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Novel Controlled Synthesis of CeO_2 Hollow Microspheres by a Simple Hydrothermal Method: Undergraduate Experiments for Nanomaterials

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Abstract Wetting chemical method is a common method for the preparation of nano-materials, which are useful for experimental study by undergraduate students. CeO_2 hollow microspheres have been successfully synthesized by hydrothermal decomposition reaction of $Ce(NO_3)_3$ on the surfaces of silica microspheres. The shell thickness of CeO_2 hollow microspheres can be controlled from 20 nm to 50 nm by adjusting the concentration of $Ce(NO_3)_3$ in the reaction solution. The morphologies of CeO_2 hollow microspheres were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), field-emission scanning electron microscopy (FE-SEM).

Keywords CeO_2 hollow microspheres, Hydrothermal decomposition reaction, Morphologies

1. Introduction

Cerium oxide is a major compound in the rare earth family that has attracted considerable attention because of their vast technological applications, such as photocatalysts, [1-3] electrochemical cells, [4] Optical and Magnetic Properties, [5] gates for metal-oxide semiconductor devices and phosphors, [6-7] biomaterials, [8] sorbents for H_2S removal, [9] and ultrviolet absorbents for sunscreens, [10] which are of great interest due to their wide applications, in particular, as redox or oxygen storage promoters in the three-way catalysts, catalysts for H_2 prodution from fuels, and solid state conductors for fuel cells. [11-12]

Cerium (IV) oxide, also known as ceric oxide, ceric dioxide, ceria, cerium oxide or cerium dioxide, is an oxide of the rare-earth metal cerium. It is a pale yellow-white powder with the chemical formula CeO_2, which is insoluble in water. It is an important commercial product and an intermediate in the purification of the element from the ores. The distinctive property of this material is its reversible conversion to a nonstoichiometric oxide. Cerium Oxide is fluorite phase structure (Fig. 1), whose molecular weight is 172.115 g/mol and chemical formula is CeO_2. The valence of cerium is +4, so it possesses strong oxidability. Its melting point and boiling point is 2400°C and 3500°C, respectively. CeO_2 can be obtained by the oxidation of Ce_2O_3:

$$2\ Ce_2O_3 + O_2 \rightarrow 4\ CeO_2.$$

Normally, CeO_2 can not be reacted with the common acid. Furthermore, CeO_2 occur the oxidation-reduction reaction with CO in the presence of high temperature:

$$4\ CeO_2 + 2\ CO \rightarrow 2\ Ce_2O_3 + 2\ CO_2 \uparrow$$

The work presented here aims at the development of an integrated research-education activity on novel controlled synthesis of CeO_2 hollow microspheres.

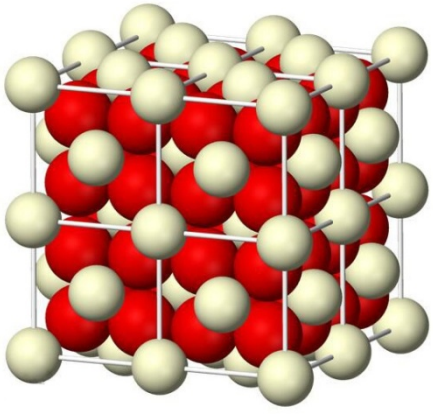

Figure 1. The structure of cerium dioxide

2. Experiment Description

2.1. Experiment Materials

Cerous nitrate (Bide Chemical Reagent Limited Company, Shanghai, China), sodium hydrate (NaOH) (Hengda Fine

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Chemical Products Limited Company, Shanghai, China), anhydrous methanol (Tianjin Fuyu Fine Chemical Co. Ltd., Tianjin, China), aqueous NH_4OH solution (Hengda Fine Chemical Products Limited Company, Shanghai, China) and tetraethylorthosilicate (TEOS) (Tianjin Fuyu Fine Chemical Co. Ltd., Tianjin, China) were purchased. All reagents were of analytical grade and used as received without further treatment. Distilled water was used in the experiment.

2.2. Instruments and Characterization

The morphologies and sizes of the resulting CeO_2 products were determined by field-emission scanning electron microscopy (FE-SEM, JSM 6700F), transmission electron microscopy (TEM, JEM-2000EX), The crystal structures of the resulting products were characterized by X-ray powder diffraction (XRD, D/MAX-500 X-ray powder diffractometer with Cu Kα radiation, λ=1.5418 Å at 40 kV and 70 mA) and an UV-vis spectrophotometer (Cary 500), respectively.

3. Experimental Procedure

3.1. Preparation of Silica Spheres

The uniform silica spheres were synthesized using Stöber method. [13] 245 mL of concentrated aqueous NH_4OH solution was added into the aqueous EtOH solution (EtOH 225 mL, H_2O 10 mL) and the resulting solution was stirred vigorously for 30 min. Then 21 mL of tetraethylorthosilicate (TEOS) was added in the solution and was stirred for 4 hrs. The mixture was centrifuged, decanted and dried in 100°C.

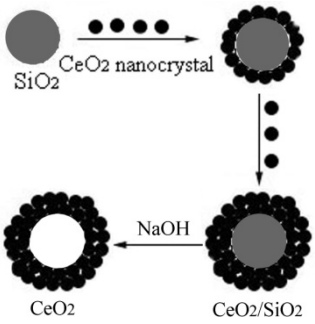
3.2. Preparation of CeO_2 Hollow Microspheres

In a typical synthesis of CeO_2 hollow microspheres, 0.868 g $Ce(NO_3)_3{\cdot}6H_2O$ was dissolved in 60 mL deionized water containing 0.1 g silica sol particles and the resulting mixture was ultrasonically irradiated for 20 min to form uniform solution. The obtained uniform solution was transferred to a Teflon- line stainless steel autoclave, which was sealed and maintained at 190°C for 24 h, and then air-cooled to room temperature. The resulting yellow precipitate was collected, washed with distilled water, and dried in air at room temperature. The yellow precipitate was treated with 0.5 M NaOH solution to remove the silica sol.

3.3. Schematic Procedure Used to Synthesize CeO_2 Hollow Microspheres

Scheme 1 shows the overall procedure used to synthesize CeO_2 hollow microspheres. Before hydrothermal treating of the reaction solution, silica microspheres are dispersed in $Ce(NO_3)_3$ solution by ultrasonic vibration. Under hydrothermal conditions, $Ce(NO_3)_3$ were decomposed to form CeO_2 nanocrystals on the surfaces of silica microspheres. The basic reaction may be expressed as follows:

$$Ce(NO_3)_3{\cdot}6H_2O \longrightarrow CeO_2+4H_2O+2H^+ +2NO_3^- +NO_2$$



Scheme 1. Schematic procedure used to synthesize CeO_2 hollow microspheres

4. Result and Discussion

4.1. X-ray Powder Diffraction (XRD) Analysis

X-ray powder diffraction (XRD) analysis was carried out to investigate the phases of the as–synthesized products. A typical XRD pattern of the as-synthesized products is shown in Figure 1. All of the diffraction peaks in Fig. 2 can be exactly indexed to the face-centered CeO_2 with lattice constants a = 5.410 Å, which are in good agreement with the literature values (JCPDS 34-0394). [14]

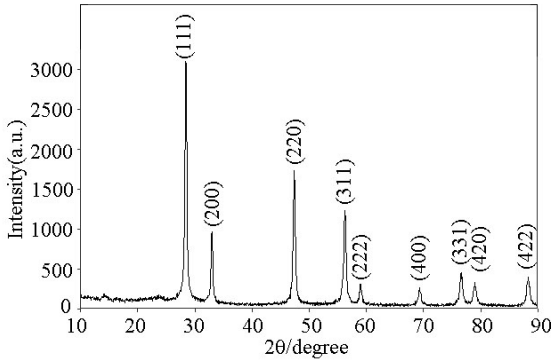


Figure 2. XRD patterns of as-synthesized CeO_2 hollow spheres

4.2. SEM Analysis of as-synthesized CeO_2 Hollow Spheres

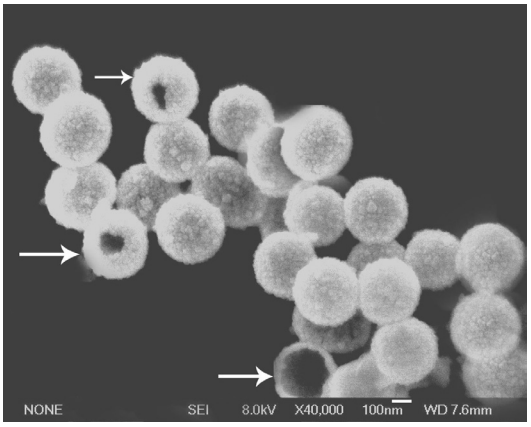


Figure 3. SEM image of as-synthesized CeO_2 hollow spheres synthesized at the concentrations of 0.1M $Ce(NO_3)_3$

Fig. 3 shows SEM image of CeO_2 hollow spheres synthesized at the concentrations of 0.1M $Ce(NO_3)_3$. The SEM photograph reveals that the as-synthesized products consist of uniform monodisperse spheres. Furthermore, it is clear that CeO_2 hollow spheres are composed of CeO_2 nanoparticles. Several individual broken hollow microspheres are present in the products as indicated by arrows in Figure 2, indicating that CeO_2 spheres possess hollow structures. The shell thickness of CeO_2 hollow spheres is 20 nm.

4.3. TEM Analysis of as-synthesized CeO_2 Hollow Spheres

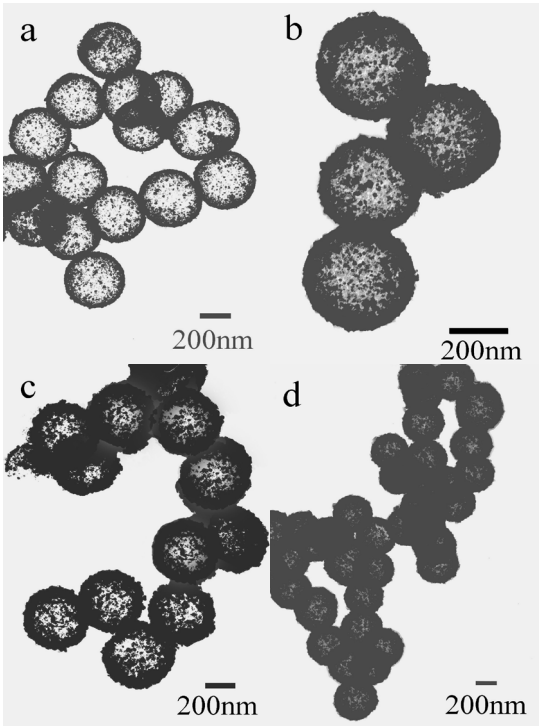


Figure 4. TEM images of as-synthesized CeO_2 hollow microspheres: the thickness of shell is (a) 20 nm (b) 35 nm, (c) 45 nm, and (d) 50 nm, respectively

Fig. 4 shows TEM images of CeO_2 hollow microspheres synthesized with different concentrations of $Ce(NO_3)_3$. The strong contrast between the core and edge indicates that CeO_2 microspheres are hollow. The shell thickness of CeO_2 hollow microspheres can be controlled by adjusting the concentrations of $Ce(NO_3)_3$ in the reaction solution. As the concentrations of $Ce(NO_3)_3$ are 0.050 M, 0.075 M, 0.100 M, and 0.125 M, the shell thickness are 20, 35, 45, and 50 nm, respectively (Table 1). The inner diameters of CeO_2 hollow microspheres are similar to that of silica microspheres.

Table 1. The relation between the concentrations of $Ce(NO_3)_3$ and the shell thickness of CeO_2 hollow spheres

The concentrations of $Ce(NO_3)_3$ / (M)	0.050	0.075	0.100	0.125
The shell thickness of CeO_2 hollow spheres / (nm)	25	35	45	50

4.4. UV/vis Analysis of as-synthesized CeO_2 Hollow Spheres

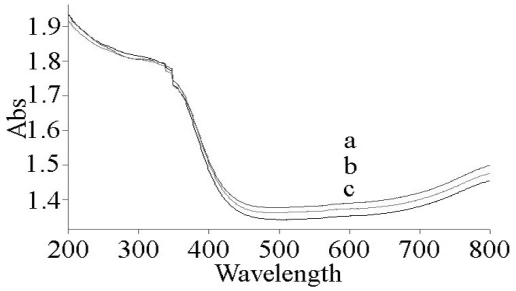


Figure 5. UV–vis absorbance spectra of CeO_2 hollow microsphere powder: the thickness of shell is (a) 20 nm, (b) 45 nm and (c) 50 nm

As ultraviolet blocking materials, CeO_2 has strong absorption properties in the ultraviolet range. Fig. 5 shows the UV/vis absorption spectra of the CeO_2 powders. As the shell thickness increases from 20 nm to 50 nm, the absorbing boundary of CeO_2 hollow microspheres is blue-shifted from 450 nm to 430 nm. The strong absorption in the spectra is due to the charge-transfer transition from O^{2-} (2p) to Ce^{4+} (4f) orbitals in CeO_2, which overruns the well-known f to f spin-orbit splitting of the Ce 4f state. [15-17] To the best of our knowledge, there was no report on them. The optical properties of CeO_2 hollow microspheres will prevent some damage from ultraviolet rays. Compared with some previous work on ultrafine CeO_2 nanoparticles, their strong absorption band is below 400 nm in the spectrum. [18] As a result, the high absorption in the UV region for CeO_2 hollow microspheres indicates that this material was suitable as a UV-blocking material.

In summary, CeO_2 hollow microspheres have been synthesized by hydrothermal decomposition reaction of $Ce(NO_3)_3$ on the surfaces of silica microspheres. The shell thickness of CeO_2 hollow microspheres can be controlled from 20 nm to 50 nm by adjusting the concentration of $Ce(NO_3)_3$ in the reaction solution. The high absorption in the UV region for CeO_2 hollow microspheres indicates that this material was suitable as a UV-blocking material. There experiments were performed at atmospheric pressure conveniently, making them suitable for materials physics and materials chemistry laboratories.

ACKNOWLEDGEMENTS

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REFERENCES

[1] Wen, X. J., Niu, C. G., Zhang, L., and Zeng, G. M., 2017, Novel p–n heterojunction BiOI/CeO_2 photocatalyst for wider spectrum visible-light photocatalytic degradation of refractory pollutants**.,** Dalton Trans., 46, 4982–4993.

[2] Wen, X. J., Zhang, C., Niu, C.G., Zhang, L., Zeng, G. M., and Zhang, X. G., 2017, Highly enhanced visible light photocatalytic activity of CeO_2 through fabricating a novel p–n junction BiOBr/CeO_2., Catal. Commun., 90, 51–55.

[3] Zhou, Q., Ma S., and Zhan S., 2018, Superior photocatalytic disinfection effect of Ag-3D ordered mesoporous CeO_2 under visible light, Applied Catalysis B: Environmental., 224, 27–37.

[4] DeCaluwe, S.C., Grass, M.E., Zhang, C., Gabaly, F.E., Bluhm, H., Liu, Z., Jackson, G. S., McDaniel, A. H., McCarty, K.F., and Farrow, R.L., 2010, In Situ Characterization of Ceria Oxidation States in High-Temperature Electrochemical Cells with Ambient Pressure XPS., J. Phys. Chem., C 114(46), 19853–19861.

[5] Niu, X. F., Zhang, X. X., and Liu, Y., 2018, Controlled Hydrothermal Synthesis, Optical and Magnetic Properties of Monodisperse Leaf-Like CeO_2 Nanosheets., Journal of nanoscience and technology., 18(4), 2622–2628.

[6] Tye, L., El-Masry, N.A., Chikyowm, T., McLarty, P., and Bedair, S. M., 1994, Electrical characteristics of epitaxial CeO_2 on Si(111)., Appl Phys Lett., 65(24), 3081–3083.

[7] Morshed, A. H., Moussa, M. E., Bedair, S. M., Leonard, R., Liu S. X., and ElMasry, N., 1997, Violet/blue emission from epitaxial cerium oxide films on silicon substrates., Appl Phys Lett., 70(13), 1647–1649.

[8] Naganuma, T., and Traversa, E., 2014, The effect of cerium valence states at cerium oxide nanoparticle surfaces on cell proliferation., 35(15), 4441–4453.

[9] Wu, M. M., Hu, C., C., Feng, Y., Fan, H., L., and Mi, J., 2015, Microwave effects on the structure of CeO_2-doped zinc oxide sorbents for H2S removal., Fuel., 146, 56–59.

[10] Si, R., Zhang, Y., W., You, L. P, and Yan C. H., 2005, Rare‐Earth Oxide Nanopolyhedra, Nanoplates, and Nanodisks., Angew. Chem., 117(21), 3320–3324.

[11] Boaro, M., Vicario, M., Leitenburg, C., Dolcetti, G., and Trovarelli, A., 2003, The use of temperature-programmed and dynamic/transient methods in catalysis: characterization of ceria-based, model three-way catalysts., Catalysis Today., 77(4), 407–417.

[12] Ghenciu, A. F., 2002, Review of fuel processing catalysts for hydrogen production in PEM fuel cell systems., Current Opinion in Solid State and Materials Science., 6(5), 389–399.

[13] Stöber, W., Fink, A., and Bohn, E., 1968, Controlled growth of monodisperse silica spheres in the micron size range., Journal of Colloid and Interface Science., 26(1), 62–69.

[14] He, Y., 2005, Synthesis of polyaniline/nano-CeO_2 composite microspheres via a solid-stabilized emulsion route., Materials Chemistry and Physics., 92(1), 134–137.

[15] Zhang, Y. W., Si, R., Liao, C. S., Yan, C. H., Xiao, C. X., and Kou, Y., 2003, Facile Alcohothermal Synthesis, Size-Dependent Ultraviolet Absorption, and Enhanced CO Conversion Activity of Ceria Nanocrystals., *J. Phys. Chem. B*, 107(37) 10159–10167.

[16] Tsunekawa, S., and Fukuda, T., 1999, Blue shift in ultraviolet absorption spectra of monodisperseCeO_{2-x} nanoparticles., J. Appl. Phys., 87, 1318.

[17] Tsunekawa, S., Sahara, R., Kawazoe, Y., and Kasuya, A., 2000, Origin of the Blue Shift in Ultraviolet Absorption Spectra of Nanocrystalline CeO_{2-x} Particles., Mater. Trans., JIM., 41(8) 1104–1107.

[18] Masui, T., Yamamoto, M., Sakata, T., Mori, H., Adachi, G., 2000, Synthesis of BN-coated CeO_2 fine powder as a new UV blocking material., J.Mater. Chem., 10, 353–357.