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Synthesis of well-dispersed $CoFe_2O_4$ nanoparticles via PVA-assisted low-temperature solid state process

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ABSTRACT

A facile PVA-assisted low-temperature solid state process using $CoCl_2{\cdot}6H_2O$, $FeCl_3{\cdot}6H_2O$, and NH_4HCO_3 as precursors and using PVA chains as a medium to synthesize well-dispersed $CoFe_2O_4$ nanoparticles was developed. The effects of the amount of added PVA and calcined temperature on the characteristics of the products were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM) and BET surface area analysis. Results showed that the facile addition of PVA chains in the reactant mixture resulted in the formation of well-dispersed $CoFe_2O_4$ nanoparticles, and the increase in specific surface area from 14.82 m^2/g to 66.92 m^2/g.

1. Introduction

Spinel ferrite nanoparticles have been intensively investigated in recent years because of their remarkable optical, electrical, and magnetic properties [1–4]. As an important spinel ferrite, cobalt ferrite ($CoFe_2O_4$) nanoparticles are candidate materials for a variety of applications, for example, high-density magnetic recording technology, ferrofluid technology, bio-medical technology, magnetic targeted delivery, and so on [5–9].

Various synthetic methods, such as sol–gel [10], microemulsion [11], chemical co-precipitation [12], hydrothermal method [13], microwave synthesis [14], ceramic method [15], and so on, have been developed to synthesize $CoFe_2O_4$ nanoparticles.

In comparison to the above-outlined techniques, low-temperature solid state process requires neither complex apparatus and sophisticated techniques nor solvent or solution. So, it is a convenient, environment-friendly, low-cost, time-saving, and low-energy consumption process [16–18]. So far, $CoFe_2O_4$ nanoparticles have been synthesized by a low-temperature solid state process using various salts, such as sulphate, acetate, nitrate, and chloride salts. It has been noted that when chloride salts were used during low-temperature solid state process, the least particle size could be obtained [19]. However, the nanoparticles were synthesized by conventional low-temperature solid state reaction generally exited in agglomeration. In order to resolve the above problem, in this paper, we reported, for the first time, a facile PVA-assisted low-temperature solid state synthesis of $CoFe_2O_4$ nanoparticles using $CoCl_2{\cdot}6H_2O$, $FeCl_3{\cdot}6H_2O$, and NH_4HCO_3 as the reactants. Our aims are to develop a simple synthetic method of good dispersibility and uniform crystallinity $CoFe_2O_4$ nanoparticles.

2. Experimental

In a typical procedure, analytically pure $CoCl_2{\cdot}6H_2O$, $FeCl_3{\cdot}6H_2O$, NH_4HCO_3, and PVA were mixed in an agate mortar at a molar ratio of 1:2:10:0.5 and ground uniformly for about 50 min. The reaction started readily during the mixing process, and accompanied by release of heat and gas. The gas evolution helped in limiting the inter-particle contact and hence, the resultant products consisted of fine and loosen particulates. After spontaneous air-drying, the products were thoroughly washed with deionized water for several times to remove ammonium chloride and excess NH_4HCO_3. Then, the products were collected by centrifugation and the precipitate was dried in an oven at 70 °C for 2 h. Finally, $CoFe_2O_4$ nanoparticles were obtained by calcining in muffle at 700 °C for 2 h.

The as-prepared product was characterized by X-ray diffraction on a Bruker Advance D8 X-ray diffractometer with Cu $K\alpha_1$ radiation ($\lambda = 0.154056$ nm) in the 2θ range from 20° to 70°, by a step of 0.02°. The working voltage was 40 kV and the current was 40 mA. The crystallite size D_{XRD} was calculated from line broadening of the (3 1 1) XRD peak by Scherrer's formula, where the Scherrer constant (particle shape factor) was taken as 0.9. Transmission electron microscopy (TEM) was carried out with a JEOL TEM-200CX microscope. The specific surface area and the adsorption isotherm curve of the powders were measured with a COULTER SA 3100 analyzer using the multipoint Brunauer, Emmett, and Teller (BET) adsorption. The particle sizes were estimated from the formula: $D_{BET} = 6/\rho S_{BET}$. The degree of agglomeration of the obtained particles was valuated via D_{BET}/D_{XRD}.

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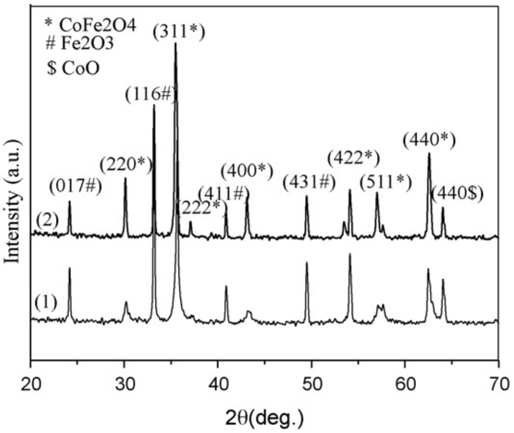

Fig. 1. XRD patterns of the as-prepared $CoFe_2O_4$ nanoparticles in the absence of PVA (1) 500 °C and (2) 700 °C.

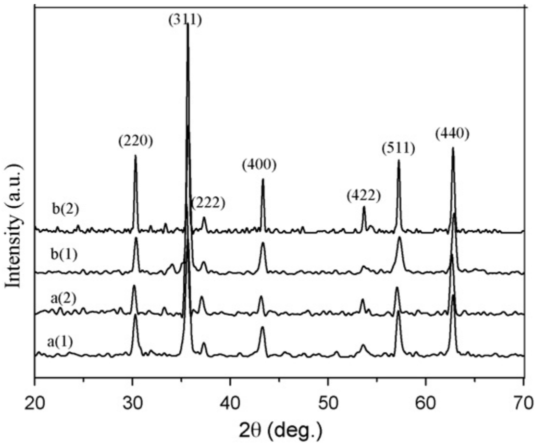

Fig. 3. XRD patterns of the as-prepared $CoFe_2O_4$ nanoparticles at different PVA addition amount (a) $CoCl_2{\cdot}6H_2O$:$FeCl_3{\cdot}6H_2O$:NH_4HCO_3:PVA = 1:2:10:1, (b) $CoCl_2{\cdot}6H_2O$:$FeCl_3{\cdot}6H_2O$:NH_4HCO_3:PVA = 1:2:10:0.5. (1) 500 °C and (2) 700 °C.

3. Results and discussion

3.1. Effect analysis of PVA addition amount

In our previous work, we found that the conventional low-temperature solid state method often produced poor crystallinity and agglomerated nanocrystallite, as shown in Figs. 1 and 2a. The grinding did not effectively disperse reactants and restrain agglomeration of resultants. Recently, we found that the introduction of PVA into reactant mixture could effectively improve crystallinity and prevent nanocrystallites from forming inseparable three-dimensional network agglomerates. We denote the method as PVA-assisted low-temperature solid state synthesis.

In our present work, the amount of added PVA was varied systematically to investigate the effect on characteristics of the as-prepared nanoparticles. Figs. 1 and 3 respectively show the XRD pattern of as-prepared $CoFe_2O_4$ nanoparticles in the absence and presence of PVA at two given temperatures. It is clear from Fig. 1 that the diffraction peaks of Fe_2O_3 and CoO phase are also observed in addition to that of $CoFe_2O_4$ phase. Further, it is evident that the sample in Fig. 3 has a more complete crystalline structure compared to the sample in Fig. 1, which suggests that the addition of PVA can significantly improves the crystallinity and composition of $CoFe_2O_4$ nanoparticles. Moreover, spinel-type $CoFe_2O_4$ nanoparticles are formed when the resultant powder is calcined at a temperature higher than 400 °C, and the crystallinity of the product improves with increasing temperature. Here, the three-dimensional network structure of PVA acts like a confined space that allows the sufficient contact and reaction of the reactants and also limits the growth of the $CoFe_2O_4$ nanoparticles, leading to the formation of $CoFe_2O_4$ nanoparticles of good crystallinity and high dispersibility.

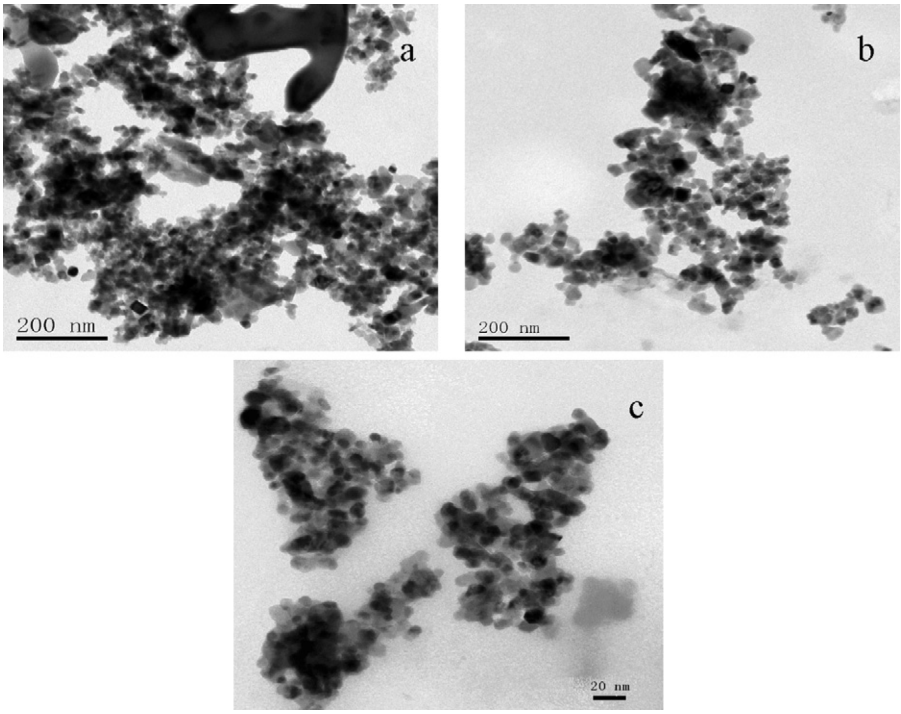

Fig. 2. TEM micrograph for the $CoFe_2O_4$ nanoparticles at 700 °C with different PVA addition amount (a) in the absence of PVA (b) $CoCl_2{\cdot}6H_2O$:$FeCl_3{\cdot}6H_2O$:NH_4HCO_3:PVA = 1:2:10:1 and (c) $CoCl_2{\cdot}6H_2O$:$FeCl_3{\cdot}6H_2O$:NH_4HCO_3:PVA = 1:2:10:0.5.

3.2. TEM analysis

The size, shape and agglomeration state of the $CoFe_2O_4$ nanoparticles via a low-temperature solid state process are showed in Fig. 2. Fig. 2a reveals that the $CoFe_2O_4$ particles prepared in the absence of PVA present the three-dimensional fractal formed by nanocrystallite agglomeration. As shown in Fig. 2b and c, the introduction of PVA chains breaks up the network structure of agglomerated nanocrystallites and results in the formation of high dispersive $CoFe_2O_4$ nanoparticles. However, the dispersibility is not in proportion to the amount of added PVA. It is evident that the size, shape and agglomeration state of the as-prepared $CoFe_2O_4$ nanoparticles in Fig. 2c are better than that in Fig. 2b. Due to the agglomeration inhibition of PVA during drying and sintering, no apparent agglomeration between particles is observed.

3.3. Reaction mechanism analysis

Unlike reactions in solution, solid state reactions are carried out directly without solution. So they have a different reaction mechanism from solution reactions. Considering that NH_4HCO_3 is decomposed by a strong heat of reaction to produce CO_2, NH_3, and H_2O, and based on the above experimental results, the mechanism of the PVA-assisted low-temperature solid state reaction can be expressed as follows:

$$\begin{aligned} &2CoCl_2{\cdot}6H_2O + 5NH_4HCO_3 \\ &\rightarrow Co_2(OH)_2CO_3 + 4NH_4Cl + NH_3 + 4CO_2 + 8H_2O \\ &\rightarrow 2CoO + 4NH_4Cl + NH_3 + 5CO_2 + 9H_2O(\text{roomtemperature}) \end{aligned} \tag{1}$$

$$\begin{aligned} &2FeCl_3{\cdot}6H_2O + 6NH_4HCO_3 \\ &\rightarrow 2Fe(OH)_3 + 6NH_4Cl + 6CO_2 + 12H_2O \\ &\rightarrow Fe_2O_3 + 6NH_4Cl + 6CO_2 + 15H_2O(\text{roomtemperature}) \end{aligned} \tag{2}$$

$$CoO + Fe_2O_3 \rightarrow CoFe_2O_4(400\,^{\circ}C) \tag{3}$$

So the solid state reaction may be generalized and be expressed as follows:

$$\begin{aligned} &2CoCl_2{\cdot}6H_2O + 4FeCl_3{\cdot}6H_2O + 17NH_4HCO_3 + PVA \\ &\quad \rightarrow 2CoFe_2O_4 + 16NH_4Cl + 17CO_2 + NH_3 + 39H_2O + PVA \end{aligned} \tag{4}$$

That is to say, when two solid phases are in contact with each other, a solid state reaction may occur in the presence of a thermodynamic driving force. However, the thermodynamic driving force is not a sufficient condition for the solid state reaction, and whether the reaction would occur also depends on the reaction kinetics. There is a kinetic barrier for the reaction, since it requires atomic diffusion in solids and nucleation of new phases. To overcome the kinetic barrier, the mobility of the atoms involved, i.e. their diffusivities, must be sufficiently high. Atomic diffusivity is proportional to temperature, and thus high atomic diffusivity can be achieved by heating the diffusion couple to an elevated temperature. This is why the solid state reaction often requires annealing of the diffusion couple at an elevated temperature.

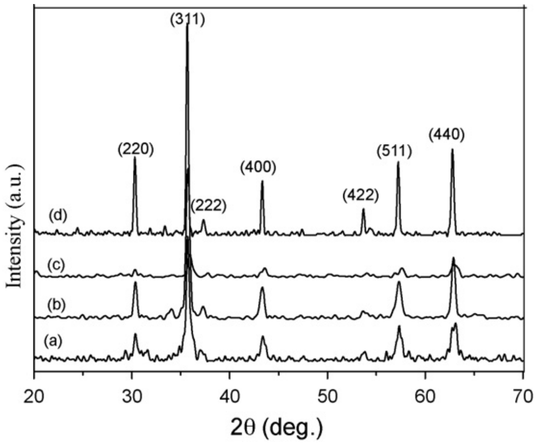

Fig. 4. XRD pattern of as-prepared $CoFe_2O_4$ nanoparticles at $CoCl_2{\cdot}6H_2O$:$FeCl_3{\cdot}6H_2O$:NH_4HCO_3:PVA = 1:2:10:0.5. (a) 400 °C, (b) 500 °C, (c) 600 °C and (d) 700 °C.

3.4. Effect analysis of calcined temperature

The influences of different calcined temperatures on characteristics of as-prepared $CoFe_2O_4$ nanoparticles are shown in Fig. 4. As is shown in Fig. 4, the crystallinity of $CoFe_2O_4$ nanoparticles improves with increasing temperature. When the sintering temperature is elevated to 700 °C, all the diffractive peaks are well indexed to spinel phase $CoFe_2O_4$ (JCPDF card no. 22-1086), and no impurities are detected. The sharp diffraction peaks manifest that the as-synthesized $CoFe_2O_4$ nanoparticles have high crystallinity.

3.5. BET analysis

The N_2 adsorption study on $CoFe_2O_4$ nanoparticles prepared at different PVA addition amount is shown in Fig. 5. The isotherms generally belong to type II of the BET classification for all samples. The volume adsorbed at same pressure of $CoFe_2O_4$ nanoparticles gradually increased with the introduction of PVA, which indicate that the introduction of PVA has a great effect on the surface area of $CoFe_2O_4$ nanoparticles.

Table 1 summarizes the effect of the amount of PVA and calcined temperature on the properties of the $CoFe_2O_4$ nanoparticles. For the $CoFe_2O_4$ nanoparticles prepared via low temperature solid state process, the D_{BET} is generally (except for sample 5) far larger than D_{XRD}, i.e. the degree of agglomeration is high, indicating that the particles are composed of agglomeration crystallites. It is very significant that the introduction of PVA into the low temperature solid state process results in increase in surface area from 14.82 m^2/g to 66.92 m^2/g and a decrease in degree of particle agglomeration from 1.55 to 0.83, which can be also confirmed by the comparative observation of TEM in Fig. 2a and c.

Table 1
The effects of PVA addition amount and calcined temperature on the properties of the $CoFe_2O_4$ nanoparticles prepared.

Sample	Molar ratio	Calcined temperature (°C)	S_{BET} (m^2/g)	D_{XRD} (nm)	D_{BET} (nm)	Degree of agglomeration (D_{BET}/D_{XRD})
1	1:2:10:0	700	14.82	39.8	61.8	1.55
2	1:2:10:1	600	17.03	35.9	53.8	1.50
3	1:2:10:1	700	26.77	28.6	34.2	1.20
4	1:2:10:0.5	600	38.79	21.8	23.6	1.08
5	1:2:10:0.5	700	66.92	16.7	13.8	0.83

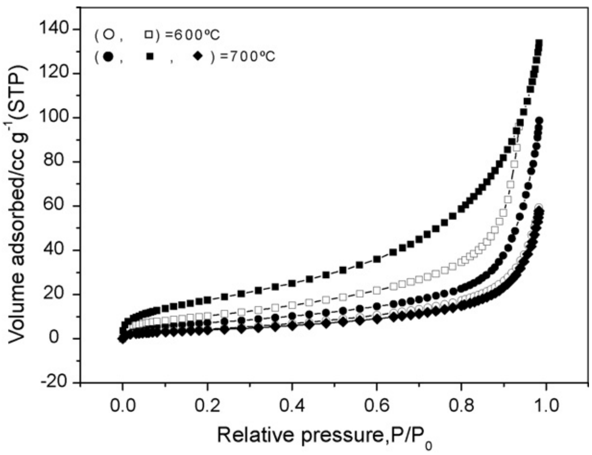

Fig. 5. The adsorption isotherm curves for $CoFe_2O_4$ nanoparticles with different PVA addition amount and different calcined temperature: (a) (●, ○) $CoCl_2{\cdot}6H_2O$:$FeCl_3{\cdot}6H_2O$:NH_4HCO_3:PVA = 1:2:10:1, (b) (■, □) $CoCl_2{\cdot}6H_2O$:$FeCl_3{\cdot}6H_2O$:NH_4HCO_3:PVA = 1:2:10:0.5 and (c) (◆) in the absence of PVA.

4. Conclusions

We demonstrate in this paper a facile and novel approach to form the good dispersibility $CoFe_2O_4$ nanoparticles via the simple introduction of PVA in low-temperature solid state process. The effects of the amount of added PVA and annealing temperature on the crystallinity of the product were studied. The addition of PVA augments the contact and reaction of the reactants inter-particle, and breaks up the three-dimensional network structure of the products, resulting in formation of the well-dispersed $CoFe_2O_4$ nanoparticles. A possible mechanism based on the experimental results is proposed. Similarly, many other spinel ferrite nanoparticles can be synthesized via PVA-assisted low-temperature solid state process.

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