
Controlled Fabrication and Optical Properties of Uniform CeO₂ Hollow Spheres

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1. Materials and Methods

¹⁵ 1.1 Synthesis of CeO₂ hollow spheres.

All chemicals were of analytical grade from Sinopharm Chemical Reagent Co., Ltd and used as starting materials without further purification. The spherical precursor compounds were synthesized by a biomolecule-assisted approach under hydrothermal condition. In a typical procedure, 1 mmol of Ce(NO₃)₃·6H₂O was loaded into a 50 ml beaker with 25 ml de-ionized water, and then 2 mmol L-
²⁰ cysteine and 0.3 g PVP were added into the solution under continuous stirring for 5 min. Then the solution was transferred into a 50 ml Teflon-lined stainless steel autoclave and was sealed and held at a temperature of 140 °C for 8 h. Subsequently, the system was allowed to cool to room temperature naturally. The resulting precipitate was collected by filtration and washed with absolute ethanol and distilled water in sequence for several times. The final product was dried in a vacuum box at 50 °C for

4 h. As prepared Ce-organic compound spheres were calcinated to produce CeO₂ hollow spheres in air at 600 °C for 2 h.

1.2 Materials characterization

The crystal structures of obtained specimens were characterized on a X-ray diffractometer (D/max2550 VB+) with Cu K α radiation ($\lambda=1.5418$ Å). The sizes and morphologies of the as-synthesized products were characterized by a field-emission scanning electron microscopy (FE-SEM, Sirion 200) with an accelerating voltage of 15 kV and transmission electron microscope (TEM, Tecnai G2 F20) with an accelerating voltage of 200 kV. The energy dispersive spectrometer (EDS) was taken on the SEM. The thermal behavior of Ce-organic compound to CeO₂ was evaluated by thermogravimetric (TG) and differential scanning calorimetry (DSC), which was obtained on a simultaneous thermal analysis (STA, NETZSCH STA 449C). The photoluminescence (PL) properties were measured on a fluorescence spectrometer (FluoroMax®-4 fluorescence spectrometer).

2. Characterization and performance

2.1 Supplemental electron microscopy data

Figure S1A shows the low magnification SEM image of the Ce-organic precursor compounds obtained with the time duration of 8 h, which indicates the uniform feature of these spheres. Figure S1B displays the low magnification SEM image of the as-prepared Ce-organic precursor spheres for 24 h, illustrating that the products were composed of two groups of spheres: large ones with mean diameter about 1.5 μm and small ones with average size of about 300 nm. Figure S1C shows the close-up shot TEM image of CeO₂ obtained by the calcination of typical spherical Ce-organic precursor for 30 min. The hollow structure with core inside can be observed.

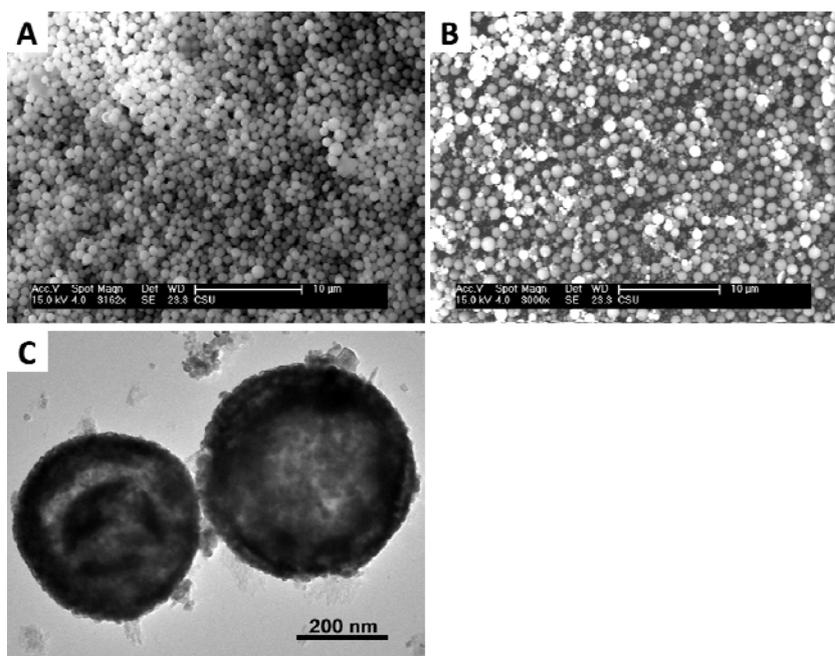


Figure S1. (A) and (B) Low magnification SEM views of as-prepared Ce-organic precursor spheres for 8 h and 24 h, respectively, (C) TEM close-up shot of CeO₂ hollow spheres with core inside.

2.2 Influence on the CeO₂ crystal phase with different amount of Sm³⁺ doped

The addition of Sm³⁺ with different concentrations ion into CeO₂ host lattice caused simultaneous effect on nanocrystal phase and size. As shown in figure S3, when 5 mol% Sm³⁺ added into the CeO₂:Sm material system, no significant change was observed comparing with XRD pattern of the pure CeO₂. However, with increasing the amount of Sm³⁺ to 10 mol%, some weak peaks of CeSO₄ could be seen in the degree range from 5 to 25°. The crystal phase of Sm₂O₂SO₄ occurred when 20 mol% and 50 mol% Sm³⁺ added. It is note worth that pure Sm₂O₂SO₄ can be prepared by the two-step biomolecule-assisted route.

EDS analysis taken on the SEM was also used to demonstrate the composition change of CeO₂:Sm as shown in figure S3. When 2 mol% Sm³⁺ was doped, the morphology of final products remains unchanged (figure S3B). With 5 mol% Sm³⁺ doped, it can be seen that the products were still composed of spheres with some broken ones (figure S3D). However, the products cannot keep the spherical structure any further when 10% mol Sm³⁺ was doped. Many particles appeared as show in

figure S3F. The approximate element ratio was displayed in the corresponding illustration of the EDS patterns. In order to improve the conductivity of the samples, all the samples were sprayed with gold. Thus, the peak of gold was displayed in the final spectrum. The EDS and SEM analysis agrees with the XRD results, demonstrating that the $\text{CeO}_2\text{:Sm}$ hollow spheres with pure CeO_2 crystal structure could be obtained only in a certain Sm^{3+} doping range.

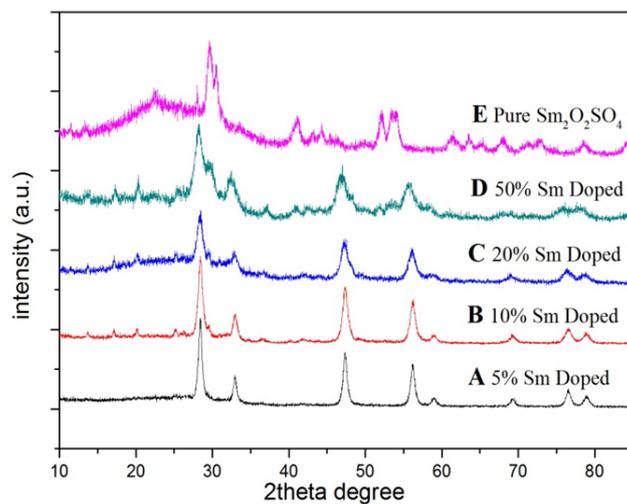


Figure S2. XRD patterns of CeO_2 with different amount of Sm^{3+} doped.

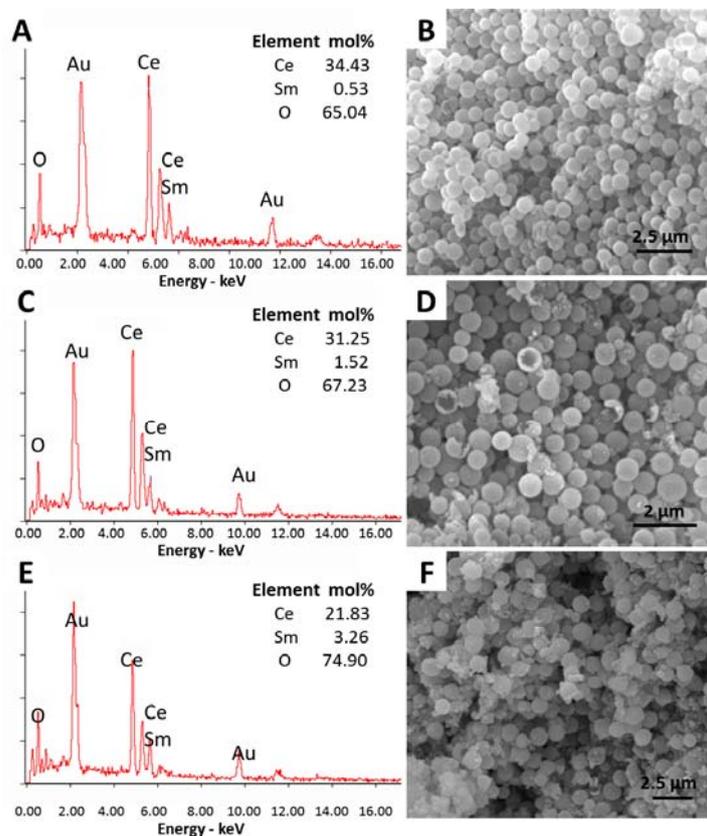


Figure S3. EDS patterns of CeO₂ with different amount of Sm³⁺ doped: (A) 2 mol%, (C) 5 mol% and (E) 10 mol%, respectively; (B), (D) and (F) are the corresponding SEM images.

2.3 Crystal structure of CeO₂

5 The point-group symmetry of Ce sites in the fluorite CeO₂ structure is O_h with eight-fold oxygen coordination as shown in figure S4, thereby providing an inversion symmetry. When Sm³⁺ ions are induced into CeO₂ crystal structure, it has the same point-group symmetry as Ce⁴⁺. Large amount of Sm³⁺ could cause inevitable distortion of lattice. The crystal structure model of CeO₂ also confirms that there exists compatibility when only the small amount of Sm³⁺ doped into CeO₂ crystal structure.

10 The energy level scheme shows that the average energy gap (E_g) between Ce and O chemical bonds is about 10.79 eV and the average charge transfer energy (E_{CT}) between Ce and O chemical bonds is about 3.61 eV.

When Sm³⁺ ions are induced into CeO₂ crystal structure, it has the same point-group symmetry as Ce⁴⁺. According to the selection rule, magnetic-dipole transitions that obey $\Delta J=0$ and ± 1 (J : the total

angular momentum) are allowed for Sm^{3+} in a site with inversion symmetry. Therefore, the ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$ ($\Delta J=0$) and the ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ ($\Delta J=1$) transitions can be observed. The above transitions are by magnetic dipole transition which follow the selection rule $\Delta J=0$ and $\Delta J=1$, respectively.

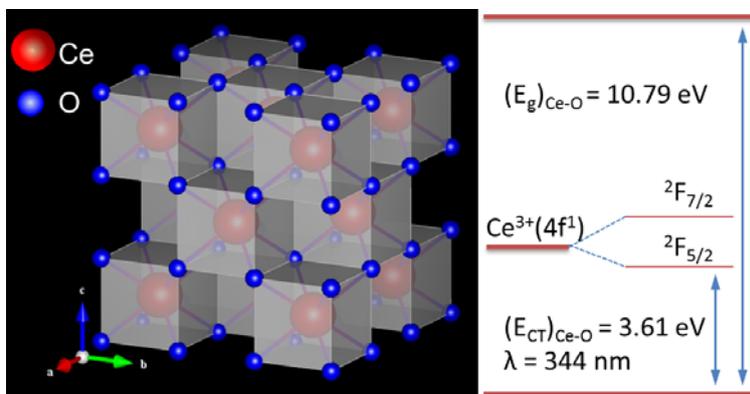


Figure S4. Ce-centered cube and skeleton construction with eight equatorial atoms of O in CeO_2 crystal structure and energy level diagrammatic sketches of nanocrystals of CeO_2 .