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Short communication

One-step synthesis of zinc ferrite nanoparticles by ultrasonic wave-assisted ball milling technology

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Abstract

Well-crystallized zinc ferrite nanoparticles with mean size of 20 nm were synthesized at low temperature (≤ 100 °C) by ultrasound wave-assisted aqueous solution ball-milling technique without subsequent calcination. $ZnCO_3 \cdot 2Zn(OH)_2 \cdot H_2O$ were used as the raw material and iron milling balls with diameter of 1.0–1.5 mm were used. As a comparison, aqueous solution ball milling without ultrasonic wave assistance was also investigated. The results showed that, this technique is simple, environmentally friendly and energy-saving for nanocrystal synthesis.

Keywords: Zinc ferrite; Nanoparticles; Ultrasonic wave; Aqueous solution ball milling

1. Introduction

The single-phased spinel structural $ZnFe_2O_4$ of excellent performance is an important magnetic material that can be widely used in ferrofluids [1], density magnetic recording media [2], biomedicine [3] and absorbent material for desulphurization of hot coal gases, etc. [4]. In recent years, several methods including hydrothermal [5], co-precipitation [6], sol–gel [7], microemulsion method [8], solid reaction process [9] and high ball-milling technique [10] have been used to synthesize magnetic zinc ferrite nanoparticles.

Ball-milling technique is the earliest nanoparticle preparation method that has been applied to industrial production among those nanoparticle synthesis technologies. Botta et al. [11] found that roughly pure $ZnFe_2O_4$ was obtained when Zn and Fe_3O_4 mixture were ball-milled for 30 min and sintered at 800 °C. Lefelshtel and his coworkers [12] successfully prepared zinc ferrite by grinding ZnO and Fe_2O_3 mixture for 400 h. Generally speaking, the conventional ball milling needs subsequent calcination at high temperature in order to get well-ordered and stable crystalline state. Because of long production period, large energy consumption and the complicated process, the commercial application of this method is restricted, to a large extent. Timothy and Mason [13] proposed that it is of potential promising to use ultrasonic wave in material synthesis. Ultrasound is environmental friendly and the cavitational energy associated with sonochemistry can be utilized to accelerate the reaction. This effect may be enhanced by combining with other process conditions.

Our research group has successfully prepared ZnO, CuO and NiO nanoparticles by aqueous solution ball milling assisted with ultrasonic wave [14,15]. In this paper, using small iron balls as milling balls, we directly synthesized magnetic zinc ferrite nanoparticles at low temperature (≤ 100 °C) via this technique without subsequent calcination. Because of the economical efficiency, environmentally friendly and energy-saving, this technique may be a potential approach for mass production of nanoparticles.

2. Experimental details

Analytical grade powders of $ZnCO_3 \cdot 2Zn(OH)_2 \cdot H_2O$ were used as starting materials. The raw material was milled in an aqueous solution ball milling device assisted by ultrasonic wave in an atmosphere of ultrapure water (1000 ml). The details of this device were shown in Ref. [14]. The diameter of the iron milling balls is 1.0–1.5 mm, and a ball to powder mass ratio is 100:1. The rotation

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speed of stirrer is 235 rpm, ultrasonic intensity and power are 40 kHz and 200 W, respectively. After a certain time interval, the as-milled products were taken out, filtered and dried at 50 °C for 24 h. For comparison, the samples obtained using other raw materials and without ultrasonic wave assistance were also prepared and studied. The phase constitution, the Raman spectra, the particle size and the magnetization of the as-milled products were characterized by X-ray diffraction (XRD, D-5000), Raman spectroscopy, transmission electron microscopy (TEM, JEOL-1230), and vibrating sample magnetometer (VSM) under an applied field of 1432 kA/m at room temperature.

3. Experimental results

Fig. 1 shows the XRD patterns of $ZnCO_3 \cdot 2Zn(OH)_2 \cdot H_2O$ ball-milled for different durations in water with small iron balls, using aqueous ball milling technique with or without ultrasonic wave assistance. The XRD patterns of $ZnCO_3 \cdot 2Zn(OH)_2 \cdot H_2O$ ball-milled with ultrasonic wave for periods of 20, 40, 60 and 80 h, respectively, can be seen in Fig. 1(a). After milling for 20 h, a remarkable decrease or disappearance of the diffracted intensities for basic zinc carbonate can be observed. At the same time, the phases of $ZnFe_2O_4$, Fe_2O_3, $Zn(OH)_2$ and ZnO started to emerge with a part of unknown composition. With further milling, the diffraction intensities of Fe_2O_3, $Zn(OH)_2$ and ZnO decreased gradually till they disappeared. One can notice that pure well-crystallized spinel $ZnFe_2O_4$ was obtained after milling for 80 h and no other phases were detected. On the other hand, the XRD patterns of as-milled production without ultrasonic wave were plotted in Fig. 1(b) for comparison. After milling for 40 h and 60 h, although the phase of $ZnFe_2O_4$ emerged too, the purity of the products is very low, with lots of impurities of Fe_2O_3, $Zn(OH)_2$ and ZnO. The effect of milling without ultrasonic for 60 h is inferior to that of milling with ultrasonic assistance for 20 h. It indicated that the mechanical force combined with ultrasonic wave significantly accelerated the synthesis reaction process.

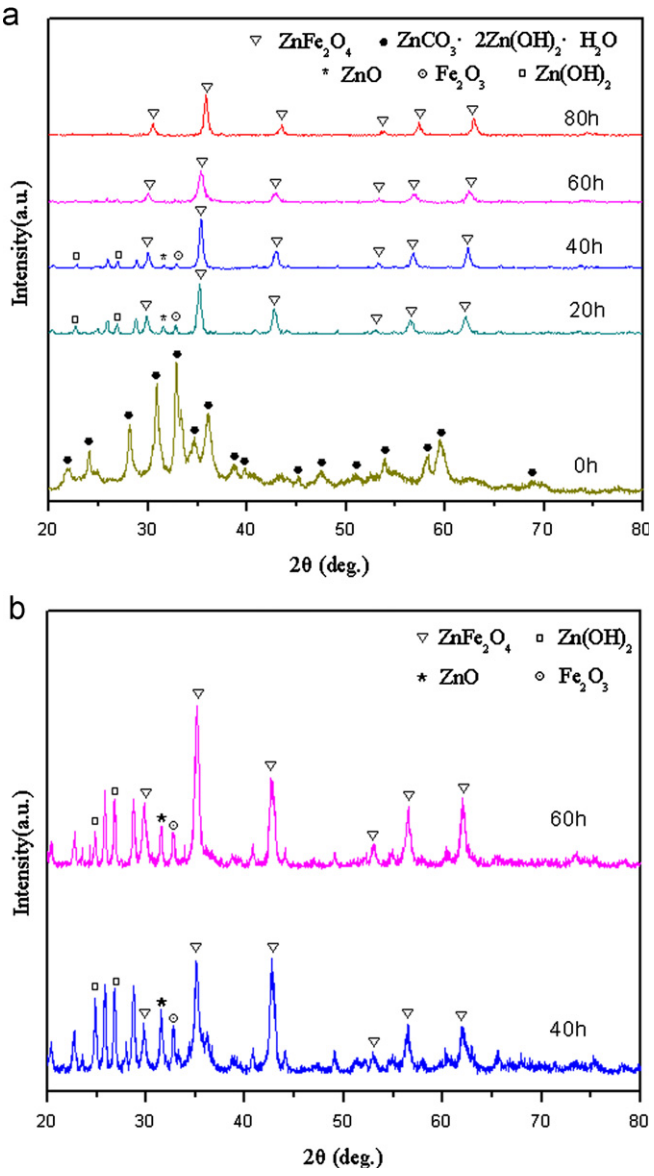

Fig. 1. XRD patterns of raw materials milled in different conditions: (a) milled with ultrasonic wave and (b) milled without ultrasonic wave.

Raman spectra of the 80 h-milled basic zinc carbonate via ultrasonic wave-assisted ball-milling is shown in Fig. 2. The spectra of the sample in the 200–800 cm^{-1} range are fitted with three broad lines at 355, 451 and 647 cm^{-1}. Wang and Schiferl [16] predict the following modes in $ZnFe_2O_4$ spinel:

$$A_{1g}(R)+E_g(R)+F_{1g}+3F_{2g}(R)+2A_{2u}+2E_u+4F_{1u}(IR)+2F_{2u}.$$

There are five first-order Raman active modes ($A_{1g}+E_g+3F_{2g}$), which are 221, 246, 355, 451, 647 cm^{-1}. In our experiment, the active mode at 647 cm^{-1} was corresponded with the motion of oxygen in tetrahedral AO_4 groups. The other low frequency modes represent the characteristics of the octahedral sites (BO_6). The three first-order Raman modes at 355, 451 and 647 cm^{-1} exhibited the broad characteristics. the results of Raman scattering measurements corresponded to the results of

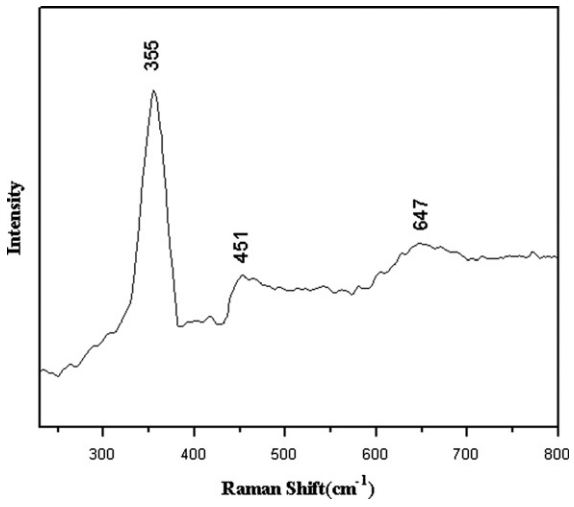

Fig. 2. Raman spectra of raw materials milled with ultrasonic waves for 80 h.

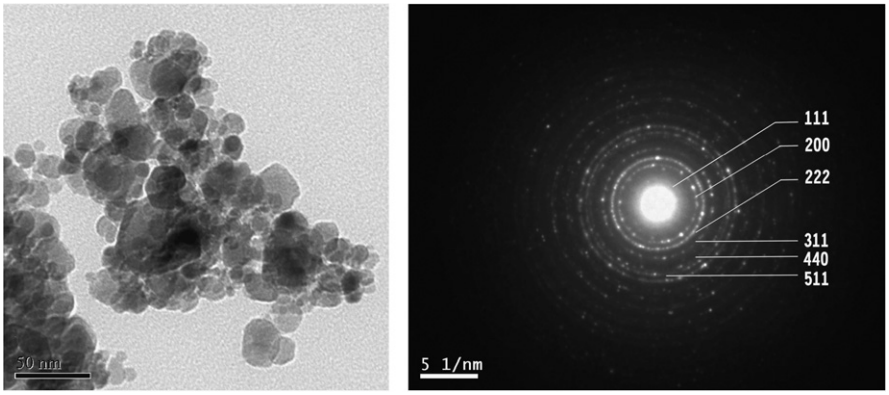

Fig. 3. SEM images of raw materials milled with ultrasonic waves for 80 h.

XRD analysis, which further confirmed that the product is $ZnFe_2O_4$.

TEM image of $ZnFe_2O_4$ obtained by milling basic zinc carbonate with ultrasonic wave assistance for 80 h is shown in Fig. 3. It is clear that most of the particles were ellipsoid with good dispersion. The sample exhibited a narrow particle size distribution with a mean size of about 20 nm, which correspond to the results of XRD analysis. The SAED patterns showed spotty ring patterns, revealing their polycrystalline structure. Through calculating *d* value of the corresponding diffraction ring, from the outside in to, continuously mark crystal indices. Based on Calibration results, it is clear that the product has face-centered cubic lattice structure. This result is in accordance with the XRD data.

The saturated magnetization of $ZnFe_2O_4$ obtained by milling basic zinc carbonate with ultrasonic wave assistance for 80 h is 56.488 emu/g, which is much higher than other reported data for $ZnFe_2O_4$ powders synthesized by high energy ball milling and thermal treatments method [11], showing ultrasonic wave-assisted ball milling method can synthesize $ZnFe_2O_4$ with high saturated magnetization.

4. Discussions

In this paper, when using $ZnCO_3 \cdot 2Zn(OH)_2 \cdot H_2O$ as raw material, the possible chemical reactions in the process of aqueous solution ball milling assisted by ultrasonic wave are given as follows:

$$2Fe + 3H_2O \rightarrow Fe_2O_3 + 3H_2\uparrow$$

$$ZnCO_3 \cdot 2Zn(OH)_2 \cdot H_2O \rightarrow 2Zn(OH)_2 + ZnO + CO_2 + H_2O$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O$$

$$ZnO + Fe_2O_3 \rightarrow ZnFe_2O_4$$

For the ball milling without the ultrasonic wave assistance, although $ZnFe_2O_4$ can be formed by long time milling, energy provided by mechanical milling is not enough,the Purity of product is very low with lots of impurities. However, in the ultrasonic wave assisted-ball milling process, the energy stored in ultrasonic wave will pass on to the reactants when it is reflected and scattered many times between small balls, then can provide much enough energy for triggering reactions and resulting in the formation of $ZnFe_2O_4$.

The synthesis of $ZnFe_2O_4$ is the result of the mutual effect of ultrasonic wave and mechanical force. Based on the principle of mechanochemistry [18–20], after enduring repeated collision, some high activity nano-sized iron powders will peel off from the surface of iron balls, revealing fresh surfaces. Both the iron scraps and the worn iron balls with active surface can react with aqueous solution easily, and then induce the intermediate reaction (1), This reaction continuously repeats in the ball milling process. Because the process of iron powders peeling off from iron balls is slow, the subsequent synthesis reaction cannot completely accomplish without the effect of ball milling.

Comparing with Fig. 1(a) and (b), it can be concluded that ultrasonic wave is of great significance to accelerate the formation of ferrite in the present work and the ultrasonic wave appears to be able to substantially reduce the onset temperature of synthesis. Generally, the cavitations caused by ultrasound can result in the formation, growth, and implosive collapse of bubbles in a liquid, accompanied by the chemical and mechanical effect [21]. Due to ultrasound wave effects, bubbles can continually absorb energy in the process of compression and expansion cycles. When the cavities implode, the gases and vapors inside them are compressed, and generate intense heat, consequently the local temperature of the liquid surrounding the cavity raises and a local hot spot is created. Suslick et al. [22] suggested that when cavitations occur in a liquid near an extended solid surface, the cavity implosion substantially differs from the ideally symmetrical spherical implosion observed in liquid-only systems. The presence of the solid particles may distort the pressure produced by ultrasound field [23]. Cavity implosion near the surfaces of particles will become markedly asymmetric. This can generate a toward-surface jet of liquid with speeds of roughly 400 km/h [24]. Such an effect, integrated with the shock waves produced by cavity implosion, will further erode solid surfaces, remove nonreactive coatings and break brittle powders and therefore reactions

are facilitated. The cavitation effects are also confirmed by lots of researchers [25].

Under the mutual effect of ultrasonic wave and mechanical force, $ZnCO_3 \cdot 2Zn(OH)_2 \cdot H_2O$ was continually crushed into smaller particles, inducing intermediate reaction (2) and generating activated ZnO. At the same time, reaction (1) is also facilitated by the effect of ultrasonic wave and produced activated Fe_2O_3. Furthermore, the ultrasonic wave-induced decrease in the pH value of solution may facilitate the transition from $Zn(OH)_2$ to ZnO (reaction (3)) [15], finally, the high reactive intermediate products ZnO and Fe_2O_3 react and generate $ZnFe_2O_4$ (reaction (4)) because of the coupling effects. Therefore, $ZnFe_2O_4$ can be synthesized directly at low temperature without subsequent high temperature calcination. The local temperature is high in the aqueous solution because of acoustic cavitation, while the whole reaction proceeds in water, so the overall temperature of the system unlikely exceeds 100 °C, which is much lower than that required for conventional solid state reaction. Compared to the commonly ball milling methods, our method does not need subsequent calcination, so it is simpler.

In addition, the $ZnFe_2O_4$ peeled off from the particles or balls can be rapidly dispersed in the solution, due to the coupling effects of ultrasonic wave and mechanical force. Therefore a large amount of fine crystals were formed in the liquid. Meanwhile, ball milling can effectively suppress the grain growth of the formed ferrite, and simultaneously prevent the agglomeration of particles. This is the reason why ultrafine $ZnFe_2O_4$ particles are obtained by ultrasonic-assisted ball milling.

5. Conclusions

Using $ZnCO_3 \cdot 2Zn(OH)_2 \cdot H_2O$ as raw material and small iron balls as milling balls, ellipsoidal zinc ferrite particles can be one-step synthesized at low temperature (≤ 100 °C) via ultrasonic wave-assisted ball milling technique, in which the calcination treatment is not needed. Meanwhile, ultrasonic wave significantly accelerated the synthesis reaction process.

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