Photocatalytic Nanomaterials for Environmental Applications



Edited by Rajesh J. Tayade Vimal Gandhi



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Photocatalytic nanomaterials have a great potential in such applications as reduction of carbon dioxide and degradation of various pollutants. They are equally important in the production and storage of energy, e.g. in the conversion of solar energy to electricity, and the production of hydrogen in photoelectrochemical cells.

Research on synthesis, characterization and specific applications is reported for titanium oxide and a number of other promising catalysts, such as silver phosphate, cerium oxide, zinc oxide and zinc sulfide.

Keywords: Photocatalytic Nanomaterials, Nanocomposites, Solar Energy Conversion, Carbon Dioxide Reduction, Hydrogen Generation, Degradation of Pollutants, Titanium Oxide, Silver Phosphate, Cerium Oxide, Zinc Oxide, Zinc Sulfide

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Preface

Concerns related to environmental problems and the energy crisis have created great challenges for scientist and technologist at a global level. For the last 3-4 decades, major attention has been given for photocatalysis to overcome these problems. Photocatalysis is an effective catalytic process with potential applications in solving above mentioned problems by degrading pollutants, reducing CO₂ levels and water splitting, respectively. Till today, various photocatalytic materials, photocatalytic reactor, degradation of various organic compound present in air and water have been studied and demonstrated. In spite of significant research work carried out in the field of photocatalysis, there are several challenges needing to be addressed such as enhancement in photocatalytic activity, development of visible light activated photocatalytic reactors based on the irradiation source. In this present special topic book entitled as "Photocatalytic Nanomaterials for Environmental Applications" we have tried to report the latest development and original applications and theoretical research in the area of photocatalysis.

This special topic book is a result from contributions experts from the international scientific community in the photocatalysis and nanomaterials development field. It thoroughly covers future prospects of various photocatalytic materials, their synthesis methods, and modifications for enhancement in photocatalytic activity as well as their application in various fields like photocatalytic degradation of environment pollutant, energy production and conversion of solar energy to electrical energy, energy storage, chemical transformation etc. It gives a comprehensive picture of photocatalytic materials and has posed several scientific and technological challenges in this area. This book will provide latest and in-depth coverage to the various photocatalytic materials used in the last decade for various applications.

The first five chapters of the book mainly focus on synthesis, characterization and various applications of titanium dioxide as photocatalyst. Chapter 1 discusses on various method of synthesis, morphological variety and application of titanium dioxide nanomaterials. To enhance the photocatalytic activity of the titanium dioxide, different TiO2-high surface area materials based composite photocatalysts are reviewed in detail in Chapter 2. A variety of visible light active photocatalysts with their synthetic methods and applications have been discussed in Chapter 3 to address the issue of UV light source in the photocatalysis. The three review chapters are supported by experimental work on synthesis of TiO₂-carbon composites, its characterization and application for degradation of isoniazid explained in Chapter 4. In Chapter 5, experimental work related to synthesis of TiO₂ nanotubes by using a low-temperature hydrothermal method without

templates and investigated the effect of annealing temperature and dissolved oxygen for the degradation of carcinogenic phenol has been discussed.

The next four chapters (Chapter 6-9) enlighten the relatively newer field of application of photocatalysis related to photoelectrochemical reduction of carbon dioxide to solar fuel and photoelectrochemical cell for the production of hydrogen. Chapter 6 mainly focused on the understanding of reaction mechanism in photon-assisted reduction of carbon dioxide including the fundamental review on photophysics and photochemistry of semiconductor materials along with possible suggestions for the design of new materials. Chapter 7 is a review article on photo-electrochemical reduction of carbon dioxide to solar fuel with appropriate case studies. In Chapter 8, Cadmium Sulphide based photoelectrochemical cells are discussed in detail to channelize solar energy directly into chemical energy and provide hydrogen fuel. Experimental work related to enhancement in hydrogen storage capacity using synthesized TiO_2 -multiwall carbon nanotube with its characterization discussed in Chapter 9.

To provide alternate photocatalytic materials of titanium dioxide, researchers are trying to synthesize/develop variety of photocatalytic materials like silver phosphate, cerium oxide, zinc oxide, zinc sulfide etc. for different purposes. Silver phosphate based photocatalytic materials review with its synthesis methods and different applications in Chapter 10. Shape-control synthesis of bare/doped ceria with its photocatalytic applications has been discussed in detail in Chapter 11. Chapter 12 focused on experimental work related to synthesis of Sm⁺³ doped ceria, its detailed characterization and photocatalytic degradation of methylene blue. Experimental work of Chapter 13 discusses about enhancement in photocatalytic transformation of diphenylamine into N-phenyo-p-benzoquinonimine in the presence of Zinc sulfide particles mixed with different photocatalytic materials due to intra particle charge transfer. A review on recent advances in Copper Zinc Tin Sulfide -CZTS (Cu2ZnSnS4) film preparation, its application in the field of solar cell development and as photocatalysts is covered in Chapter 14.

Chapter 15 focuses on modelling and optimization of photocatalytic degradation of 4-Chlorophenol (4-CP) using Response Surface Methodology (RSM) and Artificial Neural Network (ANN) using Titanium nanotube synthesized by hydrothermal method. Chapter 16 focuses on the effect of ultra sound on the synthesis of nanoparticles as well as in the removal of pollutants from the effluents.

This book is indeed the result of remarkable cooperation of many distinguished experts, who came together to contribute their research work and comprehensive, in-depth and up-to-date review chapters. We are very thankful to all contributing authors who, in spite of their busy life in research and teaching, willingly accepted the call to contribute and sent their manuscript in time. We would also like to express our gratitude to all the publishers and authors and others for granting us the copyright permissions to use their illustrations. Although sincere efforts were made to obtain the copyright permissions from the respective owners to include the citation with the reproduced materials, we would like to offer our honest apologies to any copyright holder if unknowingly, their right is being infringed.

We would like to take this opportunity to express our sincere gratitude and also like to acknowledge the sincere efforts of Mr. Thomas Wohlbier of Materials Research Forum LLC, publishing Authority and his team, for in evolving this Special Topic Book into its final shape.

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Chapter 1

TiO₂ Nanomaterials a Future Prospect

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Abstract

As a potential candidate for various applications such as self- cleaning coatings, electrode material for Li ion battery, dye sensitized solar cells, photo catalytic hydrogen generation, water purification etc. TiO_2 nanomaterials becomes an interesting topic for research all over the world. This review focuses on recent progresses in structure, methods of synthesis, morphological variety and applications of TiO_2 nanomaterials.

Keywords

Nanomaterials, TiO₂, Photocatalyst, Self-cleaning Coatings, Hydrogen Generation, Water Purification

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1. Introduction

Semiconductor photocatalysis is the most widely explored area in the current era of increased fossil fuel depletion and the resulted environmental pollution [1-5]. Photocatalysis over a semiconductor utilizes solar energy which is ultimately free of cost and highly abundant in nature. Earth absorbs approximately 51% of the total incoming solar radiation [6]. The remaining energy is reflected back into outer space and absorbed by the atmosphere which is approximately 3,850,000 EJ per year (EJ-exajoule=1018 J). Out of this huge amount of energy, we use only 500 EJ per year, i.e. earth absorbs a massive amount of solar radiation in one hour compared to the whole world uses in one year [7]. It has been a constant challenge to exploit the huge amount of sun light falling on earth. Recently technologies to harvest solar energy using nano semiconducting materials have been designed and used to meet the present and future energy crisis [8-11]. Major efforts were taken in designing metal oxide nanoparticles for superior solar energy harvesting.

Metal oxide nanomaterials have proven their efficiency in the fields of heterogeneous catalysis [12-15], photocatalysis [16-19], energy conversion and storage [20-26], sensors

[27-32], pigments [33-36], protective coatings [37-40], electronic devices [41-45] etc. When a bulk material becomes nano, the nanomaterials retain structural and mechanical stability owing to a low surface free energy [46, 47]. Also, the bulk to nano transition accompanies the modifications in size, shape, crystal structure, morphology, optical, electronic and properties and surface chemistry [48-54]. Among the various metal oxide semiconducting nanomaterials, TiO₂ garnered special attention due to its thermal and chemical stability, fine tunable optical and electronic band gap energy, non-toxicity [55-61]. After the discovery of Honda Fujishima effect in 1972 [62], extensive research works have been focused on solar light harvesting via TiO₂ based nano semiconducting systems. TiO₂ and its various modifications proved to be excellent candidate for various technological applications such as photo catalytic water splitting [63], dye sensitized solar cells [64], self-cleaning coatings [65], sensors and as electrode material for Li ion battery [66]. However, the photo conversion efficiency of TiO₂ is limited because of its large band gap energy (3.0-3.2 eV) [56]. The broad band gap energy inhibits the utilization of visible (43%) and IR (52%) region of solar spectra which comprise the major part of it. Pure TiO₂ could absorb only the remaining 5% UV radiation [67] which is a major bottle neck for TiO₂ photocatalysis. Researchers all over the world are working on extending the absorption of TiO_2 in the visible region by reducing the band gap energy and thereby attain maximum photo catalytic activity.

A variety of modification strategies have been proposed and implemented to improve the photo absorption and consequent photocatalytic activities. Metal and non-metal doping [8, 68-80], dye sensitization [81-87], semiconductor nanocomposites [88-90], reduction [91] etc. paved pathways for the fine tuning of bandgap energy of TiO_2 . This review focuses mainly on the crystal and electronic structure modifications of TiO_2 and the resulting enhancement in the photo sensitized activities. The structural aspects, basic electronic structure, morphologies and their variations upon modifications were discussed in detail.

2. Synthesis of TiO₂ nanoparticles

2.1 Sol-gel method

The sol-gel method is a widely accepted one for the synthesis of ceramic materials and metal oxide nanoparticles [92-94]. In a sol-gel process, a sol in the form of colloidal suspension is formed from the hydrolysis and polymerization reactions of the precursors. Typical precursors used in TiO_2 synthesis are of two types. Inorganic metal salts such as Titanium tetrachloride ($TiCl_4$), Titanium oxysulphate ($TiOSO_4$) and metal alkoxide compounds like Titanium isopropoxide, Titanium butoxide etc. [95]. During

polymerization, solvent is escaped from the reaction medium and the sol is transformed to a solid gel. Finally, the gel is calcined to form the required phase. The gel can be fabricated into film or sheets by dip coating or spin coating. The sol-gel method has potential applications due to the easy fabrication of powders, films, fibers, monoliths, composites and porous media. These can be transforms into ceramic material upon heat treatment. The material obtained after this processing will have high purity, homogeneity and controlled porosity [96]. The reactions involved in a sol-gel process are represented through equations (1) and (2)

Hydrolysis:
$$-T-OR + H_2O \rightarrow Ti-(OH)_4 + R-OH$$
 (1)

Condensation:
$$-\text{Ti-OH} + \text{H-OTi-} \rightarrow -\text{Ti-O-Ti-} + \text{H}_2\text{O}$$
 (2)

Where, R = alkyl group.

The various factors affecting the sol-gel process are reaction temperature, reactivity of metal alkoxide, pH of the reaction medium and nature of the solvent and additive [97]. During the condensation reaction (equation (2)), Ti-O-Ti chains were developed. Hydrolysis is favoured by the presence of excess of water and condensation is favoured by low water content in the reaction medium [98].



Figure 1. TEM images of a) Tetramethyl ammonium hydroxide capped TiO_2 and b) autoclaving the Tetramethyl ammonium hydroxide capped TiO_2 solution. Reprinted with permission from John Wiley and Sons (1999) [99].

 TiO_2 nanomaterials were synthesized with various morphological varieties through the sol-gel method using titanium alkoxide and tetramethyl ammonium hydroxide [98, 99]. Here titanium alkoxide is added to tetramethyl ammonium hydroxide in alcoholic medium and heated at 100 °C for 6 h [99]. The TEM images of tetramethyl ammonium hydroxide capped TiO₂ and the TiO₂ nanoparticles obtained after autoclaving the said solution were given in Fig. 1. Shape controlling agents can be used in the sol-gel method

which will fine tune the morphology of the resulting nanoparticles [100, 101]. Sugimoto *et al.* added Triethanolamine (TEOA) as shape controlling agent to an aqueous solution of titanium tetraisopropoxide (TTIP). They could get ellipsoidal nanoparticles instead cuboid at a pH of 11 [102, 103].

Nano TiO_2 was synthesized via the sol-gel method by P. Periyat et al. and his co-workers from titanium isopropoxide, glacial acetic acid and water mixture in the ratio 1:10:100. In their experiment, de-ionized water was added to a mixture of titanium isopropoxide and glacial acetic acid with constant stirring for 3 h followed by drying at 100 °C on water bath for 12 h [104]. SEM analysis indicated that the particles undergo agglomeration and TEM images shows a crystallite size of 16-28 nm at 700 °C.

2.2 Hydrothermal method

Hydrothermal method widely used for the production of crystalline materials and the synthesis is usually carried out in a special type of steel pressure vessel called autoclave with or without Teflon lining inside. The reaction is carried out in aqueous solution under controlled temperature and pressure. The temperature can be higher than the boiling point of water which produces the pressure of vapor saturation. The developed internal pressure depends on the temperature and volume of the solution in the autoclave. Many researchers found this method as a suitable method for the synthesis of TiO₂ nanoparticles [105-111]. For e.g., alcoholic solution of titanium tetraisopropoxide in aqueous medium was heated at 240 $^{\circ}\mathrm{C}$ for 4 h produced TiO_2 nanoparticles with a controlled size of 7-25 nm [110]. The TEM images of the as prepared TiO_2 nanomaterials with varying size on varying the composition of solvent system and the concentration of TTIP are shown in Fig.2. Andersson et al. [105] reported a low temperature synthetic method in which a reverse micro emulsion system with Triton X-100, n-hexanol, cyclohexane and Tetrabutyltitanate dissolved in HCl or HNO₃ was prepared and then the microemulsion was transferred into an autoclave. The autoclave was heated at 120 °C for 13 h, and the precipitate obtained after the hydrothermal process was washed with ethanol and dried in a desiccator. In a different strategy, the sol formed by the hydrolysis of titaniumalkoxide on prolonged hydrothermal treatment could yield monodispersed TiO₂ nanoparticles. TiCl₄ and TiCl₃ can also be used as precursors for hydrothermal synthesis of TiO₂ nanoparticles which probably have rod morphology. TiO₂ white powder on hydrothermal heating gives TiO₂ nanowires. Here bulk powder was dispersed in NaOH solution around 200 °C for 3 days.



Figure 2. TEM images of hydrothermally synthesized a) 7nm sized TiO_2 nanoparticles from 0.10M TTIP in 4:1 ethanol/water b) 15nm particles from 0.04M TTIP in 1:2 ethanol/water c) 25nm particles from 0.02M TTIP in 1:8 ethanol/water and d) HRTEM image for a 7nm particle. Reprinted with permission from the American Chemical Society (2003) [110].

In addition to TiO_2 nanoparticles, TiO_2 nanowires have also been synthesized hydrothermally by adding 1g anatase TiO_2 powder into 10M NaOH solution in a Teflonlined autoclave of 50 mL capacity at 200°C for 24 h [112] (SEM image is shown in Fig.3a). Jianming Li *et al.* found that hydrothermally synthesized TiO₂ (B) nanowires with ultrahigh surface area (TEM image is shown in Fig.3b) act as a good anode material for lithium-ion batteries, especially on fast charging and discharging performance [66].



Figure 3.a) SEM image of anatase TiO_2 nanowire b) TEM image of TiO_2 (B) nanowire. Reprinted with permission from Elsevier (2002) and the Royal Society of Chemistry (2011) [112, 66].

Wei and co-workers reported a simple hydrothermal soft chemical process for the synthesis of TiO_2 nanowires. In this procedure, they reported treatment of a layered material $Na_2Ti_3O_7$ with 0.1 M HCl and then transferred into an autoclave at a temperature of 140-170°C for 3-7 days. The resultant product was filtered, washed with water and dried at 60°C for 4h produced TiO₂ nanowires with diameters 20-100 nm [113].

2.3 Solvothermal method

The solvothermal method is similar to hydrothermal method with the only difference being the solvent used here is non-aqueous, and in effect the temperature can be raised to much higher values because a variety of high boiling organic solvents can be used [114]. This method has better control in the crystallinity, size and morphology of TiO₂ nanoparticles in comparison with the hydrothermal method. This method involves the use of a solvent in a state of moderate to high pressure (1-10000 atm) and temperature (100-1000 °C) [115]. Using this method various nanoparticle having narrow size distribution and dispersity can be prepared [116]. Solvothermal methods are favoured for reducing the overgrowth of nuclei and regulated growth process leading to the high viscosity, low polarity, surface tension and high boiling point of organic solvents [117]. The current state of art gives an idea about the synthesis of TiO₂ nanoparticles via the solvothermal method with and without the help of surfactants [118-121]. Using titanic acid nanobelts (TAN) as precursor Yuhui Cao et al. prepared anatase TiO₂ nanocrystals exposed with (001) facets by solvothermal method in HF-C₄H₉OH mixed solution [122]. The percentage of exposure of (001) facets can be varied by adjusting the amount of HF. Photocatalytic measurements reveals that the degradation of methyl orange, methylene blue and rhodamine B become higher when TiO₂ nanocrystal having 77% (001) facet. TiO₂ with varied morphologies synthesized from hydrolysis of tetrabutyl titanate in a mixture of ethanol and glycerol by solvothermal preparation combined with post annealing [123]. Wen et al. reported the synthesis of ultralong single crystalline TiO₂ nanowires by solvothermal method using commercial Degussa P25, NaOH and absolute ethanol are the precursors at a temperature of 170-200 °C [118]. The same group reported the solvothermal synthesis of bamboo shaped Ag-doped TiO₂ nanowire heterojunctions by mixing 0.2 M titanium butoxide in ethanol, 10 M NaOH solution and silver nitrate at a temperature of 200 °C/24 h [119]. The TEM images of the synthesized bamboo shaped Ag-doped nanowires are shown in Fig. 4.



Figure 3.a) SEM image of anatase TiO_2 nanowire b) TEM image of TiO_2 (B) nanowire. Reprinted with permission from Elsevier (2002) and the Royal Society of Chemistry (2011) [112, 66].



Figure 4. TEM images of the synthesized bamboo-shaped Ag-doped TiO_2 nanowires: (a) low magnification; (b) higher magnification; (c) a typical individual nanowire with two knots. Reprinted with permission from the American Chemical Society (2005) [119].

2.4 Chemical vapour deposition method

Chemical vapour deposition (CVD) is an important method for synthesizing advanced semiconductor materials [124]. In the CVD method materials in vapor state are condensed to form solid state material on reaction with a heated substrate [125]. When deposition proceeds, a chemical reaction takes place on the surface. This method is usually used to form coatings to improve the electrical, mechanical, optical, thermal, corrosion resistance and wear resistance of various materials [116].

Many precursors such as titanium tetra-isopropoxide (TTIP) [126], titanium tetrachloride [127], tetra-nitratotitanium [128] *etc.* can be used to make TiO₂ coating on a surface. For the preparation of TiO₂, Z. Ding *et al.* choose TTIP as precursor, because it is less reactive with water and results in easy handling [129]. Seifried *et al.* reported the preparation of nanocrystalline TiO₂ with particle sizes below 10 nm and thick crystalline

 TiO_2 films having grain sizes below 30 nm by pyrolysis of TTIP under a gaseous atmosphere of helium and oxygen using liquid precursor delivery [130]. The preparation of single-phase rutile TiO_2 thin films has been carried out on Pt/Ti/SiO₂/Si substrate by the Laser Chemical Vapour Deposition (LCVD) method and the developed TiO_2 thin films possess three different morphology including powder, Wulff- shaped and granules [131].

2.5 Electrodeposition method

Electro deposition is an important method for synthesizing nanomaterials and is used to produce a metallic coating on a surface by the process of reduction at the cathode. The surface to be coated is taken as cathode and the metal to be deposited as anode. The electrolyte used should be a salt solution of the metal to be deposited. Upon passing electricity the metal to be deposited, attracted towards the cathode and reduced to metallic state to form a coating on the surface of the cathode. Based on the mode of applying external current to the electro deposition system, it can be either direct or pulsed electro deposition. Compared to direct current electro deposition pulse electro deposition has the advantage of process controllable parameters such as control over structure, composition and properties [132].



Figure 5. Top view and cross-sectional SEM image of TiO_2 electrodeposited on AAM pores. Reprinted with permission from Elsevier (2005) [133].

Y. Lei *et al.* synthesized TiO_2 nanowire with the use of the template of anodic alumina membrane (AAM). SEM image was depicted in Fig. 5 [133]. The experiment involves pulse electrodeposition of 0.2M TiCl₃ solution of pH 2 as titanium and/or its compounds into the pores of AAMs [98].

3. Structural features and stability of TiO₂ nanomaterials

 TiO_2 mainly exists in four distinct polymorphs, *viz*, anatase, rutile, brookite and TiO_2 (B) [1, 134, 135]. As shown in Fig. 6, all four crystalline forms contain TiO_6 octahedra differing in their shared edges and corners leading to distortion in the polyhedral units [136]. Anatase and rutile belong to the tetragonal crystal system, while former has a zigzag chains of TiO₆ octahedra connected through four edge sharing and the later composed of linear chains of TiO₆ octahedra connected by sharing two edges [137]. Rutile is the most thermodynamically stable form of TiO₂ [138]. Brookite crystallizes in an orthorhombic system in which both edges and corners are connected [139]. Brookite commonly occurs as a minor secondary phase along with anatase and rutile, therefore it is difficult to produce Brookite as pure phase [140]. TiO₂ (B) belongs to the monoclinic crystal system in which both edges and corners are shared by the TiO₆ octahedra having a perovskite-like layered structure [135]. Among the different phases of TiO₂ (mainly anatase, rutile, brookite and TiO₂ (B)) [141], rutile is thermodynamically stable while anatase, brookite and TiO₂ (B) are metastable transform to rutile at a particular temperature range (400-700 °C) [142] depending upon the methods and conditions of preparation [143].



Figure 6. Crystalline structures of TiO_2 in different phases: (a)anatase, (b) rutile, (c) brookite, and (d) TiO2(B). Reprinted with permission from the American Chemical Society (2014) [135].

Anatase is the most widely studied crystal system among the other existing phases of TiO_2 . Rutile is the high temperature stable phase. On the other hand, anatase and brookite are stabilized with particle size ranges in the nanoscale. The heat treatment on anatase and brookite phases result in the formation of rutile-TiO₂. More precisely, anatase to

rutile, brookite to rutile, anatase to brookite to rutile and brookite to anatase to rutile transformations occur with heating. These transformations can be explained on the basis of surface energy which depends on the particle size. Surface free energy is defined as the free energy change associated with a solid when it is separated into two parts at a large distance or to increase the surface area. The thermodynamic stability is controlled by the surface energy which varies among the three polymorphs of TiO₂. The subsequent coarsening via heat treatment resulted in increased particle size and this phenomenon stabilizes the rutile at higher temperature. On the other hand, anatase and/or brookite stabilized with smaller particle size compared to rutile at moderate temperature. Significant studies are in harmony with the anatase/brookite to rutile transformations except some anomalous observations. Zang and Banfield found that the thermodynamic stability of anatase was below 11 nm, for brookite, it was between 11 to 35 nm and finally rutile was stable above 35 nm. Banfield et al. observed that after attaining rutile structure from anatase and brookite, it grew much faster compared to the rest. A similar conclusion was made by Li et al. which describe the different growth rates of anatase and rutile. As the temperature increases the anatase and rutile particle size increases, but rutile has a higher growth rate after nucleation compared to anatase. Interestingly, anatase phase have maximum photo catalytic activity due to the extent of minimum electron-hole recombination and its greater affinity towards the adsorption of organic compounds [144]. Therefore, the attainment of anatase phase stability favors photo degradation of pollutants.

4. Electronic structure and optical properties of TiO₂ nanoparticles

Theoretical calculations and experimental observations suggest that TiO₂ has an electronic band structure in which the Ti 3d orbitals form the conduction band levels and O 2p orbitals form the valance band levels. Asahi *et al.* studied the optical and electronic properties of anatase TiO₂ using first-principles calculations with full-potential linearized augmented plane-wave (FLAPW) method [145]. Outer most electrons of free Ti atoms are filled in 3d and 4s orbitals. While forming TiO₂, the 3d orbitals or conduction bands split into t_{2g} and e_g levels, while 4s are being unaffected. d_{xy} orbitals contribute to the bottom of the conduction band. Valance band composed of orbitals of oxygen, *i.e.*, σ , π and non-bonding p orbitals. The top of the valence is associated with the non-bonding p orbitals. Fig. 7 shows the molecular orbital bonding diagram for anatase TiO₂.



Figure 7. Molecular-orbital bonding structure for anatase TiO_2 : (a) atomic levels; (b) crystal-field split levels; (c) final interaction states. The thin-solid and dashed lines represent large and small contributions, respectively. Reprinted with permission from the American Physical Society (2000) [143].

5. Modifications on TiO₂

Modifications of TiO_2 nanomaterials are primarily aimed to enhance its optical properties. The wide band gap of TiO_2 limits the utility in photo assisted applications. Extensive studies have been done by the scientific community to improve the performance of TiO_2 and novels designs were contributed. One of the significant pathways is band gap engineering through doping [98, 146]. Doping with metal and/or non-metal has resulted in efficient materials for photocatalysis as well as other functional applications. Other remarkable strategies are sensitization of TiO_2 with organic (dyes) [147] or inorganic (metal or low band gap semiconductors) [137], making solid solutions [148], design of metal TiO_2 nanocomposites [149] and reduction of pure TiO_2 [91].

5.1 Doping

As structural integrity plays an important role in designing the photocatalytic activities of a semiconductor nanomaterial, doping in TiO_2 is a great challenge to the research community [150]. Doping inserts foreign elements into the crystal lattice of TiO_2 which changes the chemical composition [151, 152]. The optical properties of TiO_2 is directly related to its electronic structure where chemical composition determines the electronic structure [153]. On the other hand, changing the chemical composition through doping has significant impacts on the optical properties of TiO_2 via modifying the electronic structure.

5.1.1 Metal ion doping

Various methods are employed for doping of metal ion in TiO₂, *viz*, sol-gel, hydrothermal, solid state method *etc*. Doping with alkali [154], alkaline earth [155-157], transition [158-164] and rare earth metals [165-170] were reported for TiO₂ nanomaterials. Li, Na and K doping were attempted by Bessekhouad *et al.* [154]. S. Liu *et al.* reported the enhanced absorption properties of various concentrations of Ca doped TiO₂ nanoparticles [157]. TiO₂ nano materials doped with different amounts of cerium synthesized by Yan *et al.* via the sol-gel method creates additional electronic states above the valence band of TiO₂ capture the photo formed holes and decreases the recombination rate of photo generated electron and hole results enhanced visible light absorption. The UV-vis absorption spectra of Ce doped TiO₂ is shown in Fig.8. This will enhance the photo degradation of methylene blue compared to pure TiO₂[171].



Figure 8. UV-vis absorption spectra of Ce doped TiO_2 with different concentration of cerium. Reprinted with permission from Elsevier (2012) [169].

C. Malengreux *et al.* studied screening of the photocatalytic activity of undoped and Fe³⁺, Cr^{3+} , La^{3+} or Eu³⁺doped TiO₂ by evaluating the degradation of 4-nitrophenol under UV-visible light. The dopant nature and content with an optimal content significantly influences the photocatalytic activity of Fe³⁺ or La³⁺ single doped as well as La³⁺- Fe³⁺ and Eu³⁺- Fe³⁺ co-doped catalysts whereas Cr^{3+} doped TiO₂ shows an impairment in the photodegradation of 4-nitrophenol. While no significant effect of dopant has been observed in the case of Eu³⁺ doped TiO₂ [172].

Higher anatase phase stability of Gd^{3+} doped TiO₂ reported by Zhang *et al.* using titanium alkoxide and gadolinium nitrate as precursor shows anatase phase stability up to 800 °C[173]. Recently Mg reduction of white TiO₂ nanoparticles followed by removal of excess Mg with HCl and distilled water changes colour from white to grey to blue – grey to black and is applicable for solar water evaporation [174]. Increasing amount of Mg

produce more oxygen vacancy in TiO_2 which is responsible for its enhanced light absorption.

 La^{3+} doped anatase TiO₂ synthesized by Li *et al.* through sol-gel process inhibits the phase transformation of TiO₂, reduce the crystallite size, enhance thermal stability and increase oxygen vacancy on the surface of TiO₂ [165]. The XRD patterns of La³⁺-TiO₂ photo catalysts in different ratios were represented in Fig. 9.



Figure 9. XRD plots of La^{3+} -TiO₂ photo catalysts in different ratios. Reprinted with permission from Elsevier (2004) [163].

Cao *et al.* developed Sn^{4+} doped TiO₂ nanofilm by the plasma enhanced CVD technique resulting in more surface defects on the TiO₂ surface [175]. Recently Mn doping TiO₂ was found to be beneficial for the extended absorption of TiO₂ [176]. The resulted material had a black color and showed higher photocatalytic activity compared to P25 under sunlight.

Even though metal ion doping has positive effects on TiO_{2} , higher cost of metal ion precursor, poor thermal stability and generation of secondary impurity phases which affects the purity, in fact diminishes the photocatalytic activity are some drawbacks of metal ion doping [177].

5.1.2 Non-metal ion doping

Taking into consideration the poor thermal stability and possibility for charge carrier recombination of metal ion doped TiO_2 , in recent years non-metal ion doping is a promising way to avoid these problems. For instance, Yin *et al.* prepared N doped TiO_2

by solvothermal route showed violet in colour upon calcinations at 20-800 °C for 1 h changes to weak violet, bright yellow, weak yellow and gray. Although the colour did not change to white denoting the thermal stability of Ti-N bonding in $TiO_{2-x}N_x$ [178]. Suresh *et al.* found that incorporation of N into TiO_2 using urea tends to retains 11% anatase phase stability at 900 °C [179].

Visible light responsible S-doped TiO₂ nanocrystal powder was successfully synthesized by G. Yang *et al.* through a simple low-temperature solvothermal method using thiourea as the sulphur source. It shows higher photocatalytic activity in the visible region for the degradation of methylene blue and phenol [180] (Fig. 10). Unlike metal ion doping nonmetal ion doping is less likely to form recombination centers and hence enhances the photocatalytic activity. Yu *et al.* prepared phosphorus doped TiO₂ by sol-gel method on calcinations at 400 and 800 °C showed higher photocatalytic activity for the degradation of methylene blue compared to Degussa P25 under UV light, suggesting that P⁵⁺ restrained photocatalytic activity even at higher calcinations temperature.



Figure 10. Photocatalytic degradation Methylene Blue (MB) over TONS-1.0 and pure TiO_2 samples under visible light irradiation ($\lambda > 420$ nm.) Reprinted with permission from Elsevier (2012) [177].

However, for higher concentration of P^{5+} the activity diminishes due to the formation of secondary oxides like TiP₂O₇ and (TiO)₂P₂O₇ [181]. Fluorine doping on TiO₂ creates several advantageous effects found by Li *et al*. It includes formation of surface oxygen vacancies, the enhancement of surface acidity and the increase of defect states *ie.*, Ti³⁺ ions [182].

5.1.3 Effect of doping on electronic structure of TiO₂

As the conduction band minimum (CBM) of TiO_2 is contributed by the Ti 3d orbitals, it can be expected that d orbitals from dopant could influence the CBM [145]. Effect of transition metal doping on the band gap energy of TiO_2 was widely studied [145, 183-185]. 3d transition elements, notably, V, Cr, Mn and Fe were successfully doped into the TiO_2 lattice and found the formation of impurity levels within the band gap. Umebayashi *et al.* used full-potential linearized augmented plane wave (FLAPW) method to study the doping effects of V, Cr, Mn, Fe, Co and Ni [186]. They observed a consistent shift in the energy levels created by the dopant (Fig. 11). Metal doping creates oxygen vacancies (in case of V doping) or impurity levels in the band gap which in turn red shift the absorption edge of the metal doped TiO_2 [187]. Conversely, these factors may reduce the thermal stability and increase the chance for charge carrier recombination.

Energy states of doped anions (non-metal ions) hybridize well with the valence band states of the semiconductor oxide material, and either shift the valence band upward or broaden, resulting in the reduction of the overall band gap. Chen and Burda compared the red shift in the absorption edges of bare and C-, N-, and S-doped TiO₂ nanomaterials *via* X-ray photoelectron spectroscopy [188]. Using the FLAPW method, Asahi *et al.* analysed the electronic structures of C, N, F, P, or S doped TiO₂ [77]. Anion doping with N^{3+} , C^{4+} or S^{2-} is expected to make a photocatalyst absorb in the visible light regime [189].



Figure 11. (A) Bonding diagram of TiO_2 (B) DOS of the metal-doped TiO_2 ($Ti_{1-x}A_xO_2$: A) V, Cr, Mn, Fe, Co, or Ni). Gray solid lines: total DOS. Black solid lines: dopant's DOS. The states are labeled (a) to (j). Reprinted with permission from Elsevier (2002) [183].

Among these, nitrogen doping can be expected to give promising materials because of the ample overlapping of O 2p and N 2p states which reduces the effective band gap [190]. Doping with sulphur will also lead to the same effect but the large ionic radius of sulphur will hinder the proper incorporation of it into the oxygen lattice [146]. However, C and P doping is found to lead to recombination centers [146]. The mixing of C with O 2p states was too weak to produce a significant band gap narrowing [191].

5.2 Sensitized TiO₂

Coupling of TiO₂ with a visible light active semiconductor forms an inorganic semiconductor sensitized TiO₂. Sulphides of some p block elements and transition metals act as sensitizer to TiO₂ [192]. CdS, PbS, Bi₂S₃ and Sb₂S₃ have appropriate energy level corresponds to the TiO₂ conduction band. Here the sensitizer absorbs the visible light part of solar energy which in turn generates electron-hole pairs [193-195]. The energetically favourable positions of the photogenerated electrons and the conduction band minimum of TiO₂ makes the possible electron transfer from the sensitizer to TiO₂ [196]. Hensel *et al.* synthesized nanocomposite of N-doped TiO₂ and CdSe, which possesses visible light absorption features [197]. They demonstrated that the synergistic effect of N-doping and CdSe sensitization makes the modified TiO₂ a better candidate of photoelectrochemical activities (Fig. 12). Shen *et al.* successfully implemented coupling of p-type CuInS₂ quantum dots with TiO₂ nanoparticles [198]. It formed a p-n heterojunction through which better electron-hole separation could be achieved. A composite of MoS₂/graphene and TiO₂ was found to be efficient for H₂ generation under visible light irradiation [199].



Figure 12. Schematic representation of N-doped $TiO_2/CdSe$ nanocomposite. Reprinted with permission from the American Chemical Society (2010) [194].

Kang et al. prepared PbS sensitized TiO₂ nanoarrays for electrochemical applications [200]. Metal nanoparticle deposition on the surface of TiO₂ nanoparticles introduce new surface-active sites [201]. Redox reaction can happen on the active sites. Noble metals such as Au, Pd, Pt and Ag are deposited on the surface of the TiO₂ nanoparticles to achieve H₂ production as these noble metals possess low H₂ overpotential [202]. Pan and Xu synthesized noble metal nanoparticles deposited TiO₂ [203]. Noble metals used in their study were Ag, Au and Pd and these nanocomposites were used in the reduction of Cr(IV) and oxidation of benzyl alcohol. Zhou et al. derived a very interesting system containing ordered mesoporous anatase TiO2 channels in which Ag clusters are confined [204]. It has remarkable photocatalytic activity towards the degradation of phenol. TiO_2 nanotubes with Ag nanoparticles also found to act as anode material in dye sensitized solar cells [205]. Au@TiO₂ yolk shell nanoparticles were developed by Sun et al. The oxygen vacancies in TiO_2 and noble metal deposition play the key role in improving the visible light response and enhanced charge separation respectively [206]. Z. Lin and coworkers developed palladium quantum dots deposited on highly ordered TiO₂ nanotube arrays [207]. The charge transfer was promoted by the symbiosis of TiO₂ nanotubular morphology and the fine dispersion of Pd quantum dots on the surface of TiO₂. Bimetallic deposition is also reported in TiO₂ surfaces. Luna et al. demonstrated the enhanced H₂ generation activity of Ni-Pd deposition on TiO₂ [208]. Singhal and Kumar also attempted to develop bimetallic-TiO₂ nanocomposites [209]. They synthesized various bimetal/TiO₂ nanocomposites, viz, Pt-Pd/TiO₂, Au-Pd/TiO₂ and Ag-Pd/TiO₂ for selective conversion of CO2 to hydrocarbons [209]. Among these, Ag1%Pd1%/TiO2 was found to be the best catalyst.

5.3 Reduction

The reduction of pure TiO₂ under hydrogen atmosphere resulted in black TiO₂ nanomaterials. The first report on black TiO₂ nanomaterial was published by Chen *et al.* in 2011 [91]. This black TiO₂ nanomaterial possesses a band gap of approximately 1.5 eV. Black TiO₂ nanomaterials possess inherent self-structural modification including oxygen vacancies, self-doped Ti³⁺*etc.* which makes it absorb almost entire region of solar spectra [91, 210, 211]. These features make it as a superior candidate for various functional applications. Chen *et al.* synthesized black TiO₂ by heating white TiO₂ nanoparticles at 200 °C under 20.0 bar hydrogen atmosphere for 5 days [91, 211]. Reduction in presence of H₂/N₂/Ar at low/high pressures were reported by many groups [98, 211]. All TiO₂ nanoparticles were characterized by reduced band gap energies. Fig.13 shows the structure, photographs and HRTEM images of white and black TiO₂.



Figure 13.A) Structure and electronic DOS of black $TiO_2 B$) photographs of white and black $TiO_2 C$) HRTEM of TiO_2 and D) disordered black TiO_2 . Reprinted with permission from the Royal Society of Chemistry (2015) [207].

6. Applications of TiO₂ nanomaterials

6.1 Self-cleaning coatings

The area of self-cleaning coating is divided into hydrophilic and hydrophobic. Both perform clean-up activity through the action of water. Hydrophilic coating acts through the formation of a film of water *via* water drops spread over the surface, which removes the contaminants away along with this spreading. And for hydrophobic coating water drops roll off from the surface quickly due to the water repellent and low adhesive nature of the surface [212]. Hydrophilic coating has an additional advantage of break down dirt particles chemically under sunlight [65].

Hydrophobic surface- A hydrophobic self-cleaning coating require very high static water contact angle *i.e.* usually, $\Theta_s > 160^{\circ}$ C and a very low roll-off angle [213]. If a surface has these two properties it is known as either super hydrophobic or ultra-phobic. The waxy surface of lotus leaves along with the microscopic structures contributes towards this kind of surface [214]. I. Kartini *et al.* developed a super hydrophobic film with water contact angle 155.5° using hybrid layers of TiO₂ and dodecylamine. The film restrained hydrophobicity for 4 weeks under high relative humidity (>90%) in outdoor applications, because of the outward orientation of the hydrocarbon chains in the hybrid film [215].

Hydrophilic surface- Self-cleaning windows are coated with a transparent layer of TiO_2 which perform clean up activity by the combination of two properties, that are photo

induced chemical break down of organic dirt adsorbed onto the window and the generation of water film causes hydrophilic surface, thereby reduces the water contact angle and dirt is washed away [214]. TiO₂ has become the material of preference in self-cleaning activity, since titania is highly efficient for the photocatalytic degradation of dirt particles under direct sunlight and also it is inexpensive, nontoxic and easily available chemical [216]. The super hydrophilic character of TiO₂ was first found by Fujishima and co- workers, they reported that if the TiO₂ film is exposed to ultra violet light, water contact angle reduces to 0° causes spreading of water droplets on the surface, thereby attains removal of dirt materials from the surface [217].

6.2 Li ion battery

 TiO_2 is preferentially considered as the negative electrode for Li ion battery, because of its ability to being reduced on lithium insertion at lower potential. In TiO_2 based Li ion batteries TiO_2 nanocrystals on the surface of its anode instead of carbon has the anode surface area of about 100 m²/g compared to 3 m²/g for carbon. This facilitates electrons to enter and leave the anode easily and thus bring about fast recharging, thereby provides high current when required [218].

Porous TiO₂ urchins having superior electrochemical performance as anode for lithium ion battery including high capacity (206.2 mA h g⁻¹ at 0.5 C), superior rate performance (94.4 mA h g⁻¹ at 20 C) and stable cycling stability (94.3% capacity retention over 1000 cycles at 10 C Vs third cycle) reported by Yi. Cai *et al.* hydrothermally *via* in situ self-sacrificing template method using TiO₂/oleylamine as precursors followed by ion-exchange and calcination [219]. The improved electrochemical performance of TiO₂ nanomaterial can be ascribed to their characteristic pore structures and high structural stability. The two CV curves in Fig.14 roughly overlap with each other indicates the high redox reversibility of the as prepared TiO₂ material.



Figure 14. CV curves of a fresh electrode made of TiO_2 urchins recorded in the second sweep (a) and after galvanostatic cycling at 10 C over 5500 cycles (b). (Scan rate: 0.2 mV s_1). Reprinted with permission from Elsevier (2016) [216].

A TiO₂-CNT composite as anode material for lithium ion battery showed a superior cycling stability up to 50 cycles with a capacity of 230 mA hg⁻¹. This was synthesized by a magnetron sputtering technique onto a free-standing CNT film with paper like morphology, known as Bucky paper. The greater stability of the as prepared anode material can be attributed to the strong adhesion of TiO₂ nanocrystals on the CNT support, which already possess high electronic conductivity and good flexibility [218, 219].

 TiO_2 (B) hollow nanostructure shows excellent electrochemical performance as anode material for lithium ion batteries [220]. This high performance is due to the following reasons: i) More open TiO_2 (B) structure with significant voids and continuous channels makes the material an excellent host structure for intercalation, ii) hollow structure furnish enough space to accommodate Li^+ ion and thereby enhances the specific capacity of the battery, iii) hollow nanostructures provide large contact area between electrode and electrolyte in such a way that diffusion distance for Li^+ transport reduced and, iv) the void space in hollow structure lessen the local volume change and the problem of pulverization and aggregation of electrode material, consequently enhances the cycling performance [221].

6.3 Dye sensitized solar cells (DSSC)

In the present scenario DSSC have great attention in the field of academic research and industrial applications because it is a potential low cost technically and economically credible alternative to traditional silicon solar cells [82]. In general, DSSC consists of mesoporous TiO_2 nanofilm covered with dye molecule on a fluorine doped tin oxide (FTO) glass plate and a platinum 15 (Pt)-coated counter electrode are in contact with a liquid electrolyte (Γ/I^{3-}).

Nowadays many studies have been conducted to alleviate the problem of charge recombination. Recently M.A. Hossain *et al.* reported both ends opened TiO₂ nanotube and TiO₂ nanoparticles to form heterostructure photoanode having excellent light scattering and harvesting, long excited electron life time, unidirectional electron pathway and desirable great photo electric conversion efficiency. The hetero-nanostructure photoanode showed superior solar cell activity with higher Jsc (20.01 mA 364 cm⁻²) and PCE (8.56%) when the both-ends-opened TiO₂ nano- tubes were sandwiched between the TiO₂ nanoparticles layers [222].

At present many researchers are involved in developing and modifying photoanode by using nanoparticles, nanorods, nanotubes and nanofluids to enhance the light absorption [223], scattering [224], charge transport [225] and minimising charge recombination [226], in fact the (010) faceted leaf like anatase TiO_2 nanocrystals synthesized by *in situ*

topochemical process using exfoliated layered titanate nanosheets exhibits better performance as the light scattering layer for DSSC and can increase 28% of energy conversion efficiency by improving 33% of J_{sc} because of the enhanced light absorption [227].

6.4 Electrochromic devices

An electrochromic device (ECD) consists of a liquid or solid or gel electrolyte sandwiched between an electrochromic electrode and a counter electrode. Colour change happens in it as a result of charging/discharging this cell on the application of electric potential [228]. The principle set up of an electrochromic device is represented in Fig. 15.



Figure 15. The principle set up of an electrochromic device. Adapted from [225].

The problem of using expensive metal oxides like WO₃, NiO, MnO₃ or IrO₃ as electrochromic electrode can be solved by the low cost, non-toxic and easily available TiO_2 nanomaterials, in fact. Diasanayake *et al.* reported a novel design of an ECD using a transparent nanoparticulate TiO_2 film as the electrochromic material and SnO_2 as the counter electrode with polymethyl methacrylate (PMMA) based gel as the electrolyte. An attractive reversible colour change between blue and colourless noticed on using this ECD [229].

Electrochromic anatase TiO_2 thin film on F-doped tin oxide (FTO) substrate was successfully developed by N.N. Dinh *et al.* through the doctor blade method using colloidal TiO_2 solution with particle size 15 nm exhibits good reversible coloration and bleaching process in a solution of 1M LiClO₄ in polypropylene carbonate. The potential application of this porous nano TiO_2 film is in large area electrochromic windows [230].

S. Berger *et al.* reported an anodization process through which a thin Ti metal layer on a conductive glass fully transforms into a TiO_2 nanotubular array. The obtained layer demonstrates very good contrast behaviour and a high cycling stability, thus an electrochromic device prototype was constructed using the as prepared $TiO_2/ITO/glass$

electrode with 1 M LiClO₄ in propylene carbonate as electrolyte shown in Fig 15 [231]. TiO₂-WO₃ composite nanotube fabricated using TiW alloy anodization. This TiO₂-WO₃ composite nanotubes showed better ion insertion and electrochromic properties only when small amount of WO₃ (0.2 at %) are present [232].

6.5 Water splitting

Hydrogen is considered as the future fuel; because it is pollution - free renewable energy source can be storable with high energy density. 95% of the H₂ used for commercial purpose is derived through water splitting *via* electrolysis [233]. Among the various semiconducting metal oxides TiO_2 is the most extensively studied one, because in addition to strong catalytic activity and long-life time of electron/hole pairs it has strong chemical stability against photo corrosion and abundant reserves on the earth. Although, the energy conversion efficiency from solar to hydrogen by TiO_2 in photocatalytic water splitting is still low due to recombination of photogenerated electron – hole pairs, fast backward reaction, inability to utilize visible region (band gap energy 3.2 eV, only UV light can be utilized) of the sunlight. This difficulty can be resolved by the addition of hole scavengers, noble metal loading, ion doping (both cation and anion), composite semiconductors, dye sensitization, metal ion implantation *etc.* [233].

The fundamental requirements for the photocatalytic water splitting are, firstly a bandgap of more than 1.23 eV is the thermodynamically required energy condition whereas 2.0-2.4 eV is the energy of photon in the visible region [234]. Secondly, the bottom level of the CB of the photocatalyst should be more negative than the reduction potential of hydrogen (E_{H}^{+}/H_{2}) and the top level of the VB must be more positive than the oxidation potential of oxygen ($EO_{2}/H_{2}O$), which facilitates the efficient transportation of electrons and holes [233, 235]. A schematic representation of mechanism of photocatalytic water splitting is depicted in Fig. 16.



Figure 16. Mechanism of photocatalytic water splitting by TiO₂.

Tandem systems with separate semiconductors for water reduction and oxidation on TiO_2 based photocatalytic water-splitting are reported by Abe *et al.* [236] in which Pt-TiO₂ (anatase) preferentially catalyze water reduction using iodide as the sacrificial electron donor and TiO_2 (rutile) as the water oxidation catalyst with IO₃ as the electron acceptor under UV irradiation.

Apart from these, various other applications are also possible with TiO_2 nanomaterials with and without modifications, these includes cancer therapy [237], fuel cell [238], supercapacitor [239], water purification [240], printing ink industry [241], field emission [242], microwave absorption [243], sensor applications[30]*etc*.

7. Conclusions

Over the past decades, great efforts on TiO₂ nanomaterials have attracted extensive scientific interest for their synthesis, modifications, morphology and applications. Tremendous efforts have been made to synthesize TiO₂ nanomaterials through different methods such as hydrothermal, solvothermal, chemical vapour deposition, sol-gel and electrodeposition are briefly explained with recent research findings along with changes in properties on modification by metals and non-metals. This chemical modification results disordered surface, oxygen vacancies and Ti³⁺ to produce changes in surface, electrical, optical and electronic properties. Changes in electronic property imply bandgap narrowing or midgap states which enhances the visible light absorption and thus high photocatalytic activity. TiO₂ nanomaterials with various morphologies including nanotube, nanorod, nanowire and nanosphere are described shortly with modern synthesis routes. The most promising photocatalytic activity of TiO₂ found many industrial applications in the field of water purification, water splitting, self-cleaning coatings, dye sensitized solar cells etc. and apart from these other applications such as electrochromic devices, Li ion batteries and fuel cell were also pointed out here. Moreover, both theoretical and experimental studies based on modifications with different ions including band gap engineering and optical absorption analysis are under progress to develop this multifaceted material towards various practical applications.

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