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Preparation and performance of CeO_2 hollow spheres and nanoparticles

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Abstract: CeO_2 hollow spheres were synthesized by polystryrene sphere (PS) templates and CeO_2 nanoparticles were prepared by a facile method. The as-obtained products were characterized by scanning electron microscopy (SEM), N_2 adsorption-desorption, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and UV-vis diffuse reflectance spectra. The results showed that the structure of the obtained CeO_2 hollow spheres was hollow microsphere with a diameter of 380 nm and the average particle size of CeO_2 nanoparticles was about 1700 nm. The two samples' Brunauer-Emmett-Teller (BET) surface area was 67.1 and 37.2 m^2/g. The CeO_2 hollow spheres had a better performance than nanoparticles at UV-shielding because of higher surface area and the structure of hollow sphere.

Keywords: CeO_2; UV-shielding; hollow spheres; template; Rh B; rare earths

In recent years, people gradually realize that UV-light can induce photochemical reaction and then change our bodies' function, especially do harm to our skin, eyes and immune system. TiO_2 and ZnO[1–3] are the commonly used UV-shielding materials. But their high photocatalytic activity can oxidize and degrade other ingredients. The study finds that CeO_2 also has a potential usage as UV-shielding material[4].

CeO_2 is one of the most important functional rare earth metal oxides, widely used in catalysis[5,6], fuel cell[7], absorbents for water treatment[8,9], UV blocker[10–12] and CO oxidation[13–15] due to its high mechanical strength, oxygen ion conductivity, optical property, thermal stability, and oxygen storage capacity. Recently, the structure of hollow sphere has attracted worldwide interest because of its unique shape and attractive properties. However, most people spend their time on the properties of catalysis and CO oxidation[16–19]. CeO_2 hollow spheres have seldom been used as a UV-shielding material.

Herein, we prepared two different morphologies of CeO_2. One of them used PS microspheres as template, $Ce(NO_3)\cdot 6H_2O$ as the source of cerium and NaOH as precipitant to synthesize CeO_2 hollow spheres and the other used $Ce(NO_3)\cdot 6H_2O$ and NaOH to synthesis CeO_2 nanoparticles. To research their properties in UV-shielding, we adopted UV-vis diffuse reflectance spectra and the self-decolorization of rhodamine B solution (Rh B) in UV light.

1 Experimental

1.1 Preparation of CeO_2 nanoparticle and hollow spheres

CeO_2 nanoparticle: 30 mL cerium solution (0.002 mol $Ce(NO_3)\cdot 6H_2O$ in 20 mL deionized water) was added in a three-neck flask and then the solution was heated to 65 ºC at a suitable stirring rate for 30 min. And inject 20 mL solution (0.22 g NaOH in 20 mL deionized water), keep the temperature and stirring rate for 2 h and then stop heating, go on stirring for 2 h. In the end the suspension was centrifuged and washed with ethanol and water for two times, respectively and dried at 70 ºC, then calcinated for 2 h at 500 ºC.

CeO_2 hollow spheres: First we synthesized PS microspheres by soap-free emulsion polymerization[5]. And then weigh 4.0 g PS (solid content of 5%) microspheres suspension in a three-neck flack and add 50 mL deionized water, then ultrasonic for 10 min. The mixture solution was heated to 65 ºC at a suitable stirring rate for 30 min. And then add 20 mL cerium solution (0.002 mol $Ce(NO_3)\cdot 6H_2O$ in 20 mL deionized water). Two hours later, inject 20 mL solution (0.22 g NaOH in 20 mL deionized water), keep the temperature and stirring rate for 2 h and then stop heating, go on stirring 2 h. In the end, the suspension was centrifuged and washed with ethanol and water for two times, respectively and dried at 70 ºC, then calcinated 2 h at 500 ºC.

1.2 Characterization

The surface morphologies of samples were characterized by a HITACHI S-3400N scanning electron microscope at an accelerating voltage of 15 kV. Nitrogen adsorption and desorption experiments were performed at 77 K on a NOVA4000 gas adsorption analyzer (Quantachrome Corp.). The average diameter of the obtained

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samples was measured by Zetasizer Nano ZS (Malvern Instrument Ltd.). A PANalytical X'Pert PRO X-ray diffractometer with Cu Kα (λ=0.15418 nm) incident radiation was employed to analyze the crystal structure of the materials. The X-ray diffraction (XRD) patterns were obtained for 2θ angles from 20º to 90º at a scan rate of 0.02 (º)/min. Beijing Beifen-Ruili Analytical Instruments Fourier infrared spectrometer WQF-520 was used to analyze the FT-IR spectrogram of samples by powder tabletting method. UV absorption properties of the synthetic samples were determined by Beijing Purkinje General Instrument production of TU-1900.

The UV-shielding performance of CeO_2 hollow spheres and CeO_2 nanoparticles was also shown by the self- decolorization rate of Rh B solution in a photochemical reactor (Bilang, China), equipped with a 800 W mercury lamp as the UV-light source, which was about 10 cm from the liquid surface of the suspensions to the mercury lamp. 20 mg samples were added in 50 mL 10 mg/L Rh B solution under constant magnetic stirring. Before light up, the suspension was stirred for 1 h in dark to reach adsorption-desorption equilibrium. 4 mL suspension was timely taken out and centrifuged 3 min at a speed of 8000 r/min, the absorbance of the supernatant was measured at 554 nm. The decolorization rate W(%) was calculated according to the following formula:

$$W=(1-A_t/A_o)\times 100\% \quad (1)$$

where, A_o is the absorbance of Rh B solution before light up and A_t the Rh B solution's absorbance at different times after treatment.

2 Results and discussion

Fig. 1 shows the SEM images of PS spheres, CeO_2 hollow spheres and CeO_2 nanoparticles. These images briefly display that uniform PS microspheres with an average diameter of 360 nm were obtained (in Fig. 1 (a)), the CeO_2 hollow spheres whose average diameter is 380 nm (in Fig. 1(b)). From Fig. 1(c), we could see that various sizes of CeO_2 nanoparticles were also prepared successfully. Fig. 1(d) displays the CeO_2 nanoparticles with an average dimension of 1700 nm. And we could easily find that the morphologies of CeO_2 hollow spheres are uniform and there are some holes on the surface of CeO_2 hollow spheres which was caused by calcining PS microspheres.

Fig. 2 shows the XRD patterns of CeO_2 hollow spheres and CeO_2 nanoparticles. From Fig. 2, we can know that all the typical CeO_2 diffraction peaks are found in the as-obtained samples. The strong and sharp peaks revealed that the products synthesized by PS template could also keep a good crystal structure of CeO_2. No diffraction peaks from impurities were observed, which indicated the samples have good crystallization and high purity[9].

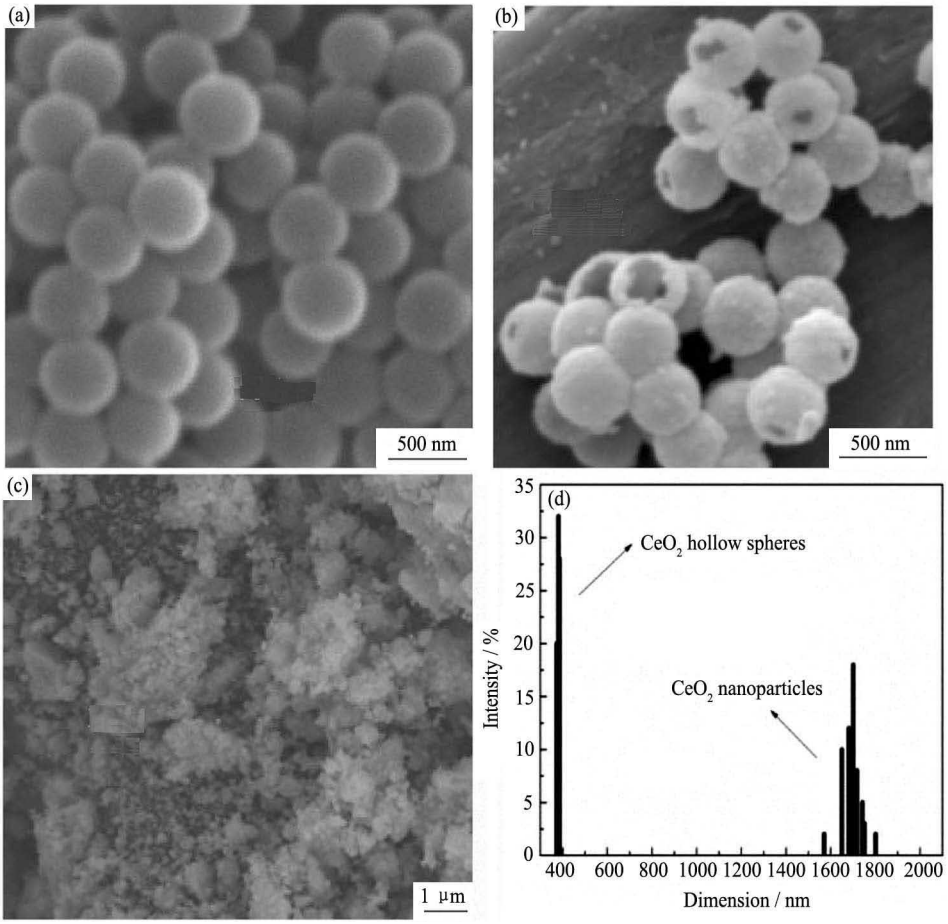

Fig. 1 SEM images of as-synthesized PS spheres (a), CeO_2 hollow spheres (b), CeO_2 nanoparticles (c) and dimension of samples (d)