



The role of ceria-based nanostructured materials in energy applications

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Ceria (CeO_2) is enjoying increasing popularity in catalytic applications, and in some cases has established itself as an irreplaceable component. The reasons for such success stem from the intrinsic structural and redox properties of ceria. Reducing the ceria particles to the nanoscale has a profound impact on the catalytic behavior. The proliferation of improved synthetic methods that allow control over the final morphology and size of the nano-structures is opening new possibilities in terms of catalytic potential, particularly for energy-related applications.

Introduction

The fast growth rate of the world population is one of the core factors accounting for the exponential increase in the yearly energy consumption. As of today, the main energy sources fulfilling global demands derive from stock or fossil fuels. However, there are rising concerns over the projected shortage of such energy supplies at the current level of *per capita* usage.

For this reason, the discovery of alternative energy sources has become a main priority in the scientific community, prompting the development of new technologies able to quench the energy thirst in the short- to medium-term future. In particular, emphasis is being given to those technological discoveries that embrace sustainability and environmental issues; in this context, there is large consensus among researchers that renewable energy sources are the only way forward to guarantee the consistent welfare of human society [1,2].

Since the 1980s, cerium dioxide, commonly known as “ceria”, has established its role as one of the most promising materials for environmental and energy applications. From an environmental point of view, CeO_2 (and more specifically the mixed oxide $\text{CeO}_2\text{-ZrO}_2$) has gained an irreplaceable role as a promoter in three-way catalysts (TWCs) for the emission control of auto-exhaust polluting gases [3–5]. In addition to this major application, there are significant examples where CeO_2 -based systems have proved to be outstanding components in the energy sector. In this context,

the latest advances have converged towards one desirable characteristic: the reduction of CeO_2 structure size to the nanoscale level.

The goal of this review is to provide some key examples on the synthetic methods to access nano-structured ceria and their use as building blocks in the hierarchical assembly of high-ordered structures. Finally, energy applications where CeO_2 nanostructures are increasingly acquiring a central role will be highlighted.

Key properties of CeO_2

Cerium has two stable oxidation states, +4 and +3, and the relatively ease of switching between these two states is the essential factor for its catalytic activity. This rapid change of oxidation state is related to its ability to store and release oxygen, a property measured by the “oxygen storage capacity” (OSC). The typical fluorite-type structure of CeO_2 is retained through the temperature range from room temperature to the melting point. However, the Ce–O phase diagrams show that under reduction conditions, CeO_2 can release oxygen, undergoing phase transformations to a series of reduced oxides (CeO_{2-x}). The process is reversible and the re-oxidation to CeO_2 occurs at higher oxygen pressures [6]. In other words, ceria can act as an efficient oxygen buffer (Fig. 1).

The mobility of oxygen ions in ceria materials is another essential aspect for catalysis and electrochemical purposes [7]. Oxygen ion diffusion is closely linked to the structural defects present in the materials [8]. Distinctive types of defects that are important in catalytic applications are the oxygen vacancies ($V_{\text{O}}^{\bullet\bullet}$), which can be introduced by doping the ceria lattice with oxides of metals with oxidation state lower than (IV) and lead to enhanced ionic

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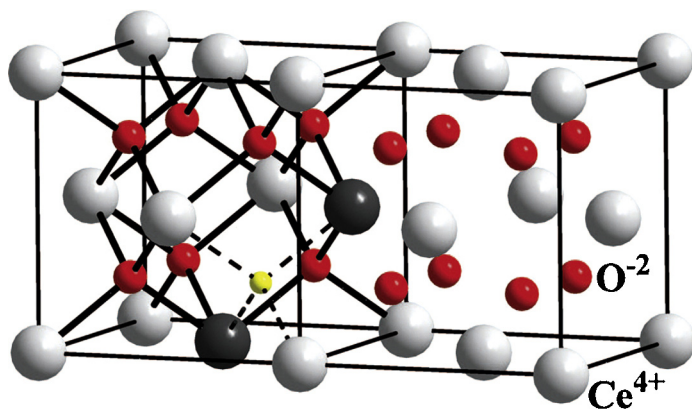


FIGURE 1

Crystal structure of doped ceria, showing undoped CeO_2 (right cube), and lanthanide-doped CeO_2 (left cube) with an oxygen vacancy (small sphere). Reprinted from ref. [10] with permission from the Copyright (2006) National Academy of Sciences, USA.

conductivity [9,10]. It is worth mentioning that other molecules can be stored within the ceria bulk, and be exploited for important energy- or environmental-related catalysis. For example, CO is one molecule that can be readily stored and this gives rise to the possibility of using ceria-based materials for processes such as CO preferential oxidation (CO-PROX) [11,12]. The stored CO can also be used to reduce environmentally malign species such as NO [13]. Quantum mechanical simulations have been used to explain the mechanism of the storage, release and transport [14].

Nano-structured ceria-based materials: synthetic methods

Upon decrease of the particle size, distinct physical and chemical properties as compared to bulk materials arise. One such property, very important in catalysis, is an increase of lattice constants (lattice relaxation), associated with the compositional and local structural changes from fluorite-type (CeO_2) to sesquioxide-type (Ce_2O_3), and consequently an increase of the oxygen vacancy content [15,16]. Hence, mobility of oxygen ions is increased.

Tailoring the shape of the nanoparticles has become a central consideration in the assembly of CeO_2 -based materials. Indeed, despite the cubic phase of the fluorite structure and therefore its isotropicity, the different facets are not equal with respect to the atomic arrangement. As a result, maximization of the exposure of certain facets can lead to significant improvements in catalytic performances. Efforts are being made to find a correlation between the surface science relative to the exposed facets and the material science for heterogeneous catalysis [17]. The surface chemistry of ceria also includes theoretical studies [18].

The development of a large arsenal of synthetic methods for the preparation of CeO_2 nanoparticles has given access to a variety of geometries including materials with zero-, one-, two- and three-dimensional control of nanostructures [19].

Zero-dimensional (0D) nanoparticles are most straight forward to obtain, given the absence of a preferential growth direction of the fluorite-type seeding crystals. Trivially, CeO_2 nanopolyhedra are synthesized by applying standard protocols applied to nanoparticles of other materials. Co-precipitation exploits the extremely low solubility of ceria and is a simple and valuable technique. It

is carried out in alkaline solutions with NaOH [20], urea [21], ammonia [22], etc. as precipitating agents. To avoid quick precipitation of too small-sized crystals the presence of surfactants such as cetyltrimethylammonium bromide (CTAB) [23] or polyvinylpyrrolidone (PVP) [24] is required, allowing better control of the particles dimensions.

Structures of higher dimensional complexity (1D, 2D and 3D) are synthetically more demanding and require accurate fine-tuning of reaction conditions. Their preparation is based on the two-stage sequence of nucleation and controlled crystal growth, both important to determine the final architecture. During nucleation, formation of many small crystallites takes place, and surface energies play a pivotal role in ensuring crystal size increase. In the second stage, aggregation of the crystals occurs and needs to be controlled in order to direct the assembly towards the desired structure.

1D CeO_2 nano-particles undoubtedly represent the most studied type of structure on account of their peculiar physical properties and their potential as components in nanodevices [25]. Accessible architectures include nanowires, nanotubes, nanorods and nanospindles and many 1D materials have been reported, together with studies of the mechanisms of formation [26,27].

In general terms, the assembly relies on two approaches differing in whether the procedure involves use of a surfactant or not.

Surfactant-free methods exploit capping agents that can specifically protect some facets during nucleation, thus altering surface energies and breaking the isotropicity of the face-center cubic system. Even simple counter-anions such as Cl^- and NO_3^- have been shown to direct the synthesis towards nanospheres, nanowires or nanorods by preferential interaction of the anion with one crystallographic facet (Fig. 2) [28,29].

In the surfactant-assisted approach, instead, the role of the surfactant is to act as a template, favoring anisotropic growth along a specific direction by spatial confinement (hard template method) or by means of preferential interaction of one surface plane with surfactant micelle systems that spontaneously self-assemble into 1D structures at critical concentrations (soft template method).

Popular hard templates for 1D geometries include anodic aluminium oxide (AAO) [30] and polycarbonate membrane filters [31]. Carbon nanotubes (CNTs) have also emerged as intriguing removable templates [32,33].

Templating by soft surfactants appears to be a more versatile method to build mono-dimensional arrangements, and a large variety of soft templates has been reported to efficiently assist formation of 1D morphologies. Common soft templates include CTAB, oleylamine, polyvinylpyrrolidone (PVP), ethylenediamine, ethylene glycol, alkyltrimethylammonium salts and others.

It must be noted that the (soft) template approach is a general technique and features chemical species that are not specific for a single type of structure, but the final geometry rather evolves by the applied synthetic conditions. Therefore, several parameters such as temperature, reaction time, cerium precursor, surfactant/cerium ratio, pH, etc. can decisively affect the final outcome, with discrimination also encompassing possible 2D and 3D structures formation.

Indicative examples include the formation of CeO_2 nanowires and nanorings assisted by sodium bis(2-ethylhexyl)sulfosuccinate (NaAOT) [34,35] and the ethylene glycol-mediated assembly of

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