Analyses of factors affecting nickel ferrite nanoparticles synthesis in ultrasound-assisted aqueous solution ball milling

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ABSTRACT

Ball milling experiments were conducted with and without ultrasound wave assistance in deionized water using $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ as raw materials. In the reaction process of $NiFe_2O_4$ prepared by ultrasound-assisted aqueous solution ball milling, some influencing factors including raw materials, ultrasonic frequency, ball to powder ratio and liquid level were changed. Samples were characterized by X-ray diffraction, fluorescence measurements and electroconductivity detections. The results indicate that more hydroxyl radicals and ions can be generated under the coupling effect of ultrasonic and ball milling. The fluorescence measurements and electroconductivity detections also reflect the reaction speed, allowing for optimal parameters to be determined.

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1. Introduction

Many methods have been used to prepare nickel ferrite [1–10], an important magnetic material with wide applications [11–20]. Among these approaches, ultrasound-assisted aqueous solution ball milling, which is a combination of ultrasound and ball milling techniques, could generate the product with shorter time [21]. In addition, using ultrasound-assisted aqueous solution ball milling can directly synthesize nickel ferrite nanoparticles at low temperatures ($\leqslant 100\,^{\circ}C$) [22]. As well known, the ultrasonic cavitation is accompanied with the generation of active hydroxyl radicals and ions, which participate in the reaction and promote the reaction [23]. Hydroxyl radical has a strong ability to get electrons. It is used to increase the degradation rate of refractory organics and the biological activity in water treatment [24]. Hydroxyl radical also causes hydroxylation of various biomolecules by reduction of unsaturated bonds present in their structures, which plays an important role in the preparation of pharmaceutical and biological applications [25].

Hydroxyl radicals generated by ultrasound-assisted aqueous solution ball milling [26,27] will accelerate chemical reactions on the new active surfaces [28,29]. By introducing radical sensitive fluorescence indicators, the fluorescence intensity of the solution can be quantitatively measured, which illustrates the number of hydroxyl radicals generated in the system [30]. The ion concentration in the solution also changes during the process of ultrasound-assisted aqueous solution ball milling. The larger the ionic concentration is, the greater the conductivity is [31]. The conductivity quantitatively measured by electroconductivity detections can be used to illustrate the number of ions [32]. Hydroxyl radicals and ions were consumed in the reaction process and the quantity of them was also changed with time [33]. When the reaction was violent, the consumption of hydroxyl radicals and ions increased with the quantity reducing. Accordingly, the amount of hydroxyl radicals and ions can indirectly reflect the reaction speed in the system.

Obviously, there are many important parameters in the system of ultrasound-assisted aqueous solution ball milling, for examples, different raw materials produced different reactions [34]. The changes of ultrasonic frequency directly affected the ultrasonic cavitation [35]. The ball to powder ratio was one of the important parameters of ball milling technology [36]. The medium volume affected the sound intensity distribution and the solution concentration [37]. Different amount of hydroxyl radicals and ions was generated under different parameters. The comparison of multiple curves of fluorescence intensity and electroconductivity with the X-ray diffractions can be used to reflect the advantages and disadvantages of the influencing factors.

In the present paper, ultrasound-assisted aqueous solution ball milling generated more hydroxyl radicals and ions than ultrasound

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or ball milling. This study fundamentally explained why ultrasound-assisted aqueous solution ball milling can synthesize the single-phase product which cannot be generated by ball milling. Various technological parameters affecting the reaction process of the ultrasound-assisted aqueous solution ball milling including raw materials, ultrasonic frequency, ball to powder ratio and medium volume were studied and the optimal parameters were determined.

2. Experiments

Nickel ferrite was synthesized by ultrasound-assisted aqueous solution ball milling in a special stainless steel milling pot ($\Phi = 165$ mm, $h = 158$ mm). 304 stainless steel milling balls ($\Phi = 1$–1.5 mm) with a total weight of 2 kg were used. The raw materials were all analytical pure (particle sizes <0.15 mm). The reaction medium was deionized water. The stirringrod was adjusted to a height of 5 mm from the bottom of the pot. The stirring speed was constant at 250 r/min. The power of the ultrasonic generator was 66 W. The average temperature of the chemical reactions in the milling pot was 50 °C. Samples were extracted at specific times, then filtered and dried at 50 °C for 24 h.

At the beginning of fluorescence determination, raw materials, a terephthalic acid (0.16 mol) catcher solution and a phosphate buffer solution (0.2 mol NaOH and 0.2 mol KH_2PO_4) were put into the milling pot in order to make pH = 7.3. During the milling process, every 30 ml samples were extracted using disposable pipettes at set times and then the same amount of catcher and buffer solutions were added. Samples were filtered many times until the solution was limpid. The fluorescence intensities of samples were recorded at 310 nm excitation and monitored for the 426 nm emission on a Fluorescence Spectrophotometer (Hitachi, Model F2500).

A conductivity meter Model DDS-11A was used to detect the electroconductivity of the reaction solution. The electrode constant measured was $J = 1021$. To ensure the accuracy of measurement, nitrogen and oxygen dissolved in the solution must be in excess. Accordingly, the experimental apparatus was refitted, as shown in Fig. 1.
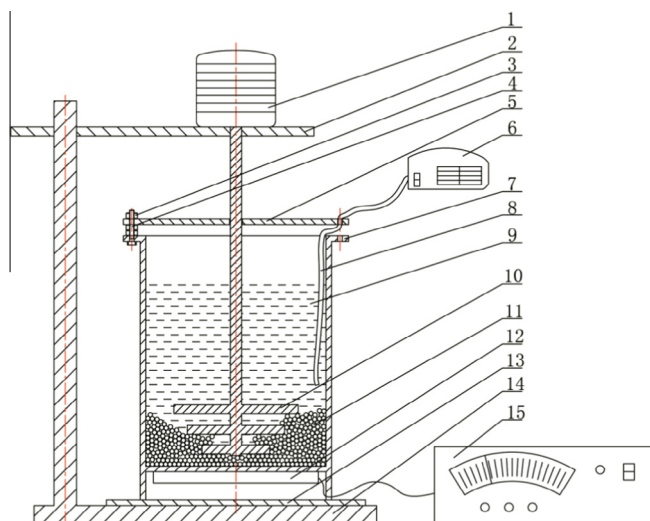

Fig. 1. Schematic diagram of ultrasound-assisted aqueous solution ball milling refitted for electroconductivity detection. 1-electromotor; 2-liftplatform; 3-nut × 9; 4-bolt × 3; 5-cover of milling pot; 6-oxygen pump; 7- stainless steel milling pot; 8-snorkel × 3; 9-reaction medium; 10-stirringrod; 11-milling balls; 12-ultrasound transducer; 13-base of milling pot; 14-supporter; 15-ultrasonic generator.

PH meter Model PHB-1 was used to determine the pH values of samples. The phase constitutes of samples were analyzed by X-ray diffraction (Model Siemens D-5000, Cu Ka, incident wavelength was 0.154056 nm).

Table 1 shows the conditions parameters for a set of experiments. Fluorescence intensity, electroconductivity and pH values were measured in experiment 1. Fluorescence intensity, electroconductivity, X-ray diffraction and pH values were measured in experiments 2, 3 and 4. Electroconductivity, X-ray diffraction and pH values were measured in experiments 5 and 6. In the contrast experiments of fluorescence intensity, the test was repeated four times. In the contrast experiments of electroconductivity, the test was repeated three times.
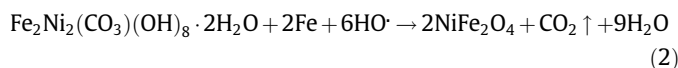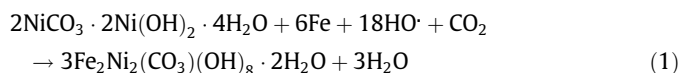
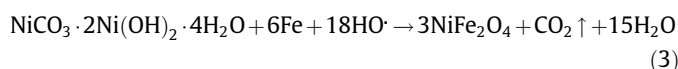## 3. Results and discussions

3.1. Deionized water

The results of fluorescence intensity and electroconductivity determined in experiment 1 are shown in Fig. 2. First, these results showed that hydroxyl radicals were generated by ball milling because the intense mechanical energy induced by ball milling can break the bonds of water molecules [38]. Ball milling allowed the N_2 and O_2 dissolved in deionized water to react to generate HNO_3 and HNO_2, increasing the ionic concentration and resulting in a change in the conductivity of the solution. The pH value was changed from 7.2 to 5.3, indicating that H^+-ions were indeed generated [39]. Second, the quantity of hydroxyl radicals generated by ultrasound-assisted aqueous solution ball milling was greater than that generated by ultrasound treatment or ball milling only. This discovery demonstrated that the coupling effect of ultrasound and ball milling techniques could accelerate the generation of hydroxyl radicals. The ionic concentration of the ultrasound-assisted aqueous solution ball milling system was also greater than that of the ultrasound or ball milling only process, which illustrated that the coupling effect of ultrasound and ball milling could accelerate the generation of ions in the system. From the view of the quantity of hydroxyl radicals and ions, the generation of ultrasound-assisted aqueous solution ball milling did not exceed the sum of the individual effect alone. This could be induced by the inverse dependence between the mechanical of ball milling and the chemical effects of ultrasound [21]. Third, the curves in Fig. 2 increased with time until they became horizontal, which implied that the quantity of hydroxyl radicals and ions generated in a fixed system could keep growing up to a constant value.

3.2. $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ and Fe powder as raw materials

The chemical reactions involving hydroxyl radicals are proposed as follows:

$$2NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O + 6Fe + 18HO^{\cdot} + CO_2$$
$$\rightarrow 3Fe_2Ni_2(CO_3)(OH)_8 \cdot 2H_2O + 3H_2O \tag{1}$$

$$Fe_2Ni_2(CO_3)(OH)_8 \cdot 2H_2O + 2Fe + 6HO^{\cdot} \rightarrow 2NiFe_2O_4 + CO_2 \uparrow + 9H_2O \tag{2}$$

The total reaction is

$$NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O + 6Fe + 18HO^{\cdot} \rightarrow 3NiFe_2O_4 + CO_2 \uparrow + 15H_2O \tag{3}$$

The results of X-ray diffraction, fluorescence intensity and electroconductivity determined in experiment 2 were shown in Fig. 3. Owing to the raw materials participating in the reaction, the pH values were all 7.2. Three curves of fluorescence intensity rose