Nanoceria

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Abstract

Cerium oxide nanoparticles (CeO_2NPs or nanoceria) is an inorganic material with many of applications and more to come. Besides being rather a chemically inert ceramic, its flurite-like electronic structure (Fig. 1) confers it a variety of interesting properties, making nanoceria one of the most interesting NPs in industry and biomedical research. What makes nanoceria very appealing is its high capacity to buffer electrons from an oxidant/reducing environment, which is due to its easy ability of being oxidized and reduced, from Ce^{3+} to Ce^{4+} and vice versa [1], followed by the capture or release of oxygen, or oxygen species (as OH·).

Since redox reactions are an important class of chemical reactions encountered in everyday processes, CeO_2 NPs are widely used in a range of industrial applications as combustion of fuels, environmental remediation [2], water purification [3], catalysis [4] and many others.

A special interesting case is metabolism where partial reduction of oxygen produces by-products, known as reactive oxygen species (ROS) including superoxide anion (O^{2-}), hydrogen peroxide (H_2O_2) and the hydroxyl radical ($OH^{\cdot}$). On one hand, ROS are an antibacterial tool in case of infection; on the other hand, high amounts of ROS are toxic for humans and the environment. Unfortunately, the heightened levels of ROS can damage significantly cellular integrity, by inducing chronic inflammation, lipid peroxidation, DNA damage, damage of oxidation sensitive proteins, or even trigger cell death (apoptosis) by a metabolic flux disruption. Therefore, the oxygen storage capacity of CeO_2NPs becomes highly useful to remove them as soon as they are generated, in situation of ROS disbalance. That property makes nanoceria a potential candidate as a therapeutic tool in prevention and treatment of a wide range of human diseases with ROS disbalance, such as: cancer, diabetes mellitus, cardiovascular disease (CDV), age-related macular degeneration (AMD) and ophthalmology. Moreover, the overproduction of ROS is critical in neurodegeneration, including Alzheimer, Parkinson, Huntington, schizophrenia among others.

What is clear is that there is a strong correlation between the cellular effects of the NPs and their engineering, including the preparation method, morphology (size, shape, surface composition, contaminants) and aggregation state of the nanoparticles [5].

Regarding its uses in medicine, morphology determines biodistribution and reactivity, therefore, for the hard task of performing precise work within the biological machinery, a fine morphological control of CeO_2 nanoparticles and their aggregation state is needed, since it drives the reactivity, colloidal stability, interaction with proteins and pharmacokinetics of the nanoparticles within the organism.

Up to now many of labored protocols of nanoceria synthesis have been described, such as high-temperature thermolysis of cerium salts, mechanochemical reactions, gas-phase methods, non-isotermal precipitation, supercritical synthesis methods, hydrothermal synthesis, sol-gel, flame-spray pyrolysis and solvothermal method, between others. Many of them require multiple steps, as use of high temperatures, refluxing, sonication or product drying. Nowadays, the wet-chemical preparations have become one of the most widely used methods of synthesis of CeO2 nanoparticles. Even so, an obtaining of pure and monodisperced CeO2 nanoparticles, with a reproducible size-control is still a challenge, since its is a highly reactive nanomaterial and tends to suffer changes in size, morphology and aggregation state (Fig.2).

Therefore, we focused our study in an understanding of the kinetic behavior of the formation of nanoceria, in order to be able to control the purity, size and aggregation state of the obtained material.

In this study we describe a preparation of CeO_2 nanoparticles in aqueous phase by a kinetic control of Ce^{3+} oxidation at room temperature. We also try to give explanations of the nucleation, selective attachment and aggregation phenomena of the nanoceria and propose storage conditions suitable for their bio-medical or industrial purposes. The size-dependent reactivity, scalability and bio-compatibility are also analyzed.

References

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Figure 1

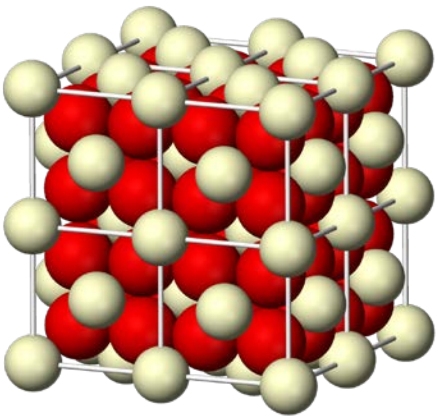

Figure 2

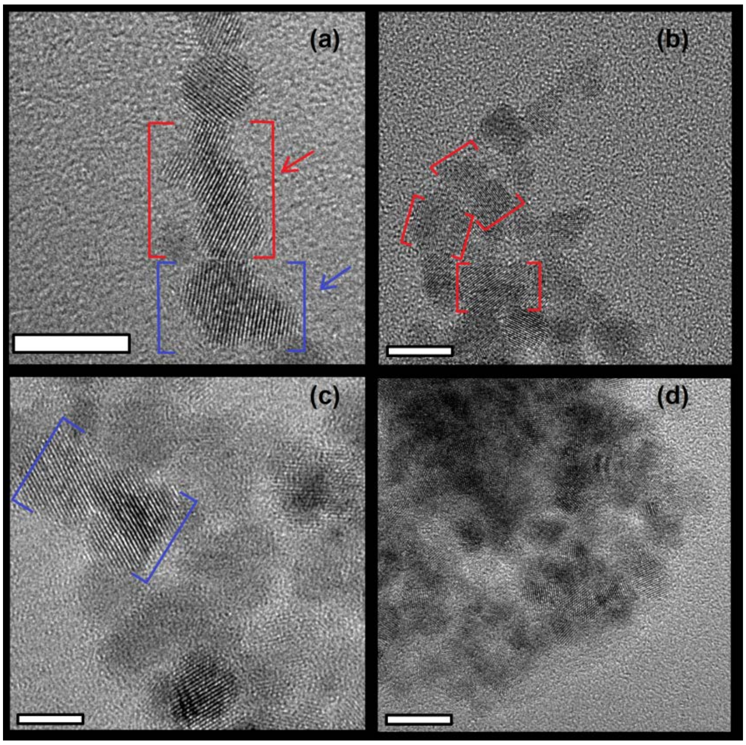

Figure 1. Electronic structure of CeO_2NPs fluorite structure, containing 8 coordinate Ce^{4+} and 4 coordinate O^{2-} .

Figure 2. HR-TEM imaging of CeO_2NPs, showing the instability of nanoceria, reflected in phenomenas as selective attachment (red brackets in (a) and (b)), morphological changes of the NPs (blue brackets in (a) and (c)) and aggregation (d).