

Microwave Fabrication and Magnetic Property of Hierarchical Spherical α -Fe₂O₃ Nanostructures

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The hierarchical spherical α -Fe₂O₃ nanostructures were obtained by polyacrylamide (PAM)-assisted microwave fabrication method. The nanostructures exhibited mesoporous structures with relatively high remanent magnetization and coercivity at 300 K. The PAM was believed to play an important role in the formation of the hierarchical spherical α -Fe₂O₃ nanostructures.

In recent years, nanostructured metal oxides play an important role in many areas of science and technology owing to their particular physicochemical properties.¹ Since the properties of nanomaterials strongly depend on their morphology, size, and microstructure, a great deal of works have been focused on the preparation of metal oxide nanostructures with novel shape and structure.² In particular, hierarchical three-dimensional (3D) nanostructures assembled by building blocks such as nanoparticles, nanorods, and nanosheets represent novel properties and potential application values in optical, electronic, and magnetic devices.³ Therefore, fabrication of novel hierarchical metal oxide nanostructures may promote development for exploring material characteristics and designing functional devices.

Among various oxides of iron, α -Fe₂O₃ is the most stable substance under ambient conditions. Because of its unique physical and chemical properties, α -Fe₂O₃ as a functional material has a wide range of applications in catalysis, gas sensors, magnetic recording materials, optical devices, electromagnetic devices, pigments, and lithium-ion batteries.⁴ To further study the special properties of nanostructured α -Fe₂O₃, a great number of efforts have been put into the preparation of α -Fe₂O₃ nanostructures, and a series of different morphologies such as nanoparticles,⁵ nanorods,⁶ nanotubes,⁷ cantaloupe-like,⁴ urchin-like,⁸ and nanoflowers⁹ have been successfully achieved by a variety of methods. Meanwhile, the microwave-assisted hydrothermal preparation of α -Fe₂O₃ nanorods and nanorings also has been reported in the literature.^{10,11} However, there is little work concerned with microwave fabrication of hierarchical spherical α -Fe₂O₃ nanostructures under reflux conditions. In this work, a quick and facile polyacrylamide (PAM)-assisted microwave fabrication method of hierarchical spherical α -Fe₂O₃ nanostructures under reflux conditions has been demonstrated. The magnetic property of the product was investigated. A role of PAM in the formation of hierarchical spherical α -Fe₂O₃ nanostructures was also discussed.

In a typical experiment, 7.5 mmol of FeCl₃·6H₂O was dissolved in 100 mL of deionized water, followed by adding 2.0 g of PAM (MW = 3000000) and 1 mmol of urea under continuous stirring for 10 min. Then the mixtures were transferred into a 250-mL round flask and heated in a microwave oven (650 W,

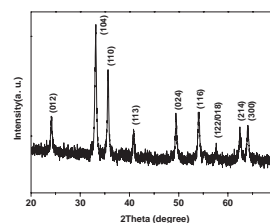


Figure 1. XRD pattern of the product.

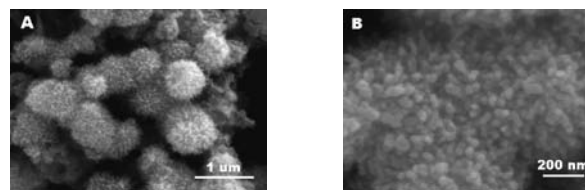


Figure 2. Typical FESEM images of the product: low magnification (A) and high magnification (B).

2.45 GHz) at refluxing for 20 min. When the flask was cooled to room temperature on standing, the product (Fe–PAM complex) was collected by centrifugation, washed using deionized water and dried 24 h at 80 °C. Then the above solid product was calcined at 550 °C for 4 h, and red powders were obtained finally.

The crystalline phases of Fe–PAM complex are shown in Figure S1,¹² it indicates that Fe–PAM complex is composed of FeOOH and unknown component before calcinations. Figure 1 shows the XRD pattern of the product. The pattern can be indexed as a pure hexagonal phase of α -Fe₂O₃ (JCPDS No. 33-0664). And no diffraction peaks of other phases or impurities appeared in the pattern.

Figure 2 shows the typical field emission scanning electron microscopy (FESEM) images of the as-prepared α -Fe₂O₃. Figure 2A indicates that the product consists of hierarchical spherical nanostructures with rough surfaces in the diameter range of 400–800 nm. In Figure 2B, at a high magnification, it can be clearly seen that the surfaces of the product are assembled by fine particles in the size range of 30–50 nm, at the same time interstices exist between fine particles. Obviously, the product conforms to the hierarchical 3D nanostructures assembled by nanoparticles. In contrast, the morphology of Fe–PAM complex before calcinations in Figure S2¹² shows packing of flower-like nanospheres. This indicates that the calcinations has removed organic impurities and promoted the formation of hierarchical spherical nanostructures.

The nitrogen sorption isotherms and the corresponding BJH pore size distribution curve of the as-prepared α -Fe₂O₃ are

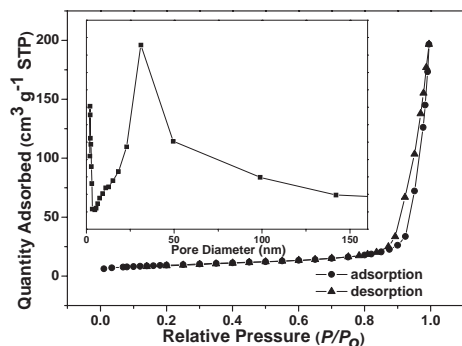


Figure 3. Nitrogen sorption isotherms and the pore size distribution curve (inset) of the product.

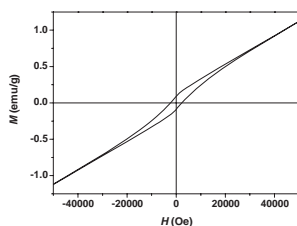


Figure 4. Magnetic hysteresis loop of the product at 300 K.

shown in Figure 3. The nitrogen sorption isotherms show the as-prepared hierarchical spherical α - Fe_2O_3 nanostructures exhibit a type IV curve, which indicates the existence of mesoporous structure in the product. The corresponding BJH pore size distribution curve shows that the maximum of pore diameter distribution is 31 nm, within the range of the mesopore (2–50 nm), and the rough surfaces of the product as well as the interspaces between the fine particles in FESEM images (Figure 2) also reflect the presence of the mesoporous structure. The total pore volume of the product is $0.30 \text{ cm}^3 \text{ g}^{-1}$, and the BET specific surface area is $31.3 \text{ m}^2 \text{ g}^{-1}$.

As well-known, the morphology and structure of nanomaterials strongly influence their physical and chemical properties. Thus, magnetic property of the product was investigated below. Figure 4 shows the magnetic hysteresis loop of the product at 300 K in the applied magnetic field sweeping from -50000 to 50000 Oe. Obviously, the magnetic hysteresis loop does not reach the saturation state even up to the maximum applied magnetic field. The similar phenomenon was reported in the literatures.^{4,8,9} Furthermore, according to the magnetic hysteresis loop, one can see that the product displays magnetic property with a remanent magnetization of $0.08947 \text{ emu g}^{-1}$ and a coercivity of 2301.5 Oe. Compared with results from other α - Fe_2O_3 nanostructures, the values of the remanent magnetization and coercivity are similar to that of cantaloupe-like superstructures⁴ but much higher than that of other, such as nanorods, nanotubes, nanoflowers, urchin-like superstructures, etc.^{5,6,8,9} Obviously, the as-prepared hierarchical spherical α - Fe_2O_3 nanostructures possess magnetic characteristic unlike other α - Fe_2O_3 nanostructures. Such a special property may be attributed to the shape anisotropy, defects, porous and hierarchical assembly way of the product.

As far as we know, rod-like or needle-like α - Fe_2O_3 nanostructures usually are obtained in conventional synthesis

methods.⁶ In this work, the hierarchical spherical α - Fe_2O_3 nanostructures assembled by nanoparticles under the microwave irradiation were obtained. However, when the reaction carried out in same conditions but without PAM, no precipitation product was obtained. The result suggests that PAM plays an important role in the formation of the hierarchical spherical α - Fe_2O_3 nanostructures. PAM is a water-soluble polymer and possesses abundant amino groups as well as carboxyl groups produced by partial hydrolysis. Based on a role of polymer in the formation of hierarchical spherical ZnS nanostructures,¹³ a possible mechanism might be described as follows: Firstly, through interaction between amino (carboxyl) groups of PAM and Fe^{3+} ion in solution, PAM and Fe^{3+} ion were combined to form certain intermediate complex, which, under the microwave irradiation, was rapidly hydrolyzed into a complex consists of iron compound nanoparticles and polymer. The complex forms spherical structures in aqueous solution owing to the hydrophobic interaction of the alkyl groups of polymer. After the removal of polymer by calcinations, the hierarchical spherical α - Fe_2O_3 nanostructures were obtained finally.

In conclusion, PAM-assisted microwave fabrication of hierarchical spherical α - Fe_2O_3 nanostructures has been successfully achieved. The product is assembled by nanoparticles and possesses relatively high remanent magnetization and coercivity at 300 K and mesoporous structures. It is suggested that PAM might play a critical role in the growth of hierarchical spherical α - Fe_2O_3 nanostructures.

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