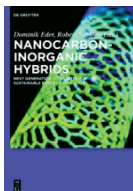


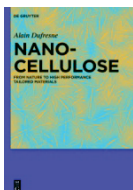
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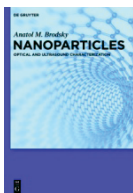
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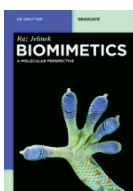
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Preface

Nowadays, it is usual to define nanocomposite “as a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm) or structures having nanoscale repeat distances between the different phases that make up the material”. Today, the use of nanocomposites has increased in various areas of engineering and technology due to their specific properties.

It has been recognized that organic-inorganic nanocomposites are very important materials for photonic crystals, coatings, adhesives, pharmaceutical, biomedical and cosmetic formulations. Furthermore, the nanoscale dimensions of nanocomposites already suggest a variety of possible industrial applications: automotive (gas tanks, bumpers, interior and exterior panels), construction (building sections and structural panels), aerospace (flame retardant panels and high performance components), food packaging, textiles, etc. Their controlled production is a goal to synthesize and design devices at the nanoscale. Moreover, hollow nanocomposites have been a subject of great scientific and industrial interest ranging from molecular biology and electronic materials to medical imaging and photonic crystals since the intrinsic properties of spherical materials can be finely tuned by changing parameters such as sphere diameter, chemical composition, and crystallinity-structure. Furthermore, they have been of interest as fillers, coatings, capsule agents, etc., because of their lower density and optical properties.

The present volume aims to provide recent information on nanocomposites (materials manufacturing and engineering) in six chapters. Chapter 1 of the book provides information on synthesis and characterization of ceramic hollow nanocomposites and nanotraps. Chapter 2 is dedicated to recent advances on preparation, properties and applications of polyurathane nanocomposites. Chapter 3 describes preparation, characterization and properties of organoclays, carbon nanofibers and carbon nanotubes based polymer nanocomposites. Chapter 4 discusses mechanical and wear properties of multi-scale phase reinforced composites. Chapter 5 describes modeling mechanical properties of nanocomposites. Finally, Chapter 6 is dedicated to polyaniline derivatives and carbon nanotubes and their characterization.

The present volume can be used as a research book for final year undergraduate engineering courses or as a topic on composites at the postgraduate level. Also, this book can serve as a useful reference for academics, researchers, materials, physics and mechanical engineers, professionals in composites and related industries. The scientific interest of this book is evident for many important centers of research, laboratories and universities as well as industry. Therefore, it is hoped that this book will inspire and enthruse others to undertake research in this field of nanocomposites.

The Editors acknowledge De Gruyter for this opportunity and for their enthusiastic and professional support. Finally, we would like to thank all the chapter authors for their availability for this work.

May, 2013

J. Paulo Davim
Constantinos A. Charitidis

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1 Synthesis and characterization of ceramic hollow nanocomposites and nanotraps

1.1 Introduction

Nanocomposite materials encompass a large variety of systems such as one-dimensional, two-dimensional, three-dimensional and amorphous materials, made of distinctly dissimilar components and mixed at the nanometer scale. Organic nanoparticles and nanospheres have been a subject of great scientific and industrial interest, ranging from molecular biology and electronic materials to medical imaging and photonic crystals. These organic materials have been prepared by heterogeneous polymerization methods [1, 2].

Past studies have demonstrated the importance of composite particles consisting of organic cores with active surfaces covered with inorganic shells [3–7] due to the customized properties of these composite dispersions (magnetic, optical, electric, adsorptive, etc.) which may be adjusted to meet specific requirements for a given application. Nanocomposites such as nanoparticles, nanospheres and micelles can be used as drug delivery and drug controlled release systems. Hollow nanocomposites are of great interest because of their ability to encapsulate substances in their hollow inner cavities and release them at a later stage. They have been of interest as fillers, coatings, capsule agents, etc., because of their lower density and optical properties [8–11]. Such “shells” are created either by hydrolysis, in situ, of the corresponding metallic salt in the presence of core materials [12–20] or calcinating polymer particles coated with uniform inorganic shells [21–32]. A very interesting topic is the production of “shells” that are constructed of corrosion inhibitor materials such as compositions of cerium oxides, cerium together with molybdenum oxides and cerium together with titanium oxides.

Some of the most effective and environmentally friendly corrosion inhibitors for aluminum alloys are derived from cerium salts. Nanostructured sol-gel coatings doped with cerium ions were investigated as pretreatments for AA2024-T3 [33]. Studies on the corrosion inhibition of cerium oxide have been made too. A process developed for the spontaneous deposition of cerium oxide conversion coatings for corrosion protection of aluminum alloy 7075-T6 showed inhibited corrosion for up to two weeks (336 h) in salt fog testing [34].

Cerium molybdate has been used as a corrosion inhibitive component to a non-chromate protective solution useful for coating iron and iron alloys, particularly steel [35]. The structure and catalytic properties of ultrafine $\text{Ce}_2(\text{MoO}_4)_3$ particles have also been studied with good results due to the high mobility of lattice oxygen ions in the oxide and the high BET surface area [36].

Another interesting topic is the loading of hollow nanocomposites with corrosion inhibiting compounds such as 8-hydroxyquinoline (8-HQ), 2-mercaptobenzothiazole (MBT), p-toluenesulfonic acid (p-TSA) and 1-H-benzotriazole-4-sulfonic acid (1-BSA). The corrosion behavior of AA2024-T3 was studied in 3.5 % NaCl solution with 8-HQ. The results revealed that 8-HQ is a mixed type inhibitor by blocking the active sites of the metal surface [37]. The effect of 8-HQ on the corrosion inhibition of copper has been investigated in neutral aqueous NaCl solutions. It was stated that a protective film is formed on the surface by polymerization of Cu (II)–hydroxyquinoline complexes, films that play an essential role in the inhibition of Cu corrosion [38]. Moreover, 8-HQ exhibits antiseptic, disinfectant, and pesticidal properties. It functions as a bacteriostat and fungistat agent to prevent adverse growth of micro-organisms on red blood cells [39]. Furthermore, 1-BSA is a derivative of benzotriazole which has been used as a corrosion inhibitor for the protection of magnesium and aluminum alloys [40, 41].

8-HQ and MBT compounds were studied as corrosion inhibitors by S.V. Lamaka and coworkers for AA2024-T3 [42]. They found that these inhibitors provide anticorrosion protection for AA2024-T3 forming a thin organic layer of insoluble complexes on the surface of the alloy. Inhibiting action is the consequence of suppression of dissolution of Mg, Al and Cu from the corrosion active intermetallic zones [43, 44]. K.A. Yasakau *et al.* examined the addition of 8-HQ at different stages of the synthesis process to understand the role of possible interaction of the inhibitor with the components of the sol-gel system [45]. MBT was evaluated by Zheludkevich *et al.* as a corrosion inhibitor for protection of AA2024-T3 in neutral chloride solutions [46].

A lot of attention has been focused on hollow spheres of titania. The reason is their photocatalytic activity and low density, which make them suitable for a number of applications such as catalysts, white pigments and filters. Photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. The photocatalytic process includes chemical steps that produce reactive species that in principle can cause fatal damage to micro-organisms [47–49]. A heterogeneous photocatalytic system consists of semiconductor particles (photocatalyst) which are in close contact with a liquid or gaseous reaction medium. Titanium dioxide nanocontainers have been synthesized using PS cores as templates [50], using carbon spheres as templates [51], or by using $\text{Ti}(\text{SO}_4)_2$ instead of organometallic titanium as precursor [26]. Moreover, hollow microspheres of mesoporous titania with a thin shell of anatase structure have been prepared by a procedure of surfactant poly(ethylene oxide) assisted nanoparticle assembly [52]. Other methods for producing hollow titania spheres are the Kirkendall effect [53], the Ostwald ripening [54] and the gas phase synthesis [55].

Magnetic containers have received a lot of interest during the last years. Hematite and iron hollow spheres have been synthesized using PS templates [30, 56]. Moreover, iron oxide spheres were produced using hollow latex cages as templates [24]. Magnetic hollow spheres with a surface layer enriched in silica were fabricated using

aerosol-assisted methods [25]. Magnetic biocompatible hybrid hollow spheres were prepared by a core-template-free route [57]. Hollow magnetic microspheres were fabricated by plasma treatment from precursor core-shell particles [58].

Encapsulation of various molecules with bioactivity is also a property that raises both scientific and industrial interest. In the last decade several works have focused on the preparation of nanospheres. Silica nanobottles [31], silica nanospheres with a magnetic core and a charged surface [59], fluorescent silica nanospheres [60], polypyrrole-magnetite-silica particles [61], CdS-SiO₂ core-shell particles [62] and silica nanospheres encapsulating enzyme [63] are some remarkable results in this area. Significant progress has also been observed in sol-gel bioglasses, where complex systems have been developed so as to improve bioglass properties [64]. In the last years there has been an attempt to decrease patients' convalescence time and enforce bioglass functionality by the encapsulation of bio-molecules in the sol-gel silica networks [65]. These characteristics promote bioglasses for clinical use.

Materials with the ability to absorb water have been known since the mid-1960s. Since then, many studies about these materials followed with the aim to develop super absorbent polymers (SAPs), which absorb water several hundred to a thousand times their own dry weight. SAPs are three-dimensional polymer networks, partially cross-linked, having the capability to expand during the absorption process and used in many fields, such as baby diapers, agricultural applications and other advanced technologies [66]. Among the disadvantages of these materials are the loss of their ability to absorb water after repeated absorption-drying cycles, the remarkable increase in their size during swelling and their scraggly shape both in dry and in expanded form.

This review is focused on the preparation and characterization of cerium molybdate, cerium titanium oxide, ceria with/without conductive polymer coatings, magnetic and photocatalytic hollow nanocomposites. Furthermore, the nanocomposites are loaded with corrosion inhibitors to produce an inhibitor delivery system. Encapsulations of the corrosion inhibitors are proven by heat treatments and FT-IR spectroscopy. TGA measurements reveal the amount of inhibitors incorporated in the nanocontainers. The performance of the complex system (nanocontainers and inhibitors) in a corrosive environment is tested via potentiodynamic, electrochemical impedance spectroscopy, UV-vis spectroscopy measurements showing good results.

Furthermore, experiments of the hollow nanocomposite antibacterial action on pure culture of *E. coli* are reported. *E. coli* are the most encountered bacterium in the clinical laboratory due to its clear structure. Additionally, the laboratory strains produce well-defined individual colonies when culturing the organisms on agar plates. A decrease of *E. coli* concentration is observed for the TiO₂ and ceria nanocomposites with/without conductive polymer coatings.

Finally, the production of nanocomposites that have the ability to absorb water without extensive swelling as well as to trap corrosive agents is reported. The water trapping nanocomposites can be regenerated after water removal by drying or washing with an excess of organic solvent, like ethanol. Such a system with nearly

constant dimension before and after water absorption can be incorporated into coatings to prevent interaction of water with the metal without causing cracks.

The incorporation of the aforementioned complex inhibitors and trap nanocomposites into coatings on metals via sol-gel or electro-polymerization of conductive polymers can demonstrate efficient multiscale anticorrosion protection in systems used for airplanes, ships, and automobiles (Fig. 1.1).

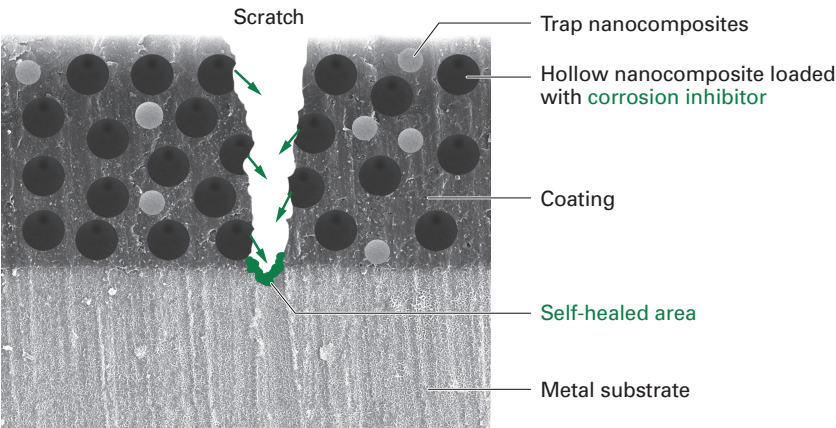


Fig. 1.1: Multiscale anticorrosion protection system.

1.2 Hollow nanocomposites

1.2.1 Cerium oxide hollow nanocomposites

The synthesis of cerium oxide hollow nanocomposites is based on an organic templates process [67]. The method of emulsion polymerization with potassium persulfate (KPS) as the initiator is used to produce anionic PS latex. The reaction is carried out in a 1,000 cm³ container under the conditions of Table 1.1. To eliminate the effect of oxygen, the solution is purged with nitrogen before the process is initiated. The

Table 1.1: The conditions used in the preparation of PS latex at 80 °C

Material	Quantity (g)
Styrene	4.53
KPS	0.65
Sodium dodecyl sulfate	0.21
Water	460

polymerization process lasts for 12 hours. The resulting dispersions are centrifuged at 14,000 rpm for 30 min, the supernatant solutions are discarded, and then the particles are resuspended in doubly distilled water using a sonicator. This process is repeated three times.

The PS lattices are coated via the sol-gel method to form a ceria oxide layer. The sol-gel coatings are prepared by controlled hydrolysis of cerium (III) acetylacetonate ($\text{Ce}(\text{acac})_3$) aqueous solution in the presence of PS latex, urea and polyvinylpyrrolidone (PVP). These dispersions are aged in an oven preheated to 100 °C for 24 hours (Table 1.2). The resulting dispersions are centrifuged at 14,000 rpm for 30 min, the supernatant solutions are discarded, and then the particles are resuspended in doubly distilled water with a sonicator. This process is repeated three times, and the purified powders are dried in a desiccator.

Table 1.2: Conditions of preparation of coated nanospheres

Material	Quantity (g)
PS	1.130
PVP	1.6
$\text{Ce}(\text{acac})_3$	2.4
Water	160

The production of hollow cerium dioxide nanocomposites encompasses the removal of the PS cores by calcination. The composite is calcinated for 4 h in air in a furnace at 600 °C with a heating rate of 10 °C min⁻¹. Furthermore, the hollow ceria nanocomposites (approximately 90 nm in diameter) are coated with a conducting polymer layer via electrodeposition using cyclic voltammetry (CPCeO_2). For this purpose, 0.1 g of the nanocomposites are added in 100 ml aqueous solution which contains 0.1 M pyrrole, 0.1 M aniline and 0.3 M oxalic acid. An aluminum panel is used as the working electrode, a platinum sheet as the counter while a saturated calomel electrode (SCE) serves as reference. Under these conditions, electropolymerization preferably occurs on the working electrode forming a conducting polymer layer containing ceria spheres. However, simultaneously the spheres remaining in the solution act as polymerization sites and are thus covered by a mixed conducting polymer layer. The potential is scanned between -1 and 3 V vs. SCE at a rate of 30 mVs⁻¹. After the polymerization process, the coated spheres are collected by filtration, washed thoroughly with distilled water in order to eliminate solution residues (monomers, oxalic acid) and left in air to dry for 24h.

The synthetic process leads to the formation of uniform hollow nanocomposites with a diameter 90 ± 10 nm (Fig. 1.2). The X-Ray Diffraction (XRD) analysis confirms the formation of crystalline cerianite CeO_2 (4-0593 cerianite).

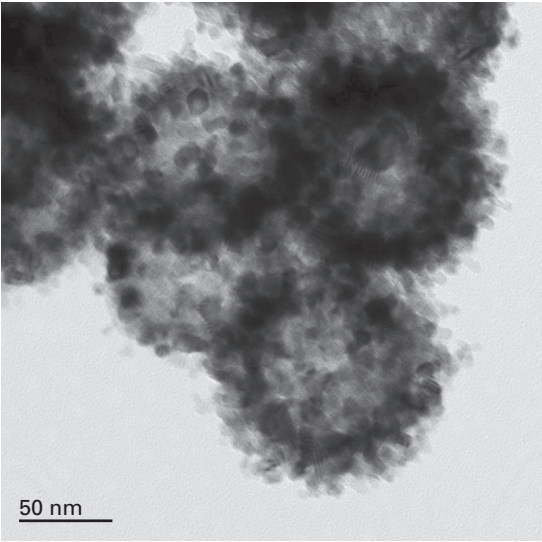


Fig. 1.2: Transmission electron micrographs of CeO_2 hollow nanocomposites [67].

1.2.2 Titanium oxide hollow nanocomposites

The synthesis of titanium dioxide hollow nanocomposites consists of three experimental steps [50]. The first step involves the preparation of organic templates. Positive charged PS latex is synthesized via polymerization in suspension using 2,2'-Azobis (2-methylpropionamidine) dihydrochloride (AMPA) as the initiator. For this purpose, the reaction is carried out in a 500 cm^3 container under the conditions listed in Table 1.3.

Table 1.3: The conditions used in the preparation of PS latex at 70°C

Material	Quantity (g)
Styrene	4.53
AMPA	0.6521
Water	400

To eliminate the effects of oxygen, the solution is purged with nitrogen before the process is initiated. The polymerization duration is 12 hours. The resulting dispersions are filtered, centrifuged at 14,000 rpm for 30 min, the supernatant solutions are discarded, and then the particles are resuspended in absolute ethanol using a sonicator. This process is repeated three times. The PS particles prepared by this procedure (Table 1.3) are homogeneous.

The coating procedure consisted of controlled hydrolysis of ethanolic solution of titanium tetraisopropoxide (TTIP) in the presence of PS latex. PVP and NaCl 5mM solution are added to the mixture reaction to prevent aggregation of the core particles [84]. The resulting dispersions are centrifuged at 14,000 rpm for 30 min, the supernatant solutions are discarded, and then the particles are resuspended in absolute ethanol with a sonicator. This process is repeated three times, and the purified powders are dried in a desiccator. The conditions of preparation of coated spheres are listed in Table 1.4.

Table 1.4: Conditions of preparation of coated spheres

Material	Quantity
Ethanol (ml)	400
PVP (g)	4.0
NaCl 5mM (ml)	10
PS (g)	4.5
TTIP (ml)	4.5

The hollow titanium dioxide nanocomposites are produced after the removal of PS cores by calcination. Initially, the coated spheres are placed on a glass slide and dried, first at room temperature and then for 1 h at 60 °C. After that, the composite is further calcinated for 3 h in air in a furnace at 600 °C, at a heating rate of 10 °C min⁻¹.

After calcination the hollow titania dioxide nanocomposites have a diameter of approximately 240 ± 10 nm. The EDX analysis shows that the basic elements that constitute the spheres are titanium and oxygen (Fig. 1.3). The XRD analysis indicates that

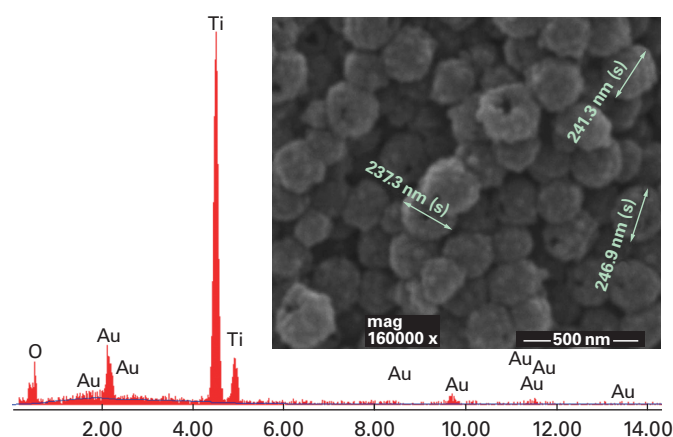


Fig. 1.3: Scanning electron micrographs of hollow TiO₂ nanocomposites after calcination at 600 °C.

the TiO_2 nanocomposites formed at temperature 600 °C are crystalline and consist of anatase (00-021-1272 Anatase, syn) and rutile (00-021-1276 Rutile, syn) type.

1.2.3 Cerium molybdate hollow nanocomposites

Cerium molybdate hollow nanocomposites are synthesized using a two-step process [32]. First, PS nanospheres are produced using emulsion polymerization. Second, the PS spheres are coated via the sol-gel method to form a cerium molybdate layer. Finally, the nanocontainers are made by calcination of cerium molybdate coated PS nanospheres.

The method of emulsion polymerization is employed to produce anionic PS latex, used as core particles. The experimental conditions for the PS preparation are similar to those in section 1.2.1 on cerium oxide nanocomposites. The PS lattices are coated via the sol-gel method to form a cerium molybdate layer. The sol-gel coatings are prepared by controlled hydrolysis of $\text{Ce}(\text{acac})_3$ and sodium molybdate aqueous solution in the presence of PS latex and PVP. These dispersions are aged for different time intervals in test tubes and placed in an oven preheated to 96 °C (Table 1.5). The resulting dispersions are centrifuged at 14,000 rpm for 30 min, the supernatant solutions are discarded, and then the particles are resuspended in doubly distilled water with a sonicator. This process is repeated three times, and the purified powders are dried in a desiccator.

Table 1.5: Conditions of preparation of coated spheres

Material	Quantity (g)
Polystyrene	10.0
PVP	10.0
$\text{Ce}(\text{acac})_3$	5.0
sodium molybdate	0.5
Water	1000

Hollow cerium molybdate nanocomposites are produced after the PS burn-off by calcination. Initially, the coated nanospheres are placed on a glass slide and dried, first at room temperature and then for 1 h at 60 °C. Then, the composite is calcinated for 4 h in air in a furnace at 550 °C with a heating rate of 10 °C min^{-1} . After calcination of the coated nanospheres, the resulting hollow nanocomposites have an external diameter of 145 ± 10 nm (Fig. 1.4). The EDX analysis illustrates that the nanocomposites consist of cerium, molybdenum and oxygen. The XRD analysis depicts that the nanocomposites' structures formed at temperature 550 °C are crystalline and consist of cerium molybdenum oxide (33-0330) type.

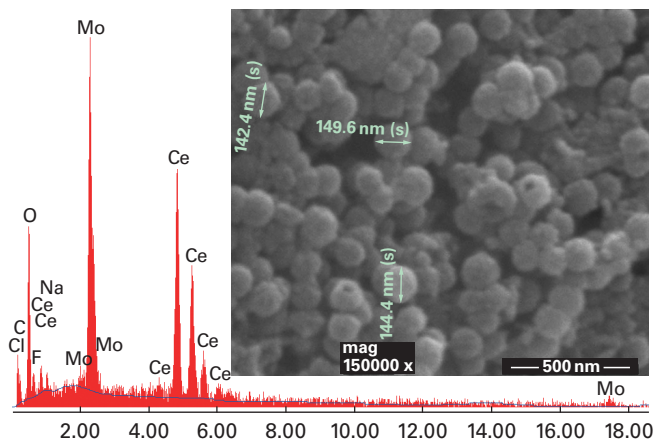


Fig. 1.4: Scanning electron micrographs of cerium molybdate hollow nanocomposites.

1.2.4 Cerium titanium oxide hollow nanocomposites

The synthesis of cerium titanium oxide hollow nanocomposites consists of three experimental steps [69]. The first step involves the preparation of positive charged organic templates based on PS. Styrene is polymerized by polymerization in suspension. The conditions for the polymerization process of PS are similar to those of in section 1.2.2 above. During the second step the PS nanospheres are coated via sol-gel method. Sol-gel coating is prepared with controlled hydrolysis of the alcoholic solution of TTIP and $\text{Ce}(\text{acac})_3$ in presence of PS nanospheres, NaCl and PVP (Table 1.6). The positive charged polystyrene reacts with the negative charged product of the hydrolysis of TTIP and $\text{Ce}(\text{acac})_3$. Monomers or oligomers of hydrolyzed TTIP and $\text{Ce}(\text{acac})_3$ are condensed on the surface of the polystyrene. Aging of the solutions at 60 °C, centrifugation and washing of the coated nanospheres is followed. The formation of hollow nanospheres is achieved after heat treatments of the composites at 600 °C with heating rate 10 °C min⁻¹, where the polystyrene cores are burned off.

Table 1.6: Conditions of preparation of coated spheres

Material	Quantity (g)
Ethanol (ml)	800
PVP (g)	8.0
NaCl 5mM (ml)	20.0
PS (g)	9.0
TTIP (ml)	9.0
$\text{Ce}(\text{acac})_3$	1.0

The size of the nanocomposites is 180 ± 10 nm as determined by Scanning Electron Microscopy (SEM) (Fig. 1.5). The EDX analysis shows that titanium, cerium and oxygen constitute the spectrum of the nanocomposites. XRD illustrates that the hollow nanoparticles consist of anatase and cerianite crystalline phases.

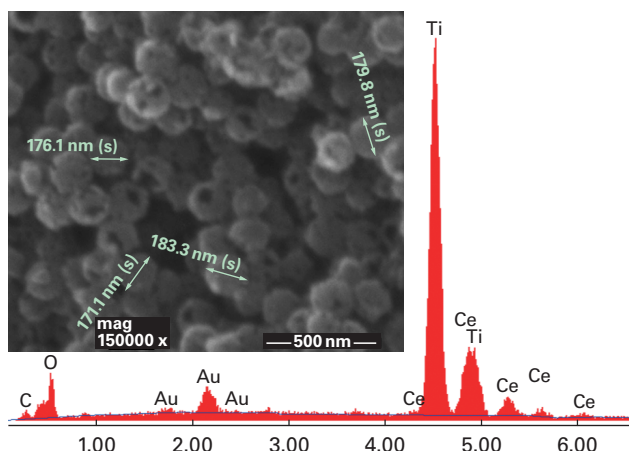


Fig. 1.5: SEM image and EDX analysis of cerium titanium oxide hollow nanocomposites.

1.2.5 Magnetic hollow nanocomposites

Magnetic hollow submicrocomposites are synthesized through a two-step process [21]. First, PS spheres are produced in order to be used as core particles. Second, the PS spheres are coated via the sol-gel method to form an iron oxide layer. The composite is treated in air to burn off the PS latex. The method of emulsion polymerization is employed to produce anionic PS latex, used as core particles. The process is described in section 1.2.1 above. The size of the PS spheres is controlled by the concentration of the monomer (styrene), the initiator (KPS) and the emulsifier (sodium dodecylsulfate). The coating procedure involves the controlled hydrolysis of aqueous solution of iron (III) chloride in the presence of PS latex. PVP and urea are added to the mixture reaction to prevent aggregation of the core particles. For this purpose, dispersions containing polystyrene latex, iron (III) chloride, PVP and urea are aged for 3 days in test tubes, placed in an oven preheated to 95 °C. The resulting dispersions are centrifuged at 7,000 rpm for 15 min. The supernatant solutions are discarded and then the particles are resuspended in doubly distilled water with a sonicator. This process is repeated three times. The purified powders are dried in a desiccator (Table 1.7).

Hollow hematite composites are synthesized via heat treatments where the PS cores are burnt off. Initially, the coated spheres are placed on a glass slide and dried,

Table 1.7: Conditions of preparation of coated spheres

Material	Quantity (g)
PS	0.25
PVP	2.25
Urea	3.30
HCl 0.75×10^{-2} M	2.80
Iron (III) Chloride	0.40
Water	250

first at room temperature and then for 2 h at 80 °C. Then, the composite is further calcinated for 3 h in air in a furnace at 500 °C at a heating rate of 5 °C min⁻¹. Moreover, the hollow hematite (Fe₂O₃) composites are heated for 1, 4, 12 and 24 h at 350 °C in a hydrogen oven and this results in hollow magnetite (heated for 1 h) and hollow composites containing both maghemite and iron phases (heated for 4, 12, 24 h). Calcination of the coated composites gives hollow spheres with a diameter of 400 ± 10 nm (Fig. 1.6). These spheres consist of hematite phase (XRD-Analysis). The thickness of the container’s wall is approximately 45 nm.

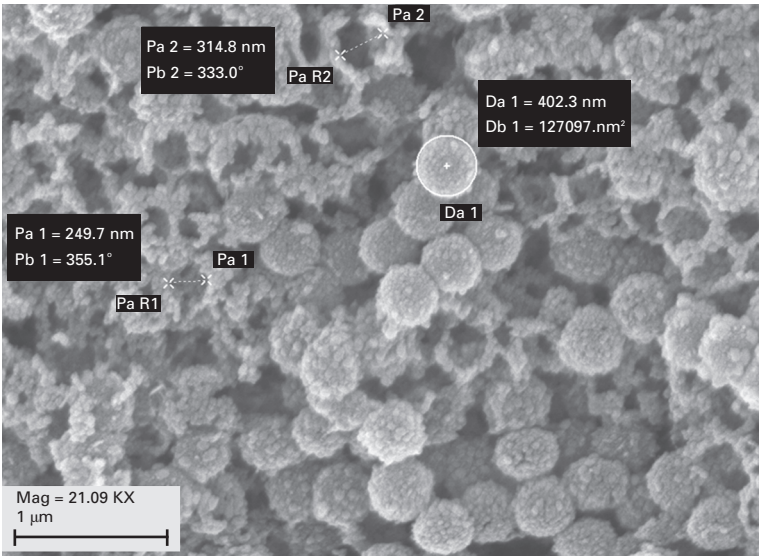


Fig. 1.6: SEM of hollow hematite spheres after calcination [21].