas. Boron nitride bamboo-like structures were

obtained [146] in the solid-state process, consisting the steps of the conversion of h-BN crystals into a powder with a ball mill and subsequent annealing.

Good agreement between the experimental IR and Raman spectra of single-walled bamboo-like, zigzag, and armchair nanotubes (and also plates and the “cones”) of boron nitride, which are obtained by the carbothermal method [151], with those calculated for low-frequency modes, gives hope that similar spectra corresponding to various chiralities, diameters, and thicknesses can be helpful in determining the composition of a sample.

The high-pure bamboo-like BN nanotubes with high yield were synthesized [152] via an effective CVD method by annealing porous precursor under NH_3 atmosphere. Nanotube content is estimated as 90 wt.%.

Coral-like boron nitride nanostructures were synthesized [153] via a simple method in a quasi-static atmosphere of nitrogen. The results of characterization have shown that the coral-like morphology is constructed by a main bamboo-shaped nanotube stem and a large amount of h-BN crystalline flakes growing outward from it.

BN tassel-like and treelike nanostructures were synthesized [154] through a CVD method. The tassel-like morphology is made up of a BN bamboo-shaped nanotube and numerous polyhedral particles attached onto it. The “tree” consists of a BN main stem and many BN nanotube branches grow outward from it. The formation of these unusual structures is proposed to arise from a two-stage deposition process: First, primary BN stems are formed followed by subsequent precipitation of amorphous clusters onto the rough outer surfaces. Second, polyhedral particles or BN nanotubes are nucleated and grew on the outer surface as a result of further deposition from the vapor phase.

A self-propagation high-temperature synthesis and annealing are a route to synthesis of wavelike boron nitride nanotubes [155].

Boron nitride fiber-like clusters and nanotubes were synthesized by evaporation of the layered BN under the nitrogen atmosphere [156]. Their associations in tree like and coral-like aggregates were obtained.

Boron nitride whiskers with diameter and aspect ratio of (2–3) μm and 40–100, respectively, were prepared [157] by calcining the precursors that were synthesized.

Rectangular nanotubes with line defects on the edges are also possible. For example, in an electric arc between electrodes of ZrB_2 in molecular nitrogen, N_2 , atmosphere [145], rectangular BN nanotubes were synthesized, having triangular “kinks” at the ends. Here, along with preferred hexagons and squares, energetically unfavorable rings with odd number of constituents—pentagons and heptagons—were found too. DFT calculations were performed [158] to investigate the availabilities and properties of boron nitride nanotubes with quadrangular cross sections. To achieve the purposes, the original structure of a representative BN nanotube was individually decorated by the carbon and silicon atoms to make the C–BN and Si–BN models. The optimized results indicated that the investigated models could be stabilized; however, they showed different properties.

APPLICATIONS

From the theoretical point of view, boron nitride nanotubes are interesting in that methods and approaches developed for the calculation of their constitution and electronic structure can be successfully transferred to the quantum chemistry [159]. On the other hand, they exhibit a number of properties that will have to find a variety of practical applications [160].

Fibers and Reinforcement

At once behind synthesizing BN nanotubes, for them, a number of probable applications in techniques have been offered [4], for example, fiber formed from a system of collinear BN nanotubes.

Consequently, the understanding of their mechanical properties is important. The theoretical studies carried out using a total-energy nonorthogonal tight-binding parameterization on the elastic properties of single-walled BN nanotubes were reported in Ref. [161]. Tubes of different diameters, ranging from 0.5 to 2 nm, were considered, and it was found that in the limit of large diameters, the mechanical properties of nanotubes approach those of the monolayer sheet. The stiffness and plasticity of BN nanotubes were investigated [162] using generalized tight-binding MD and *ab initio* total-energy methods. Due to B–N bond rotation effect, the compressed zigzag nanotubes were found to undergo anisotropic strain release followed by anisotropic plastic buckling. The strain is preferentially released toward N atoms in the rotated B–N bonds. The tubes buckle anisotropically toward only one end when uniaxially compressed from both. Based on these results, a skin-effect model of smart nanocomposite materials was proposed, which localizes the structural damage toward the surface side of the material. B–N bond-rotation mode of plastic yield in BN nanotubes in Ref. [163] was investigated combining *ab initio* computations with a probabilistic rate approach to predict the kinetic and thermodynamic strength. BN nanotube yield defects have low activation, but high formation energies. Elastic characteristics of BN nanotubes in Ref. [104] were also calculated applying MNDO method.

An analysis of the size effect's role in the properties of nanostructured materials was provided [164]. In particular, the possibility to reveal the superplasticity was mentioned as their interesting feature, which is found in several nanocomposites such as Si_3N_4 –BN nanotubes.

The nature and mechanism of interfacial reactions between boron nitride nanotubes and aluminum matrix at high temperature (650°C) were studied using high-resolution transmission electron microscopy (HRTEM) [165]. This study analyzes the feasibility of the use of BN nanotubes as reinforcement in aluminum matrix composites for structural application, for which interface plays a critical role. A theoretical prediction on Al/BN nanotube interface in macroscale composite suggests the formation of a strong bond between the matrix and reinforcement phase. As multiwalled BN nanotubes have very attractive mechanical and thermal properties, for example, elasticity, tensile strength, and high resistance to oxidation,

they may be considered as ideal reinforcing agents in light-weight metal matrix composites, especially, aluminum ribbons [166].

Nanomechanics

Other opportunities of application of the BN nanotubes are connected with the features of their phonon spectrum [27,167]. Such dielectric tubes without inversion center can be used as phonon laser in GHz–THz range or hypersound quantum generator. Because of the presence of the special nanotubular oscillatory modes, there is a strong enhancement of electron–phonon interaction in comparison with a bulk material, and it is not excluded that close-packed 1D BN nanotubes will serve as high-temperature superconductors.

Using a simple six-exponential potential acting between B and N atoms on two h-BN sheets and BN nanotubes, the frequencies of the various motions of BN nanotubes on h-BN surface were calculated [168]. Bulk modulus was calculated to be 37.03 GPa. Thus, an application of a small pressure compresses it to a greater extent, and this property can be best employed for making good shock absorbers.

Cantilevered single-walled boron nitride nanotube-based nanomechanical resonators can be prepared in both zigzag and armchair forms [169]. The vibration response analysis [170] of single-walled boron nitride nanotubes treated them as thin-walled tubes. The resonant frequency variations as well as the resonant frequency shift are caused by the changes in the size of BN nanotubes in terms of length as well as the attached masses. The results indicate that the mass sensitivity of cantilevered BN nanotube nanomechanical resonators can reach 10^{-23} g and the mass sensitivity increases when smaller size nanomechanical resonators are used in mass sensors. The dynamics analysis of single-walled BN nanotubes as a resonant nanomechanical sensor by using the finite-element method was reported in Ref. [171].

Piezoelectricity

BN from C distinguishes partial heteropolarity of the chemical bonding, and for this reason, one more sphere of the possible applications for BN nanotubes can become an elaboration of new piezoelectric materials. The threefold symmetry of BN sheet, the groups III–V analog to graphite, prohibits an electric polarization in its ground state. But this symmetry is broken when the sheet is wrapped to form a BN tube. It was shown [172] that this leads to an electric polarization along the nanotube axis that is controlled by the quantum mechanical boundary conditions of its electronic states around the tube circumference. Thus, the macroscopic dipole moment has an intrinsically nonlocal quantum mechanical origin from the wrapped dimension.

Combining *ab initio* and tight-binding methods, and analytical theory, the piezoelectricity of a heteropolar, in particular, BN nanotube was found [173] to depend on its chirality and radius. The effect can be understood starting from the piezoelectric response of an isolated sheet, along with a structure-specific mapping from the sheet onto the tube surface. It was demonstrated that a linear coupling between the

uniaxial and shear deformations occurs in chiral nanotubes, and the piezoelectricity of nanotubes is fundamentally different from its counterpart in bulk material.

Ab initio calculations of the spontaneous polarization and piezoelectric properties of BN nanotubes showed [174] that they are excellent piezoelectric systems with response to values larger than those of piezoelectric polymers. The intrinsic chiral symmetry of the nanotubes induces an exact cancellation of the total spontaneous polarization in ideal, isolated nanotubes of arbitrary indices. But the breaking of this symmetry by the intertube interaction or elastic deformations induces spontaneous polarization comparable to that of wurtzite bulk semiconductors [104].

As, in addition to their weak damping properties, BN nanotubular structures possess good piezoelectric characteristics, they are able to serve as powerful converters in the specified frequency range [103]. Taking into account that ultrasound can propagate in a crystal, such hypersonic generator and detector based on BN nanotubes were synthesized in a SiC shell.

The results of electro-thermo-nonlocal axial vibration analysis [175] of single-walled BN nanorods under electric excitation can be used for micro- and nano-electro-thermo-mechanical devices and nanoelectronics.

Heterojunctions

The theory [176] developed for structural and electronic properties of nanotubular heterojunctions, in which one of the layers is nanotubular boron nitride (viz., for C/BN and $\text{BC}_2\text{N}/\text{BN}$ systems), leads to a conclusion that on the basis of it, different electronic devices can be elaborated.

In particular, sandwich nanostructures with C layers both in the center and at the periphery separated by a few BN layers may allow creation of nanotubular electronic devices [177]. Within the special semiempirical approach [178], C/BN superlattices and isolated junctions had been investigated as specific examples by the wide variety of electronic devices that can be realized using such nanotubes. The bottom of the conduction bands in pure BN nanotubes is controlled by a nearly free-electron state localized inside the tube suggesting interesting electronic properties under doping.

Multielement nanotubes comprising multiple SiC core, an amorphous SiO_2 -intermediate layer, and outer shells made of BN and C layers separated in the radial direction, with diameters of a few tens of nm and lengths up to 50 μm , were synthesized by means of reactive laser ablation [179]. This resembles a coaxial nanocable with a semiconductor–insulator–semiconductor geometry and suggests applications in nanoscale electronic devices that take advantage of this self-organization mechanism for multielement nanotube formation.

The development of high-emission B–N–C nanostructured materials for solar-to-electric energy converters was proposed [180]. Nanotubular emission cathodes were fabricated in nitrogen flow as a result of surface modification induced by laser treatment of the compacted samples of fine-grained h-BN powders and 25 wt.% black composite.

The transport properties and differential conductance of the heterostructures constructed by single-walled carbon nanotube and single-walled boron nitride nanotube were investigated using DFT [181]. Such tunable by bias differential conductance of BN/C nanotube heterostructure mainly derives from the blockage of the transport channels induced by the semiconducting BN segment.

Optics

In zigzag BN nanotubes, radial deformations that give rise to transverse pressures decrease the gap from 5 to 2 eV, allowing for optical applications in the visible range [182].

Importantly, both the zigzag and chiral tubes are found [183] (see also Ref. [184]) to exhibit large second-order nonlinear optical behavior with the second-harmonic generation and linear electro-optical coefficients being up to 15 times larger than that of bulk BN in both denser zincblende and wurtzite-like structures, indicating that BN nanotubes are promising materials for nonlinear optical and optoelectronic applications. The bandgap progression with BN nanotube diameter that is of crucial importance for device applications was presented and analyzed in detail in Ref. [185].

Electronic structure of BN nanotubes can be tuned in a wide range through covalent functionalization [186] (see also Ref. [187]). The ultraviolet (UV) and visible absorption spectra indicate that their electronic structure drastically changes under functionalization. *Ab initio* calculations revealed that the covalently functionalized BN nanotubes can be either *n*- or *p*-doped depending on the electronegativity of molecules attached, and their energy gap can be adjusted from UV to visible optical range by varying concentration of functionalizing species.

Boron nitride nanotubes were functionalized and solubilized [188] in organic solvents by using conjugated poly(*p*-phenyleneethynylene)s (PPEs) and polythiophene. The functionalization with PPEs enhanced planarization of PPEs with red shifts in both absorbance and emission of the composite materials with reference to free PPEs, whereas the functionalization of BN nanotubes with polythiophene results in blue shifts in both the absorption and emission.

Noncovalent functionalization of disentangled boron nitride nanotubes can lead to strong and stable visible light emission devices [189]. Eu-doped boron nitride nanotubes are a nanometer-sized visible light source [190].

Radiation and Shielding

A theoretical description of electron irradiation of single-walled BN nanotubes was presented in Ref. [191]. These calculations of the total knock-on cross section for nanotubes can be used as a guideline for TEM experimentalists using high-energy focused beams to shape nanotubes and also more generally if electron irradiation is to be used to change nanotube properties such as their optical behavior or conductivity.

Isotopically enriched ^{10}BN nanotubes not only have lightweight, excellent mechanical properties and a strong resistance to oxidation but also a radiation shielding property,

which offer a multifunctional material with promising aerospace applications [192].

An attempt to develop an effective ionizing shielding material on the basis of thermally stable phosphates (widely used in aerospace applications) filled with the micro- and nano-sized boron compounds including BN nanotubes together with carbon compounds was reported [193].

Absorbers and Sensors

In general, the effect of a gas molecule adsorption was investigated [194] on zigzag BN nanotube within a random tight-binding Hamiltonian model. The results have shown that the adsorption of carbon dioxide gas molecules by boron atoms only leads to a donor-type semiconductor while the adsorption by nitrogen atoms only leads to an acceptor. In all cases, increasing the gas concentration causes an increase in the height of the peaks in the bandgap. This is due to an increasing charge carrier concentration induced by adsorbed gas molecules.

Tremendous spin-splitting effects in absorbing open boron nitride nanotubes make their application to nanoscale spintronic devices possible [195].

One-dimensional crystals of potassium halides, including KI, KCl, and KBr, were inserted [196] into BN nanotubes for their functionalization. The wetting properties (static contact angles of the liquids and surface tension) of individual BN nanotubes were studied [197] experimentally using a nanotube-based force to measure the interactions between nanotubes and liquids *in situ*.

From thermodynamics and chemical bonding dynamics, antisite atom segregation in porous BN nanotubes, with respect to perfect counterparts, was studied [198] using DFT. There was a proposal that different structures allow antisite atom segregation to offer many promising applications in new fields, such as biolabeling, purification, and chemical and biological separations. The results on giant osmotic energy conversion measured in a single transmembrane BN suggest [199] that BN nanotubes could be used as membranes for osmotic power harvesting under salinity gradients.

By using the DFT, CO molecules adsorbed on palladium atom-doped boron nitride nanotubes were investigated [200]. This indicates that Pd-doped nanotubes can be considered as nanogas-sensitive material. The adsorption of CO onto Ni-doped boron nitride nanotubes was investigated using the DFT [201]. It was found that the strength of adsorption of CO onto Ni-doped perfect BN nanotubes is higher than that on defective ones.

Carbon dioxide (CO_2) emitted from large-scale coal-fired power stations or industrial manufacturing plants has to be properly captured to minimize environmental side effects. From the results of *ab initio* calculations using PW and LCAO, strong CO_2 adsorption on boron antisite B_N in boron-rich boron nitride nanotube was reported [202]. This implies that boron-rich BN nanotubes could capture CO_2 effectively at ambient conditions.

The physisorption of methane in homogeneous armchair open-ended single-walled boron nitride nanotube triangular

arrays was evaluated [203] using Monte Carlo simulation. According to the results, it is possible to reach 108% and 140% of the US Department of Energy's target for CH_4 using such arrays.

The adsorption properties of acetone on zigzag single-walled BN nanotubes were investigated [204] using DFT calculations. The results obtained show that acetone is strongly bound to the outer surface on the top site directly above the boron atom. The ability of zigzag BN nanotubes to adsorb acetone is significantly stronger than the corresponding ability of zigzag carbon nanotubes.

In the communication [205], the humidity-sensing properties of single boron nitride nanotubes with and without Au decoration were investigated. The good humidity-sensing properties of the Au-BN nanotube combined with its excellent chemical stability make it a promising candidate for the fast detection of humidity in various wild environments.

According to the *ab initio* investigation [206], Al- and Ga-doped single-walled boron nitride nanotubes serve as ammonia sensor.

Ab initio calculations based on DFT method were used [207] to investigate the adsorption properties of OCN^- by single-walled BN nanotubes. One can conclude that BN nanotubes play an important role as suitable sensor.

Platinum nanoparticle-modified polyaniline-functionalized boron nitride nanotubes can serve as amperometric glucose enzyme biosensor [208].

Hydrogen Storage

Hydrogen adsorption in multiwalled boron nitride nanotubes and their arrays was studied using grand canonical Monte Carlo simulation [209]. The results show that hydrogen storage increases with tube diameter and the distance between the tubes in multiwalled boron nitride nanotube arrays. Also, triple-walled boron nitride nanotubes present the lowest level of hydrogen physisorption, double-walled boron nitride nanotubes adsorb hydrogen better when the diameter of the inner tube diameter is sufficiently large, and single-walled boron nitride nanotubes adsorb hydrogen well when the tube diameter is small enough.

Hydrogen uptake capacities of 1.8 and 2.6 wt.% were obtained [210] on multiwalled BN nanotubes and bamboo-like nanotubes, respectively, under 10 MPa at room temperature. The results have shown that chemical interactions mainly take place between hydrogen and BN. Taking into consideration the ultimate stable chemical and thermal stability, BN nanotubes may exhibit some interesting possibilities in storing hydrogen. Compressive buckling of open-ended boron nitride nanotubes could be useful [211] in hydrogen storage applications as well.

Ab initio simulations on the interaction of molecular hydrogen H_2 with the native and substitutional defects of small-diameter (8,0) BN nanotubes were performed in Ref. [72]. The adsorption of H_2 on structures was found to be endothermic with respect to dissociation, with the small-diameter nanotube possessing the smaller barrier. Although chemisorption along the tube axis is energetically preferred, the

barrier for dissociation is lower for chemisorption across the tube axis, implying that chemisorbed hydrogen can be kinetically trapped in a higher-energy state. Dopants can maximize hydrogen-binding energies: Si dopants for N provide H_2 -binding energies of 0.8 eV, at the upper end of the range required for hydrogen storage. The surface stress induced by nanotube curvature boosts the hydrogen storage capabilities of vacancies, with the nitrogen vacancy chemisorbing 4H and allowing a H_2 molecule to enter the interior of the tube. Thus, the hydrogen-binding properties of BN systems are strongly dependent on the defects and dopants present. Pretreating of these systems so as to partially remove nitrogen should enhance H_2 adsorption properties.

It was tentatively concluded [212] that the improvement of the electrocatalytic activity by surface modification with metal or alloy would enhance the electrochemical hydrogen storage capacity of BN nanotubes.

The hydrogen absorption capacity of Ti-covered single-walled BN nanotube was investigated using *ab initio* PW method [213]. The weak interaction of H_2 molecules with the outer surface of bare nanotube can be significantly enhanced upon functionalization by Ti atoms: each Ti atom adsorbed on tube can bind up to four H_2 molecules with an average binding energy suitable for room temperature storage. The adsorption of H_2 on Ce-doped boron nitride nanotubes was investigated [214] by using DFT. It was found that Ce preferentially occupies the hollow site over the BN hexagon. The results indicated that seven H_2 per Ce can be adsorbed and 5.68 wt.% H_2 can be stored in Ce_3/BN nanotube system. Among nanotubes doped with metals, Ce exhibits the most favorable hydrogen adsorption characteristics in terms of the adsorption energy and the uptake capacity.

Biomedicine

Boron nitride nanotubes represent an innovative and extremely intriguing class of nanomaterials, and encouraging studies about their applications in biomedicine have emerged. As a consequence, a systematic investigation of their biosafety has become of fundamental importance in the biomedical research. In Ref. [215], the biocompatibility data of BN nanotubes injected in rabbits were presented. No significant adverse effects were found, and no impairments in blood, liver, and kidney functionality were highlighted. All the collected data are very promising, suggesting the optimal biocompatibility of BN nanotubes and thus enabling their exploitation in nanomedicine as nanotransducers and nanocarriers.

It was demonstrated [216] that boron nitride nanotubes are noncytotoxic and can be functionalized for interaction with proteins and cells.

Electrothermal transverse vibration of fluid-conveying double-walled boron nitride nanotubes embedded in an elastic medium such as polyvinylidene fluoride, which is a piezoelectric polymer, was investigated [217]. The results could be used in designing nano-electro-mechanical devices for measuring the density of a fluid such as blood flowing through such nanotubes with great applications in medical fields.

The interaction of thiazole drug with zigzag single-walled BN nanotube of finite length in gas and solvent phases was studied [218] by means of DFT calculations. This study may provide new insight into the development of functionalized BN nanotubes as drug delivery systems for virtual applications. Boron nitride nanotube functionalized with glucosamine is a potential novel carrier system for radioisotope and drug delivery [219].

Irreversible lethal electroporation uses short pulses of high amplitude static electric fields to create irreversible pores in the cell membrane, thus causing cell death. BN nanotube-mediated irreversible electroporation has high potential on cancer cells. It was speculated [220] that BN nanotubes, when interacting with cells exposed, amplify locally the electric field.

Mass Production

Various techniques including plasma-arc, laser ablation, and chemical vapor-phase synthesis were employed to produce bulk amounts of BN nanotubes with some success, but in general the yields are low. In Ref. [221], a high-yield plasma-arc method that easily and reliably produces macroscopic amounts of pure BN nanotubes is described. Interestingly, the method produces almost exclusively double-walled nanotubes; these in turn self-assemble into BN nanotube bundles or ropes. This synthesis also produces BN-coated crystalline nanoparticles, whose cores can be preferentially etched leaving behind hollow BN “nanococoons.”

High growth temperatures (above 1100°C), a low production yield, and impurities had prevented progress in the applications of BN nanotubes. Relatively recently, it was shown that these tubes can be grown on substrates at lower temperatures (of about 600°C) [222]. High-order tubular structures were constructed, which can be used without further purification.

An effective route of growing boron nitride nanotubes was developed in Ref. [223]. By reacting boron, silica, and iron oxide catalysts supported on alumina, gas-phase reactants and liquid-phase catalyst could be generated *in situ*. When ammonia is introduced, boron nitride nanotubes could be formed by the reaction of boron oxide and ammonia inside the liquid-phase catalysts. The synthesized boron nitride nanotubes are highly crystallized and have multiwalled structures with 10–30 nm in diameter. The growth process can be explained based on vapor–liquid–solid wirelike growth mechanism.

Selective growth of boron nitride nanotubes was demonstrated [224] by means of plasma-enhanced pulsed laser deposition. Although it is a physical vapor deposition technique for the growth of BN thin films, ion sputtering induced by the plasma can eliminate the formation of BN thin films and lead to the so-called total resputtering region, in which a pure phase of BN nanotubes can be grown at 600°C–700°C using Fe catalyst.

A method for producing long, small-diameter, single- and few-walled, boron nitride nanotubes in macroscopic quantities was reported in Ref. [225]. The pressurized vapor/condenser method produces, without catalysts, highly crystalline, very

long, small-diameter, BN nanotubes. Palm-sized, cotton-like masses of BN nanotube raw material were grown by this technique and spun directly into centimeters-long yarn. Nanotube lengths were observed to be 100 times that of those grown by the most closely related method.

FULLERENES

As is known, the term *fullerene* was introduced and established in due time to identify cage molecules of carbon. At the 13th International Symposium on Boron, Borides, and Related Compounds (September 5–10, 1999, Dinard, France), it has been proposed to name the similar structures built of boron and nitrogen atoms as “fulborenes” [167]. However, during the discussion, attention was drawn at inadmissibility of word building by breaking a surname, as Fuller is the name of an inventor of the so-called geodesic dome. It seems appropriate not to introduce a new term, but expand the concept of *fullerene* in a way that it would characterize just the structure, rather than a specific chemical composition of the molecule.

GEOMETRY

Semiempirical MO method calculation performed for the $B_{12}N_{12}$ of fullerene-like spheroid geometry had led to the following values structural parameters [226]. Valence angles B–N–B in rhombuses and hexagons equal to 79.92° and 106.44°, while bond lengths equal to 1.504 and 1.418 Å, respectively. The same lengths tested by *ab initio* HF method fall in intervals 1.475–1.508 and 1.433–1.438 Å confirming semiempirical results.

Boron nitride nanocage materials have a great potential of the low-dimensional materials with the isolated environment. By controlling the nanostructure, BN fullerene materials are expected to show various electronic, optical, and magnetic properties. A number of studies were made on BN fullerene materials and BN nanocapsules, which are expected to be useful as electronic devices, high-heat-resistant semiconductors, and insulator lubricants. The purpose of the work [227] was to synthesize and characterize the BN nanocage materials and to indicate a guideline for designing and synthesizing the BN fullerene materials, which are expected as the future nanoscale devices.

In practice, mainly $B_{36}N_{36}$ structures are formed. Comparative analysis of a number of possible structural models of BN fullerenes does lead to the conclusion [85] that, in contrast to the six- and four-membered rings, the $B_{36}N_{36}$ cluster is stable. In this way, it is possible to find some explanations for other similar structures of boron nitride [86].

A simple and efficient method was presented [228] for the enumeration of substitution isomers for polyhedral molecules of BN with face spirals. For these molecules, it is convenient to find a set of symmetry-equivalent vertex sequences, each corresponding to a symmetry operation of the point group of the parent framework. This enables to represent each symmetry operation as permutation of vertices, with which the isomorphic configurations and the

symmetry of a substitution isomer are readily found, thus solving the enumeration problem. The method was applied to the BN fullerene-24 cage and the truncated octahedron for enumerating the related $B_{24-m}N_m$ isomers and for assigning their maximal symmetry.

HREM, mass spectrometry, and molecular mechanics/orbital calculations of the boron nitride-based clusters showed [229] the formation of $B_{36}N_{36}$. Image simulations of these clusters confirmed the proposed structure model.

The boron nitride cages having the form of the fullerene-like molecules serve as alternative nanostructures to tubular boron nitride. However, considering a corresponding geometrical problem, it is known that, in contrast to tubes, such closed structures cannot be faceted only by hexagons. Like the obvious fullerenes, BN fullerenes can form fullerite crystals and compounds (e.g., with metals)—fullerides. For any structural analysis of BN fullerene-like systems, the presence of a certain model of the atomic structure is obligatory.

Modeling of the BN fullerene structures as well as fullerites (Figure 47) and fullerides constructed of them can be based on several empirically established rules [27]. The comparison of the measured values of formation enthalpies it yields is that B–N chemical bonds are essentially stronger than B–B and N–N bonds. For this reason, it is believed that the structure of the stable BN fullerenes is close with stoichiometric one, that is, ratio $B/N \approx 1:1$. But such systems can be built up only from atomic rings with even number of vertices, which are alternatively occupied by atoms B and N. This statement is *Rule 1*. Further, the structures of BN fullerenes are searched among Archimedean polyhedra, all vertices of which lie at a sphere surface, under the additional condition that for each atom three nearest neighbors are available. It is the essence of *Rule 2*. The search of the BN fullerite structures is governed by two additional rules. *Rule 3* states the coordination and

type of molecular lattices are determined by a number and orientation of faces of the constituent molecules. *Rule 4* states the number of covalent double bonds on both conjugated faces equals to a necessary number of intermolecular single bonds between two adjacent faces.

The conditions of the formation of covalence crystals from the binary fullerene-like molecules, in particular, B_nN_n , were more detailed in Ref. [230]: these clusters should be the hollow convex polyhedra satisfying Euler's rule, that is, their faces should be constructed only by even-membered rings and satisfy the so-called isolated ring's rule; the number of the isolated faces should be coincident with the symmetry of the forming crystal; it should exist only alternating chemical bonds (i.e., B–N bonds). In the case of 4, 6, 8, or 12 isolated faces, these conditions lead to tetrahedral, cubic, and hexagonal symmetries. Thus, bonding of the clusters with similar faces forms close-packed crystal structures with sphalerite-like, rock salt, bcc (body centered cubic), fcc (face centered cubic), and hcp (hexagonal close packed) lattices.

The concept of a regular boron nitride fullerene has been introduced in Ref. [90–93,102,111, and 230]. The structure of the BN fullerene is considered as regular if it meets the following conditions: (1) the structure consists of equal numbers of B and N atoms, (2) only threefold chemical bonds are realized (i.e., analogs of the bonds in layers of h-BN-, r-BN-, and t-BN-layered crystals, as well as in regular BN nanotubes, but with distinguished valence angles), and (3) atomic rings represent plane or broken (along diagonals between B and N sites) regular polygons with even number of vertices alternatively occupied by B and N atoms. The given definition yields equal B–N bond lengths. Denote this only structural parameter for (n)-fullerene ($n = 1,2,3,\dots$) by $d_{(n)}$. The chemical formula of a regular BN fullerene should

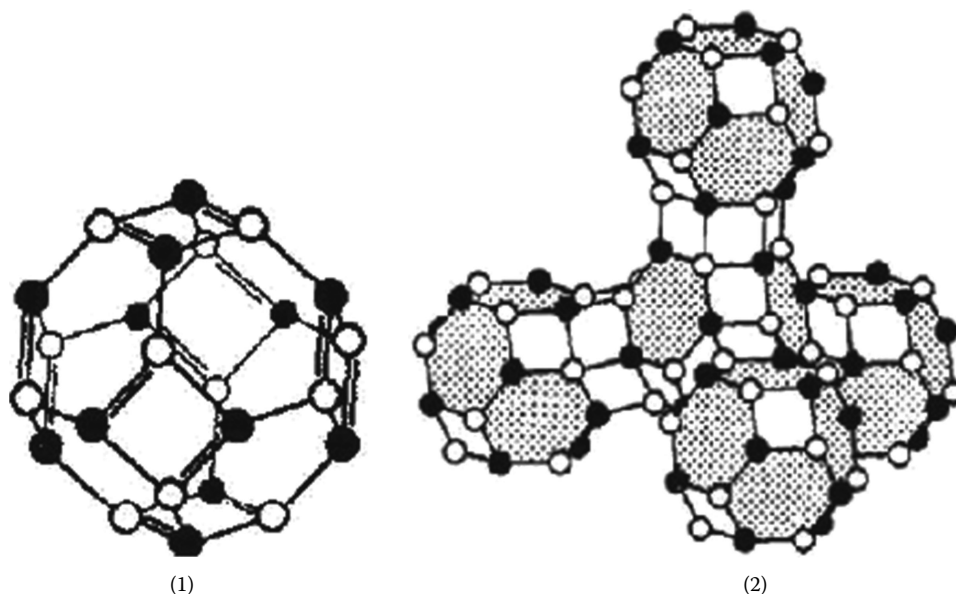


FIGURE 47 Structure of the regular fullerene $B_{12}N_{12}$ and $B_{24}N_{24}$ coordination tetrahedron, the building block of zinc-blende and wurtzite-like boron nitride fullerite lattices.

be $B_{2n(n+1)}N_{2n(n+1)}$. As the regular fullerene is inscribed in sphere, the spherical or, more precisely, geographical (r, ϕ, λ) coordinates are useful to describe atomic site positions. Evidently, the geographical coordinate r for all atomic sites equals to fullerene radius $r_{(n)}$:

$$r_B = r_N = r_{(n)}.$$

The latitudes ϕ are determined as

$$\phi_B = \phi_N = \text{sgn } m \arccos \frac{r_{n,m}}{r_{(n)}},$$

while longitudes λ as

$$\lambda_B = \arcsin \frac{d_{Bn,m}}{r_{n,m}} + \pi \left(\frac{(4l-3-(-1)^m)}{2n} - 1 \right)$$

and

$$\lambda_N = \arcsin \frac{d_{Nn,m}}{r_{n,m}} + \pi \left(\frac{(4l-3-(-1)^m)}{2n} - 1 \right).$$

Here, indices $m = \pm 1, \dots, \pm(n+1)$ and $l = 1, \dots, n$ are the number of atomic rings in parallel planes and B and N atoms in planes, respectively.

Radius $r_{n,m}$ of the ring in m -plane can be calculated from the following relation:

$$r_{n,m}^2 = \frac{d_{Bn,m}^2 + 2d_{Bn,m}d_{Nn,m} \cos \pi/n + d_{Nn,m}^2}{4 \sin^2 \pi/n}.$$

For planes with $m \neq \pm 1$, $d_{Bn,m}$ and $d_{Nn,m}$ are certain interatomic distances in m -plane, which equal to one of the diagonals $d_{n,k,j}$ between certain B and N vertices in regular $2k$ -gon ($k = 1, 2, 3, \dots$ and $j = 1, \dots, k$) with side $d_{(n)}$ and vertices occupied by B and N atoms:

$d_{n,k,j}/d_{(n)} = (\sin \pi j / 2k) / (\sin \pi / 2k)$. But if $m = \pm 1$, that is, in planes adjacent or coincident with equatorial plane, one from the parameters $d_{Bn,m}$ and $d_{Nn,m}$ equals to $d_{(n)}$, while another equals to parameter $D_{(n)}$ expressed as

$$\frac{D_{(n)}}{d_{(n)}} = \frac{\sin \pi j_B / 2k_B}{\sin \pi / 2k_B} + \frac{\sin \pi j_N / 2k_N}{\sin \pi / 2k_N} - 1,$$

where j_B and j_N are the j -values in planes with $m = \pm 1$.

And, nally, radius $r_{(n)}$ of regular (n) -fullerene is determined as

$$\frac{2r_{(n)}^2}{d_{(n)}^2} = 1 + \frac{1}{8 \sin^2 \pi/n} \left(\frac{\sin \pi j_B / 2k_B}{\sin \pi / 2k_B} + \frac{\sin \pi j_N / 2k_N}{\sin \pi / 2k_N} \right)^2.$$

In particular, in the case of $n = 2^0, 2^1, 2^2, \dots$, that is, for fullerenes $B_4N_4, B_{12}N_{12}, B_{24}N_{24}$, etc., planes with $m = \pm 1$ coincide with equatorial one and one can obtain the simplified formula:

$$\frac{r_{(n)}^2}{d_{(n)}^2} = \frac{1}{\sin^2 \pi / 2n} \left(\frac{3}{4} + \frac{\cos \pi / 2n}{\sqrt{2}} \right).$$

Based on this model of regular fullerene of BN, the asymptotic (at high index, $n \gg 1$) expression of BN fullerene radius shows [94] that it is almost proportional to n .

Based on the stated relations, the explicit expressions (in terms of B–N bond length $d_{(n)}$) of the interatomic distances in regular boron nitride fullerene have been obtained:

$$\begin{aligned} & (Bn, m', lm' - Nn, m'', l'')^2 \\ &= 2r_n^2 - 2 \text{sgn } m' m'' \sqrt{(r_{(n)}^2 - r_{n,m'}^2)(r_{(n)}^2 - r_{n,m''}^2)} \\ &\quad - (d_{Bn,m'} d_{Nn,m''} + d_{Nn,m'} d_{Bn,m''}) \frac{\cos(4(l' - l'') + (-1)^{m'} + (-1)^{m''}) \pi / 2n}{4 \sin^2 \pi / 2n} \\ &\quad + (d_{Bn,m'} d_{Bn,m''} - d_{Nn,m'} d_{Nn,m''}) \frac{\sin(4(l' - l'') + (-1)^{m'} + (-1)^{m''}) \pi / 2n}{2 \sin \pi / n} \\ & (Nn, m', l' - Bn, m'', l'')^2 \\ &= 2r_n^2 - 2 \text{sgn } m' m'' \sqrt{(r_{(n)}^2 - r_{n,m'}^2)(r_{(n)}^2 - r_{n,m''}^2)} \\ &\quad - (d_{Nn,m'} d_{Bn,m''} + d_{Bn,m'} d_{Nn,m''}) \frac{\cos(4(l' - l'') - (-1)^{m'} - (-1)^{m''}) \pi / 2n}{4 \sin^2 \pi / 2n} \\ &\quad + (d_{Nn,m'} d_{Nn,m''} - d_{Bn,m'} d_{Bn,m''}) \frac{\sin(4(l' - l'') - (-1)^{m'} - (-1)^{m''}) \pi / 2n}{2 \sin \pi / n} \\ & (Bn, m', l' - Bn, m'', l'')^2 \\ &= 2r_n^2 - 2 \text{sgn } m' m'' \sqrt{(r_{(n)}^2 - r_{n,m'}^2)(r_{(n)}^2 - r_{n,m''}^2)} \\ &\quad - (d_{Bn,m'} d_{Bn,m''} + d_{Nn,m'} d_{Nn,m''}) \frac{\cos(4(l' - l'') + (-1)^{m'} - (-1)^{m''}) \pi / 2n}{4 \sin^2 \pi / 2n} \\ &\quad + (d_{Bn,m'} d_{Nn,m''} - d_{Nn,m'} d_{Bn,m''}) \frac{\sin(4(l' - l'') + (-1)^{m'} + (-1)^{m''}) \pi / 2n}{2 \sin \pi / n} \\ & (Nn, m', l' - Nn, m'', l'')^2 \\ &= 2r_n^2 - 2 \text{sgn } m' m'' \sqrt{(r_{(n)}^2 - r_{n,m'}^2)(r_{(n)}^2 - r_{n,m''}^2)} \\ &\quad - (d_{Nn,m'} d_{Nn,m''} + d_{Bn,m'} d_{Bn,m''}) \frac{\cos(4(l' - l'') - (-1)^{m'} + (-1)^{m''}) \pi / 2n}{4 \sin^2 \pi / 2n} \\ &\quad + (d_{Nn,m'} d_{Bn,m''} - d_{Bn,m'} d_{Nn,m''}) \frac{\sin(4(l' - l'') - (-1)^{m'} + (-1)^{m''}) \pi / 2n}{2 \sin \pi / n}. \end{aligned}$$

BOND POLARITY

The analysis of the atomic orbital population in nonstoichiometric molecule $B_{36}N_{24}$ (with structure like the carbon C_{60}

fullerene) carried out [231] by the X_α -method gives the following values of the atomic charges: B(1) + 0.47, B(2) + 0.41, and N - 0.66 (there are two nonequivalent B sites—see their definitions in subsection ‘Binding Energy’).

Using a semiempirical method of MNDO, the average charge per B atom (positive) and per N atom (negative) in $B_{12}N_{12}$, $B_{24}N_{24}$, and $B_{60}N_{60}$ fullerenes have been evaluated, respectively, as ± 0.260 , ± 0.311 , and ± 0.300 [27].

Optimization of the smallest BN cage molecule conformation by a gradient-search method also leads to the necessity to transfer certain electron charge from B atoms to N atoms and, hence, to a certain deal of ionicity in interatomic bonds together with the formation of *rippling* surfaces [232]. Because positive B ions leave inside, while negative N ions leave outside, it results in the formation of a thin dipole layer.

BINDING ENERGY

For the first time, $B_{36}N_{24}$ fullerene, which is the boron nitride structural analog of the well-known carbon C_{60} fullerene, was calculated [231]. It is very difficult for synthesizing, because of a strong deviation from the stoichiometric composition: its traces are hardly observable by mass spectrometry. For this reason, the bond lengths in $B_{36}N_{24}$ molecule were not measured. The B(1)–B(1), B(2)–B(2), B(1)–N, and B(2)–N distances were only estimated by means of MD: 1.972, 2.016, 1.670, and 1.695 Å, respectively. Here, B(1) designates the sites of the pairs of adjacent B atoms, which form the sides of the five-membered rings, and B(2) are the sites of the pairs constituent of the pairs, which form the common side of the adjacent six-membered rings (unlike B sites, all N sites in this structure are equivalent).

Semiempirical MO method calculation performed for the $B_{12}N_{12}$ of fullerene-like spheroid geometry [226] testifies in favor of the presence of stationary points on potential energy surfaces of $(BN)_{12}$ fullerenes. The molar heat of formation is estimated as 0.86 eV/mol. HF test calculations also confirm a conclusion about their stability: system total energy is negative and its absolute HF value ranged in an interval from 945.77688 up to 950.56265 eV.

The optimization by the DFT method of possible structures, originated from fully deformable graphs of B_3N_3 and B_4N_4 , leads to the conclusion [233] that such systems are able to compete with other finite structures of boron nitride and, in particular, with fullerenes.

In Ref. [44], energies of the $B_{12}N_{12}$ fullerene cage were obtained taking the energy of an isomer in the form of a ring as a reference value. The HF method gave -1.58, -1.06, and -0.88; the DFT with the LDA -8.21, -7.46, and -7.35; and the DFT with gradient corrections -1.93, -1.10, and -1.00 eV. Despite the considerable differences in the absolute values obtained for the difference energies, its negative sign and, therefore, the stability of fullerene molecules $B_{12}N_{12}$ raise no doubts.

The study, using the DFT, of ionized clusters $B_nN_n^+$ with the number of atoms $n = 3, \dots, 10$ showed [234] that, as in the case of their neutral counterparts, structures with even indices n have lower energy.

It had been noticed that boron nitride fullerene-like systems mainly obtained in experimental conditions are $B_{36}N_{36}$ molecules. The comparative analysis of some possible structural models of BN fullerenes indeed leads to a conclusion [85] that unlike the isolated atomic rings, $B_{36}N_{36}$ cluster is a stable structure in spite of the existence of distorted six- and four-membered rings. It is an explanation for the other similar BN microstructures too [86].

The growth mechanism for BN fullerenes in Ref. [27] was investigated theoretically by means of MD using original B–B, B–N, and N–N interatomic potentials. Semiempirical MNDO method predicts the stability of $B_{12}N_{12}$, $B_{24}N_{24}$, and $B_{60}N_{60}$ fullerenes as their total potential energies are negative. On magnitude, they equal to 10.26, 11.12, and 11.26 eV/mol, respectively (at heats of formation of 6.857, 8.098, and 29.280 eV/mol).

On the other hand, the theoretical analysis of the relative stability of B_nN_n molecules with $n = 8, \dots, 11$ carried out in Ref. [235], using various versions of the HF method and DFT, leads to the following conclusions. The cage is more stable than the ring, if at least two of the four-membered rings are separated by hexagons. This situation occurs first when $n = 11$, so that the $B_{11}N_{11}$ cage is clearly more stable than the ring. The B_8N_8 cage, on the contrary, is obviously less stable. As for the B_9N_9 and $B_{10}N_{10}$ cages, by their stability, they are comparable with the corresponding ring structures.

In Ref. [236], the *ab initio* DFT calculations within the GGA were applied to study the relative stabilities of stoichiometric fullerenes $B_{16}N_{16}$, $B_{36}N_{36}$, and $B_{64}N_{64}$, as well as non-stoichiometric ones $B_{12}N_{16}$, $B_{32}N_{36}$, $B_{60}N_{64}$, $B_{16}N_{12}$, $B_{36}N_{32}$, and $B_{64}N_{60}$. Following classification of BN fullerenes has been offered. As small, intermediate, and large ones, the fullerenes with a diameter of ~5, 8, or 12 Å, respectively, should be considered. Quantitatively, the relative stabilities of BN fullerenes with nearly the same sizes were estimated based on calculated molar energies of formation: $B_{12}N_{16}$ 8.28, $B_{16}N_{16}$ 8.54, and $B_{16}N_{12}$ 8.08; $B_{32}N_{36}$ 8.77, $B_{36}N_{36}$ 8.77, and $B_{36}N_{32}$ 8.61; and $B_{60}N_{64}$ 8.89, $B_{64}N_{64}$ 8.89, and $B_{64}N_{60}$ 8.1 eV. The generalization of similar results leads to the conclusion that for large fullerenes the dependence of the formation molar energy on the number n of B–N pairs is expressed by the formula $E/n = A + B/n + C/\sqrt{n}$, where A is the energy of formation per B–N pair in isolated BN plane sheet with respect to layered h-BN crystal (it corresponds to a limit of fullerene with infinite diameter), B/n describes the contributions from the stresses caused by the presence of “wrong bonds,” and the term $C/\sqrt{n}$ is caused by edge formation after achieving the sizes when polyhedral form becomes more suitable.

Total and cohesion energies of the smallest stoichiometric boron nitride fullerene-like clusters were also considered by the HF method in Gaussian-orbital basis [232]. Calculations revealed their stability. The stability and geometry of the $B_{12}N_{12}$ fullerene-like cages were studied [237] by using DFT calculations. It was found that the $B_{12}N_{12}$ structure is thermodynamically stable at ambient conditions.

It is possible to obtain some inequalities between total ground-state energies of polyhedral carbon clusters and their

derivatives with substitution by boron and nitrogen atoms $(\text{BN})_x\text{C}_{n-2x}$ ($n - 2x \geq 0$), which do not depend on a used theoretical method of analysis and on this reason are suitable in *ab initio* calculations as well as for semiempirical estimations [238]; the difference between these energies is expressed by the simple sign-variable sum over substituted sites.

VIBRATION FREQUENCIES

According to the semiempirical MO calculations [226], the lowest vibration frequency for $(\text{BN})_{12}$ fullerene spheroids is estimated as 340.3 cm^{-1} .

By another semiempirical method, MNDO, frequencies of the vibration modes dominant over the BN fullerenes IR spectra were found [27] as follows: $\text{B}_{12}\text{N}_{12}$ 294 and 825 and $\text{B}_{24}\text{N}_{24}$ 1356, 1336, and 772 cm^{-1} .

MULTISHELLED FULLERENES

In Ref. [27], it was noted that the difference between the effective radii of the spheroidal molecules $\text{B}_{12}\text{N}_{12}$ and $\text{B}_{60}\text{N}_{60}$, which is equal to $3.36 \text{ \AA}$, is close to the interlayer distance of $3.33 \text{ \AA}$ in h-BN. This analogy can be extended to bonds at fullerene surfaces: calculating the fullerene molecules $\text{B}_{12}\text{N}_{12}$, $\text{B}_{24}\text{N}_{24}$, and $\text{B}_{60}\text{N}_{60}$, the same authors have successfully used the interatomic potential of B–N interaction with the equilibrium distance of $1.4457 \text{ \AA}$, which corresponds to the length of the bonds within the layers of an h-BN crystal. By the carbothermal synthesis, multishelled fullerenes—BN “onions”—were obtained.

Extrapolating the simplified formula of radius over all regular BN fullerenes and assuming $d_{(n)}$ as the intralayer bond length in BN 3D layered crystals ($1.4457 \text{ \AA}$), their radii were calculated. Then, assuming interwall distances as interlayer bond length in BN 3D layered crystals ($3.3306 \text{ \AA}$), their most stable aggregates in the form of double-shelled fullerenes were predicted [90–94]. From the obtained values, one can find that for regular fullerenes with indices of $n + 3$ and n , deviations of the difference between radii from the expected intershell distance value are almost zero. This result does not seem accidental. Maybe, the formula obtained for fullerene radius reveals general relation between intralayer and interlayer structural parameters a and c in all the layered boron nitride structures, such as layered crystals, multiwalled nanotubes, and multishelled fullerenes, $c/a = 2.6621$ in real h-BN-layered crystals $c/a = 2.6602$.

FULLERITES AND FULLERIDES

Consideration of $\text{B}_{12}\text{N}_{12}$, $\text{B}_{24}\text{N}_{24}$, and $\text{B}_{60}\text{N}_{60}$ molecules as analogs of carbon fullerenes allows to predict [27,232,239,240] the existence of inorganic polymeric chains and at least 10 boron nitride fullerite crystals and calculate their lattice parameters and density. It has been constructed that a number of small clusters B_nN_n (with $n = 12, 16, 18, 24, 34, 60$) are able to form zeolite-like covalence crystals. The comparison between these structural calculations and available

experimental data allows identifying the fullerite with simple cubic symmetry constructed from $\text{B}_{12}\text{N}_{12}$ molecules with BN intermediate explosive phase.

Using DFT calculations, it was predicted [241] that single-walled hemispherical-caped boron nitride BN nanotubes with small diameters can be produced via the coalescence of stable nanoclusters. Specifically, the assembly of B_nN_n ($n = 12, 24$) clusters exhibiting particularly high stability and leading to armchair (3,3) and (4,4) BN nanotubes, respectively, was considered.

Maps of the distribution of electron density in the boron nitride fullerite with diamond-like structure having the $\text{B}_{12}\text{N}_{12}$ molecules at the vertices have been calculated [167] using an *ab initio* full potential augmented plane wave method.

Considering the problem how BN fullerenes could be assembled in molecular solids, the work [242] was focused on the smallest synthesized BN fullerene, $\text{B}_{12}\text{N}_{12}$, which is built by squares and hexagons. First, the interaction between two of these fullerenes was analyzed, using the hybrid density functional methods. Two different interactions have been studied in the dimer, a square facing a square (S–S) and a hexagon facing a hexagon (H–H). In both cases, B is facing N. The most stable dimer was found to be S–S facing, with covalent interactions between the monomers, but other dimers with weak interactions have been found as well, which opens possibilities of new systems, as in the case of fullerene dimers and solids. The solids resulting from the infinite repetition of the characterized dimers were optimized, finding two different solids, with covalent and weak interactions between monomers, respectively.

Molecular and solid forms of BN, based on stoichiometric and nonstoichiometric fullerenes, were predicted in Ref. [243] by means of *ab initio* calculations. The study of the energetics of dimer formation indicated that the reactivity of BN fullerenes depends strongly on the stoichiometry. The stoichiometric fullerenes form strong covalence bonds between the tips of neighboring cages, while the tips of nitrogen-rich fullerenes “repel” each other. Calculations predict the large interstitial channels, with diameters of $5\text{--}8 \text{ \AA}$, but the hardness comparable to that of hard metals. In contrast, nitrogen-rich units (with the exception of $\text{B}_{12}\text{N}_{16}$) should form loosely bound molecular solids (like the standard carbon fullerenes). The following values of binding energy per intermolecular bond were predicted: $\text{B}_{12}\text{N}_{16}$ and $\text{B}_{16}\text{N}_{16}$ dimers 0.47 and 0.45 and $\text{B}_{12}\text{N}_{16}$, $\text{B}_{16}\text{N}_{16}$, and $\text{B}_{36}\text{N}_{36}$ fullerite crystals 0.34, 0.30, and 0.29 eV. In contrast to this, nitrogen-rich cells of boron nitride (except $\text{B}_{12}\text{N}_{16}$) are to be associated with weakly bound molecular solids like conventional carbon fullerenes.

As for BN polymorphic modification with diamond-like structure and $\text{B}_{12}\text{N}_{12}$ molecules instead atomic sites [244], structure of which earlier called by E-phase, it was named [27] as “hyperdiamond”. The experimental value for its lattice parameter, $11.14 \text{ \AA}$, is in good agreement with the predicted one, $11.52 \text{ \AA}$.

First-principle methods were applied [130] for calculations of new cluster and crystalline nanophases of refractory