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ORIGINAL CONTRIBUTION

Ceria Nanoparticles, a Mixed Valent Oxide Material

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(Received Date 25th May 2016; Revised Date 30th June 2016; Acceptance Date: 06th July 2016)

ABSTRACT

We report a simple room temperature based aqueous route to synthesize nearly mono-dispersed ultra small (~ 3 nm) ceria nanoparticles (NP). The NPs were characterized by using X-ray diffraction and transmission electron microscopy to ascertain their crystalline phase and sizes. Detail x-ray photoelectron spectroscopic studies revealed the mixed valent state of the ceria NPs. It was observed that the despite of possessing the CeO₂ crystal structure the NPs contained a mixture of Ce³⁺ and Ce⁴⁺ valencies.

KEYWORDS—Ceria, Nanoparticles, Mixed valent oxide

1. INTRODUCTION

Cerium oxide (ceria, CeO₂) is a rare earth oxide that has attracted a great deal of interest owing to its unique properties, including high mechanical strength, oxygen ion conductivity, and oxygen storage capacity, autocatalytic property and free-radical scavenging property.¹⁻¹⁴ Because of these characteristics, ceria has been widely used as an oxygen ion conductor in solid oxide fuel cells^{4, 7}, oxygen sensors¹⁵. In very recent years, ceria nanoparticles (NPs) having mixed valence state of Ce ions are found to have free radical scavenging property. Because of this property ceria NPs can prevent radiation induced cellular damage, retinal degeneration etc^{2, 16-18}. Several methods have been employed to synthesize ceria nanoparticles including flame combustion method,^{19, 20} hydroxide co-precipitation of a precursor solution composed of cerium ammonium nitrate and zirconyl chloride followed by sonication,²¹ hydrothermal/solvothermal process^{22, 23}, microemulsion process^{11, 24}, sonochemical and

microwave-assisted heating methods,²⁵ sol-gel method²⁶ etc.

To date, the ceria NPs synthesized by above-mentioned methods are often highly aggregated, and large scale synthesis of monodisperse NPs is quite challenging. Only a few organic solvent assisted synthesis²⁶, or post surface engineering could produce well dispersed, water-soluble ceria nanoparticles. It is therefore important to develop a robust synthesis method to produce water-soluble, ultra-small ceria nanoparticles with high yield to meet the growing demand of high-quality ceria NPs in biomedical applications. In this communication we report a simple, eco-friendly, cost-effective room temperature aqueous route to produce water-soluble, ultra-small (~ 3 nm) ceria NPs.

2. EXPERIMENTAL DETAILS

Ceria NPs were synthesized by adding 0.434 g Ce(NO₃)₃.6H₂O to a basic solution (0.1 g

NaOH dissolved in 32 ml water) followed by 48 hrs magnetic stirring. The resulting white precipitate was collected and washed several times in water. Ceria NPs remained highly dispersed in DI water for several days studied herein. For particle characterization using transmission electron microscopy (TEM), the precipitate was re-dispersed in ethanol and deposited on a thin carbon film coated Cu grid. UV-visible and auto-catalytic activity of ceria NPs were studied using water-dispersed particles. For the X-ray diffraction (XRD) and X-ray photo electron spectroscopic (XPS) studies, vacuum desiccated particles were used. The XRD study was carried out to determine the crystalline phase identity of the products whereas, the XPS study was carried out to determine the chemical composition and valence state of the elements in the ceria nanocrystals.

3. RESULTS AND DISCUSSIONS

The XRD pattern of the dried sample as shown in Figure 1 reveals the formation of pure CeO_2 with cubic phase (fluorite structure, JCPDS 34-0394, space group $Fm-3m$), having lattice constants of 5.414(3), 5.436(3), and 5.405(3) Å,

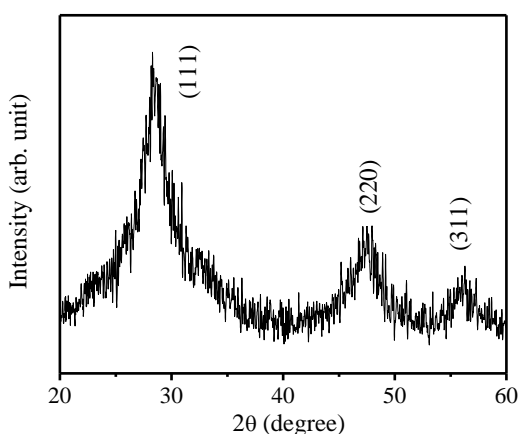


Figure 1: XRD pattern of the ceria nanoparticles.

respectively. The broadening of the diffraction pattern could be ascribed to the formation of ceria

NPs. Within the limit of the XRD sensitivity, we could not detect the formation of any hydroxide phase [$\text{Ce}(\text{OH})_3$].

Morphology and particle size of the ceria NPs were investigated through high resolution TEM (HRTEM). Figure 2a reveals the formation of nearly mono-dispersed ceria NPs with particle size 3 ± 0.5 nm. Image in the inset of Figure 2a shows the HRTEM image of a single ceria NP. The HRTEM image clearly demonstrates the formation of single crystalline nanoparticles even at room temperature. Figure 2b represents the

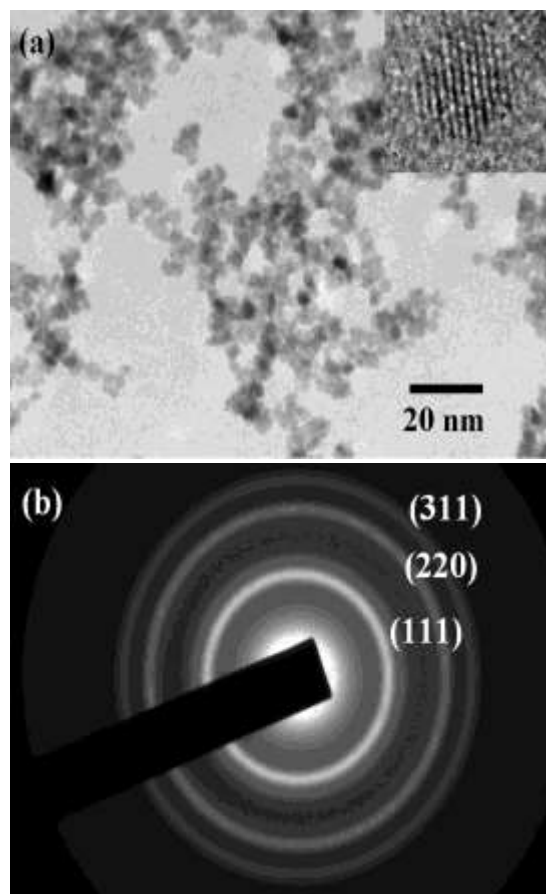


Figure 2: (a) TEM image shows the formation of mono-dispersed ceria NPs. The image in the inset depicted the high resolution TEM image of an individual NP. (b) SAED pattern of the nanoparticles indicating the formation of crystalline ceria NPs.

selected area electron diffraction (SAED) pattern recorded on a bunch of ceria nanoparticles. The appearance of bright white rings demonstrates the formation of NPs. Through proper analysis the rings were indexed to the various crystalline plane of ceria. The results are in good agreement with the XRD pattern. In our synthesis approach, it is important to keep the NaOH concentration low in order to have a controlled reaction condition allowing proper periodic arrangement of the constituent atoms to form well-faceted nanocrystals. It was observed that the use of high concentration of NaOH triggered rapid and uncontrolled precipitation producing undefined aggregated ceria structures.

In order to determine the chemical composition and the valence state of the elementary components in the products we have carried out the XPS studies. Figure 3a

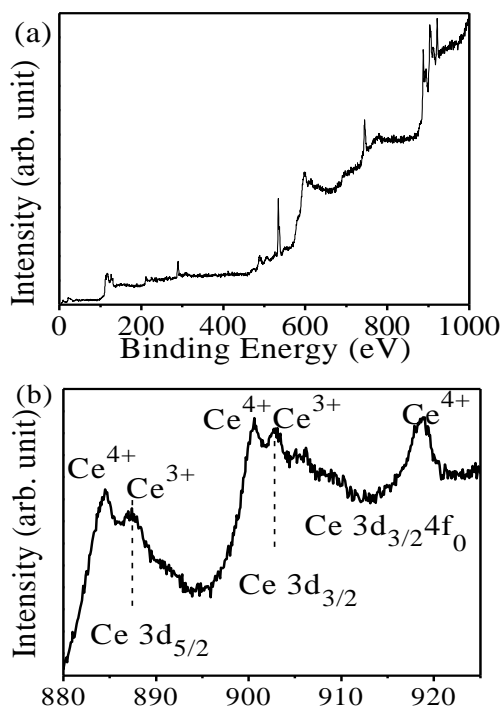


Figure 3: XPS spectra of the ceria nanoparticles: (a) survey scan and (b) high-resolution scan showing the valence states for Ce in the ceria NPs.

demonstrates the survey XPS spectrum of the samples exhibiting the presence of Ce and O as the elementary components in near stoichiometric condition. It is well known that the valence state of the Ce is important in determining the properties and applicability of the ceria nanoparticles. In this study we have therefore investigated in details the valence state of Ce using high resolution XPS spectra in the region of 880-925 eV. The XPS spectrum (Figure 3b) shows the presence of a mixed valence state (Ce³⁺ and Ce⁴⁺) for the synthesized cerium oxide NPs. The Ce³⁺ ions are introduced in the ceria nanocrystal lattice because of oxygen vacancies of Ce³⁺ ions created by surface chemical reactions.

Based on our experimental findings, we propose the formation mechanism of ultra-small ceria NPs as follows. The controlled conversion of solvated cerium ions to ceria NP is mediated by the mild basic environment. Basic reaction condition instantaneously converts cerium hydroxide to ceria nuclei. The mild reaction condition is crucial for promoting controlled nucleation. During the growth process, hydroxide ions are populated to the surface bound cations, providing a unique capping environment. Such environment restricts grain growth by preventing further diffusion of the constituent atoms.

4. CONCLUSIONS

In summary, we have synthesized nearly mono-dispersed, ultra small (3±0.5 nm) ceria NPs by simple aqueous solution route at room temperature. Studies reveal the formation of single crystalline ceria NPs with mixed valence state of Ce ions (Ce³⁺ and Ce⁴⁺). The NPs exhibited autocatalytic behavior as investigated through a H₂O₂ test coupled with UV-visible transmission measurements. These studies indicated that the present NPs could be directly used as an anti-oxidant in various biomedical applications.

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