Cerium Oxide Nanoparticles: Properties, Synthesis, Applications, and Future Perspectives

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Introduction:

Cerium oxide nanoparticles (CeO_2 NPs), commonly known as nano ceria, have emerged as one of the most extensively studied rare-earth nano materials due to their remarkable physicochemical properties, including reversible Ce^{3+}/Ce^{4+} redox behaviour, high oxygen storage capacity, excellent thermal stability, and strong catalytic activity. These characteristics originate primarily from the defect-rich fluorite crystal structure and high surface-to-volume ratio at the nano scale. CeO_2 nanoparticles have found widespread applications in heterogeneous catalysis, environmental remediation, energy conversion and storage devices, biomedical science, sensors, and industrial polishing processes. This review comprehensively discusses the structural, electronic, and surface properties of CeO_2 nanoparticles, various synthesis strategies, and their diverse applications. Additionally, toxicity concerns, challenges in practical implementation, and future research directions are critically analyzed.

Keywords: Cerium oxide nanoparticles, nano ceria, oxygen vacancies, catalysis, biomedical applications, energy materials

Introduction :

Basically, nano materials have totally changed material science because we can now mess with stuff at the tiny nano meter level. At this size, materials act pretty differently, physically, chemically, and biologically, compared to when they're in bigger chunks. Out of all the nano metal oxides, cerium oxide, or CeO_2, is a big deal because it's got this really cool way of handling oxidation and reduction, and it's super stable [1,2].

One such lanthanide element is cerium, which may readily transition between being Ce^{3+} and Ce^{4+}. For any process involving these kinds of chemical reactions, CeO_2's ability to essentially grasp and release oxygen is fantastic. When you shrink CeO_2 down to nano size, it gets a lot more surface area, more places where oxygen can be missing (called vacancies), and it just reacts better. That's why you see it used everywhere, like in car exhaust systems, fuel cells, for polishing stuff, as an antioxidant, and even in medicine [3,4].

This review aims to present a detailed overview of CeO_2 nanoparticles, covering their fundamental properties, synthesis routes, applications, toxicity concerns, and future prospects.

Crystal Structure and Properties

Cerium, which comes after lanthanum, is the second most abundant element in the lanthanide group, and it's also the most reactive among them. Both the +3 and +4 oxidation states are present in this electropositive ion. Compared to Ce_{+3} ([Xe] $4f_1$), the Ce^{4+} ion is more stable due to its empty f- orbital ([Xe] $4f_0$). Cerium oxide (CeO_2) and cerium sesquioxide (Ce_2O_3) are the two most frequent forms of cerium. The most stable of them is cerium oxide (CeO_2), which has the space group F3m3 and a face-centered cubic fluorite structure.

In this structure, cerium ions are situated in alternating cube centers within a simple cubic oxygen lattice, with each metal ion being surrounded by eight oxygen atoms. Pure ceria, which has a 5 eV band gap, can become a decent N-type semiconductor when crystal defects and impurities are introduced. Research and data suggest that CeO_2 isn't purely an ionic compound. Studies using optical reflectance and photoelectron spectroscopy reveal a significant metallic characteristic in the oxide, even after the metal and oxygen orbitals have hybridized and the valence band is largely composed of oxygen's 2p character. This indicates that the formal charge on the metal cation is less than +4, suggesting that CeO_2 can be described as an ionic covalent compound [8,9].

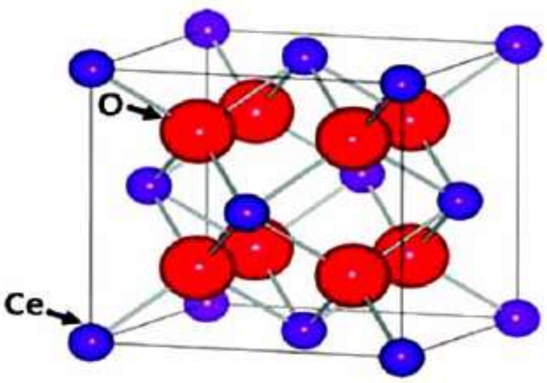

Fig.1 Cubic fluorite structure of cerium oxide

CeO_2 is a wide bandgap semiconductor with a bandgap of 2.8–3.5 eV. The presence of Ce^{3+} ions and oxygen vacancies introduces defect states within the bandgap, influencing electrical conductivity and optical absorption [10,11].

Nano ceria exhibits:

- Mixed ionic and electronic conductivity
- Strong UV absorption
- Size-dependent photoluminescence behaviour

These properties are crucial for photo catalysis, sensing, and energy applications.

Synthesis Methods for Cerium Oxide Nanoparticles

Chemical Synthesis Methods

Sol–Gel Method

The sol-gel method is the process of forming inorganic compounds through chemical reactions in solution at low temperatures. In this process, there is also a phase change from colloidal suspension (sol) to form a continuous liquid phase (gel). After the gel is formed, ripening will occur which can occur in a few days. Finally, the gel will be processed at high temperatures to decompose organic compounds and remove volatile reagents to produce nanoparticles. The sol–gel technique involves hydrolysis and condensation of cerium precursors, followed by drying and calcination. This method offers excellent control over particle size and homogeneity but requires careful temperature control [12,13].

Precipitation and Co-precipitation Methods

Cerium salts are precipitated using alkaline agents in this straightforward and scalable process. Despite being economical, particle agglomeration is a frequent problem. The most used technique for creating CeO_2 nano particles is the precipitation approach. This process typically uses cerium nitrate hexahydrate as the precursor for the synthesis of CeO_2 nano particles in the presence of bases such potassium carbonate (K_2CO_3), sodium hydroxide (NaOH), ammonium carbonate ($(NH_4)_2CO_3$), and ammonia solution. Usually, the co-precipitation process yields nanoparticles that are more pure and have a smaller size distribution. This is because more uniform particle nucleation and growth are made possible by the simultaneous mixing of the precursor and the precipitating agent. However, compared to the precipitation approach, the co-precipitation method is typically more complicated and time-consuming [14–16].

Hydrothermal and Solvothermal Methods

These methods employ high-temperature and high-pressure conditions to produce well-crystallized nanoparticles with controlled morphology such as nanorods, nanocubes, and nano spheres. A solvothermal process is a process inducing a decomposition or a chemical reaction between precursors in a closed reaction vessel with the presence of a solvent at a temperature higher than the boiling temperature of the solvent. Hydrothermal engineering is becoming one of the most important tools for advanced material processing, mainly because of its advantages in processing nanostructured materials for various technological applications such as electronics, optoelectronics, catalysis, ceramics, magnetic data storage, biomedicine, bio-photonics, etc. The hydrothermal technique not only helps in the processing of monodispersed and highly homogeneous nanoparticles but also acts as one of the most interesting techniques for processing nano-hybrid materials and nano composites [17,18].

Combustion Synthesis

Combustion conflation produces nano-crystalline CeO_2 with great purity by exothermic redox reactions between essential nitrates and energy. For the conflation of CeO_2 nano particles, the outcome combustion system is an easy-to-use and efficient system. It entails burning a substance that contains cerium chloride or nitrate and energy comparable to that of glycine or urea. The heat produced by the exothermic combustion response is enough to propel the conformation of CeO_2 nano particles. The reaction takes only a few seconds, and the end result is a fine CeO_2 greasepaint. The resulting combustion apparatus for the conflation of CeO_2 nano particles is easy to use and reasonably priced. It is a quick system that also requires very low temperatures and has a short response time [19,20].

Green Synthesis Methods

Green synthesis employs biological agents such as plant extracts, bacteria, fungi, and algae. These techniques:

- Minimize the impact on the environment
- Enhance the biocompatibility
- Steer clear of hazardous substances

The use of green-synthesised CeO_2 nanoparticles in biomedical applications is being more and more investigated. The green synthesis of CeO_2 nano particles from various sources has been the subject of numerous investigations. An affordable, environmentally responsible, and secure substitute for conventional chemical synthesis techniques is the green synthesis of CeO_2 nano particles. Cerium ions are reduced to cerium oxide in the production of CeO_2 nano particles using natural plant extracts or other biological agents [21, 22].

Applications of Cerium oxide nanoparticles

Catalytic Applications

Ceria is an essential component for catalytic applications and reactions because of its propensity for oxygen uptake and release brought on by the reversible transition between Ce^{3+} and Ce^{4+}. Numerous nano-micro ceria structures have been created, and in recent years, their catalytic uses have been widely documented. In three-way catalytic converters, CeO_2 nanoparticles are essential parts that control oxygen content, promote the oxidation of CO and hydrocarbons, and lower NOx emissions [23, 24].

Nano ceria finds extensive application in:

- Oxidation of CO
- Reaction of water-gas shift
- Reforming methane
- Conversion of biomass

Its strong heat stability and oxygen mobility greatly improve catalytic activity.

Environmental Applications

Water Treatment: Photo catalysis

A promising approach is to transfigure carbon dioxide (CO_2) into renewable, high value-added products with minimum environmental impact and maximum effectiveness. Numerous problems, including energy dearths and environmental declination, are caused by high CO_2 situations, but this can help. Photo catalytic reduction styles are a promising technology for working these problems. Cerium dioxide (CeO_2) is one of the most important rare earth oxides, and cerium dioxide grounded print catalysts have gained a lot of attention in recent times due to their distinctive features, similar as their tunable electronic structures and their excellent print catalytic performances. Still, the wide energy band of cerium oxide limits its application of light. Colorful strategies uses for the revision of cerium oxide, encompassing external snippet doping, hetero structure fabrication, disfigurement fabrication, and crystal clear aeroplane modulation, to ameliorate the catalytic performance of CeO_2 [25- 27].

Cerium oxide print catalysis uses CeO_2's semiconductor parcels, especially its tunable bandgap and capability to switch between Ce^{3+}/ Ce^{4+} countries, to induce reactive oxygen species (ROS) under light, driving environmental remediation like contaminant declination(colorings, organic composites, Cr (VI)) and CO_2 conversion, frequently enhanced by doping or compound conformation(e.g., with graphene) to boost visible light immersion and catalytic spots, making it promising for wastewater treatment and solar energy product [27,28].

Energy Applications

Solid Oxide Fuel Cells (SOFCs)

Solid oxide fuel cells (SOFCs) are considered to have great eventuality in furnishing clean and dependable electric power; thus, exploration in this area attracts great attention in recent times. Numerous reports suggest that ceria-grounded ion operators retain huge resistance to carbon deposit and have implicit to allow impregnable force of dry hydrocarbon energies to the anode. CeO_2 grounded accoutrements are used as electrolytes and electrode factors due to the high ionic conductivity, chemical and thermal stability and the reduced operating temperatures [29,30].

Batteries and Super capacitors

CeO_2 nanoparticles enhance electrode stability and electrochemical performance in lithium-ion batteries and cold-blooded super capacitors. Cerium oxide (CeO_2) shows great pledge in batteries and super capacitors due to its excellent redox parcels (Ce^{3+}/ Ce^{4+}), low toxin, and environmental stability, acting as a mock capacitive material for high charge storehouse, though its innately low conductivity and face area bear mixes (with graphene, carbon nanotubes, or other essence oxides) to significantly boost performance for practical energy storehouse bias [31,32].

Hydrogen Production

Nano ceria plays a crucial part in thermochemical water- splitting cycles and catalytic hydrogen generation. Cerium oxide (CeO_2) is pivotal for advanced hydrogen product, primarily through solar thermochemical water splitting(two- step cycle heat to release O_2, also reply with brume for H_2) or as a catalyst enhancer, using its unique capability to cycle between Ce^{3+} and Ce^{4+} countries, creating oxygen vacuities that grease redox responses and ameliorate oxygen exchange. It boosts hydrogen yield by enhancing oxygen storehouse, modifying catalyst electronic structures, and cranking biomass in gasification processes, offering implicit for effective, sustainable hydrogen generation [33,34].

Biomedical Applications

Cerium oxide nanoparticles have also been used in biomedicine as antibacterial, antioxidant, and cancer treatments. It has been discovered that cerium is a long-lasting and promising biocide for stopping bacterial infections. Compared to other metal ions, its distinct antibacterial action and greater safety for human cells make it a suitable choice for a range of biomedical applications. Since numerous research have reported diverse designs of cerium-related nano materials against pathogenic bacteria, cerium and cerium oxide-based antimicrobials have garnered a lot of attention [35–37].

Sensors and Industrial Applications

Gas and Biosensors

Cerium oxide is an excellent material for both gas and humidity sensing due to its high oxygen storage capacity, oxygen vacancy properties, and good electrical conductivity, enabling high-sensitivity detection of gases like CO, H_2S, and various VOCs, as well as precise monitoring of relative humidity with fast response/recovery times, often enhanced by nano structuring or compositing with other materials for improved performance [38,39].

Also the Cerium oxide nanoparticles are excellent biosensor materials due to their unique redox properties, enzyme-mimetic activities (like peroxidase, SOD), large surface area, and biocompatibility, enabling highly sensitive detection of biomarkers, DNA, metal ions, and food spoilage markers through electrochemical, optical (colorimetric, fluorescent), and chemi/luminescent methods, acting as recognition/transducer elements in simplified, cost-effective diagnostic platforms [40,41].

Polishing and Protective Coatings

Nano ceria is considerably used in chemical mechanical polishing and as UV- blocking and erosion- resistant coatings. It's a superior, fine abrasive used for high- perfection polishing (glass, optics, semi-conductor) to achieve ultra-smooth, clear homestretches, removing scrapes and defects without damage. It also serves as an advanced defensive coating, particularly for aluminium and magnesium blends, offering excellent erosion resistance by forming a stable, unresistant subcaste that enhances continuity and performance in colourful artificial operations [42-45].

Challenges and Future Perspectives

Key challenges include:

- Controlling defect concentration
- Preventing agglomeration
- Long-term toxicity assessment
- Scalable green synthesis

Future studies should concentrate on multifunctional composites and safe-by-design nano ceria. [46].

Conclusion :

Cerium oxide nanoparticles represent a multifunctional material with immense eventuality across catalysis, energy, environmental remediation, and biomedicine. Advances in conflation, functionalization, and safety evaluation will further enhance their real- world connection. Although there are still some undetermined issues and challenges, the unique physical and chemical parcels of Cerium oxide nanoparticles and the achieved significant advances of it easily demonstrate that Cerium oxide nanoparticles is a fascinating and protean material that's promising for multitudinous artificial and biomedical operations

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