CERIUM OXIDE

SANTOSHI S. NAIK
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INORGANIC CHEMISTRY

INTRODUCTION

Cerium belongs to lanthanide series and available most abundantly in the crust of the earth with an average concentration of 50 ppm as a rare earth element. Elemental cerium is a flexible and malleable lustrous metal. Cerium metal is iron-gray in color and is highly reactive. It is also known as a strong oxidizing agent and exists as cerium oxide in association with oxygen atoms. It exists as either cerous (Ce^{3+}, trivalent state) or ceric (Ce^{4+}, tetravalent state) in the form of compounds.

Cerium oxide (CeO_2) which is one of the important transition metal oxides acting as n-type semiconductor materials. It possesses several features resulted from the combination of high amount of oxygen in its structure and the facile change between the reduced and oxidized states (Ce^{3+} and Ce^{4+}) [2]. The CeO_2 has cubic fluorite structure, in which each cerium atom is surrounded by eight equivalent oxygen atoms and each oxygen atom is surrounded by a tetrahedron of four cerium atoms. Ideally, CeO_2 should have a formal charge of −2 and distance between oxygen–oxygen atoms should be 2.705 Å, in which the formal charge of cerium ions is +4 .

The main unique characteristics of cerium oxide involve a band gap of 3–3.6 eV, high value of dielectric constant up to $\kappa = 23–26$, high refractive index of n: 2.2–2.8, and high dielectric strength reached to 2.6 MV cm^{-1} [4. Such properties qualify cerium oxide-based materials to be employed in various applications, especially when they are in nanosized particles. The cerium oxide is a famous member of nanostructured materials having a wide range of applications. Cerium oxide materials/nanomaterials have been utilized in numerous fields including adsorption, catalysis, photocatalysis, sensing, fuel cells, hydrogen production, semiconductor devices as well as biomedical uses.

Commercial uses of CeO_2 could be utilized in the pure form or in a concentrated dose as a polishing powder for glasses as well as ophthalmic lenses or precision optics. Cerium oxide is also employed as a glass constituent for preventing solarization and discoloration, particularly in television screens. The CeO_2 contributes in heat-resistant alloy and ceramic coatings. Cerium oxide is also used in petroleum refining and emission controlling system in gasoline engines as well as a diesel fuel-borne catalyst to reduce particulate matter emissions. In recent years, CeO_2 nanoparticles have gained more consideration in biomedical research community since they could be used as inhibiting cellular agent along with their antimicrobial and antioxidant activity.

Owing to the dramatical and widespread industrial uses of cerium oxide materials, the National Institute of Environmental Health Sciences is suggested and nominated CeO_2 for toxicological characterization because of its limited toxicity data, and a lack of toxicological studies for nanoscale

CeO_2. CeO_2, which is one of important transition metal oxides, acts as n-type semiconductor materials that have diverse applications such as adsorption, catalysis, photocatalysis, sensing, fuel cells, hydrogen production, semiconductor devices as well as biomedical uses.

Cerium, a rare earth metal, is the first element of the lanthanide series in the periodic table. The 4f orbitals of rare earth metals are adequately shielded by 5p and 4d electrons, leading to interesting catalytic properties . Unlike most rare earth metals, cerium can exist in both 3+ and 4+ states . Thus, cerium oxide exists as both CeO_2 and Ce_2O_3 in the bulk state. At the nanoscale, however, cerium oxide has a mix of cerium in the 3+ and 4+ states on the nanoparticle surface. With a decrease in nanoparticle diameter, the number of 3+ sites on the surface increase and oxygen atoms are lost (oxygen vacancies) . This is depicted by an overall structure of CeO_{2-x}.

Cerium oxide nanoparticles (CeNPs, nanoceria) are widely used in chemical mechanical polishing/planarization , corrosion protection , solar cells , fuel oxidation catalysis , and automotive exhaust treatment. Pertinent to this review, CeNPs also display many bio-relevant activities-mimicking superoxide dismutase (SOD),catalase, peroxidase, oxidase, and phosphatase , and scavenging hydroxyl radicals, nitric oxide radicals, and peroxynitrite .

Reactive Oxygen Species (ROS) are released as by-products in aerobic metabolism and they are routinely linked to oxidative stress (increased levels of intracellular ROS contributing to many diseases). However, ROS primarily act as signaling molecules in physiological processes. For a current and detailed understanding of ROS, readers are referred to an extensive review by Schieber et al. that describes the two faces of ROS—redox signaling and oxidative stress. In this context, antioxidants can be defined as substances that scavenge ROS or inhibit their production. Interest in studying antioxidants grew after a study that described the potential benefits of vitamin E on cardiac health. The activity of metal and metal-based nanoparticle systems and their interactions with ROS depend on their microenvironment. It is well established that metal and metal oxide nanoparticles exhibit antioxidant properties. Since naturally occurring small antioxidant molecules have limited absorption into the body, nanoparticles have been investigated as carriers for antioxidant molecules. On the other hand, metal and metal-based nanoparticle systems can also be used for prooxidant treatment strategies.

The bio-relevant activities of CeNPs earmark them for use in potential pharmacological agents, drug delivery and bioscaffolding The basis for these activities of CeNPs is the thermodynamic efficiency of redox-cycling between 3+ and 4+ states on their surface and their unique ability to absorb and release oxygen. While it was initially thought that both oxygen vacancies and the redox-cycling between cerium in 3+ and 4+ states are involved in the antioxidant activities of CeNPs, it is now accepted that redox-cycling is solely responsible for all antioxidant properties. This suggests that the surface ratio of Ce^{3+}/Ce^{4+} plays a key role in all of the bio-relevant activities of CeNPs. It is worth noting that CeNPs can also show prooxidant properties at lower pH values and high doses, and they are known to exhibit potential toxicity based on their synthesis method, concentration, and exposure time, as detailed in a review by Yokel et al. As explained by Xu et al. in their review on CeNPs and their applications, cerium is not found in the human body and there are no known clearance mechanisms for it. This implies that exposure to cerium would lead to systemic toxicity. These reasons necessitate careful optimization of synthesis parameters to generate non-toxic CeNPs that have either pro-oxidant or antioxidant properties that are based on the treatment strategy being used.

The interactions of a nanoparticle system with its microenvironment need to be considered while designing effective nanocarriers. It is important to note that polymeric nanocarriers and smart polymer systems can be used to encapsulate enzymes for drug delivery applications and offer good biocompatibility. Such systems can also offer dual responsive programmable drug release. However, CeNP-based treatment strategies have a unique advantage in that they have a self-regenerative antioxidant capability .

Cerium oxide nanoparticle has wide range applications in the diverse fields. The unique property such as high reactivity and characteristics of cerium oxide nanoparticle has the popularity in agricultural field. It plays critical role in food security and agricultural sustainability. Cerium oxide nanoparticle can be applied in polluted soil to enhance the crop growth and provide tolerance against salt and heavy metal stress. Unfortunately, the application of cerium oxide nanoparticle in agriculture field is still controversial because of their unknown effects and fate in the body of humans. In high concentration, cerium oxide compete with the essential nutrients and reduce their uptake in plants. Application of these particles to field crops shows toxic effects and reduce the nutrients availability to plant in very high concentrations. Due to its toxic effects on plants, yield of field crops ultimately reduce. Cerium oxide nanoparticles application according to the crop physiology and physiochemical properties of soil is recommended. A wide range of careful investigations is needed to check possible mechanisms behind nanoceria interaction in plants and their impact on soil biota. Authors urge and recommend researchers around the world to work on CeO_2 NPs so a clear demarcation between is feasibility and toxicity can be made.

Cerium oxide as such is only seldom used as adsorbent for removing pollutants from liquid effluents, the adsorption phenomena play necessarily the key role in catalytic and photocatalytic applications. Ji et al. studied the adsorption of azo dye Acid Orange 7 on CeO_2 in relation to its photocatalytic activity and concluded that superior adsorption properties of CeO_2 in comparison with TiO_2 cause its better photodegradation efficiency. An effect of pH on the sorption behaviour of CeO_2 was studied in detail in this work. Effects of the synthetic conditions (synthesis in acidic and alkaline media) on the adsorption properties of cerium oxide were studied by Brigante and Schulz . Nevertheless, the (liquid-phase) adsorption behaviour of various forms of cerium oxides prepared by various synthetic routes is still understood insufficiently. In the present work, we prepared a series of cerium oxides by calcination of cerium carbonate at various temperatures ranging from 200 to 1000°C and examined their sorptive properties towards Acid Orange 7 azo dye as the most popular model compound in photocatalytic applications. The adsorption kinetic dependencies were measured and possible mechanisms of adsorption were discussed. It was proven that the adsorption efficiency correlates closely with the degradation efficiency of CeO_2 for organophosphate pesticide parathion methyl, even though both processes were studied in quite different media.

Applications of ceria

Being technologically important functional material, ceria has remarkable applications in many diverse fields. In this section, a brief discussion on some of the most widely known commercial and industrial applications of ceria and nanoceria is presented.

Solid oxide fuel cells

Solid oxide fuel cells (SOFCs) are considered to have great potential in providing clean and reliable electric power; therefore, research in this area attracts great attention in recent years. Many reports suggest that ceria-based ion conductors possess huge resistance to carbon deposition and have potential to allow unstoppable supply of dry hydrocarbon fuels to the anode .

Gorte and Vohs first demonstrated a direct electrochemical oxidation of hydrocarbons such as methane and toluene using SOFC at 973 and 1073 K with copper and ceria composite. The anode was designed as $Cu/CeO_2/YSZ$, with Cu primarily utilized as the current collector and the function of CeO_2 was to impart catalytic activity for the required oxidation reactions. These anodes were found to have inherently high redox stability, large sulphur tolerance and were operative with sulphur contents up to 400 ppm without losing its significance performance . Ceria-based ceramics are well known to exhibit mixed ionic and electronic conductivity in a reducing atmosphere due to reversible redox transition between Ce^{3+} and Ce^{4+}. Additionally, their excellent catalytic activities also correspond to ease in an oxygen-vacancy formation mechanism. Another effective method to increase the reforming reactions of hydrocarbon, i.e. to facilitate C–H bond breaking process is the addition of noble metals, such as Pt, Rh, Pd and Ru.

Catalytic applications

The tendency of oxygen uptake and release of ceria due to reversible transition between Ce^{3+} and Ce^{4+} makes this material a key ingredient for catalytic applications and reactions. Various nano-micro ceria structures have been fabricated, and their catalytic applications are extensively reported in recent years.

Carbon monoxide (CO) oxidation is the most exclusively studied reaction in this category. During CO oxidation, ceria nanomaterials can elevate the oxygen storage capability of catalysts at low temperatures. Generally, high surface area occupied nanomaterials are considered ideal for this application. The high surface area provides a greater tendency to active species to contact with reactants, and therefore an enhanced catalytic performance can be expected. There are different reports that discuss various morphologies to evaluate the CO oxidation performance. For instance, nanotubes exhibit inner and outer surfaces that unadventurously provide active sites for the reactants adsorption that leads to better catalytic performance in CO oxidation. On the other hand, nano-sized particles also exhibit high surface area, but demonstrate poor catalytic performance; while nanorods, with low surface area and larger diameter, were found to be more active in CO oxidation. This unusual behaviour of diverse morphologies is mainly attributed to the exposed planes. For example, the nanoparticles have dominant (111) exposed planes, whereas the nanorods' edges are terminated by (110) and (100) planes. The (110) and (100) planes are considered to be more active than the (111) plane and hence are found to express significantly enhanced redox properties required for excellent catalytic activities in CO oxidation.

Photocatalysis

Globally, efficient visible light photocatalytic water splitting is an active area of research for renewable energy as well as water and air purification. A novel and efficient Au-supported CeO_2 nanoparticle-based photocatalysts were fabricated, and its visible light activities were reported by Primo et al. Excellent photocatalytic activity of ceria nanoparticles was observed for oxygen generation from water .

Synthesis of CeO_2 NPs

Nanoparticles are synthesized through various physico-chemical methods.However, both methods require toxic solvents, high temperature, and pressure, which pose threats to the environment. Moreover, higher cost, laborious downstream processing, lesser biocompatibility, instability, and low yield make them further inefficient.There is a growing need to fabricate nanostructures which have the potential to solve these problems. Presently, researchers have exploited the green method to overcome all these challenges. For instance, plants, microbes, and other biological products have been used as reducing and/or stabilizing agents in the fabrication of ecofriendly NPs.CeO_2 NPs have also been synthesized using various physical, chemical, and biological methods. The latter is extensively utilized for its biomedical, pharmacological, and food applications due to their safe and biocompatible nature. Moreover, features like high yield, everlasting stability, and better morphologies can be obtained using a greener approach.

Green Synthesis from Plants

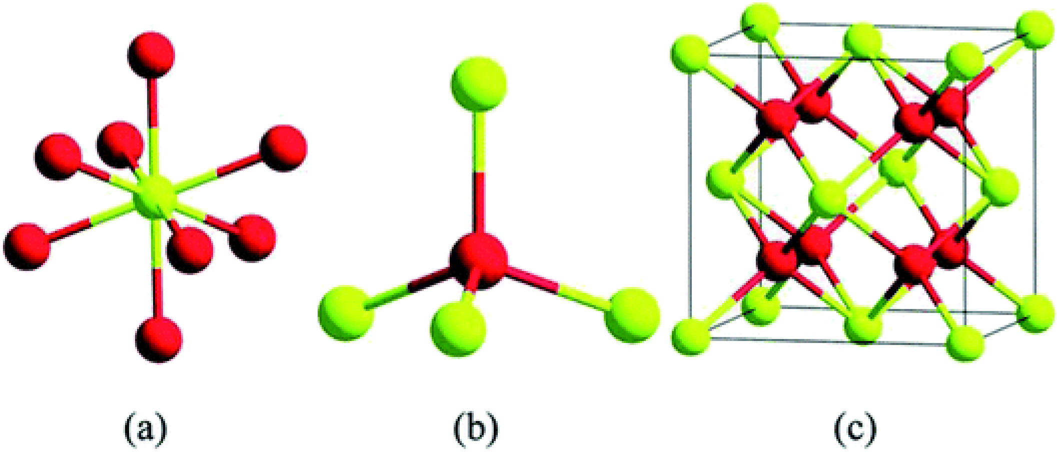
Green syntheses of CeO_2 NPs have been reported using plant extracts, microbial, and other biological derivatives. Plants in this regard have been the most efficient source due to their abundance, safe nature, and rich source of reducing and stabilizing agents. Various parts of plants such as leaves, flower, and stem have been used for the synthesis of CeO_2 NPs. Till date the majority of green synthesis studies have been conducted on leaves extracts, as it is a rich source of metabolites.A broad variety of metabolites/phytochemicals in plant extracts such as ketones, carboxylic acids, phenols, and ascorbic acid are used as reduction and stabilizing agents. Plants based CeO_2 NPs are produced through a simple approach in which bulk metal salt is mixed with the extract and the reaction completes in minutes to a few hours in ordinary lab conditions.[28,29,34] The metallic salt solution is reduced into respective nanoparticles via the phytochemicals whose synthesis is confirmed firstly through color change from colorless to yellowish, brownish, or whitish, and then characterized through various spectroscopic and imaging techniques.

Leaf extract of *Moringa oleifera L* was used to synthesize CeO_2 NPs with spherical morphologies and size of 100 nm. The synthesized NPs showed potential antimicrobial and wound healing properties. *Gloriosa Superba* leaf extract was used as a reducing and stabilizing agent in synthesis of CeO_2 NPs and has shown potential antibacterial properties.[37] *Hibiscus sabdariffa* natural extract yielded crystalline CeO_2 with a diameter of 3.9 nm.[30] Spherical shaped nanoparticles of size 63.6 nm synthesized from Gel extract of medicinally important plant *Aloe Barbadensis*.[38] The resultant CeO_2 NPs showed high antioxidant potential. Green synthesis of CeO_2 nanoparticles was demonstrated using *Jatropha curcus* leaf extract having high photocatalytic activity and a monodispersed shape of 3–5 nm. Spherical shaped cerium oxide nanoparticles are synthesized using Leaf extract of *Oleo Europaea*, with a size of 24 nm having high antimicrobial activity against both gram-negative and positive strains of bacteria. *Origanum majorana* extracts were used to synthesize CeO_2 NPs, having pseudo spherical shape (20 nm). FT-IR confirmed that the reduction is attributed to the presence of different phenolic and flavonoids compounds in the extract. CeO_2 was synthesized using *Rubia cordifolia* leaf fusions. Spectroscopic and microscopic analysis revealed hexagonal shaped NPs having a size of 26 nm. The biogenic CeO_2 NPs also showed excellent anti-cancer potential. Nano rod size ranges from 5–55 nm CeO_2 NPs resulted when *Pedalium murex* L. was added to the aqueous solution of salt at room temperature having high antibacterial activity. *China rose* petal was used as a robust bio template for the facile fabrication of novel ceria Nano sheet with a size of about 7 nm.[39] The deviation in size and morphology noticed among the reported studies might be due to the different influence of reaction temperature, pH, time, concentration of salt precursor or plants extracts, and part of the plant being used. Moreover, plants based CeO_2 NP's showed excellent stability at diverse conditions. For instance, green mediated ceria NP's remain stable at liquid solution and no physiochemical changes were observed. Similarly, biogenic CeO_2 NP's also showed high thermal stability at high temperature and remained stable for a longer period of time, which indicates their long durability and everlasting stability. Until now, various plants have been used in the biogenic synthesis of CeO_2 NPs

Physicobiochemical properties

Physicochemical properties

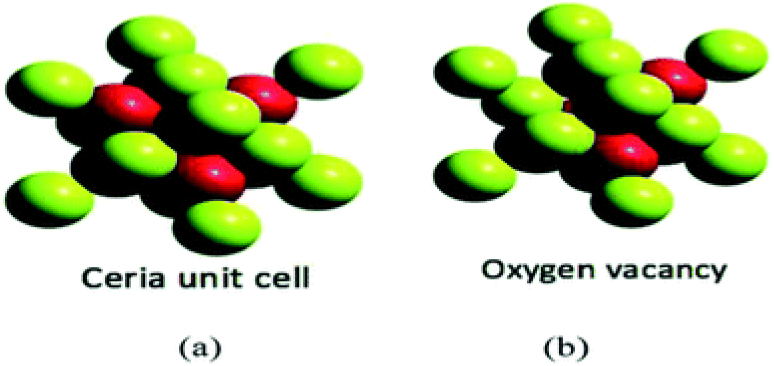
Cerium is the most abundant rare earth alkali element which is listed in the F block of the periodic table, and they are found in minerals, namely synchysite, hydroxyl bastnasite, monazite, zircon, rhabdophane, sallanite, and bastnasite. Cerium exhibits exceptional character of cycling between the two ionic states, which is Ce^{3+} and Ce^{4+}, and this is possible due to the presence of ground-state electron in the 4f (Xe $4f^1 5d^1 6s^2$) orbital which enables it to exhibit redox properties. Further, the cerium oxide nanoparticle (Ce_4O_8) is a face-centered cubic (fcc) fluorite lattice comprising of eight oxygen atoms bonded to the cerium atom, and the complete unit cell (Ce_4O_8) measures 5.1 Å on an edge. The building blocks of nanoparticles are the crystallite nature of the particle, and in the cerium oxide nanoparticle, polycrystallinity is more common. Generally, the crystallite unit depends on the synthesis method, and the crystallites are analyzed through the X-ray diffraction technique. Moreover, hierarchal assembly of the unit's cells into crystallites and crystallites to particles can be done by self-assembly of particles into sheets, rods, hollow variants, *etc.* which are larger structures.



Density and molar mass of cerium is 6.770 gm cm^{-3} (approximately) and 140.12 g mol^{-1} respectively; it is malleable and at room temperature oxidizes very readily. It also shows excellent thermal properties with melting and boiling temperature of 798 °C and 3424 °C respectively. Cerium in its oxide form represents the cubic fluorite structure, and at the nanoscale range, it maintains the same structure along with oxygen deficiencies, which provide it with redox reaction sites. Further, the cubic fluorite structure shows three low-index planes (100), (110), and (111), and the dipole moments perpendicular to the surface shows charged plane, neutral, and none respectively. Interactions between the adsorbed molecules with the cerium's surface are dependent on the crystal surfaces and plane properties exhibited by the cerium nanoparticles. The structure also enhances the catalytic property. Unlike the (100) and (111), (110) does not present the o-terminal endings, rather it has a Ce center with O-ions (C1, C2). The ability of cerium oxide nanoparticles to exists in +3 and +4 valence states helps them to exhibit two oxidation states, which are Ce^{3+} and Ce^{4+}. Cerium oxide is highly unsaturated, which contributes to the instability and promotes restructuring of the surface. Further, this also affects the microstructure and physicochemical environment, which affects their chemical reactivity. They can also switch between two oxidation states that are from trivalent +3 to tetravalent +4, giving them the capability to show redox reactions. The elimination of the oxygen ions by cerium oxide leads to the non-stoichiometric and reduced metal oxide, which clears the presence of certain binding energy between Ce^{3+} and oxygen atoms.

Oxygen vacancy

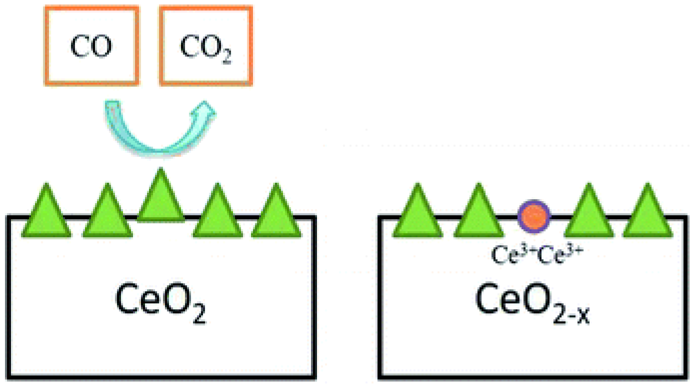
Esch and co-workers utilized scanning tunneling microscope to determine the oxygen vacancy, and clustering of oxygen on the (111) surface of CeO_2 and further, this study revealed a better understanding of rare-earth oxides reduction by oxidation. The absence of one or more oxygen atom from the eight octants found in the ceria unit cell is the concept of oxygen vacancy . The debate on the charge which cerium atom has and their link with oxygen vacancies, till date, is unanswered but many researchers have made some assumptions like the single oxygen vacancy is due to the reduction of the Ce^{4+} atoms, and the location of resulting Ce^{3+} atom will be adjacent called as a triplet, and the reason behind this is size and the method utilized to synthesize crystals of ceria. Further, many researchers have tried to determine the Ce^{3+} concentration value, but all the results were contradicting and varying.Hence, it can be considered that particle size decides the percentage of cerium atoms; the particle size when decreases, the percentage of cerium atom increases and *vice versa*.



(a) (b)

Measurement of the Ce^{3+}/Ce^{4+} ratio can be useful to understand the concentration of oxygen vacancy. Oxygen vacancy can construct itself, and they can also be quantified by a numeral called oxygen storage capacity (OSC). This numeral can be expressed as oxygen micromoles released per-gram of starting material. The OSC value of cerium dioxide in the gas phase is 1452.47 μmol per O_2 per g and can be explained from the below-mentioned equilibrium reaction:$CeO_2 \leftrightarrow CeO_{2-x} + x/2O_2$ for $x = 0.5$ then $CeO_{1.5}$ (Ce_2O_3)(1)

Further, commonly used cerium oxide is prepared as micro- or nano-scale crystals but not as a gas phase molecule. The entirely reduced commercial cerium oxide can be just a fraction of the OSC value calculated theoretically in eqn (1). OSC equilibrium equation signifies a reversible reaction and it justifies that this material can act as a catalyst, as it’s an idea that is fundamental. Indeed, solid cerium oxide particles can be assumed as oxygen buffer; this provides/removes oxygen from the surrounding environment by reacting to lack/excess of oxygen in the existing environment. This ability to extract oxygen atoms reversibly from the lattice can be utilized for catalytic oxidation of various materials, namely CO and other exhaust gases which are partially oxidized .



There are two different thoughts for the mechanism of cerium oxide on the SOD-mimetic and hydrogen peroxide catalase. The initial thought is that the Ce^{3+}/Ce^{4+} ions, interact directly to neutralize superoxide and destroy peroxide, and this is known as the ionic mechanism. The other thought is that SOD-mimetic and hydrogen peroxide catalase reactions proceed by annihilation and oxygen vacancy creation with the cerium ionic states by interchanging between +3 and +4 to support the oxygen vacancy state. Further, referring to the ionic mechanism, the SOD mimetic component is favored by an increase in the Ce^{3+}/Ce^{4+} ratio, and on the other hand, catalase reaction is favored by a decrease in this ratio. Apart from focusing on ratios of ions, let's explore the thermodynamic aspect of the Ce^{3+}/Ce^{4+} in detail by investigative dynamic reaction chemistry. The unique and complete balanced reaction is embodied in the eqn (2) and (3), which represents the SOD-catalytic like dismutation reaction.$3Ce^{4+} + 3O_2^- \rightarrow 3Ce^{3+} + 3O_2$ (Ce^{4+} reduction)(2)$Ce^{3+} + O_2^- + 2H^+ \rightarrow Ce^{4+} + H_2O_2$ (Ce^{3+} oxidation)(3)

Size and reactivity

The size of the nanoparticle does matter in case of the reactivity, and if the cerium oxide nanoparticle size is small, it shows a greater lattice expansion which further leads to reabsorption and decline in oxygen release; this was explained using a comparison between lattice expansion of bulk ceria with cerium oxide nanoparticle.

Lattice doping

The doping of transition metal and lanthanide in the cerium oxide nanoparticle's sub-lattice helps in the prediction of oxygen vacancy defect concentration and particle reactivity in cerium. When the La ion was doped with the cerium oxide, the oxygen vacancy increased with the increase in the surface area. Interestingly, another study showed a decrease in the oxygen vacancy concentration when doped with the smallest atomic radii ion (Yb).

Considering a point that which type of cations can be doped in cerium lattice, for the same, it can be assumed that cations with low ionic radii than cerium ion can be the ideal candidate for doping, but this is not always true. The thermodynamic aspect specially enthalpy of incorporated dopant must be taken into consideration, in this regard modern computational quantum mechanical methods can be useful. Further, K. Reed *et al.* investigated and found that substitution of the small iron atom of 78 pm to 97 pm cerium was endothermic by 4.3 eV per Fe_2O_3 unit, but in the case of 116 pm lanthanum, the substitution was exothermic by 3.3 eV per La_2O_3 unit. Hence, from the studies, its well understood that approx. 2–4% of iron is doped into cerium lattice in low-temperature conditions, and the iron associated was in amorphous form.

Catalytic activity

Cerium oxide nanoparticles are very capable of maintaining their catalytic behavior in harsh environments; they can also decompose ROS by the action of catalysation. Cerium oxide nanoparticles have low $3^+/4^+$ ion ratios and thus show high catalyse mimetic activity, which is responsible for the decomposition of a potentially harmful oxidizing agent known as H_2O_2 and produces H_2O and O_2. H_2O_2 is the product generated from the superoxide, which is produced in the mitochondria during the NADPH oxidases. From the earlier experiments, it is well known that cerium oxide nanoparticles depend on the size, morphology, *etc.* of the particle to show catalytic effects. Researchers revealed that the Ce^{4+} reduced by H_2O_2 accomplishes by the initial reduction of Ce^{4+} into Ce^{3+}. The catalyse type activity is supposed to rely on the Ce^{4+} fraction, and further studies have shown that the smaller surface area of large Ce^{3+} fraction enhances the enzyme-like catalytic activity.An investigation was performed to identify the key factors which affect the catalytic activity of cerium oxide nanoparticles, and this study also showed adsorption of H_2O_2 on cerium oxide nanoparticles surface. The observation of this study shows that the efficacy of the disproportionation process is modulated by adsorption of the H_2O_2 molecules on cerium oxide nanoparticles surface and this depends on the particle size.Hence, cerium oxide nanoparticles depend on the surface area to the volume ration, giving them the capability to act as a catalyst. The increase in the surface area to volume ration is considered as the major reason behind the extraordinary catalytic activity of the cerium oxide nanoparticles