A Simple Route to Preparation and Characterization of Er_2O_3 Microspheres

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Large scale, uniform Er_2O_3 microspheres have been prepared with $CO(NH_2)_2$ as the precipitant through a hydrothermal method. The obtained products were characterized by X-ray powder diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, and field-emission scanning electron microscopy. The Er_2O_3 microspheres are composed of nanoparticles, and the diameter is in the range of 200–300 nm. In addition, a possible formation mechanism of Er_2O_3 microspheres was discussed.

Rare earth oxides have drawn much attention because they are an interesting group of materials with potential applications in the fields of infrared, laser, biological, optical, magnetic, catalytic, and fluorescent materials, and sensitivity sensor.[1] In the rare earth oxide family, erbium oxide (Er_2O_3) and erbium-doped materials have been used in catalysis, optics, sensing, optical communication, and optoelectronics owing to their excellent physical and chemical properties.[2] However, the property of a material is strongly related to the size, shape, and dimensionality.[3] Therefore, it is necessary to discuss the preparation of Er_2O_3 micro- and nanostructures with complex shapes because of their potential applications, but few studies have been focused on the fabrication of Er_2O_3 nanocrystals with various morphologies.[1]

Recently, micro- and nanomaterials with spherical morphology have been widely reported, most existing chemical solution routes to them demand the utilization of extra surfactants,[4] templates,[5] or other additives such as citric acid[6] to fabricate of nanospheres. To the best of our knowledge, no studies have been made on the synthesis of Er_2O_3 with these uniform microspheres. Therefore, we report here a simple route to preparation of Er_2O_3 microspheres using $CO(NH_2)_2$ as the precipitant without any surfactant and template. The molar ratio of $CO(NH_2)_2$ to Er_2O_3 is a dominant factor for the formation of Er_2O_3 microspheres.

In a typical experiment, 0.0015 mol of Er_2O_3 was dissolved in 9.3 mL of 1 M HNO_3, and 0.009 mol of $CO(NH_2)_2$ was added to the solution with stirring. After some minutes, the mixture was transferred into a 60-mL Teflon liner, and some deionized water was poured into till 80% of the total volume under vigorous stirring. Then, it was put into a stainless autoclave and maintained at 210 °C for 4 h. After that, the autoclave was allowed to cool to ambient temperature. The precipitate was washed several times with distilled water and absolute ethanol and dried at 80 °C for 6 h.

Figure 1 shows the typical X-ray diffraction (XRD) patterns of the products obtained at the different reaction temperatures. All the peaks of the samples a–c can be indexed to pure cubic phase (JCPDS card No. 08-0050, $a = 1.054$ nm) with high crystallinity. When the reaction temperature is 230 °C, the sample d is not pure cubic phase Er_2O_3. Further evidence for the composition was obtained by the XPS of the products. The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing the C1s to 284.60 eV. The survey of XPS spectrum of the products (Figure 2a) suggests that there are no other elements on the surface of the samples; the O1s peak at about 530.55 eV can be assigned to the O (−2) in the Er_2O_3. Figure 2b shows that the binding energy of Er4d is 168.53 eV.

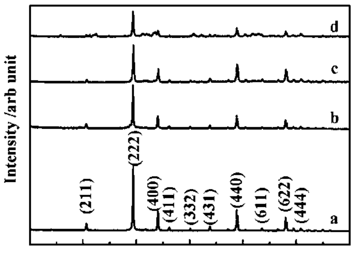


Figure 1. XRD patterns of the products obtained at different reaction temperatures. (a) 120 °C; (b) 170 °C; (c) 210 °C; (d) 230 °C.

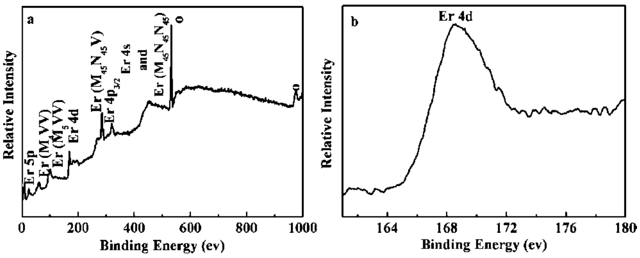


Figure 2. X-ray photoelectron spectra (XPS) of the as-obtained products: (a) survey spectrum, (b) Er4d region.

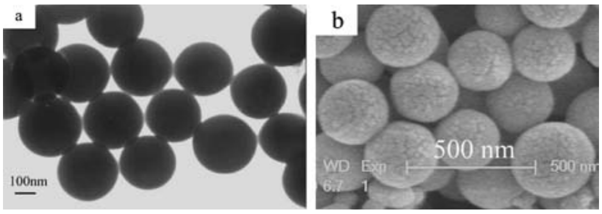


Figure 3. (a) Bright field TEM image of the as-obtained products. (b) FESEM image of the as-obtained products.

The TEM image of these microspheres shows the solid nature by a strong contrast between the pale edge and dark center (Figure 3a). Figure 3b shows an overview FESEM image of the sample obtained at 210 °C for 4 h with the 6:1 molar ratio of $CO(NH_2)_2$ to Er_2O_3, large-scale Er_2O_3 microspheres are formed with the diameter in the range of 200–300 nm, and most

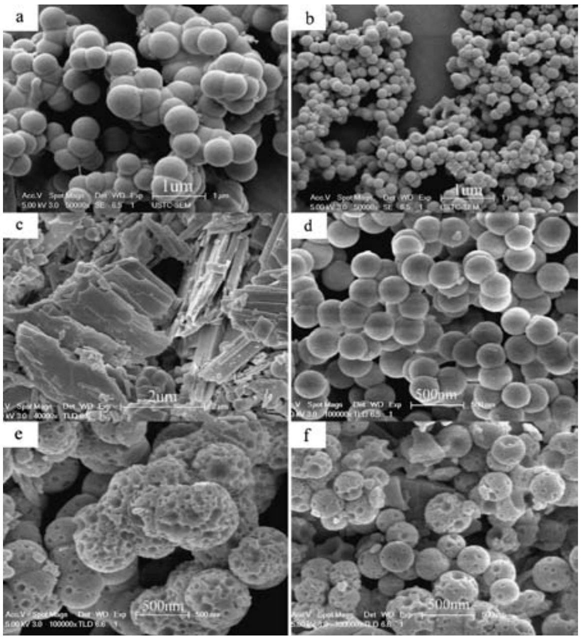
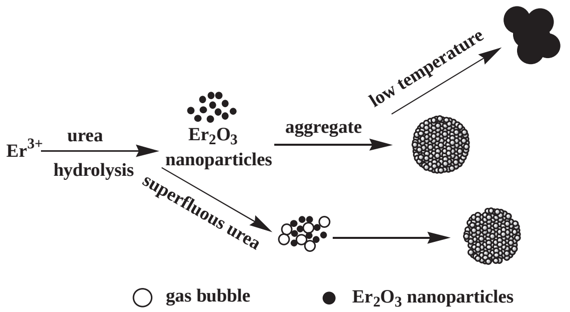


Figure 4. FESEM images of the products obtained at 120 °C (a) and 170 °C (b). FESEM images of the products obtained with the molar ratio of $CO(NH_2)_2$ to Er_2O_3 being 2:1 (c), 6:1 (d), 10:1 (e), and 16:1 (f).



Scheme 1. Formation process of the uniform Er_2O_3 microspheres.

of the structures are uniform; the microspheres are composed of nanoparticles, and the size is about 20 nm.

The morphologies of the products obtained at different reaction temperatures and with different molar ratios of the starting reagents were examined by a field-emission scanning electron microscope (FESEM). It can be seen from the Figure 4a that the microspheres have grown together when the temperature was 120 °C. After the temperature reached 170 °C, the microspheres were formed in about 70% morphological yield (Figure 4b), which is lower than those at 210 °C (Figure 3b). When the molar ratio of $CO(NH_2)_2$ to Er_2O_3 is 2:1, pure phase cannot be obtained, and flake structures were formed with the thickness of about 150 nm (Figure 4c). Large-scale and uniform Er_2O_3 microspheres with diameters in the range of 200–300 nm were formed when the molar ratio of $CO(NH_2)_2$ to Er_2O_3 is 6:1 (Figure 4d). However, when the molar ratios of $CO(NH_2)_2$ to Er_2O_3 are 10:1 and 16:1, the surface of most Er_2O_3 microspheres was corrupted with many different size holes, it was resulted from the superfluous $CO(NH_2)_2$ producing a lot of NH_3 bubbles (Figures 4e and 4f). These results reveal that the molar ratio of $CO(NH_2)_2$ to Er_2O_3 is a dominant factor for the formation of Er_2O_3 microspheres.

From the morphologies of the products obtained at different reaction temperatures and with different molar ratios of the starting reagents, we speculate that the growth of the Er_2O_3 microspheres is through a self-assembly process. As illustrated in Scheme 1, the presence of $CO(NH_2)_2$ plays an important role in the formation of Er_2O_3 microspheres. The $CO(NH_2)_2$ was hydrolyzed to provide alkaline condition slowly, which is in favor to crystal growth with some morphologies. When $CO(NH_2)_2$ was added to the reaction mixture under optimum conditions, Er_2O_3 nanoparticles were formed in the alkaline condition caused by hydrolysis of $CO(NH_2)_2$. These particles would rapidly self-assembled into Er_2O_3 microspheres to lower its interfacial energy. When the temperature was relatively low (120 °C), the microspheres were grown together, possiblly because of the hydrolysis rate of $CO(NH_2)_2$ was slow at relatively low temperature. When the concentration of $CO(NH_2)_2$ is above the optimum conditions, the superfluous $CO(NH_2)_2$ was hydrolyzed to produce a lot of NH_3 gas bubbles, which could result in the surface of microspheres corrupted. We also have carried out the experiment in the presence of palmitic acid, and monodispersed nanoparticles were obtained (The TEM image appears in the Supporting Information), which farther supported that the Er_2O_3 microspheres are self-assembled nanoparticles. This growth process is similar to the growth of these reported previously.[7]

In summary, uniform Er_2O_3 microspheres in the cubic phase were prepared by a hydrothermal method. The XRD, TEM, FESEM, and XPS were used to characterize the products. The Er_2O_3 microspheres are composed of nanoparticles, and the diameter is in the range of 200–300 nm. This reaction process for the formation of Er_2O_3 microspheres is free of any template and surfactant. Various experiment parameters were examined, and a possible formation mechanism of Er_2O_3 microspheres was presented. This method brings forward a wide idea to synthesize other rare-earth compounds with various morphologies and novel properties.

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