

# Synthesis and characterization of $\text{CoFe}_2\text{O}_4$ nanoparticles<sup>①</sup>

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**Abstract:** The reverse microemulsion composition consisting of 37.0% cyclohexane, 26.0% surfactant (TX-10 and AEO9), 13.0% *n*-pentanol and 24.0% aqueous phase was investigated and chosen for the preparation of cobalt ferrite nanoparticles. Then silicon dioxide was coated onto the surface of the magnetite nanoparticles. The two kinds of nanoparticles were characterized by means of X-ray diffractometry (XRD), scanning electron microscopy (SEM), infrared spectroscopy (IR), and energy dispersion spectrometry (SEM-EDS). The SEM results indicate that both nanoparticles have narrow size distribution, less agglomeration and are in the size range of 10–60 nm. XRD patterns show that there is not any peak detected except for the peaks of  $\text{CoFe}_2\text{O}_4$ , and imply that the coated silicon dioxide is amorphous. IR absorption spectra of the samples show the characteristic bands of Si—O—Si group and Fe—O group. SEM-EDS indicates that the molar ratio of Fe to Si is 96.11:3.89. These results prove that a thin film of  $\text{SiO}_2$  is coated on the surface of the magnetite nanoparticles. And the characterization of cobalt ferrite nanoparticles prepared by conventional precipitation method are compared.

**Key words:**  $\text{CoFe}_2\text{O}_4$ ; nanoparticle; microemulsion; silicon dioxide; coating

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## 1 INTRODUCTION

Recently, the nanoparticles in the size range of 1–100 nm have been received increasing attention because of their unusual physical and chemical properties compared with larger particles<sup>[1, 2]</sup>. Various nanoparticles have been prepared by different kinds of methods, such as coprecipitation method<sup>[3]</sup>, shock wave treatment<sup>[4]</sup>, sol-gel process<sup>[5]</sup>, hydrothermal process<sup>[6]</sup> and microemulsion approach<sup>[7–10]</sup>. In comparison, microemulsion system is more attractive than other processing routes, so various organic or inorganic nanoparticles have been prepared via microemulsion approach. For example, Wang et al<sup>[11]</sup> reported the preparation of  $\alpha$ -Fe nanoparticles by a microemulsion system consisting of saturated  $\text{Fe}^{2+}$  solution, isopropanol and PVP; Chen et al<sup>[11]</sup> synthesized colloidal gold nanoparticles by a reverse microemulsion system consisting of CTAB, *n*-pentanol, hexane and water; Capanetli et al<sup>[2]</sup> prepared CdS nanoparticles by a microemulsion system containing water, AOT and *n*-heptane.

Ferrite nanoparticles are the promising materials for extensive investigation and application because of their excellent catalytic activity and mag-

netic characteristics. At present, several synthesis methods of  $\text{CoFe}_2\text{O}_4$  nanoparticles have been developed, such as chemical coprecipitation method<sup>[12]</sup>, sol-gel process<sup>[13]</sup> and microemulsion approach<sup>[14]</sup>. For example, Xu et al<sup>[15]</sup> synthesized nanoparticles by combustion method; Shah and Pillai<sup>[14]</sup> prepared the precursor of  $\text{CoFe}_2\text{O}_4$  by microemulsion approach, and these precursors were then calcined to prepare  $\text{CoFe}_2\text{O}_4$  nanoparticles. Ferrite nanoparticles have been applied to biomedical research for the last decade. Although ferrite nanoparticles have good magnetic characteristics, their poor biocompatibility restricts their application. While  $\text{SiO}_2$  has good biocompatibility. In this paper, we attempted to synthesize  $\text{CoFe}_2\text{O}_4$  nanoparticles using a new reverse microemulsion system consisting of water(or brine), TX-10, AEO9, cyclohexane and *n*-pentanol. TX-10 and AEO9 were used as a new mixed surfactant with the mass ratio of 1:1. And then we prepared silica-coated  $\text{CoFe}_2\text{O}_4$  with good biocompatibility and magnetic characteristics by coating process. The characterization of uncoated  $\text{CoFe}_2\text{O}_4$  and  $\text{SiO}_2$ -coated  $\text{CoFe}_2\text{O}_4$  nanoparticles were investigated using

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XRD, SEM, IR and EDS techniques, and the characterization of  $\text{CoFe}_2\text{O}_4$  nanoparticles prepared by conventional precipitation method was also compared.

## 2 EXPERIMENTAL

### 2.1 Chemical reagents

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (99.0% pure),  $\text{Co}(\text{NO}_3)_2$  (99.0% pure), cyclohexane (99.0% pure), *n*-pentanol (99.0% pure) and ammonia (> 36%,  $\text{NH}_3$ ) were produced by the Second Chemical Reagent Plant of Shanghai, China. Methanol (99.0% pure) and acetone (99.0% pure) were purchased from the Chemical Reagent Plant of Hunan Normal University. TX-10 (99.0%, technical grade) and AEO9 (99%, technical grade) were supplied by Hunan Licheng Groups and double-distilled water was used to prepare the samples.

### 2.2 Microemulsion composition

In order to prepare reverse microemulsions, a high-purity cyclohexane was used as the continuous oil phase; *n*-pentanol was used as cosurfactant; mixture of AEO9 and TX-10 (mass ratio of 1: 1) was used as surfactant; and an aqueous solution was used as the dispersed phase. The composition was indicated in Table 1. Two microemulsions (I and II) with identical compositions but different aqueous phases were prepared. The aqueous phase in microemulsion I was a mixture of cobalt (II) nitrate and ferric nitrate solution with the molar ratio of 1: 2. The aqueous phase in microemulsion II was the precipitation agent, ammonia, with a sufficient concentration for the precipitating of  $\text{Co}^{2+}$  and  $\text{Fe}^{3+}$  ions. In order to identify the oil-continuous compositions of these two reverse microemulsions, we determined the two partial ternary phase diagram (at room temperature) with the mixed nitrate solution or ammonia solution as aqueous phase. The oil-continuous microemulsions were checked by the measurement of electrical conductivity.

**Table 1** Composition of microemulsion system

Component	Microemulsion I	Microemulsion II	Mass fractions/%
Aqueous phase	0.20 mol/L $\text{Fe}(\text{NO}_3)_3 +$ 0.10 mol/L $\text{Co}(\text{NO}_3)_2$	0.40 mol/L $(\text{NH}_4)\text{OH}$	24.0
Surfactant	TX-10+ AEO9	TX-10+ AEO9	26.0
Cosurfactant	<i>n</i> -pentanol	<i>n</i> -pentanol	13.0
Oil phase	Cyclohexane	Cyclohexane	37.0

### 2.3 Nanoparticle preparation

$\text{CoFe}_2\text{O}_4$  nanoparticles were prepared via two

processing methods: 1) the conventional precipitation method and 2) the microemulsion method. In the precipitation method, aqueous  $\text{NH}_3$  solution (24%, mass fraction) was added to 0.10 mol/L  $\text{Co}^{2+}$  and 0.20 mol/L  $\text{Fe}^{3+}$  solution, then the system was refluxed at 85 °C for 5 h. Finally  $\text{CoFe}_2\text{O}_4$  nanosized product was dried under vacuum at 60–70 °C.

For the microemulsion method, these two reverse microemulsions (I and II) were mixed under constant stirring. Within the nano-sized aqueous droplets of the reverse microemulsion, the reaction of  $\text{Co}^{2+}$  and  $\text{Fe}^{3+}$  ions with  $\text{OH}^-$  anions happened and the cobalt-iron hydroxide precipitate formed. The process of the reaction was controlled by the pH value through modulating the amounts of ammonia reverse microemulsion. After 10 min, the system was warmed to 95 °C, refluxed for 5 h, and the  $\text{CoFe}_2\text{O}_4$  nanoparticles appeared. Being naturally cooled to room temperature, the  $\text{CoFe}_2\text{O}_4$  nanoparticles were separated from the reaction media by centrifugation and washed with absolute ethanol and distilled water for several times. Finally,  $\text{CoFe}_2\text{O}_4$  nanosized product was dried under vacuum at 60–70 °C for 7 h.

The  $\text{CoFe}_2\text{O}_4$  powders were added into the glycol solution, and then the water glass solution was added into the mixed solution. The pH value of the solution was adjusted to about 10 using 1 mol/L HCl. The mass fraction of  $\text{CoFe}_2\text{O}_4$  was 7%. The gelation time was longer than 2 h with the temperature of 80 °C. After being coated, the particles were filtered and washed using double-distilled water and then dried at 120 °C for 3 h.

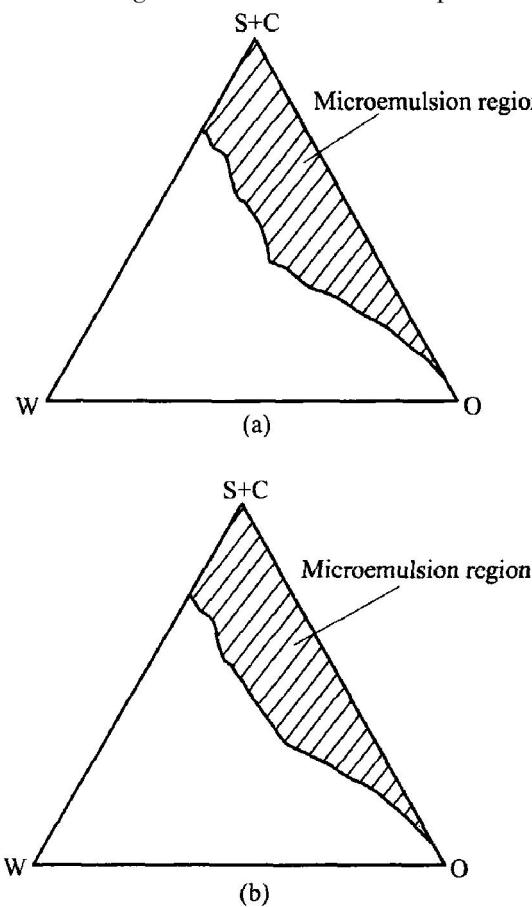
### 2.4 Characterization

All products were characterized using X-ray diffractometry (Cu  $\text{K}\alpha$ , Philips PW1729). The powders were also characterized for particle/agglomeration size distribution using laser scattering technique (Horiba LA-910). Observation of crystallites by scanning electron microscopy (SEM) was performed on LEO 1430 VP SEM. The element composition of the coated particle was analyzed by energy dispersion spectrometry (SEM-EDS, KYKY-2800). Infrared spectroscopy (IR, Nicolet, 750) of the samples was used to study the chemical bonds between uncoated  $\text{CoFe}_2\text{O}_4$  and  $\text{SiO}_2$  coated  $\text{CoFe}_2\text{O}_4$  powders.

## 3 RESULTS AND DISCUSSION

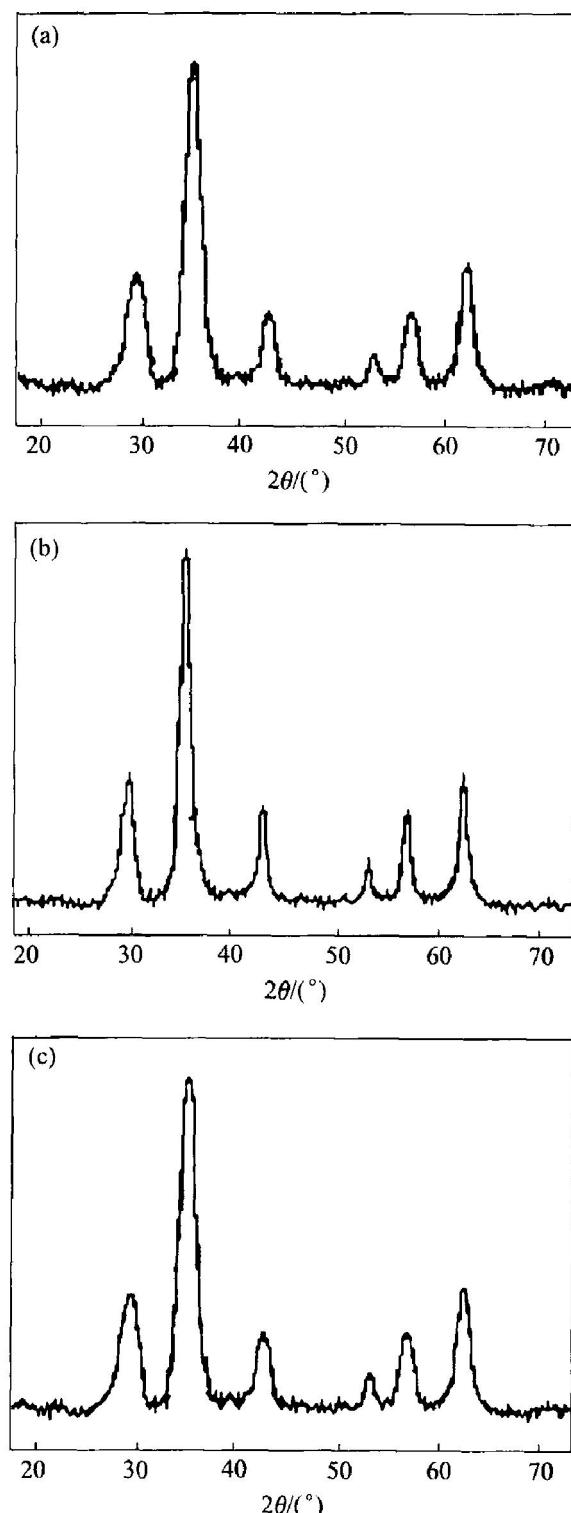
The partial quasiterinary phase diagrams of the reverse microemulsion systems of TX-10, AEO9, *n*-pentanol, cyclohexane and Brine at 30 °C are shown in Figs. 1(a) and (b), where S (surfactant) and C (cosurfactant) represent the total mass

of TX-10, AEO9 and *n*-pentanol, O is the mass of oil phase and W is the mass of brine. Two aqueous solutions are not the same in two figures: one is mixed nitrates of 0.10 mol/L  $\text{Co}(\text{NO}_3)_2$  and 0.20 mol/L  $\text{Fe}(\text{NO}_3)_3$  in Fig. 1(a) and the other aqueous solution is 0.4 mol/L ammonia solution in Fig. 1(b). But the oil, surfactant and cosurfactant used are the same in two figures. The reverse microemulsion region is represented by the shaded area in two figures. The two phase diagrams are similar and the reverse microemulsion region is widened with increasing mixed surfactant/oil phase ratio.



**Fig. 1** Partial phase diagram established for ternary system comprising coclohexane, TX-10+ AEO9, *n*-pentanol and different aqueous solutions at room temperature  
 (a) —Aqueous solution containing mixed nitrates of 0.10 mol/L  $\text{Co}(\text{NO}_3)_2$  and 0.20 mol/L  $\text{Fe}(\text{NO}_3)_3$ ;  
 (b) —Aqueous solution containing 0.4 mol/L ammonia

Figs. 2(a) and (b) show the XRD patterns for the particles prepared with the microemulsion and precipitation method, respectively. It is evident that these powders contain only spinel ferrite.  $\text{CoFe}_2\text{O}_4$  can be formed by two methods and all the peaks in the two patterns match well with JCPDS card. No impurity peaks can be found on the XRD patterns. However, it can be observed that the peaks for the particles obtained by the microemulsion method have broader and weaker intensity patterns than those by the precipitation method.

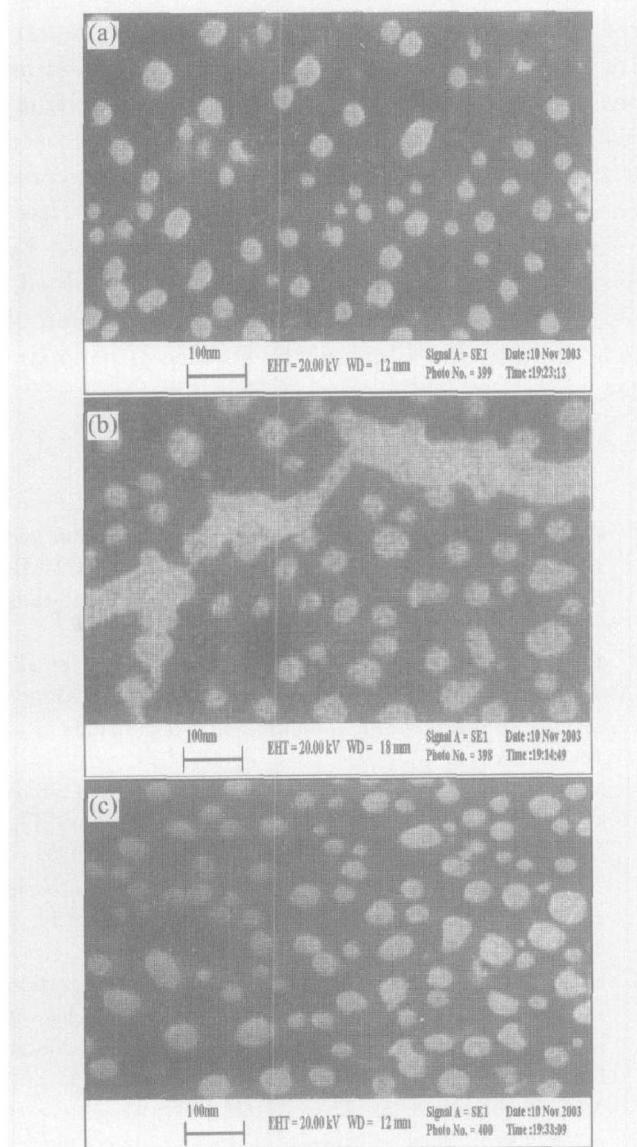


**Fig. 2** X-ray diffraction patterns of nanoparticles prepared by different methods  
 (a) —Microemulsion method and uncoated;  
 (b) —Precipitation method and uncoated;  
 (c) —Microemulsion method and silica-coated

This phenomenon is not resulted from lower crystallinity or amorphous structure. Fig. 2(c) shows the X-ray diffraction pattern of the silicon dioxide-coated  $\text{CoFe}_2\text{O}_4$  which is similar to that in Fig. 2(a). No diffraction peak characteristic of crystalline silica is observed, whereas the six characteristic diffraction peaks of  $\text{CoFe}_2\text{O}_4$  are examined by X-ray diffractometry. This result implies that the

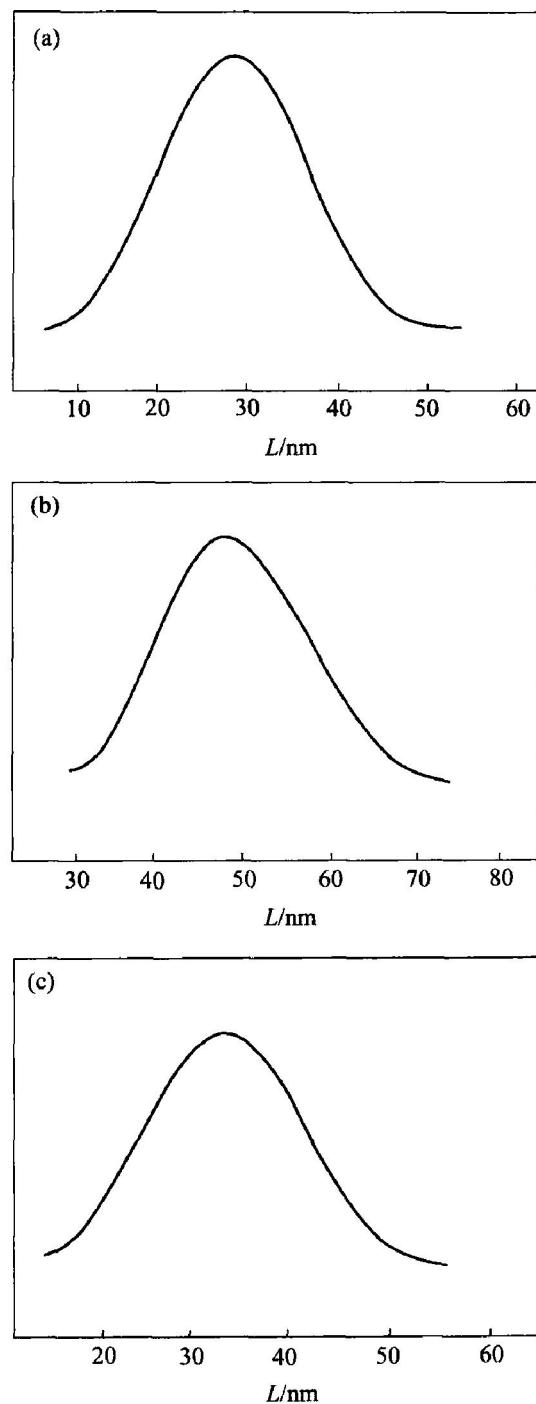
coated silicon dioxide is amorphous.

The SEM images of the particles prepared by the microemulsion and precipitation method are shown respectively in Figs. 3(a) and (b). It is obvious from these figures that the sizes and morphologies of the particles show little difference. The particles prepared by the microemulsion method are spherical and regular (Fig. 3(a)). Their diameters are in the range of 10–50 nm and narrow particle size distribution is shown in Fig. 4(a). Whereas the particles prepared by precipitation method are less regular and some are agglomerated (Fig. 3(b)). Their diameters are in the range of 30–70 nm and a very broad particle size distribution is shown in Fig. 4(b). Fig. 3(c) shows the SEM image of the magnetite nanoparticles prepared by the microemulsion and coated with silicon dioxide, which shows that most of the particles are spherical with an average diameter of 35 nm. The distribution of particle diameters is shown in Fig. 4(c).



**Fig. 3** SEM micrographs of nanoparticles prepared by different methods

- (a) —Microemulsion method;
- (b) —Precipitation method; (c) —Coating

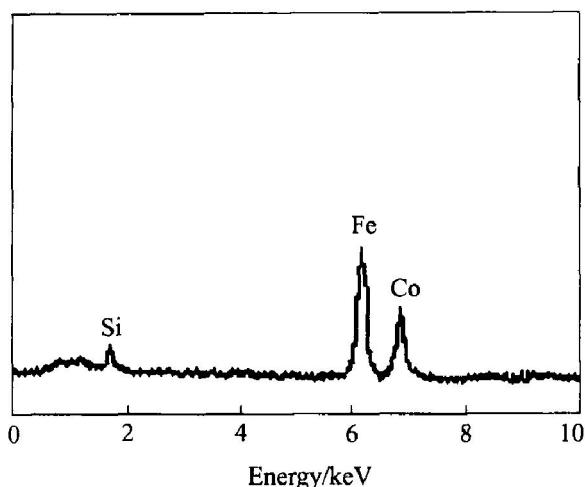


**Fig. 4** Size distribution of nanoparticles prepared by different methods

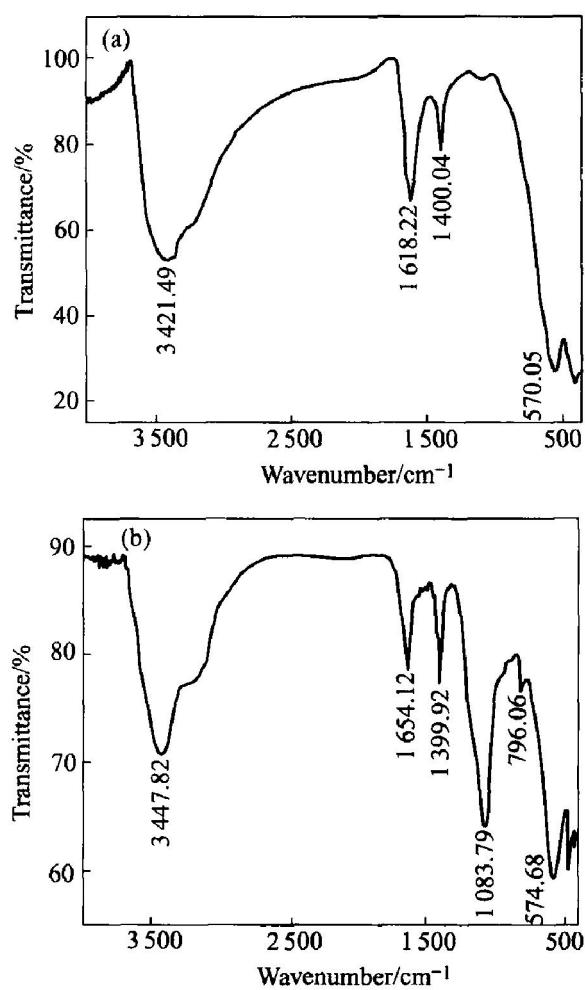
- (a) —Microemulsion method and uncoated;
- (b) —Precipitation method and uncoated;
- (c) —Microemulsion method and coated

EDS is used to identify the elements of the powder. Fig. 5 shows a typical SEM-EDS elemental analysis result of silica-coated  $\text{CoFe}_2\text{O}_4$  nanoparticles. Si element peak at 1.76 keV can be seen from the figure. The molar ratio of Fe to Si is 96.11 : 3.89. We can conclude that a thin film of silicon dioxide is coated on the surface of  $\text{CoFe}_2\text{O}_4$  particles.

IR spectroscopy analysis is also used to evaluate the presence of silicon dioxide on the surface of  $\text{CoFe}_2\text{O}_4$  nanoparticles. Figs. 6(a) and (b) show



**Fig. 5** SEM-EDS elemental analysis of  $\text{SiO}_2$ -coated  $\text{CoFe}_2\text{O}_4$  nanoparticles



**Fig. 6** IR spectra of samples  
(a) —Uncoated; (b) —Coated

the IR spectra of uncoated and coated  $\text{CoFe}_2\text{O}_4$  nanoparticles respectively. Three absorption peaks appear in the spectra, and they are related to the characteristic vibrational transverse optical modes of  $\text{Si}—\text{O}—\text{Si}$  chemical bond. The band which appears at about  $453.17\text{ cm}^{-1}$  is the rocking vibrational mode; the  $796.06\text{ cm}^{-1}$  absorption band corresponds to the bending vibration; and the band

near about  $1083.79\text{ cm}^{-1}$  corresponds to an asymmetric stretching vibration of  $\text{Si}—\text{O}—\text{Si}$  bond. The characteristic absorption bands (at  $574.68$  and  $413.14\text{ cm}^{-1}$ ) of the  $\text{Fe}—\text{O}$  bond of  $\text{SiO}_2$ -coated  $\text{CoFe}_2\text{O}_4$  compared with those of uncoated  $\text{CoFe}_2\text{O}_4$  (at  $570.05$  and  $410.11\text{ cm}^{-1}$ ) are also found. In addition, in Figs. 6(a) and (b) the absorption bands near  $3400$  and  $1630\text{ cm}^{-1}$  refer to the vibration of remainder  $\text{H}_2\text{O}$  in the samples. And there also exists the contribution of adsorbed  $\text{CO}_2$  for the band near  $1400\text{ cm}^{-1}$  in Figs. 6(a) and (b). From these results of IR spectra and SEM-EDS, it is proven that the  $\text{CoFe}_2\text{O}_4$  nanoparticles can be coated with silicon dioxide.

#### 4 CONCLUSIONS

A new reverse microemulsion system consisting of TX-10, AEO9, cyclohexane *n*-pentanol and water(brine) was studied and successfully used to synthesize  $\text{CoFe}_2\text{O}_4$  nanoparticles. We have prepared  $\text{SiO}_2$ -coated  $\text{CoFe}_2\text{O}_4$  with good biocompatibility and magnetic characteristics by coating process. Then, the difference among microstructures, crystallogram, and IR spectra of uncoated and silica-coated products prepared from reverse microemulsion method was investigated. The characterization of  $\text{CoFe}_2\text{O}_4$  nanoparticles prepared by conventional precipitation method was also valued. These results are utilized to prove the formation of silicon dioxide thin films on the surface of nanoparticles.

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