A novel atmospheric pressure hydrolysis without stirring and combustion–calcination process for the fabrication of magnetic Fe₃O₄/α-Fe₂O₃ heterostructure nanorods

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Abstract

Atmospheric pressure hydrolysis without stirring and a combustion–calcination method were utilized to fabricate magnetic Fe₃O₄/α-Fe₂O₃ heterogeneous nanorods. First, the β-FeOOH nanorods were fabricated via hydrolysis, and the concentration of Fe³⁺, hydrolysis temperature, and hydrolysis time were optimized. The optimal fabrication conditions were as follows: a 0.1 M FeCl₃ solution was hydrolyzed at 90 °C for 2 h. The average length and diameter of the β-FeOOH nanorods fabricated under the optimal conditions were approximately 216 and 58 nm, respectively. Subsequently, Fe₃O₄/α-Fe₂O₃ heterogeneous nanorods were fabricated via a combustion–calcination process. The volume of absolute ethanol, calcination temperature, and calcination time were investigated to optimize the fabrication conditions of Fe₃O₄/α-Fe₂O₃ heterogeneous nanorods under the following conditions: absolute ethanol: 50 ml; calcination temperature: 300 °C; and calcination time: 2 h. Magnetic Fe₃O₄/α-Fe₂O₃ heterogeneous nanorods fabricated under optimal conditions were characterized with an average length of 199 nm, an average diameter of 51 nm, a zeta potential of +17.2 mV, and a saturation magnetization of 13 emu·g⁻¹.

1. Introduction

As a new generation of materials, nanomaterials have several novel properties that are different from those of traditional materials, including the quantum tunneling, surface, and quantum size effects [1]. Nanomaterials have broad applications, including crop production [2], medicine and health [3], aerospace [4], environmental [5], aviation and space exploration, resources and energy [6], and biosensors [7].

Magnetic iron oxide materials have been widely used as nanomaterials in science and technology. Magnetic iron oxide materials typically have three crystal types: magnetite (Fe₃O₄), hematite (α-Fe₂O₃), and maghemite (γ-Fe₂O₃) [8]. Magnetic ferrite materials have been widely applied in biomedicine, reaction catalysis, and electronic components owing to their excellent magnetic and catalytic properties, low cost, simple preparation, and high chemical stability. α-Fe₂O₃ is the most common polycrystalline compound in nature in the form of minerals [9]. It is widely found in rocks and soil and has antiferromagnetic or weak ferromagnetic properties at room temperature. Fe₃O₄ exhibits good catalytic activity, strong stability, low cost, and several morphologies. Furthermore, α-Fe₂O₃ is paramagnetic above 956 K (Curie temperature) [10], and has a rhombohedral structure consisting of O²⁻ and Fe³⁺ [11]. α-Fe₂O₃ is simpler to synthesize than other forms of iron oxide, because it is an end product of other forms of iron oxide. Furthermore, it is highly stable under natural conditions. In contrast, Fe₃O₄ [12] has ferromagnetic properties at room temperature. It differs from other
forms of iron oxide in that its structure contains both bivalent and trivalent iron. Fe₃O₄ is easy to magnetize; therefore, it exhibits a high magnetic response when affected by an external magnetic field. Fe₂O₃ is a metastable oxide of iron oxide because it can be oxidized to α-Fe₂O₃ at temperatures above 673 K [13]. Fe₂O₃ nanoparticles have become a research hotspot for magnetic separation materials because of their high specific surface area, excellent biocompatibility, quantum size effect, and easy surface modification. However, Fe₂O₃ has weak magnetism, limiting its further application. Simultaneously, the strong magnetism of Fe₃O₄ causes it to agglomerate. To solve this problem, magnetic Fe₃O₄/Fe₂O₃ heterogeneous nanomaterials have been developed [14, 15], which exhibit a series of advantages such as stable performance, strong tolerance, and low toxicity. In addition, the saturation magnetization is between that of Fe₂O₃ and Fe₃O₄, which further improves the directional transport ability [16].

From the perspective of polymer modification, nanomaterials with a large aspect ratio can provide polymers with excellent rigidity. Compared with three-dimensional spherical particles of the same size, two-dimensional rod-shaped nanoparticles have a longer circulation time and better transport and penetration performance in porous tissues, such as tumor sites. Moreover, the large surface area of the nanorods can result in stronger interactions [17]. Hence, rod-shaped nanoparticles have important application prospects in tumor imaging, diagnosis, and targeted drug delivery.

Various methods can be used to prepare ferrite nanomaterials, which can be roughly divided into liquid-[18], solid-[19], and gas-phase methods [20]. Among them, the liquid-phase method is the most widely used, including the coprecipitation [21], sol-gel [22], microemulsion [23], thermal decomposition [24], and hydrothermal methods. The coprecipitation method has attracted the attention of several studies because of its lack of pollution and controllable particle size. The sol-gel synthesis method can control the composition, microstructure, purity, and shape of ferrite by adjusting the sol concentration, stirring rate, and annealing temperature. Thermal decomposition, which is economical and environmentally friendly, is the simplest method for synthesizing ferrite. The properties of ferrite nanomaterials are closely related to their preparation method. Owing to their excellent physical and chemical properties, ferrite nanomaterials have been widely used in biomedicine, electronic components, reaction catalysis, and absorbing materials. Although ferrite nanomaterials are magnetically recyclable and easy to separate, their catalytic activity is not high; therefore, there are significant opportunities for further development.

In this study, atmospheric pressure hydrolysis without stirring and the combustion–calcination method were introduced for the fabrication of magnetic Fe₃O₄/α-Fe₂O₃ nanorods, and the effect of all the factors in the process was determined. Some studies have investigated the effect of the solubility product of divalent metal hydroxides on the size and magnetism of nanoparticles formed in the process of co-precipitation [25]. Moreover, it has been reported that the synthesis of pure magnetite nanoparticles by the co-precipitation technique proved that the initial pH, temperature of the iron salt solution, and the final pH are key parameters in the controllable preparation of nanoparticles [26]. The atmospheric hydrolysis method is simple to operate with low cost raw materials. Compared with pure Fe₂O₃ or Fe₃O₄ nanomaterials [27], the magnetic properties of Fe₃O₄/α-Fe₂O₃ heterostructure nanorods are moderate, do not agglomerate easily, and are convenient for later applications.

2. Experimental

2.1. Fabrication of β-FeOOH nanorods

5.41 g FeCl₃·6H₂O (0.1 M) was placed in 200 ml distilled water with magnetic stirring. The obtained homogeneous solution was then transferred to a round flask, heated at 90 °C for 2 h, and hydrothermally reacted without magnetic stirring. The resulting suspension was centrifuged to obtain the sediment. β-FeOOH nanorods were successfully fabricated by rinsing, drying, and grinding. The effects of initial Fe³⁺ concentration (0.05, 0.1, 0.2, 0.3, and 0.5 M), hydrolysis time (2, 4, 6, 8, 10, 12, and 16 h), and hydrolysis temperature (60, 70, 80, and 90 °C) were investigated to optimize the fabrication process. First, various concentrations of Fe³⁺ were heated at 90 °C for 2 h in a water bath to prepare the β-FeOOH nanorods. Subsequently, the solution with the optimal concentration of Fe³⁺ was hydrolyzed at 90 °C for various periods. Finally, the effect of the hydrolysis temperature on the β-FeOOH nanorods was investigated.

2.2. Fabrication of magnetic Fe₃O₄/α-Fe₂O₃ heterostructure nanorods

The combustion–calcination process was employed to fabricate Fe₃O₄/α-Fe₂O₃ heterogeneous nanorods. 5.41 g FeCl₃·6H₂O (0.1 M) was rapidly dissolved in 200 ml ultrapure water and heated in a water bath at 90 °C for 2 h. The suspension was then centrifuged and alternately rinsed six times with absolute ethanol and water. After drying for 12 h, the precipitate was mixed with varying volumes of absolute ethanol (20, 30, 40, 50, and 100 ml) to optimize the fabrication conditions. Subsequently, the mixture composed of the precipitate and absolute
ethanol was placed in a crucible and then ignited, which was evenly dispersed by ultrasound. When the flame extinguished and the combustion product cooled to room temperature, the combustion product was calcined at 300 °C for 2 h in a programmed temperature-controlled furnace [28]. Hence, a sample group was prepared to investigate the amount of ethanol. Subsequently, the products prepared using the optimal amount of ethanol were calcined at various temperatures (200, 250, 300, 350, and 400 °C) for 2 h. After optimizing the amount of ethanol and calcination temperatures, the calcination times (0.5, 1, 2, 3, and 4 h) were investigated to determine the optimal fabrication conditions. The products obtained using the optimal amount of ethanol calcinated at the optimal temperature, were then calcinated for various periods. Magnetic Fe3O4 heterogeneous nanorods were successfully fabricated after grinding. In summary, the amount of absolute ethanol, calcination temperature, and calcination time were varied to optimize the fabrication process.

2.3. Characteristics of β-FeOOH and magnetic Fe3O4/α-Fe2O3 nanorods
The phases of the β-FeOOH and Fe3O4/α-Fe2O3 nanorods were characterized by x-ray diffraction (XRD). Their morphologies were analyzed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). A vibrating sample magnetometer (VSM) was used to measure the magnetic properties, and the zeta potential of the Fe3O4/α-Fe2O3 nanorods was measured using a laser particle size analyzer.

3. Results and discussion

3.1. Structural characteristics of β-FeOOH nanorods
Figure 1 (A) shows the XRD pattern of the β-FeOOH nanorods heated in a water bath at 90 °C for 2 h. The peaks of the β-FeOOH nanorods at 26.7, 34.0, 35.2, 39.2, 46.4, 52.9, 55.9°, and 64.4° belonged to the (310), (400), (211), (301), (411), (431), (521), and (541) diffraction crystal faces, respectively. This corresponds to the standard card of β-FeOOH (ICPDS No. 34–1266). Hence, the products contained β-FeOOH. The SEM morphology of the β-FeOOH nanorods in figure 1(B) indicates that the products had rod-shaped structures with good dispersion. After the measurements, the average length and diameter of the nanorods were approximately 216 and 58 nm, respectively. The reason for the rod-shaped structure may be that FeCl3 was heated and hydrolyzed to produce Fe(OH)3 and HCl, and then Fe(OH)3 was further decomposed to produce β-FeOOH. HCl was easily volatilized during heating, owing to its low boiling point, resulting in rod-shaped β-FeOOH that was not corroded. Figure 1(C) shows that β-FeOOH had a rod-like structure and uniform size, and the average length and diameter were approximately 218 and 59 nm, respectively, which were consistent with the SEM morphology (figure 1(B)).

3.2. Effect of reaction conditions on β-FeOOH nanorods
3.2.1. Effect of Fe3+ concentration
The SEM morphologies of the β-FeOOH nanorods with various initial Fe3+ concentrations and their relative yields are shown in figure 2. It is evident from figure 2(A) that when the initial Fe3+ concentration was 0.05 M, the fabricated products were a mixture of nanoparticles and nanorods with significant agglomeration. The reason for this phenomenon may be the small amount of β-FeOOH caused by the low initial Fe3+ concentration, which limits the formation of the rod-like structure. As clearly shown in figures 2(B)–(E), the resulting products were all rod-like structures with uniform size when the concentration was 0.1–0.5 M. However, the yield of β-FeOOH became lower with an increase in the initial Fe3+ concentration (figure 2(F)). Simultaneously, the amount of FeOOH generated by hydrolysis was limited. When the initial Fe3+ concentration was 1.0 M, the yield of β-FeOOH was 74%.
concentration was increased, the morphologies of the β-FeOOH nanorods remained similar. Hence, the optimal initial Fe$^{3+}$ concentration was determined as 0.1 M.

3.2.2. Effect of hydrolysis time

Figure 3 shows the SEM morphologies of β-FeOOH nanorods heated at 90 °C for varying hydrolysis times and their relative yields. The products were all rod-like structures upon investigation of hydrolysis time. The β-FeOOH nanorods exhibited a uniform size after less than 12 h. However, when the time was extended to 16 h, the nanorods agglomerated significantly, and the dispersion of the materials was poor. The plethoric β-FeOOH grains and long growth time caused by the extended hydrolysis time may be explained by the large size of the nanorods and their poor dispersion. The yields of the β-FeOOH nanorods after 12 h were not significantly different. When the hydrolysis time was 16 h, the yield increased slightly, indicating that the hydrolysis time had little impact on the yield when the hydrolysis time was less than 12 h. Hence, a hydrolysis time of 2 h was selected as the best condition owing to it being time-independent.

3.2.3. Effect of hydrolysis temperatures

A 0.1 M FeCl$_3$ solution was hydrolyzed for 2 h at various temperatures. The SEM images of the morphologies are shown in figure 4. The products had rod-like structures with good dispersion (figures 4(A)–(D)). The yields of β-FeOOH nanorods fabricated under different hydrolysis temperatures are shown in figure 4(E), exhibiting an upward trend with increasing temperature. This may be attributed to the accelerated speed of hydrolysis and the increase in β-FeOOH grains. Because the yield was affected by temperature, an optimal temperature of 90 °C was selected.

3.3. Characterization of magnetic Fe$_3$O$_4$/α-Fe$_2$O$_3$ heterogeneous nanorods

The SEM morphology of the magnetic Fe$_3$O$_4$/α-Fe$_2$O$_3$ heterogeneous nanorods calcined at 300 °C for 2 h with 50 ml absolute ethanol (figure 5(A)) indicated that the heterogeneous nanomaterials exhibited rod-like structures with good dispersion. The average length and diameter was 199 and 52 nm, respectively, which were slightly lower than those of the FeOOH nanorods. The reason for this phenomenon may be that the nanorods appeared more stable with an increase in calcination temperature. Therefore, the size of the nanorods decreased with decreasing specific surface area and surface energy. The TEM image of the heterogeneous nanorods in figure 5(B) indicates that the rod-like structure was loose because of the rapid decomposition of FeOOH under high-temperature calcination. After the measurement, the average length and diameter of the magnetic Fe$_3$O$_4$/α-Fe$_2$O$_3$ nanorods were approximately 198 and 49 nm, respectively, which were consistent with the SEM morphology. Figure 5(C) shows the XRD pattern of the magnetic Fe$_3$O$_4$/α-Fe$_2$O$_3$ heteroplasmon nanorods compared with the standard PDF cards of Fe$_3$O$_4$ and Fe$_2$O$_3$. It can be observed from the figure that the XRD pattern was similar to that of the hematite (Fe$_2$O$_3$). The diffraction peaks at 24.1°, 33.2°, 35.6°, 40.9°, 49.5°,
Figure 3. SEM morphologies of $\beta$-FeOOH fabricated with various hydrolysis times of 2 h (A), 4 h (B), 6 h (C), 8 h (D), 10 h (E), 12 h (F), 16 h (G), and the corresponding yields (H).

Figure 4. SEM morphologies of $\beta$-FeOOH nanorods fabricated at different hydrolysis temperatures of 60 $^\circ$C (A), 70 $^\circ$C (B), 80 $^\circ$C (C), 90 $^\circ$C (D), and their yields (E).
54.1°, 62.4°, and 63.9° are attributed to Fe₂O₃ (JCPDS No. 33–0663) [25]. However, the diffraction peak intensities at 33.2°, 35.6°, 62.4°, and 63.9° are attributed to Fe₃O₄. The diffraction peaks at 30.2° and 43.3° are attributed to pure Fe₃O₄ (JCPDS No. 03–0863). In addition, Figure 5(D) depicts the hysteresis loop of magnetic Fe₃O₄/α-Fe₂O₃ heterogeneous nanorods, with a saturation magnetization of 13 emu·g⁻¹, exhibiting a superparamagnetic nature with negligible remanence and coercivity. The coercivity and remanence magnetization obtained from the VSM measurements were 0.186 kOe and 2.46 emu·g⁻¹, respectively. The saturation magnetization of the magnetic Fe₃O₄/α-Fe₂O₃ nanorods was lower than that of pure Fe₃O₄, which made it difficult for magnetic Fe₃O₄/α-Fe₂O₃ nanorods to reunite and easily modify the surface with sufficient magnetism. Moreover, the area surrounded by the hysteresis loop represents the energy consumed by the ferromagnetic material during the magnetization cycle, which is often converted into heat energy.

3.4. Effect of fabrication conditions on Fe₃O₄/α-Fe₂O₃ heterogeneous nanorods

3.4.1. Effect of anhydrous ethanol amount

Figure 6(A) shows the hysteresis loops of the magnetic Fe₃O₄/α-Fe₂O₃ heterogeneous nanorods fabricated with different volumes of anhydrous ethanol. Figure 6(B) shows the hysteresis loops of magnetic Fe₃O₄/α-Fe₂O₃ heterogeneous nanorods fabricated when the volume of anhydrous ethanol was 30 ml. It can be observed from the figure that all the as-fabricated heterologous nanorods had magnetic properties. The saturation magnetization of the magnetic Fe₃O₄/α-Fe₂O₃ nanorods decreased when the volume of anhydrous ethanol was less than 30 ml. The combustion time decreased with less anhydrous ethanol and produced fewer reducing substances, resulting in weak magnetism of the Fe₃O₄/α-Fe₂O₃ nanorods. Inadequate combustion resulted in low levels of Fe₃O₄. Hence, the presence of Fe₃O₄ may cause an increase in magnetism, whereas Fe₂O₃ exhibited extremely low magnetism. The saturation magnetization exhibited an upward trend with an increase in the anhydrous ethanol amount. As the volume of anhydrous ethanol increased, the combustion time also increased, and the magnetic properties of the Fe₃O₄/α-Fe₂O₃ heterologous nanorods increased owing to the increasing content of Fe₃O₄. When the volume of anhydrous ethanol was 100 ml, the saturation magnetization of the magnetic Fe₃O₄/α-Fe₂O₃ heterologous nanorods reached a maximum value. However, the amount of
anhydrous ethanol was so large that it affected the ignition operation, and the combustion time was excessive, which increased the solvent and time related costs. With a change in ethanol content, the coercivity exhibited no clear change, however the area of the hysteresis loop first decreased and then increased. Therefore, 50 ml anhydrous ethanol was determined as the optimal volume for fabricating magnetic Fe$_3$O$_4$/Fe$_2$O$_3$ heterologous nanorods.

### 3.4.2. Effect of calcination time and temperature

Figure 7(A) shows the hysteresis loops of the magnetic Fe$_3$O$_4$/α-Fe$_2$O$_3$ heterologous nanorods fabricated at different calcination temperatures. When calcinated at 200 to 300 °C, the saturation magnetization of the magnetic Fe$_3$O$_4$/α-Fe$_2$O$_3$ nanorods exhibited an upward trend. The reason for this phenomenon is that the reductive substance generated by combustion cannot be completely decomposed at low calcination temperatures. Fe$_2$O$_3$ could not be reduced sufficiently to form significant amounts of Fe$_3$O$_4$. With an increase in temperature, the content of Fe$_3$O$_4$ also increased owing to the increase in the reduction of Fe$_2$O$_3$. Hence, the saturation magnetization of the Fe$_3$O$_4$/α-Fe$_2$O$_3$ heterologous nanorods decreased owing to the low content of Fe$_3$O$_4$. When the calcination temperature was higher than 300 °C, the reduced Fe$_3$O$_4$ could be further oxidized to α-Fe$_2$O$_3$, and the saturation magnetization of the Fe$_3$O$_4$/α-Fe$_2$O$_3$ heterologous nanorods decreased owing to there being less Fe$_3$O$_4$. It can be observed that the saturation magnetization of the Fe$_3$O$_4$/α-Fe$_2$O$_3$ nanorods reached a peak value at 300 °C. With an increase in the calcination temperature, the coercivity exhibited no clear change, however the area of the hysteresis loop first increased and then decreased. Therefore, 300 °C was determined as the optimal calcination temperature for fabricating the magnetic Fe$_3$O$_4$/α-Fe$_2$O$_3$ nanorods.
Figure 7(B) shows the hysteresis loops of the magnetic Fe3O4/α-Fe2O3 heterologous nanorods calcined for different periods. The saturation magnetization of magnetic Fe3O4/α-Fe2O3 nanorods increased slightly when calcinated for less than 2 h. This may be because Fe2O3 was reduced to a greater extent by the reducing materials generated from the incomplete combustion of ethanol with longer calcination times, leading to an improved saturation magnetization of magnetic Fe3O4/α-Fe2O3 heterologous nanorods. However, the saturation magnetization of the as-fabricated nanorods decreased when they were calcined for more than 2 h. The reason for this phenomenon may be that the reduced Fe3O4 was re-oxidized to α-Fe2O3 when calcined for a longer time, thus weakening the magnetic properties of the heterologous nanorods. With increasing calcination time, the coercivity exhibited no clear change, however the area of the hysteresis loop first increased and then decreased. Therefore, 2 h was selected as the optimal calcination time for the fabrication of the Fe3O4/α-Fe2O3 nanorods.

In summary, the optimal fabrication conditions for magnetic Fe3O4/α-Fe2O3 heterologous nanorods were as follows: anhydrous ethanol: 50 ml; calcination temperature: 300 °C; and calcination time: 2 h.

4. Conclusions

The fabrication and optimization conditions of β-FeOOH nanorods and magnetic Fe3O4/Fe2O3 heterologous nanorods were introduced, and the following conclusions were made.

(1) The atmospheric pressure hydrolysis process was used to fabricate β-FeOOH nanorods. Various effects including the concentration of Fe3⁺, hydrolysis time, and hydrolysis temperature were optimized for 0.1 M FeCl3 hydrolyzed at 90 °C for 2 h. All the obtained β-FeOOH nanomaterials fabricated under the optimized conditions were rod-like structures with uniform size, and the average length and diameter were approximately 216 and 58 nm, respectively.

(2) Magnetic Fe3O4/α-Fe2O3 heterogeneous nanorods were successfully fabricated via a combustion–calcination process. A calcination temperature of 300 °C, 50 ml of absolute ethanol, and calcination time of 2 h were determined as the optimal fabrication parameters. The average length and diameter of the fabricated heterogeneous nanorods were approximately 199 and 51 nm, respectively, which were lower than those of the β-FeOOH nanorods. Moreover, the saturation magnetization was 13 emu·g⁻¹, exhibiting a super-paramagnetic nature.

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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).

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