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Preparation and characterization of superparamagnetic \(\alpha\)-Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\)@Si\(_2\) nanocomposites via a citric-TEOS-ethanol solution combustion process

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Abstract

Superparamagnetic \(\alpha\)-Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\)@Si\(_2\) nanocomposites were prepared by the citric-TEOS-ethanol solution combustion method. Four key influencing factors, i.e. the calcination temperature, the volume of anhydrous ethanol, the volume of tetraethyl orthosilicate (TEOS), and the molar ratio of iron nitrate and citric acid (IN:CA) were investigated. The calcination temperature and the volume of anhydrous ethanol mainly affected the phase composition of \(\alpha\)-Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\)@Si\(_2\) nanocomposites, and the volume of TEOS and the ratio of IN:CA had a great influence on the crystallinity of \(\alpha\)-Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\)@Si\(_2\) nanocomposites. The tendency for the properties of superparamagnetic \(\alpha\)-Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\)@Si\(_2\) nanocomposites changing with the conditions was explored and the mechanism was analyzed.

1. Introduction

Magnetic iron oxides have been widely applied in information storage, solid-phase separation, biosensor, magnetic resonance imaging contrast agent, magnetic ink, and many other fields [1, 2]. Among them, magnetic Fe\(_2\)O\(_3\) and \(\alpha\)-Fe\(_2\)O\(_3\) nanomaterials are the most common. Magnetic Fe\(_2\)O\(_3\) nanomaterials, which have specific surface area effect, good biocompatibility, and magnetic property, have attracted lots of interest [3, 4], and they can be separated from liquid under an external magnetic field, which is convenient for material recovery. However, magnetic Fe\(_2\)O\(_3\) nanomaterials are at a high energy state and have unsaturated bonds on the surface, which enable them to bond with other atoms and to be agglomerate easily [5]. While, the magnetic \(\alpha\)-Fe\(_2\)O\(_3\) nanomaterials have good electrochemical properties, optical properties, high stability, low toxicity, and good biocompatibility [6], except that the saturation magnetization (Ms) of them is relatively small, which is not conducive for the magnetic recovery and limits their applications [7]. For the appropriate magnetic property to be applied and by combining the characteristics of Fe\(_2\)O\(_3\) and \(\alpha\)-Fe\(_2\)O\(_3\) nanomaterials, the magnetic \(\alpha\)-Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\) heterostructure nanomaterials have been prepared [8, 9].

Silica, which has good biocompatibility and chemical stability, is one of the ideal materials for modifying magnetic nanomaterials [10]. Moreover, it can not only shield the dipole effect between particles, prevent the reunion, and improve their stability and dispersion, but also form complex pore structure and increase specific surface area [11–14]. The magnetic nanomaterials modified by silicon dioxide can better combine the amino and carboxyl functional groups, which enables them to have good surface functions. Pan et al prepared magnetic Ni\(_{0.5}\)Cu\(_{0.5}\)Fe\(_2\)O\(_4\)/SiO\(_2\) nanocomposites which performed well in absorbing dyes [15]. Yu et al prepared Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\)/SiO\(_2\) and modified the surface of them to obtain the immobilized penicillin G acylase with good performance [16]. However, there are few researches on magnetic \(\alpha\)-Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\)/SiO\(_2\) nanocomposites at present.
Magnetic $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$@SiO$_2$ nanomaterials with particle size less than the critical size can produce superparamagnetism, which can be rapidly magnetized under the external magnetic field and can be rapidly demagnetized when the external magnetic field is removed [17]. Superparamagnetic $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$@SiO$_2$ nanocomposites not only have good chemical stability and biocompatibility, but also have the potential advantages of fast magnetic response, good targeting, long half-life of blood circulation, high tissue specificity in vivo, and low toxic and side effects. These advantages have entitled superparamagnetic $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$@SiO$_2$ nanocomposites potential applications in magnetic resonance imaging, biological separation, tumor thermotherapy, loading drugs, enzyme immobilization, catalysis and other fields [18–20].

At present, a variety of synthetic methods have been developed to prepare nanomaterials, such as solution combustion synthesis method, thermal decomposition method, coprecipitation method, sol-gel method, microemulsion method, and etc. [21, 22]. Among them, the solution combustion synthesis method has the advantages of simple equipment, simple operation, short reaction time, and controllable preparation [23, 24]. In this project, a novel solution combustion synthesis method using ferric nitrate as oxidant, citric acid as reducing agent, anhydrous ethanol as solvent, and TEOS as silicon source was introduced, which could realize the one-step preparation of superparamagnetic $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$@SiO$_2$ nanocomposites. The effects of the calcination temperature, the volumes of anhydrous ethanol and tetraethyl orthosilicate (TEOS), and the molar ratio of iron nitrate to citric acid (IN:CA) on phase structure, crystallinity, and magnetic properties of the nanocomposites were investigated.

2. Experimental

Superparamagnetic $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$@SiO$_2$ nanocomposites were prepared by a citric-TEOS-ethanol solution combustion method. Fe(NO$_3$)$_3$·9H$_2$O (9.25 g), citric acid, and TEOS were added in anhydrous ethanol, followed by magnetic agitation for 2 h. The obtained homogeneous solution was then ignited. After the solution was completely burned, it was calcined at a certain temperature for 2 h. Finally, superparamagnetic $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$@SiO$_2$ nanocomposites were obtained by grinding. On this basis, the effects of four factors on the sample were investigated, and the specific operating conditions were shown in table 1. The microstructure of superparamagnetic $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$@SiO$_2$ nanocomposites were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The element composition and proportion were obtained from an energy dispersive x-ray spectrometer (EDS). The crystal structure was analyzed by x-ray diffraction (XRD). The magnetic properties of nanocomposites were measured by vibration sample magnetometer (VSM). The components of the nanocomposites were identified and analyzed by Fourier Transform infrared spectroscopy (FTIR).

3. Results and discussion

3.1. Characteristics of $\alpha$-Fe2O3/Fe3O4@SiO2 nanocomposites

Figure 1 showed the characterization of superparamagnetic $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$@SiO$_2$ nanocomposites which were treated at 400 °C for 2 h with citric acid (13.02 g), anhydrous ethanol (20 ml), and TEOS (2.62 ml). The SEM image (figure 1(a)) showed the average particle size of $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$@SiO$_2$ nanocomposites was approximately 40.8 nm. The nanocomposites had good dispersion and were well-formed with obvious boundaries. The morphology was further demonstrated by TEM (figure 1(b)), showing that the polycrystalline nanocomposite was composed of amorphous silica and crystalline $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$. The EDS energy spectrum (figure 1(c)) revealed the presence of silicon. From the FTIR (figure 1(d)), peaks at 462 cm$^{-1}$ and 551 cm$^{-1}$ are corresponded to the Fe–O bond [25], confirming the existence of spinel ferrite. The strong absorption band of 1063 cm$^{-1}$ and 791 cm$^{-1}$ are corresponded to the Si–O bond [26], which indicated the presence of silica in the nanocomposites. The peak of 3430 cm$^{-1}$ was corresponded to –OH. The peak of 1384 cm$^{-1}$ indicated the presence of NO$^–$, which was not fully decomposed at this calcining temperature. The XRD patterns of

| Table 1. Operating conditions when exploring different influencing factors. |
|---------------------------|----------------|-----------------|----------------|----------------|
| operation conditions | the calcination temperature (°C) | anhydrous ethanol (ml) | TEOS (ml) | IN:CA |
| the calcination temperature (°C) | 200–500 | 400 | 400 | 400 |
| anhydrous ethanol (ml) | 20 | 15–35 | 20 | 20 |
| TEOS (ml) | 2.62 | 2.62 | 1.31–3.92 | 2.62 |
| IN:CA | 1:3 | 1:3 | 1:3 | 1:9–1:3 |
α-Fe₂O₃/Fe₃O₄@SiO₂ and the standard patterns of Fe₃O₄ (JCPDS No. 03-0863) and α-Fe₂O₃ (JCPDS No. 33-0664) were shown in figure 1(e). The absence of silica diffraction peaks in the patterns was attributed to the amorphous nature of the silicon coating. The diffraction peaks of the 2θ = 24.1° (012), 33.1° (104), 35.6° (110), 40.8° (113), 49.4° (024), 54.0° (116), 62.4° (214), 64.0° (300) corresponded to the standard card of α-Fe₂O₃ (JCPDS No. 33-0664). The peaks of the 30.2° (220), 35.5° (311), 43.3° (400), 56.8° (511), 62.7° (440) were observed, which could be indexed to the Fe₃O₄ nanocrystalline structure (JCPDS No. 03-0863). Through the comparison among the three patterns, the existence of the two different iron oxide crystal structures could be confirmed, which indicated the existence of α-Fe₂O₃/Fe₃O₄. The average grain size calculated by Scherer’s formula was 15.84 nm. Scheler’s formula was as follows:

\[
D = \frac{0.89\lambda}{\beta \cos \theta}
\]

Where, D was the grain size, λ was the wavelength, β was the full width half maximum, and θ was the diffraction peak angle. The low coercive force and narrow hysteresis loop indicated a soft magnetic material (figure 1(f)).

Figure 1. SEM image (a), TEM image (b), EDS image (c), FTIR spectra (d), XRD patterns (e), M–H curve (f) of superparamagnetic α-Fe₂O₃/Fe₃O₄@SiO₂ nanocomposites.
was 39.7 emu g\(^{-1}\), which was convenient for material recovery under an external magnetic field. The residual magnetization was 6.86 emu g\(^{-1}\), and the coercivity was 42.43 Oe.

3.2. Effects of Influence Factors on Superparamagnetic \(\alpha\)-Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\)@SiO\(_2\) Nanocomposites

Figure 2 (a) displayed the XRD patterns of superparamagnetic \(\alpha\)-Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\)@SiO\(_2\) nanocomposites calcined at different temperatures. The diffraction peak of \(\alpha\)-Fe\(_2\)O\(_3\) at 33.1° and the diffraction peaks of Fe\(_3\)O\(_4\) at 30.2° were observed, which suggested that \(\alpha\)-Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\) could be obtained at the temperature range of 200 °C to 500 °C. As the calcination temperature increased, the strength of peaks and the width of half-peak changed obviously, indicating that the molar ratio of \(\alpha\)-Fe\(_2\)O\(_3\) and Fe\(_3\)O\(_4\) in the nanocomposites changed significantly. According to the comparison between the relative intensity of the diffraction peaks at
35° and 33.1°, the phase content of $\alpha$-$Fe_2O_3$ increased significantly when the temperature was above 350 °C. It revealed the calcination temperature could affect the phase composition of $\alpha$-$Fe_2O_3/Fe_3O_4@SiO_2$. With the increase of calcining temperature, the oxidation degree was deepened, and the $Fe_3O_4$ phase changed to the $\alpha$-$Fe_2O_3$ phase. It can be seen from figure 2(e) that the average grain size first decreased and then increased with the increase of calcination temperature. When the calcination temperature was 350 °C, the minimum average grain size was 11.09 nm.

The hysteresis loops (M–H curves) of superparamagnetic $\alpha$-$Fe_2O_3/Fe_3O_4@SiO_2$ nanocomposites calcined at different calcination temperatures were shown in figure 2(b). According to the M–H curves, the range of residual magnetization was 2.43 emu g$^{-1}$ to 7.61 emu g$^{-1}$, and the range of coercivity was 20.75 Oe to 120.5 Oe. The variation trends of remanent magnetization and coercivity increased first and then decreased at 200 °C–450 °C. At 350 °C, the remanent magnetization and coercivity had the maximum value, and the Ms was the highest of 40.5 emu g$^{-1}$. When the calcination temperatures were above 350 °C, the content of magnetic $Fe_3O_4$ in $\alpha$-$Fe_2O_3/Fe_3O_4@SiO_2$ nanocomposites decreased, leading to the lowest Ms in the nanocomposites, which was consistent with the results from XRD patterns. Moreover, the excessive temperature led to structural defects and spin disorders of the obtained nanocomposites, resulting in lower Ms.

Figure 2(c) revealed the XRD patterns of superparamagnetic $\alpha$-$Fe_2O_3/Fe_3O_4@SiO_2$ nanocomposites prepared with various volumes of anhydrous ethanol. The diffraction peaks of $\alpha$-$Fe_2O_3$ and $Fe_3O_4$ could be observed in the XRD patterns, indicating that the $\alpha$-$Fe_2O_3/Fe_3O_4@SiO_2$ nanocomposites were successfully prepared when the volumes of anhydrous ethanol were 15 ml to 35 ml. When the volume of anhydrous ethanol was 20 ml, the average grain size was the smallest (figure 2(f)), and the Ms was the highest (figure 2(d)). The insufficient volume of anhydrous ethanol resulted in less reducing agents produced during the combustion process, thus producing less magnetic $Fe_3O_4$. The excessive amount of anhydrous ethanol resulted in prolonged combustion time and deepened oxidation degree. When the volume of anhydrous ethanol was 30 ml, the minimum residual magnetization was 0.53 emu g$^{-1}$ and the minimum coercivity was 5.72 Oe.

When the amount of TEOS was 1.31 ml, the XRD pattern of the product only contained the diffraction peaks of the $Fe_3O_4$ phase (figure 3(b)). Correspondingly, it had the highest Ms (figure 3(b)). When the volume of TEOS was 2.62 ml, the diffraction peaks of $\alpha$-$Fe_2O_3$ and $Fe_3O_4$ could be observed and the crystallinity was good, indicating that the $\alpha$-$Fe_2O_3/Fe_3O_4@SiO_2$ nanocomposites were successfully prepared. It was observed from figure 3(b) that the Ms decreased with the volume of TEOS increasing from 1.31 ml to 3.92 ml. The amount of TEOS directly affected the thickness of the silica layer in the nanocomposites. As the volume of TEOS increased, the non-magnetic silicon layer was completed gradually, and the layer thickness increased, resulting in a decrease in the mass fraction of the superparamagnetic $\alpha$-$Fe_2O_3/Fe_3O_4$, with their Ms being decreased.

The XRD patterns and M–H curves of superparamagnetic $\alpha$-$Fe_2O_3/Fe_3O_4@SiO_2$ nanocomposites prepared with various ratios of IN: CA were indicated in figures 3(c), (d). When the ratio of IN:CA was 1:3, the produced superparamagnetic $\alpha$-$Fe_2O_3/Fe_3O_4@SiO_2$ nanocomposites had high crystallinity and the diffraction peaks were consistent with the JCPDS cards of $\alpha$-$Fe_2O_3$ and $Fe_3O_4$ (figure 3(c)). It was observed from figure 3(d) that the Ms decreased with the increase of citric acid. Citric acid could be mixed with metal ions to disperse metal ions to reduce the degree of grain agglomeration. However, excessive citric acid made it difficult for anhydrous ethanol to ignite, thus the production of reducing agents was reduced, leading to a decrease in Ms.

4. Conclusions

The superparamagnetic $\alpha$-$Fe_2O_3/Fe_3O_4@SiO_2$ nanocomposites were prepared by the citric-TEOS-ethanol solution combustion method. The above discussion suggested the volume of anhydrous ethanol and the calcination temperature affected the phase ratio of $\alpha$-$Fe_2O_3$ and $Fe_3O_4$ in the superparamagnetic $\alpha$-$Fe_2O_3/Fe_3O_4@SiO_2$. The $\alpha$-$Fe_2O_3/Fe_3O_4@SiO_2$ nanocomposites with larger Ms could be obtained when the calcination temperature was 350 °C and the volume of anhydrous ethanol was 20 ml, respectively. TEOS and citric acid had a great influence on the crystallinity of $\alpha$-$Fe_2O_3$ and $Fe_3O_4$. When the volume of TEOS was 2.62 ml and the ratio of IN:CA was 1:3, the superparamagnetic $\alpha$-$Fe_2O_3/Fe_3O_4@SiO_2$ nanocomposites with good crystallinity could be prepared. It demonstrated that the controlled preparation of the $\alpha$-$Fe_2O_3/Fe_3O_4@SiO_2$ nanocomposites could be achieved.
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of interest

The authors declare no conflict of interest.

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