Synthesis of amorphous \( \text{Fe}_2\text{O}_3 \) nanoparticles by microwave irradiation

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Abstract

Amorphous \( \text{Fe}_2\text{O}_3 \) nanoparticles of about 3–5 nm in size have been synthesized by microwave irradiation heating of an aqueous solution, containing ferric chloride, polyethylene glycol-2000 and urea. The \( \text{Fe}_2\text{O}_3 \) nanoparticles were characterized by the techniques of TEM, XRD, DSC, TGA and magnetization measurements. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Amorphous metal oxides have many important applications including solar energy transformation, magnetic storage media, use in the electronics industry and also as catalysts [1–5]. Much research has been carried out in the last 20 years on the manufacture of amorphous oxides and their characteristics. Almost all of the amorphous transition metal oxides that have been conventionally produced exhibit superparamagnetic or paramagnetic behavior [6]. Amorphous metal oxides can be obtained by rapidly quenching a molten mixture of metal oxides and a glass former such as \( \text{P}_2\text{O}_5 \), \( \text{V}_2\text{O}_5 \), \( \text{Bi}_2\text{O}_3 \), \( \text{SiO}_2 \), \( \text{CaO} \), etc. [1.6–8], or by thermal decomposition of some easily decomposed metal compounds [4,9]. Amorphous metal oxide thin films on a substrate can be prepared by means of ion beam sputtering, electron beam evaporation or thermal evaporation [10]. So far, only a few pure amorphous metal oxides such as \( \text{Cr}_2\text{O}_3 \), \( \text{V}_2\text{O}_5 \), \( \text{MnO}_2 \) and \( \text{PbO}_2 \) powders have been successfully prepared by means of thermal decomposition [4,9]. Amorphous \( \text{Fe}_2\text{O}_3 \) have been successfully prepared by means of sonication [11]. Other amorphous metal oxides are usually obtained in the form of hydrous oxides [5,12]. Cooling rates of ca. \( 10^5–10^7 \text{ K s}^{-1} \) are generally required to prepare amorphous metals [13]. The thermal conductivities of metal oxides are usually much lower than those of metals. Therefore, it seems to be more difficult to prepare amorphous metal oxides than amorphous metals, since larger cooling rates are required for
their preparation. This is the reason why amorphous metal oxides can only be obtained in the form of thin films, and why a glass former must be used to prevent crystallization of metal oxides if the quenching method is applied.

Since 1986, microwave irradiation as a heating method has found a number of applications in chemistry. The microwave heating technique has been developed [14–21]. The microwave synthesis has been widely used to zeolites. Compared with the usual method, microwave synthesis has the advantages of very short time, small particle size, narrow particle size distribution, and high purity. Janse et al. [14] suggested that these advantages could be attributed to fast homogeneous nucleation and the easy dissolution of the gel. Unfortunately, the exact nature of the interaction of the microwaves with the reactants during the synthesis of materials is somewhat unclear and speculative. However, it is well known that the interaction of dielectric materials, liquids or solids, with microwaves leads to what is generally known as dielectric heating. Electric dipoles present in such materials respond to the applied electric field. In liquids, this constant reorientation leads to friction between molecules, which subsequently generates heat [22].

In this paper, we report a novel method for the preparation of amorphous iron oxide nanoparticles. In this method, amorphous Fe$_2$O$_3$ nanoparticles were successfully prepared by microwave irradiation, by means of the hydrolysis of FeCl$_3$·6H$_2$O in aqueous solution containing polyethylene glycol and urea. The nanoparticles were characterized by X-ray diffraction (XRD), electron microscopy (TEM), etc. Using the same method, amorphous Cr$_2$O$_3$ nanoparticles were also successfully prepared.

2. Experimental

2.1. Materials

The starting materials for the preparation of amorphous Fe$_2$O$_3$ powders were ferric chloride, FeCl$_3$·6H$_2$O from Jinshan chemical reagent factory (China), polyethylene glycol-2000 (PEG) from Tianjin third reagent factory (China), and urea from Shanghai chemical reagent factory (China). All the chemicals were used as received. Distilled water was used throughout the experiment.

2.2. Instruments

Microwave oven with 650 W (Sanle General Electric, Nanjing, China) was used. A refluxing system was connected with microwave oven.

Powder X-ray diffraction (XRD) patterns were recorded on Shimadzu X-ray diffractometer XD-3A (Cu K$_\alpha$ radiation, $\lambda = 0.15418$ nm).

Transmission electron micrographs were obtained with a JEOL-JEM 200CX electron microscope (TEM). The samples used for TEM observations were prepared by dispersing some products in ethanol followed by ultrasonic vibration for 30 min, then placing a drop of the dispersion onto a copper grid coated with a layer of amorphous carbon.

Thermogravimetric and differential thermal analysis (TG–DTA) was conducted in N$_2$ at a heating rate of 10°C/min, in the temperature range of room temperature–1000°C, with Thermal Analyst 2100 TA Instruments (TA Instruments Ins.).

The differential scanning calorimetric (DSC) spectrum was recorded using a Shimadzu DT-40 at 10°C/min.

Magnetization measurements were performed on a Lakeshore Series 7300 vibrating sample magnetometer.

3. Synthesis of amorphous Fe$_2$O$_3$ powder

The mixture solution, containing 1 wt.% PEG, 1.0×10$^{-2}$ M FeCl$_3$·6H$_2$O, and 1 M urea, was reacted in a microwave refluxing system for 10 min with 50% power (i.e., microwave operates in 30-s cycle, on for 15 s, off for 15 s; the total power is still 650 W). After cooling to room temperature, the precipitate was centrifuged, washed with distilled water and air-dried. The final brown product was collected for characterization.

4. Results and discussion

The amorphous nature of the product is demonstrated by the XRD spectrum as well as by electron diffraction patterns. A diffuse ring pattern is detected.
for the as-prepared product, indicating its amorphous nature. The XRD of the product before and after heat treatment is depicted in Fig. 1 and demonstrates clearly the amorphicity of the as-prepared microwave product. The conversion of the amorphous Fe$_3$O$_4$ into the crystalline form occurs when the sample is sintered at 400°C, and Fe$_3$O$_4$ is obtained. All peaks in the Fig. 2a pattern could be indexed to Fe$_3$O$_4$. The grain size of the sample, as calculated from the half-width of the diffraction peaks using the Debye–Scherrer equation, was ca. 12 nm.

Fig. 2 shows the TEM images of as-prepared Fe$_3$O$_4$ nanoparticles sintered at 400°C for 2 h. In Fig. 2a, it is apparent that amorphous Fe$_3$O$_4$ consists of small particles with 3–5 nm-diameter. The amorphous Fe$_3$O$_4$ powder is an agglomerate of small particles. Most of the particles are aggregated in a porous, spongelike form. In Fig. 2b, it is apparent that Fe$_3$O$_4$ consists of riziform particles. The diameter of the riziform particles is ca. 10 nm, and the length is ca. 30 nm.

The DSC curve is shown in Fig. 3. It reveals a distinct exothermic peak at ca. 340°C, which is attributed to the crystallization of amorphous Fe$_3$O$_4$.

Fig. 4 shows the TGA curves for amorphous Fe$_3$O$_4$ powder. In the TGA curve, 28% weight loss is observed between 50°C and 500°C. Weight loss of 22.5%, between 50°C and 200°C, comes from the evaporation of free adsorbed water. Another 5.5% weight loss from 200°C to 500°C may come from the decomposition of residual PEG. Higher than 500°C, no weight loss is observed in the TGA curve.

Room temperature magnetization curves of the as-prepared and sintered samples of Fe$_3$O$_4$ are shown in Fig. 5. The curve of the amorphous Fe$_3$O$_4$ does not reach saturation and no hysteresis is found, indicating that the as-prepared amorphous Fe$_3$O$_4$ particles are superparamagnetic. It is well known that the magnetization of ferromagnetic materials is very sensitive to the microstructure of a particular sample. If a specimen consists of small particles, its total magnetization decreases with the particle size owing to an increase in the dispersion of the exchange integral [23], which finally reaches the superparamagnetic state when each particle acts as a big “spin” with suppressed exchange interaction between the particles.

The proposed mechanism of the microwave heating hydrolysis preparation of Fe$_3$O$_4$ nanoparticles may be similar to general hydrolysis process. First, hydrated Fe$^{3+}$ ions can form complexes with H$_2$O molecules or OH$^\cdot$ ions. Further polymers of this hydroxide, Fe(H$_2$O)$_x$(OH$^-$(3−$x$)$^+$, can serve as
precursors for the oxide. The starting precipitate from the Fe(III) salt may be formed by accompanying numbers of nucleation of the hydrated Fe(H₂O)₆(OH)₃⁺ salt, and consists of very fine precursors for the final oxide. In aqueous solution, H₂O as polar molecules tends to take protons.
away from hydroxide, and can be expressed as follows:

\[
\text{Fe(OH)}_3(\text{OH}^-)^{3-} + \text{H}_2\text{O} \\
\rightarrow \text{Fe}_2\text{O}_3 \cdot n(\text{H}_2\text{O}) + \text{H}_3\text{O}^+ .
\]

In the microwave heating environment, the fast, homogeneous heating results in a rapid and more simultaneous nucleation than heating with conventional method. Moreover, because of the simultaneous nucleation and homogeneous heating, uniformly small particles can be synthesized. In addition, PEG, as a dispersion stabilizer, can inhibit nonhomogeneous precipitation to obtain homogeneous precipitation. The pH of the solution was adjusted by hydrolysis urea, which is favorable for hydrolysis Fe(III) reaction.

In the same method with as-prepared \( \text{Fe}_2\text{O}_3 \) nanoparticles, amorphous \( \text{Cr}_2\text{O}_3 \) has also been successfully synthesized from an aqueous solution consisting of \( 5.0 \times 10^{-2} \text{ M Cr(NO}_3)_3 \cdot 9\text{H}_2\text{O}, 1 \text{ wt.}\% \text{PEG} \) and \( 2 \text{ M urea} \). Fig. 6 shows the TEM images of as-prepared \( \text{Cr}_2\text{O}_3 \) nanoparticles sintered at 650°C for 2 h. It is apparent that amorphous \( \text{Cr}_2\text{O}_3 \) are small particles, 2–3 nm in size. After heat treatment, the product shows 20–50-nm polymorphous particles.

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**Fig. 5.** Magnetization curve of the amorphous \( \text{Fe}_2\text{O}_3 \) at room temperature.

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**Fig. 6.** Transmission electron micrographs of the \( \text{Cr}_2\text{O}_3 \) nanoparticles. (a) amorphous \( \text{Fe}_2\text{O}_3 \); (b) sintering at 650°C.
5. Conclusions

In this work, a microwave heating hydrolysis method has been successfully used for the preparation of amorphous Fe$_2$O$_3$ nanoparticles and amorphous Cr$_2$O$_3$ nanoparticles. Compared with other synthesis methods, microwave synthesis method can be carried out under the conditions of shorter reaction time and lower reaction temperature, and particles of smaller size can be obtained.

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