CERIUM-BASED MATERIALS:
SYNTHESIS, PROPERTIES AND APPLICATIONS

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Cerium-Based Materials: Synthesis, Properties and Applications

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CONTENTS

PREFACE

Cerium is the most abundant metal of rare-earth elements. It can be utilized in various fields of application, such as phosphors, alloys, magnetics, catalysis, catalytic converters and gas mantles. China has been the biggest producer of rare-earth elements in the last decades. Cerium shows +4, +3, +2, and +1 oxidation states but +4 is the most stable oxidation state. It is biologically inactive as well as non-toxic for humans. Cerium oxide (Ceria or CeO_2) and ceria-based materials have been explored in various applications in academia and industries such as catalysts, pharmaceuticals, electrochemistry, sensor, *etc.* Cerium-based materials are mostly used in heterogeneous catalysis and other various fields. As per our knowledge, there is no such book that can summarize the cerium-based materials. Hence, in this book, Cerium-based materials are summarized with their application in various fields such as industrial, catalytic, biomedical, and so on. This book will explain the history of cerium/ cerium-based materials, their synthesis, and their properties chapter wise. We sincerely hope that this book will be a great help to the researchers. We look forward to your observations.

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CHAPTER 1

Introduction to Cerium and Cerium-based Materials

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Abstract: The redox behavior of cerium is responsible for its high technological importance since ceria serves as a potential material in assorted applications. Changes in the optical, electrical, magnetic, and catalytic behavior of ceria can be brought about by employing different methodologies and reaction conditions. The high thermal and structural stability of ceria offers its utilization as a host lattice for various doping schemes. The incorporation of dopant elements beautifies the lattice by generating oxygen vacancies and thereby creating various interesting properties. Aiming with the stabilization of ceria and ceria-based compounds in nano-dimensions also opens up various new possibilities to explore it further for numerous useful applications.

Keywords: Cerium, Cerium-based materials, Characterization, Nanomaterials, Synthesis.

INTRODUCTION

Cerium is a well known abundant rare-earth element. Its minerals such as silicate, carbonate, phosphate, and hydroxide can be utilized in various fields of applications, like phosphors, alloys, magnetics, catalysis, catalytic converters and gas mantles. In the last decades, China is the biggest producer of cerium. Even the price of cerium oxide is cheaper than lanthanum oxide. It can be extracted from its ores. Cerium exhibits variable oxidation states such as +4, +3, +2 and +1 oxidation states but among them, +4 is the most stable. In addition to this, Ce^{3+} compounds are also known to be stable such as $Ce(NO_3)_3$ and many more. Cerium oxide (ceria, CeO_2) and ceria-based materials have been explored for various applications in academia and industries such as a catalyst, [1-20] a pharmaceutical

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Ramesh Chandra and Ravi Tomar (Eds.)

[21 - 23], in electrochemistry [24 - 28], as a sensor [29, 30], as an interlayer/sublayer/buffer layer [31, 32], and so on [33 - 37]. Cerium-based materials are most commonly used in heterogeneous catalysis.

Ceria is pale yellow powder which is obtained by the combustion of cerium, oxalate or hydroxide. Ceria received much attention due to its redox property, thermal stability, transport properties as well as oxygen storage capacity [38, 39]. It was first used industrially by Ford Motor Company in 1976 in catalytic converters as an oxygen storage component. On the other hand, ceria was considered to be an "inert" support. In past decades, ceria was used for the stabilization of catalytically active nanoparticles. After that it had been considered as a co-catalyst in catalytic reactions. But in recent times, experimentally it has been proved that it is a highly promising catalyst in numerous organic and inorganic reactions. Majorly it helps in the construction of three-way-catalyst (TWCs). Since 1950 till date, there are more than 26000 publications including the study related to CeO_2 and ceria-based materials having a wide range of applications. The golden year of ceria materials in terms of publications was from 2014 to 2018. During these years, more than 2500 papers were published on ceria materials. Moreover available reports based on pristine and doped ceria show their applications in superoxide dismutase mimetic activity, hydroxyl radical scavenging, in the reduction of ischemic brain damage by disruption of the blood-brain barrier after ischemia, as a catalyst for intracellular drug delivery, as a support for stem cells in cultured vitro, peroxidase mimetic activity, oxidase mimetic activity, phosphate mimetic activity, nitric oxide radical scavenging and many more.

Ceria in its crystal structure is known to exist with fluorite lattice having space group *Fm-3m* (Fig. **1**). In its structure, 8-coordination is exhibited by cerium ions and 4-coordination by oxygen ions. The availability of mixed oxidation state or redox properties makes it accountable for various applications. Usually, doping of ceria is carried out by substituting cerium ion with lower valence cations which introduces oxygen vacancies to maintain the overall charge neutrality in the lattice. Doping induced oxygen vacancies provide equal sites to migrate oxygen ions by hopping mechanism and are thereby responsible for high ionic conductivity of the lattice. Moreover, ceria is significantly capable of bringing out high degree of substitution which results in non-stoichiometric ceria. Consequently, non-stoichiometry of ceria provides highly disordered structures. Usually, in order to improve oxide ion conductivity of ceria, cerium ions are substituted by rare earth ions [40]. Reported literature includes that ceria can be doped with numerous metals as dopant which contribute to tuning the oxygen storage capacity, oxide-ion conductivity and redox behavior too. Dopant cations involve isovalent (Zr^{4+} and Sn^{4+}), aliovalent (Y^{3+}, Gd^{3+}, Sm^{3+}, La^{3+}, $Pr^{4+/3+}$ and Sr^{2+})

and transition-metal ions (Ti^{4+}, Cu^{2+}, Fe^{3+} and Pd^{2+}) to enhance oxide-ion conductivity [41 - 54].

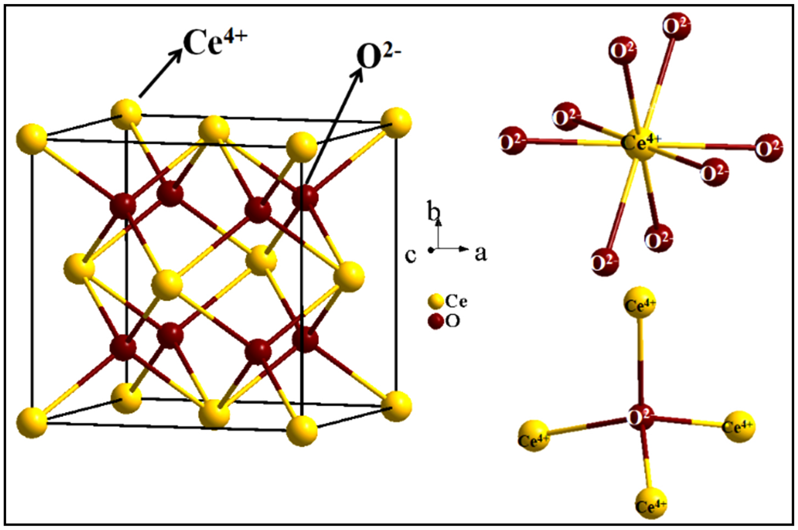

Fig. (1). Crystal structure of ceria along with representation of cerium ion (8-coordinated) and oxygen ion (4-coordinated).

CERIA-BASED MATERIALS

Scientists throughout the world gave two major directions for ceria-based materials that are of high interest in catalysis. From the industrial point of view, the first one is in car convertors, which can be fulfilled by increasing the surface area and thermal stability of ceria based materials. With this idea, solid solutions of transition or rare earth metals especially those containing zirconium have been prepared and found to be highly promising. These achievements facilitate their usages as closed coupled catalysts (CCC) that will be stable up to a temperature of 1000 ºC. One of such examples is ceria-zirconium based TWCs that play a role as environmental catalysts. Although continued debate is going on the necessities of phase homogeneity exhibited by ceria-based materials, other than zirconium, palladium-cerium based materials have a broad range of applications in organic synthesis for example in cross-coupling reaction, oxidation, hydrogenation, methane activation and many more.

CERIUM-BASED AS NANOMATERIALS

Nanotechnology provides materials with a controlled shape and size (in nanodimensions). Although, low thermal stability of nanomaterials is a

CHAPTER 2

Synthesis and Characterization of Cerium-based Nanomaterials

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Abstract: Pristine ceria is an extensively explored nanomaterial. In order to improve physiochemical properties of ceria and ceria based materials, a different synthetic strategy has been employed which has been highlighted in the current chapter. The high stability of pristine ceria offers an opportunity to utilize it as a host lattice against the doping/substitution of alkali metals, alkaline earth metals, transition metals, rare earth and noble metals. This way incorporation of different valence metals ion into ceria causes structural distortion which further facilitates alteration of the physical and chemical properties of host lattice. Diverse synthetic conditions are used to stabilize ceria and ceria-based materials in nano-resime having morphologies such as nanowires, nanocubes, nanospheres, nanotubes and many more. Thus, different morphologies of ceria and ceria-based materials are mainly applicable for their high technological importance. The synthesized samples can be characterized by using powder X-ray diffraction, Raman scanning electron microscopy, energy dispersive spectroscopy, transmission electron microscopy and X-ray photoelectron spectroscopy.

Keywords: Catalyst, Methodology, Morphology, Nanostructure, Pristine ceria, Surface area.

INTRODUCTION

Compositional and structural changes arising during the progress of a reaction can be noticed by employing advanced spectroscopic and microscopic analysis [1 - 4]. For the complete exploration of structure-property relationship pristine ceria and ceria-based nanomaterials with a particular shape, size and surface demonstrate ideal catalyst models. Ceria and ceria-based materials have potential applications in thermal catalysis and photocatalysis [5 - 9]. It is well known that ceria stabilizes in fluorite structure where each cerium cation is coordinated by eight nearest-neighbor oxygen anions and oxygen anion is coordinated by four nearest-neighbor cerium cations (Fig. **1**) [10].

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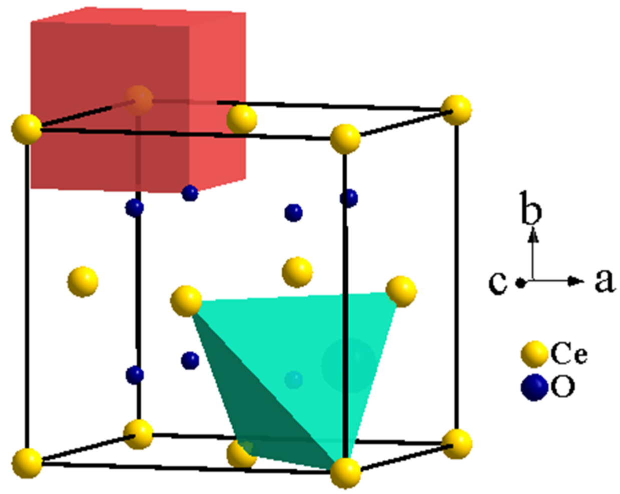

Fig. (1). Crystal structure of CeO_2.

The redox nature of ceria offers and opens up numerous opportunities to dope/substitute it with four types of cations (with different valence) such as: (1) Zr, Hf and rare-earth metals, (2) transition metals, (3) alkali and alkali-earth metals and (4) noble metals [11]. Such doping or substitution schemes might be leading to structural distortion which further causes alteration of physical and chemical properties of host lattice.

In previous years, enormous part of research has been devoted to improve the chemical synthetic methodology in order to prepare well-defined CeO_2 and CeO_2-based nanostructures. Untill now, reported synthetic strategies mainly are of two types: (1) Crystallographic structure-directed and (2) Template-directed synthesis methods [16 - 18]. The first type includes hydrothermal/solvothermal treatment, coprecipitation synthesis and sol-gel method [12 - 15]. Though the second type of synthetic strategy involves self-template and soft/hard template-directed synthesis methods [16 - 18]. All these methodologies require capping reagents since these can be selectively absorbed on specific facets of nanocrystals and their direct growth with desired morphology [19]. Nowadays, electrochemical deposition and electrospinning are gaining attention of researchers due to simplicity in methods, ease of scale-up, low cost and environmental friendliness [20, 21]. Other than this, large number of other methods such as microwave-assisted synthesis, ultrasonic irradiation, flame spray pyrolysis, chemical vapor deposition and many more are also found to be useful in the preparation of ceria-based nanomaterials [22 - 25]. High thermal and chemical stability of ceria are responsible for its use in post-modification methods such as in phosphorization, sulfuration, impregnation and special annealing treatment [26 - 28]. Additionally, ceria nanocomposites are also doped with various metals in order to prepare CeO_2-supported and CeO_2-modified with high electrocatalytic performance [29].

SYNTHESIS OF PRISTINE CERIA

Ceria (CeO_2) is a very well-known compound exhibiting redox behavior and can be synthesized by numerous methodologies [30 - 48] (Fig. **2**). Among them, some of the easy techniques that can be performed under normal laboratory conditions are explained in this section:

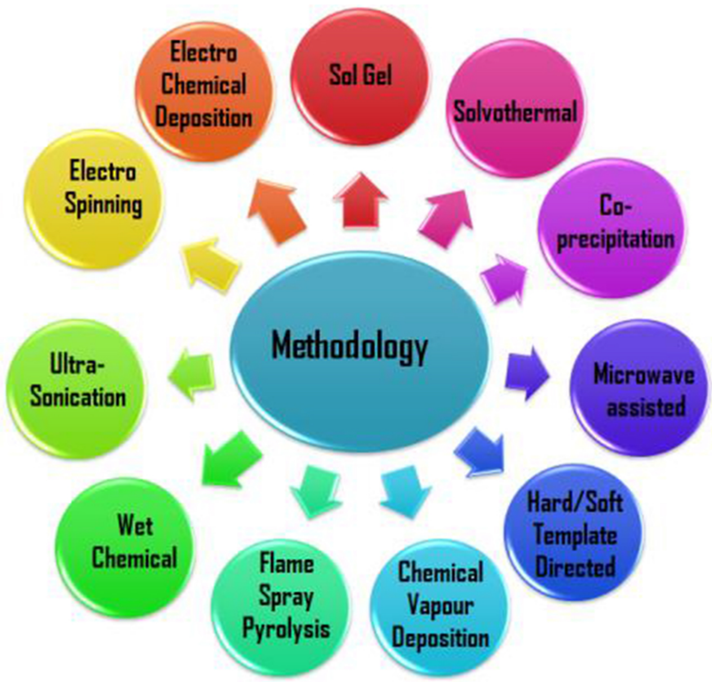

Fig. (2). Pictorial representation of various methodology used for synthesis of CeO_2.

Solvothermal Method

In this method, usually a chemical reaction between the reaction mixtures took place above the boiling point of the used solvent [30, 32]. Ceria preparation using this method requires 0.05 $molL^{-1}$ of $Ce(NO_3)_3.6H_2O$ or $(NH_4)_2Ce(NO_3)_6$ and added to the known volume of ethanol, mixed well and then transferred into a Teflon bottle. pH of the reaction mixture was adjusted by adding KOH or NaOH and finally the reaction was performed at 180 °C for 24hrs in an electric oven. By controlling the potential and pH under hydrothermal conditions, the product can be synthesized in a way of controlled oxidation state which leads to the stabilization of a product with a metastable and micro-porous structure.

CHAPTER 3

Catalytic Applications of Cerium-based Materials

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Abstract: This chapter pivots on the employment of Ce-based catalysts in numerous catalytic applications glancing at the foremost commercial technologies due to their high abundance in the earth's crust. Ceria in essence to their proficiency to harmonize Ce (III) & Ce (IV)-oxidation states depending on oxygen availability, which is known as oxygen-storage capacity, is at the heart of the potentiality of Ce-based materials to exemplify as a catalyst in numerous reactions. Ceria being one of the most auspicious materials in use since 1980 onwards, has strongly dilated to affect several processes for chemical transformations by and large for energy and environmental applications. In this chapter, we will review some of the ingrained applications of Ce-based catalysts and, we will try to display a brief rundown of emerging technologies in this ongoing field to encourage further reading.

Keywords: Aerobic oxidation, Cerium-based MOFs, CO-oxidation, Knoevenagel (toluene) oxidation, One-pot synthesis, ORR, Oxidation, Photo-oxidation, Reduction, Solid-base catalysts, Solvent-free aerobic oxidation, TWC application, Waste-water treatment.

INTRODUCTION

Cerium (Ce) is a common rare earth metal element that is abundant, affordable, and non-toxic. Ce-based catalysts are gaining popularity due to their two stable valence states: Ce (III) and Ce (IV). Cerium's position in the periodic table explains its unique and plentiful qualities, which are also mirrored in the chemistry and features of metal organic frameworks (Fig. **1**). Without a doubt, its most important technological advancement is in the field of catalysis, where Ce-based catalysts are used as a promoted or co-catalyst in amalgamation with noble or transition metals and also other oxides in widespread application related to the removal of virulent compounds from internal combustion engines, essentially as a constituent of two way catalyst (TWC) for the removal of CO, HC (hydrocarbons)

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Ramesh Chandra and Ravi Tomar (Eds.)

and NO (nitrogen oxides) from gasoline [1 - 3]. Furthermore, there are a number of processes that are emphatically extravagant in the presence of Ce-based formulations, such as favorable CO oxidation and syngas mixture creation *via* water gas shift reaction in steam and dry methane reformation [4, 5]. Moreover, a combination of Ceria with noble metals or other oxides uplifts further oxidation or hydrogenation reactions. Likewise, specific interaction between Ce and Pd/Pt gives rise to a highly active catalyst for methane [6] and CO oxidation [7, 8].

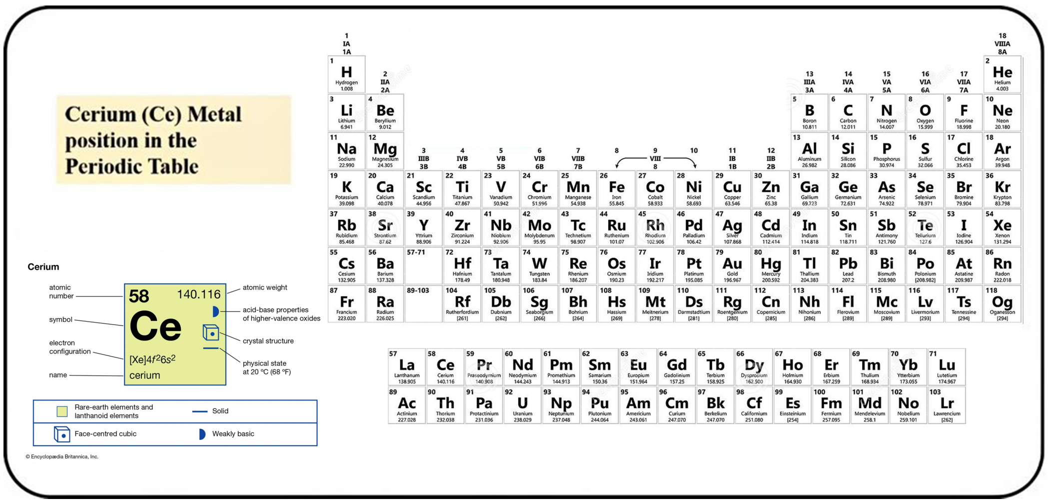


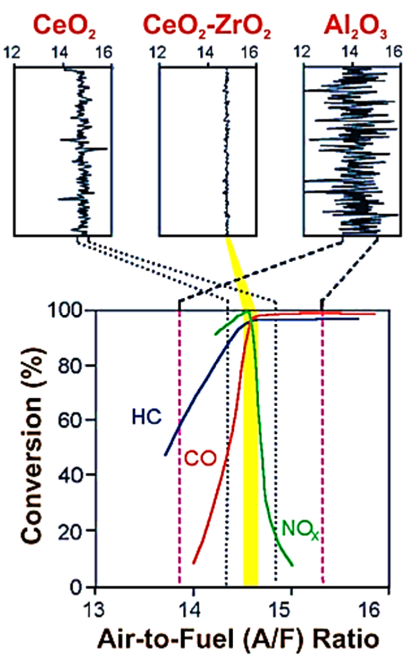
Fig. (1). Cerium (Ce) metal position in the periodic table.

Despite the fact that the advancement of ceria is associated with its industrial utilization in catalysis, there are numerous principal non-catalytic applications where Ce-based catalysts such that CeO_2, conceivably exploited as an ultraviolet absorber [9], anticorrosion coatings [10], glass decolorization [11] or as an abrasive powder for polishing glass and hard stone [12]. Furthermore, very recently, the authors exploited biomimetic and antioxidant activity of ceria in several biomedical applications [13, 14]. Owing to the low toxicity and high bio-compatibility, Ce-nanoparticles were incorporated with their efficiency in neutralizing radicals, which is the basis of utilization in biomedicine for antibacterial agents and MRI-contrast enhancers [15, 16] or several oxidative-stress related diseases [17]. Recently, a Ce-based catalyst has been widely studied as an n-type semiconductor with a bandgap of 3.1 eV for photocatalytic applications, where the broad band gap of ceria requires UV light to operate the mechanism [18]. This chapter includes all the applications of Ce-based catalysts in this rapid growth field. This chapter shed light on the variety and properties of Ce-based catalysts and their applications in different fields such as TWC application, support for metal *i.e.*, Ce (III) and Ce (IV)-metal organic framework

(MOFs) applications and features, solid-base catalyst, oxidation and reduction reactions, one-pot synthesis and waste-water treatment. Moreover, future research supervisions of Ce-based catalysts are also suggested.

THREE-WAY CATALYST (TWC) APPLICATION

Momentarily, self-propelled emission is a major cause of air pollution. Nowadays, the catalytic converter is one of the most admirable and efficient solutions for automotive contamination control [19]. In this context, TWC has been demonstrated to be a satisfactory substitute to simultaneously reduce the elimination of hydrocarbons (HC), carbon monoxide (CO) and nitrogen oxide (NO), to command fatigue emissions from gasoline engine powered vehicles [3], which was proposed by Gross *et al.* in 1963. The authors discovered that utilising an A/F ratio close to stoichiometry maximises the conversion of three species; however, CO, HC, and NOX conversion drops sequentially under rich and lean conditions as depicted in (Scheme **1**), descending rapidly when the engine intervenes outside of a sharp window, approximately air/fuel = 14.6 by weight [20].



Scheme (1). Based on the different supports used in TWC, the conversion efficiency of HO, CO and NO_X, with the control of the A/F ratio. Copyright 2016 [2], with permission from American Chemical society; scheme of a TWC with lambda sensors.

CHAPTER 4

Photocatalytic Application of Cerium-based Nanomaterials

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Abstract: This chapter pivots on Ce-based catalysts' employment in numerous catalytic applications glancing at the foremost commercial technologies due to their high abundance in the earth's crust. Ceria - CeO_2 is considered the most stable oxide which confirms that Ce^{3+} prefers the oxidation state than the Ce^{4+} oxidation state. This is also known as oxygen - storage capacity. CeO_2 shows good photocatalytic activity. This chapter explores the important properties of Ce and CeO_2 with a comparison of their bulk properties with their properties at the nanoscale. Further, different synthesis processes of Ce and CeO_2 nanoparticles have been discussed. Later, the chapter addresses the mechanism of photocatalysis using CeO_2 nanoparticles. Further, the chapter discusses applications and studies of doped CeO_2 based photocatalysts, and we will try to display a brief rundown of emerging technologies in the ongoing field to encourage further reading.

Keywords: Cerium, Cerium-oxide, Heterogeneous photocatalysis, Photocatalysis, Waste water treatment, Water-splitting.

INTRODUCTION

One of the biggest problems in front of human beings is pollution. In the process of prosperity and advancement of human life, industrial development started all over the world. Mankind succeeds in that way, and we have better transportation, clothes, electronic gadgets, electrical appliances, shelter, *etc.* But all these things brought all kinds of pollution around us [1, 2]. Now there is a massive problem of water pollution, air pollution and soil pollution [3 - 6]. These problems open the research scope, such as the search for an improved way to clean water, air and soil pollution [7 - 10]. The methods for cleaning all these kinds of pollution are to find good filters or photocatalyst materials.

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Photocatalysis and photocatalysts have developed a great interest and are considered as a green chemical pathways for water purification, air purification, water - splitting, water remediation *etc.* In this process, chemical reaction starts in the presence of light, and the photocatalyst enhances the response speed. It has been over 50 years now researchers have been extensively working on photocatalysis. However, research over it was highlighted by Fujishima and Honda in 1972 when these two researchers from Japan managed to perform electrochemical photolysis of water using TiO_2 and platinum rod [11]. It is a cost-effective source for the production of hydrogen and oxygen molecule [11 - 13].

The primary role of a photocatalyst is to speed up photoreaction in the presence of light. In photocatalysis, light is absorbed by photocatalysis, and produces electron holes pairs and generates free radicals. These free radicles initiate secondary reactions [14 - 16].

The photocatalysis is divided into two categories: homogeneous and heterogeneous photocatalysis [17 - 19]. If the phase of the reactant and photocatalysis is the same, then photocatalysis is referred to as a homogeneous photocatalysis [19, 20]. For example, photo - Fenton systems (Fe^+ and Fe^+/H_2O_2)-hydroxyl radicals are produced in Fenton systems with the formation of Fe^{3+} while in photo - Fenton type process, Fe^{3+} is reduced to Fe^{2+} in the presence of ultra - violet light, as shown below [21, 22].

In contrast to homogeneous photocatalysis, when the reactant phase is different from photocatalysis, this catalysis is known as a heterogeneous photocatalysis. Metal - oxide, carbides, nitrides and semiconductors are common heterogeneous photocatalysis. TiO_2 is the most studied photocatalysis used for several applications. There are certain limitations of current photocatalysis such as recombination light, absorption of visible light and conduction band, *etc*. [9, 10, 13].

This limitation opens up opportunities for higher performance under visible light, coast - effectiveness, thermal stability and corrosion-free photocatalysis materials, which can be applicable for commercial purpose. The lanthanide/rare - earth doped materials and lanthanide/rare - earth oxide materials are studied extensively so as to improve the stability and performance of traditional heterogeneous photocatalysis. It is observed that CeO_2 shows photocatalytic behavior due to their excellent semiconductor and redox properties [23 - 27].

CERIUM AND CERIUM DIOXIDE

Cerium is the most reactive and most abundant rare - earth element in the rare - earth series [28]. It is present in four known isotopes; therefore, it is found in many mineral forms like monazite, cerite, orthite and bastenaesite [29, 30]. The extracted Ce is soft, ductile and malleable metal and its color changes from gray to silver with purity. It shows strong paramagnetic behaviour at room temperature and shows antiferromagnetic nature under 13 K. Under severe conditions - in mill kelvin range and very high pressure 20 kbar, it becomes superconductors. However, it is not widely used due to its specific properties (like easy oxidation, reaction with water; it is highly flammable or ignites upon a simple scratch with a sharp object). It is oxidized easily when it comes in contact with air even at room temperature. Cerium has also shown good optical characteristics when doped with metal - oxides or luminescence phosphors [29, 31, 32].

The important properties of cerium are mentioned in Table **1**. The energy of inner 4f is closer to the 6s level, allowing variable occupancy of these two energy levels. Thus, Ce possesses variable electronic structures and hence it has two oxidation states: Ce^{3+} and Ce^{4+}. These two states provide two oxides: cerium dioxide (CeO_2), and cerium sesquioxide (Ce_2O_3). Out of these two, CeO_2 is considered as the most stable oxide of cerium. It is observed that the Ce^{4+} state is more stable(as the 4+ oxidation state, all 4f, 5dand 6s orbitals are empty and Ce gains the stable configuration of xenon) than Ce^{3+}, as the electronic configuration $[Xe]4f^0$ (of Ce^{4+}) is more stable compared to $[Xe]4f^0$ (of Ce^{3+}). Further, it shows that Ce has a wide - bandgap of 3.19 eV with high excitation energy, which is used for photocatalysis and photovoltaic applications [33, 34].

Table 1. Important properties of cerium.

Properties	Earth Crust	Oxidation State	Electronic Configuration	Atomic Number	Density	Atomic Radius
Ce	46.1 ppm	3 and 4	[Xe]4f26s2	58	6.78 g/cm3	1.84 Å

Cerium dioxide (also called ceria) based materials are promising materials for photocatalyst activities, as they can have a redox exchange between Ce^{3+} and Ce^{4+}. Moreover, Ce is a more abundant rare - earth metal in the earth crust than other rare - earth elements, and it is even more than some transition metals like tin and copper. This makes Ce and CeO_2 more economical advantages over tradition photocatalyst materials. Switching between +3 and +4 oxidation states also opens up several vital applications like semiconductors used for solar cells, sensors and polishing materials. However, this chapter is focused on photocatalytic properties Ce and CeO_2 based materials [35, 36].

CHAPTER 5

Biological, Biomedical and Pharmaceutical Application of Cerium-based Materials

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Abstract: Cerium-based materials have established themselves as biologically active materials with a wide range of pharmacological benefits. In particular, Nanoceria has been proven to be the most versatile and effective therapeutic agent due to its surface area-to-volume ratio. In this chapter, we made an attempt to discuss all important therapeutic applications of Cerium based materials. Also, the mechanistic course of action of cerium-based materials has been emphasized in this chapter. Moreover, the possible toxicity of cerium-based materials in the biological system has been reviewed in the later section of this chapter.

Keywords: Antiseptic, Anti-inflammatory, Cerium, Nanoceria, Pharmacology.

INTRODUCTION

Rare earth elements are unique due to the presence of well-shielded 4f orbitals. Cerium is a rare earth metal that has ubiquitous applications in many fields. Cerium can act as a catalytic converter, a source of electrolytes as well as a UV absorber [1]. Apart from its industrial applications, cerium shows paramount presence in several biological and biomedical dimensions [2].

The antiseptic properties of Cerium (III) compounds like Cerium (III) nitrate date back to the late 19th century. Cerium (III) stearate and cerium (III) acetate were the major constituents of several solutions to skin problems. Apart from this, Cerium (III) iodide used to be intravenously injected to treat inoperable solid tumours.

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Ramesh Chandra and Ravi Tomar (Eds.)

Except for others, the antioxidant property of Cerium has significant eminence. This is because oxidative stress can cause severe chronic ailments [3]. The anti oxidant property and related catalytic activity of cerium oxide are expected due to the presence of Cerium (III) and Cerium (IV) redox couple.

The catalytic property of cerium oxide results from the oxidative vacancy and valence defect present. Moreover, these catalytic properties are enhanced when cerium oxide is in the form of a nanoparticle that is Nanoceria. This improvement is due to Nanoceria's larger surface area, as the valence defects and oxygen vacancies are more on this enlarged surface [4]. Further significance of Nanoceria is accounted for because of Cerium's auto regenerative property (III) after it undergoes the catalytic cycle. Studies have shown that Nanoceria exhibits neuroprotective behavior, irrespective of the particle size. Neuroprotection is just one of several critical applications and other fascinating properties of Nanoceria [5].

Nanoceria can potentially adsorb blood serum, which can affect biological activity. However, this property is related to zeta potential, thus can be solved by size and surface tailoring. Alongside this, the controversial cytotoxic behavior of cerium compounds is studied to be time and dose-related [6]. Cerium particles are preferably used over lead particles to capture inorganic phosphate released during enzymatic hydrolysis by any phosphatases [7].

Another prominent reason for the biological application of Cerium is its resemblance to calcium. Cerium has a size analogous to calcium and hence can replace calcium. Thereby, Cerium can potentially inhibit Calcium-based reactions. It must be noted that due to a similarity in the size of Ca and Sr, the replacement of Ca by Sr may occur, which is not considered beneficial for bone health. However, references also stated that moderate-level strontium supplementation could improve calcium absorption in bones [8]. Alongside, some studies also revealed that Sr substituted Ca-Silicate ceramic scaffolds can help in better regeneration of osteoporotic bones [9]. Although, no corresponding reference stating the replacement of Ce with Sr was found, few studies concluded that the co-substitution of Ce and Sr in fluorohydroxyapatite ($Ca_{10}(PO_4)_6F_{0.5}(OH)_{1.5}$), used as an implant material, triggers bone formation around the implant material. Further, the co-substitution increases the fracture strength as well as the hardness at the micro-level [10]. We will ponder these and other biological and pharmaceutical aspects of cerium-based compounds in the other sections.

Although free radicals are inevitable for human survival, they can even cause cell death when present in excess. This emphasizes that both free radicals and antioxidants in a proper balance are necessary for human well-being. In the imbalance between the reactive oxygen species (ROS) and antioxidants, oxidative stress arises. This oxidative stress is the root cause of several health disorders and is the primary reason behind aging.

Biological antioxidants do not eliminate but regulate the amount of free radicals present. Both exogenous or endogenous antioxidants are essentially required in biological systems. These antioxidants work by scavenging the excess free radicals produced during normal metabolism. These free radicals or reactive oxygen species (ROS) include superoxide, peroxide, nitrate, and hydroxyl radicals.

Among various natural and synthetic pro-oxidant, cerium compounds acquired a considerable point of interest. On the surface of cerium oxide, Cerium is present in two oxidation states, *i.e.*, Ce^{3+} and Ce^{4+}. There is a cyclic shuffling between these two oxidation states of Cerium present on the surface of Cerium oxide particles. This cyclic switching between two oxidation states creates oxygen vacancy defects, which scavenge excess free radical species produced during cell metabolism.

The size and structure of the cerium particles are optimized to overcome the drawbacks of particle size, such as less biocompatibility and shorter circulation time. Nanoparticles have a high surface-area-to-volume ratio, thus showing better surface activity. Considering the above facts, optimum-sized nanoparticles are preferred in many biological applications [11].

Cerium (IV) salts are unstable in aqueous solutions at a pH greater than 3 due to their hydrolytic behavior and lack of biological applications. The metastability of Cerium (+IV) is well indicated by the redox potential of Ce^{3+}/ Ce^{4+} couple, which is 1.7V.

However, the concentration of Ce^{3+} compared to Ce^{4+} increases as the size of the cerium oxide particle decreases. This increase in Ce^{3+} concentration is directly associated with increased oxygen vacancy and therapeutic efficiency of cerium oxide nanoparticles. Nevertheless, considering the cytotoxic effects of nanoparticles, Nanoceria, or cerium oxide nanoparticles' size is tailored to obtain nanoparticles with minimum or no cytotoxicity and maximum pharmaceutical potential.

Nanoceria has a fluorite structure. This structure with oxygen defects due to the cyclic shift between the two oxidation states, Cr^{3+} and Cr^{4+}, bestows a strong antioxidant advantage on Nanoceria [12].

SUBJECT INDEX

A

B

Ramesh Chandra and Ravi Tomar (Eds.)

F

G

H

I

K

L

M

N

O

P

R

S

T

U

V

W

X

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Ramesh Chandra is an accomplished and revered teacher, distinguished scientist, outstanding researcher and exceptionally successful administrator who excels in institution building. He is a Professor of Chemistry and Founder Director of ACBR at the University of Delhi, which has acquired international status through its original and creative research output. He has been Vice-Chancellor, Bundelkhand University, Jhansi for six years from 1999-2005, and also chaired as the President of the Indian Chemical Society from 2004-2006, Member, Planning Commission, Govt. of U.P., India and Secretary - Zaheer Science Foundation. He has distinguished administrative experience of establishing 36 Institutes of Higher learning at Bundelkhand University, Jhansi with minimal support from the state government, which is now rated as the best University of U.P. Over the past 38 years, he has contributed a great deal to the field of Biomedical Sciences. He has supervised 81 Ph.D. and 10 M. Phil. Students, in all, trained more than 100 research scholars. His personal accomplishments are half a dozen patents, 263 scientific Research Papers in International journals of repute and several books edited or authored by him. He is the recipient of several professional national/ international recognitions and has been a member of the Governing Council, BOG, Executive/ Academic Councils of several Universities/ Institutions, Advisor to various academic institutions, non-official Director of PSU's. He is a prolific writer and displays extraordinary flair for writing on themes particularly like Higher Education and social issues.

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