Self-assemblage of Single/Multiwall Hollow CeO_2 Microspheres through Hydrothermal Method

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(Received May 11, 2006; CL-060558; E-mail: zyj@ustc.edu.cn)

Novel single/multiwall hollow CeO_2 microspheres were synthesized by self assemblage through hydrothermal method without any surfactant, the shells of which were consisted of CeO_2 nanoparticles with mean size of 70 nm. The influence of the molar ratio of urea to $Ce(NO_3)_3{\cdot}6H_2O$ on the morphology of the products was investigated and the formation mechanism of single/multiwall hollow CeO_2 was proposed.

Cerium oxide is one of the most widely used rare earth metal oxides because of its oxygen deficiency, oxygen storage capacity, and electronic conductivity.[1] An important factor that influences the performance of CeO_2 is morphology. Up to now, CeO_2 with different morphologies has been synthesized, such as nanoparticle,[2] nanowire,[3] nanotube,[4] nanorod,[5] nanocube,[5] mesoporous,[6] solid sphere,[7] and single shell hollow spheres.[8] As far as we know, there is no reports on synthesis of multiwall hollow CeO_2 microspheres through hydrothermal method. In this paper, novel single/multiwall hollow CeO_2 microspheres were synthesized through hydrothermal method which is simple and convenient.

In a typical procedure, 0.54 g of urea is dissolved with 10 mL of distilled water in a beaker and then transferred into a Teflon liner. Ten milliliters of 0.3 M $Ce(NO_3)_3{\cdot}6H_2O$ solution, 5 mL of H_2O_2 (w/w 30%) and some more distilled water are added into the Teflon liner. The above Teflon liner is put into a stainless autoclave and maintained at 230 °C for 10 h. The precipitate is filtered off and washed with distilled water and absolute ethanol. Finally, some light yellow powders are obtained after drying in vacuum at 80 °C for 6 h.

Figure 1a illustrates that the products sythesized at 230 °C for 10 h are cubic phase CeO_2.[9] When the reaction temperature is 180 °C, the products are not pure cubic phase CeO_2[9] (shown in Figure 1b). Figures 2a–2d show the dark field TEM image, the bright field TEM image, select area electron diffraction (SAED), and the SEM image of the products, respectively. The strong contrast between the different regions in Figures 2a and 2b suggests that the products are the single/multiwall hollow sphere structure. There is a clear space between every shells. The polycrystalline diffraction rings in Figure 2c correspond to the (111), (220), and (311) peaks of XRD pattern, which indicates that the shell of the microsphere is made up of CeO_2 nanoparticles. From Figure 2d, it can be observed that the products are a mixture of single wall and multiwall hollow microspheres, the yield of microspheres in products exceeds 90%. Some microspheres broke after being treated in an ultrasonic water bath for 2 h. The inset of Figure 2d shows an individual broken multiwall hollow microsphere. It can be clearly seen that the thickness of the microsphere shell is about 70 nm, and the shell is composed of nanoparticles with mean size of 70 nm.

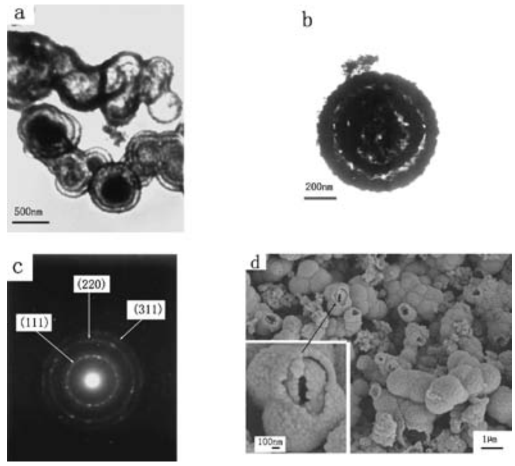

Figure 2. TEM images, SAED, and SEM image of the products. (a) Dark field TEM image; (b) bright field TEM image; (c) SAED; (d) SEM image.

Figure 3 shows the X-ray photoelectron spectra (XPS) of the products. Figure 3a indicates that there are no other elements except for Ce and O on the surface of the samples. The Ce 3d spectrum (Figure 3b) can be assigned as follows: The peaks labeled u and v are due to $3d_{3/2}$ and $3d_{5/2}$ spin orbit states.

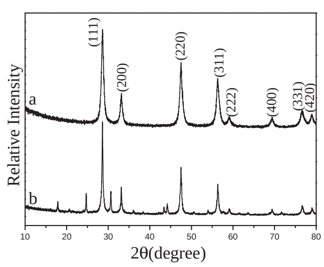

Figure 1. XRD pattern of the products. (a) 230 °C; (b) 180 °C.

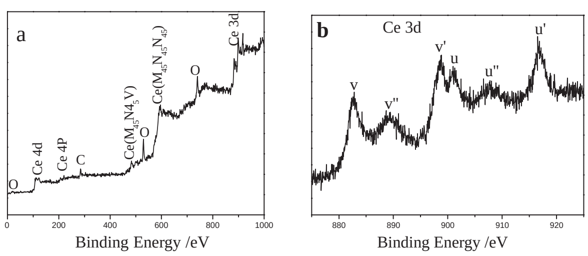

Figure 3. XPS analysis of the products. (a) Survey spectrum; (b) Ce 3d region spectrum.

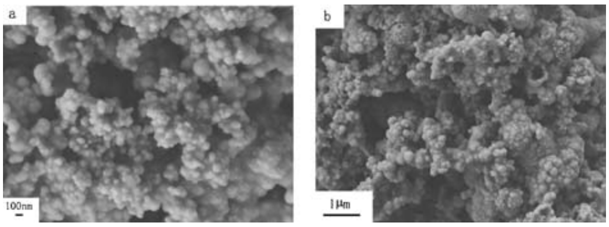

Figure 4. SEM images of the products obtained under the ratio of urea to $Ce(NO_3)_2$ of 1:1 (a) and 2:1 (b).

The u′/v′ doublet is due to the primary photoemission from $Ce(IV)O_2$. The u″/v″ doublet is shakedown features resulting from the transfer of one or two electrons from a filled O 2p orbit to an empty Ce 4f orbit.[10]

The urea plays an important role in the formation of single/multiwall hollow microspheres. NH_3 gas bubbles produced by urea (shown in Eqs 1 and 2) act as the soft-templates to fabricate single/multiwall hollow microspheres in the hydrothermal process.

$$CO(NH_2)_2 + 3H_2O \rightarrow 2NH_4^+ + 2OH^- + CO_2(g), \quad (1)$$

$$NH_4^+ + OH^- \rightleftharpoons NH_3{\cdot}H_2O \rightleftharpoons H_2O + NH_3(g). \quad (2)$$

When the molar ratio of urea to $Ce(NO_3)_3{\cdot}6H_2O$ is 1:1, the products are all nanoparticles (shown in Figure 4a) because the urea mainly acts as a precipitant and there is little NH_3 gas bubbles. The proportion of single/multiwall hollow microspheres rises when the molar ratio of urea to $Ce(NO_3)_3{\cdot}6H_2O$ increases from 1:1 to 3:1. Figure 4b shows the SEM image of the products under the molar ratio of urea to $Ce(NO_3)_3{\cdot}6H_2O$ of 2:1. The optimal molar ratio of urea to $Ce(NO_3)_3{\cdot}6H_2O$ is from 3:1 to 6:1.

From the above observations, an aggregation mechanism to form single/multiwall hollow microspheres can be proposed. The formation mechanism of the single/multiwall hollow microspheres is shown in Figure 5, referring to preparation of ZnSe microspheres.[11] Firstly, CeO_2 monomers grow into nanoparticles, and some NH_3 gas bubbles are newly produced in the reaction system (step a). Secondly, the CeO_2 nanoparticles assemble to form the first shell of the sphere on the surface of gas bubbles. Several NH_3 gas bubbles will possibly congregate to form the bigger irregular gas bubbles, so some of the products are irregular hollow microspheres (step b). The second shell will be formed under the assistance of the NH_3 gas bubbles around the first shell of the sphere (steps c and d). Similary, the other shells will self-assemble one after the other and the polywall microshpere come into being.

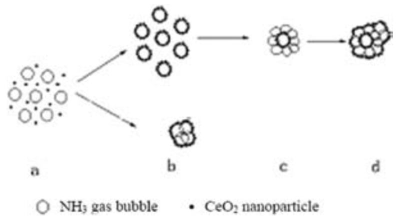

Figure 5. The possible formation mechanism of the CeO_2 single/multiwall hollow microspheres.

In summary, novel single/multiwall hollow CeO_2 microspheres were synthesized by self-assemblage through a hydrothermal method at 230 °C. XRD, TEM, SEM, and XPS were used to characterize the products. The influence of the molar ratio of urea to $Ce(NO_3)_3{\cdot}6H_2O$ on the morphology of the products was investigated and the formation mechanism of single/multiwall hollow CeO_2 was proposed.

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Published on the web (Advance View) July 15, 2006; doi:10.1246/cl.2006.944