

Research Article

Preparation of $\gamma\text{-Fe}_2\text{O}_3/\text{Ni}_2\text{O}_3/\text{FeCl}_3(\text{FeCl}_2)$ Composite Nanoparticles by Hydrothermal Process Useful for Ferrofluids

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Using a hydrothermal process in FeCl_2 solution, $\gamma\text{-Fe}_2\text{O}_3/\text{Ni}_2\text{O}_3/\text{FeCl}_3(\text{FeCl}_2)$ composite nanoparticles were obtained from the $\text{FeOOH}/\text{Ni}(\text{OH})_2$ precursor prepared by coprecipitation. The precursor and the as-prepared nanoparticles were investigated by vibrating sample magnetometer (VSM), X-ray diffraction (XRD), energy disperse X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). The experimental results showed that the paramagnetic amorphous precursor, in which $\text{Ni}(\text{OH})_2$ is formed outside FeOOH , is transformed to ferrimagnetic $\gamma\text{-Fe}_2\text{O}_3/\text{Ni}_2\text{O}_3$ composite when it is processed in FeCl_2 solution (0.25, 0.50, 1.00 M) in an autoclave at 100°C for 1 hr. In addition, the dismutation reaction of FeCl_2 produces FeCl_3 and Fe. Some FeCl_3 and little FeCl_2 can be absorbed to form $\gamma\text{-Fe}_2\text{O}_3/\text{Ni}_2\text{O}_3/\text{FeCl}_3(\text{FeCl}_2)$ composite nanoparticles in which Ni_2O_3 forms outside the $\gamma\text{-Fe}_2\text{O}_3$ core and the outermost layer is $\text{FeCl}_3(\text{FeCl}_2)$. The content of $\text{FeCl}_3(\text{FeCl}_2)$ in the particles increased, and the magnetization of the particles decreased with the concentration of FeCl_2 solution increasing in the hydrothermal process. The $\text{FeCl}_3(\text{FeCl}_2)$ surface is chemically passive and nonmagnetic (paramagnetic). Accordingly, the composite nanoparticles are chemically stable, and their aggregation is prevented. The specific saturation magnetization of such composite nanoparticles can get to 57.4–62.2 emu/g and could be very suitable for synthesizing ferrofluids.

1. Introduction

Magnetic nanoparticles with diameters less than 100 nm have attracted increasing interest in the fields of basic science and technology [1–3]. Studies of magnetic nanoparticles have focused on the development of novel synthetic technology [2]. A nanocomposite is a material composed of two or more phases where the combination of different physical or chemical properties may lead to completely novel materials [4]. Magnetic nanocomposites have applications ranging from ferrofluids to separation science and technology [5]. Synthesis of nanoparticles of several kinds of materials can be achieved by the coprecipitation method. Generally, the precursor, synthesized by chemical coprecipitation, needs to be further processed (by drying, calcinations, etc.) to form oxide nanoparticles [6]. During the chemical reaction,

followed by calcination or annealing, a new phase is formed. However, in addition to the transition from amorphous to crystalline, the particle size increases with the calcination temperature and also aggregation of crystallites occurs [7]. Therefore, for the synthesis of ferrofluids, nanoparticles prepared by calcination could be unsuitable.

The hydrothermal process is a successful way to grow crystals of many different materials [8]. In the present work, composite nanoparticles based on $\gamma\text{-Fe}_2\text{O}_3$, Ni_2O_3 , and $\text{FeCl}_3(\text{FeCl}_2)$ were prepared by processing the amorphous $\text{FeOOH}/\text{Ni}(\text{OH})_2$ precursor in FeCl_2 solution in an autoclave at 100°C . The effect of the concentration of FeCl_2 solution on the product's magnetization, crystal structure, chemical composition, and morphology was investigated. A new route for the preparation of magnetic composite nanoparticles is proposed.

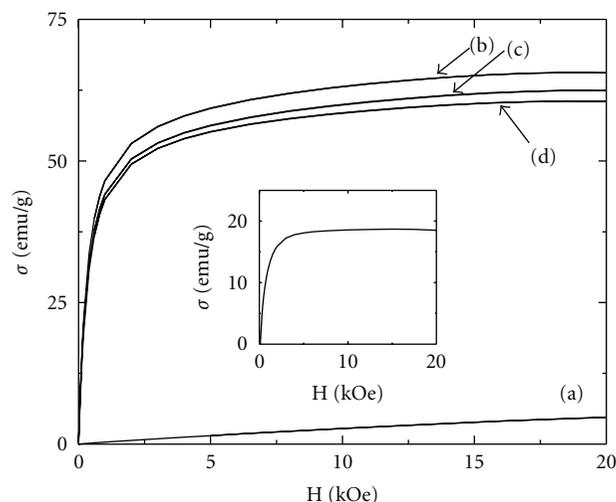


FIGURE 1: The magnetization curves of the precursor (a) and the processed sample in 0.25 M (b), 0.50 M (c), and 1.00 M (d) FeCl_2 solution, respectively. The magnetization curve of Ni_2O_3 particles about $1 \mu\text{m}$ in diameter is shown in the insert. The Ni_2O_3 particles is commercial availability.

TABLE 1: The elemental analysis from EDX for the precursor (a), and the processed sample in 0.25 M (b), 0.50 M (c), and 1.00 M (d) FeCl_2 solution.

Fe	Ni	Cl	Fe:Ni
(a) 66.58	33.42		2:1
(b) 89.02	9.91	1.07	8.98:1
(c) 87.61	10.01	2.38	8.75:1
(d) 89.52	7.95	2.53	11.26:1

2. Experiment

The preparation of the nanoparticles can be divided into two steps. First, the precursor was synthesized using the coprecipitation method. An aqueous mixture of FeCl_3 (40 mL, 1 M) and $\text{Ni}(\text{NO}_3)_2$ (10 mL, 2 M in HCl 0.05 mol), in which the ratio of Fe^{3+} to Ni^{2+} was 2:1, was added to NaOH solution (500 mL, 0.7 M). Then, the solution was heated to boiling for 5 minutes with stirring. After the heating was stopped, the black precursor gradually precipitated. The precursor was washed with a low concentration of HNO_3 solution (0.01 M) to $\text{pH} = 7\sim 8$. The second step was to obtain the composite nanoparticles. The precursor was added to FeCl_2 solution, whose concentration was 0.25 M, 0.50 M, or 1.00 M, to form a mixture solution (200 mL). This was then poured into a stainless steel autoclave with a Teflon liner (whose volume is 400 mL), heated to 100°C for 1hr and allowed to cool naturally to room temperature. Finally, the particles were washed with acetone and allowed to dry naturally.

The magnetization, crystal structure, chemical composition, and morphology of both the precursor and processed samples were analyzed using vibrating sample magnetometry (VSM, HH-15), X-ray diffraction (XRD, XD-2), energy dispersive X-ray spectroscopy (EDX, Norton 8000), X-ray

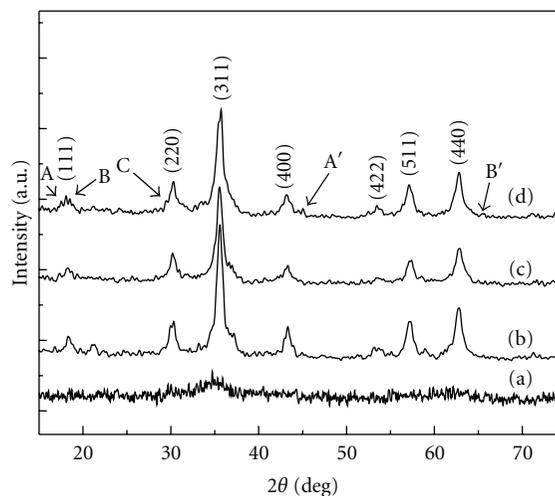


FIGURE 2: XRD patterns of the precursor (a) and the processed sample in 0.25 M (b), 0.50 M (c), and 1.00 M (d) FeCl_2 solution, respectively.

photoelectron spectroscopy (XPS, Thermo ESCA 250), and transmission electron microscopy (TEM, PHILIPS TECNAI 10).

3. Results and Analysis

Figure 1 shows the magnetization curves at room temperature for the precursor and the three processed samples. Clearly, the precursor appears to be paramagnetic, and the processed samples are ferromagnetic. It can be deduced from Figure 1 that the magnetization of the processed samples weakens as the concentration of FeCl_2 solution increases. The specific saturation magnetization σ_s of ferromagnetic materials can be estimated from the linear relationship of σ versus $1/H$ at high field [9]. The particles prepared by the hydrothermal process in 0.25 M, 0.50 M, and 1.00 M FeCl_2 solution give σ_s values of 62.2, 59.2, and 57.4 emu/g , respectively.

Figure 2 displays the XRD patterns for the precursor and the three processed samples. The results indicate that the precursor is amorphous, and the three processed samples are crystalline, mainly containing $\gamma\text{-Fe}_2\text{O}_3$. According to Scherrer's formula, the $\gamma\text{-Fe}_2\text{O}_3$ grain sizes of the particles may be calculated from the width of the (311) diffraction peak. This gives nearly the same size, about 8 nm, for all samples. For the processed samples in 1.00 M FeCl_2 solution, in addition to the diffraction peaks of the $\gamma\text{-Fe}_2\text{O}_3$ phase, a few new peaks can be observed. Three new peaks correspond to crystal face spacings d of approximately 0.507, 0.480, and 0.304 nm, as indicated by arrows A, B, and C, respectively, in Figure 2(d). These values are close to the $d = 0.508$, 0.450, and 0.298 nm of the strongest peaks of $2\text{FeCl}_3 \cdot 5\text{H}_2\text{O}$. This demonstrates that $2\text{FeCl}_3 \cdot 5\text{H}_2\text{O}$ has formed after the hydrothermal process, and its presence increases with the concentration of FeCl_2 . In addition, little peaks at $2\theta = 44.8^\circ$

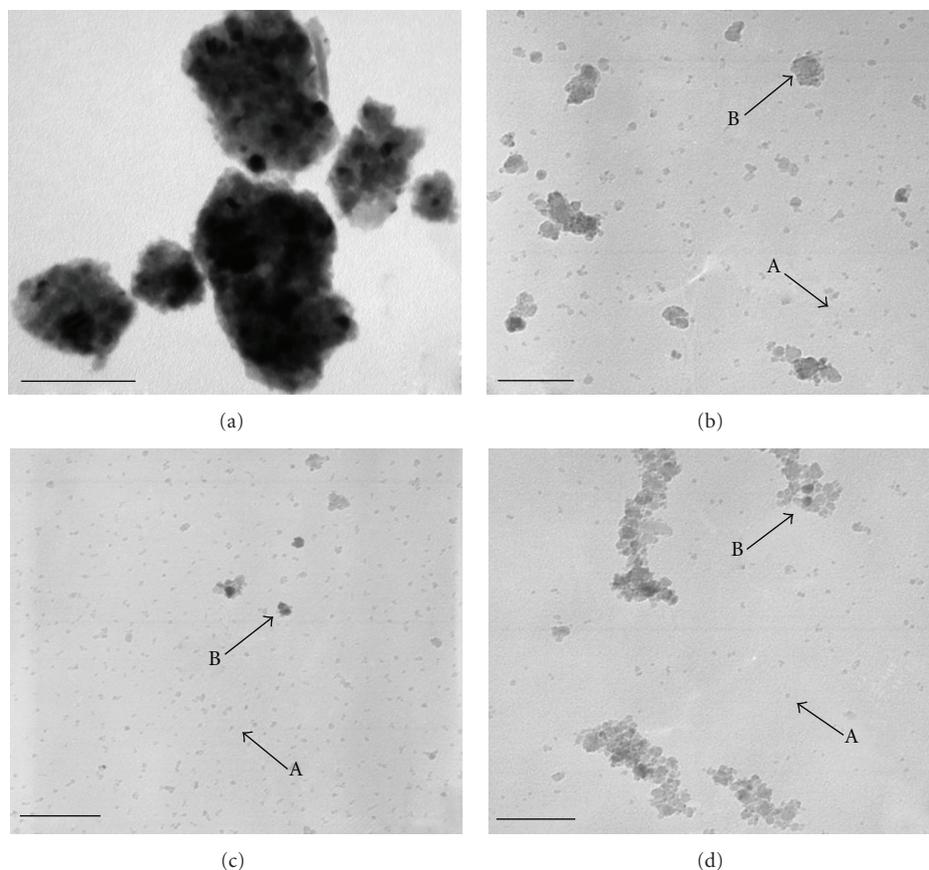


FIGURE 3: TEM images of the precursor (a) and the processed sample in 0.25 M (b), 0.50 M (c), and 1.00 M (d) FeCl_2 solution, respectively. The size bar is 100 nm.

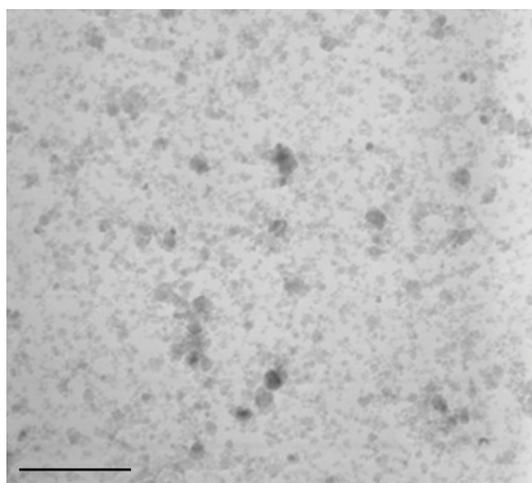


FIGURE 4: TEM images of the ferrofluid particles. The size bar is 100 nm.

and 65.2° may be seen in Figure 2(d) as indicated by arrows A' and B', and they belong to (110) and (200) diffraction peaks of Fe, respectively.

EDX results show that the precursor was constituted from Ni and Fe, although the processed samples contained

some Cl as well. Quantitative analysis indicated that the mole ratio of Fe to Ni in the precursor was about 2 : 1, which is the same as that of the starting reagents, but the ratios in the processed samples are far larger than that of the starting reagents or the precursor. The detailed data are listed in Table 1. The XPS results indicated that the precursor consisted of Fe, Ni, and O, and the processed samples contained some Cl in addition. It was found by quantitative analysis that the ratio of Fe to Ni in the precursor is less than 2 : 1, but in the processed samples are greater than 2 : 1. In addition, the concentration of Cl in the processed samples increased with increasing concentration of FeCl_2 solution in the hydrothermal process. These data are listed in Table 2. The values of the binding energy of the measured samples showed that the precursor consisted of both FeOOH and $\text{Ni}(\text{OH})_2$, and the processed samples consisted of Fe_2O_3 , Ni_2O_3 , and FeCl_3 (FeCl_2). The complete data of the binding energies are listed in Table 3.

Typical TEM photographs of the precursor and the processed samples are shown in Figure 3. It can be seen from the TEM observations that the precursor is loosely aggregated and the processed samples contain quasispherical particles with nearly uniform size of a few nanometers (as indicated by arrow A) in addition to some aggregates (as indicated by arrow B).

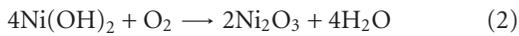
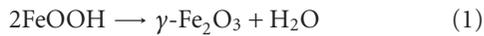
TABLE 2: The elemental analysis from XPS for the precursor (a) and the processed sample in 0.25 M (b), 0.50 M (c), and 1.00 M (d) FeCl₂ solution.

Fe	Ni	Cl	Fe:Ni
(a) 55.22	44.78		1.23 : 1
(b) 66.51	23.92	9.57	2.78 : 1
(c) 70.05	13.96	15.99	5.02 : 1
(d) 65.37	10.46	24.17	6.25 : 1

4. Discussion

The experimental results show that the precursor is an amorphous composite of FeOOH and Ni(OH)₂. Since the ratio of Fe to Ni measured by XPS is less than that of the starting reagents and the EDX measurement is in agreement, it can be concluded that the Ni(OH)₂ species has formed outside the FeOOH species in the precursor because the XPS information comes from the surface layer, less than 3 nm thick, but the EDX information comes from a depth of about 1 μm. Similarly, it can also be concluded that the FeCl₃ (FeCl₂) is formed outside the outermost layer of the particles.

From the experimental results, it can be seen that when the amorphous precursor, consisting of FeOOH/Ni(OH)₂, was hydrothermally processed in FeCl₂ solution, a transition process took place to form the Fe-Ni oxide composite. The schematic main reactions in the hydrothermal process can be described as



In the starting reagents, the content of Ni(NO₃)₂ is 0.02 mol, so that the one of Ni(OH)₂ is so. If the Ni transforms completely into Ni₂O₃ following the schematic reaction (2), the reaction needs 0.005 mol O₂ which is about 112 mL O₂, that is, about 530 mL air. Obviously, the stainless steel autoclave is not as bigger enough to contain so much air. This means that only partial nickel hydroxide (Ni(OH)₂) species transformed into Ni₂O₃, and other Ni(OH)₂ species dissolved in water. This agrees with the measured results of both EDX and XPS in which the ration of Fe to Ni is much larger than 2 : 1 for the processed samples. The dissolution of Ni(OH)₂ can enhance the pH value of the solution, which would assist precipitation. In addition, it is noted that for the processed samples, the concentrations of both Ni and Cl measured by XPS are larger than the ones measured by EDX. From the difference between the XPS and EDX data, it can be determined that the particle core consists of γ-Fe₂O₃ and Ni₂O₃ is formed outside the γ-Fe₂O₃, a result which is in agreement with the precursor structure consisting of both FeOOH and Ni(OH)₂.

The FeCl₃ could result from the dismutation reaction of some FeCl

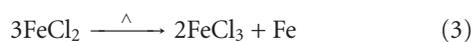


TABLE 3: Binding energy data from XPS (eV) for the precursor (a) and the processed sample in 0.25 M (b), 0.50 M (c), and 1.00 M (d) FeCl₂ solution.

	Fe2p	Ni2p	O1s	Cl2p
(a)	711.15	855.81	530.75	
FeO*O**H	711.40		*530.10 **531.20	
Ni(OH) ₂		855.80	531.50	
(b)	710.83	855.25	530.16	198.78
(c)	710.90	855.39	530.27	198.82
(d)	710.97	855.25	530.23	198.85
γ-Fe ₂ O ₃	710.90		529.80	
Ni ₂ O ₃		855.60	531.80	
FeCl ₃ /FeCl ₂	711.10/710.40			198.80/198.60

Note. The standard data for FeO*O**H, Ni(OH)₂, γ-Fe₂O₃, Ni₂O₃ and FeCl₃ are taken from PHI 5300 ESCA Data Bank and the Handbook of X-ray Photoelectron Spectroscopy.

The Fe could form into iron nanoparticles. And, since pure FeCl₃ is very easy to dissolve in water, the FeCl₃ would be absorbed on γ-Fe₂O₃/Ni₂O₃ particles to form the outermost layer of the composite nanoparticles. XRD measurements of the processed samples in which there are new peaks of both FeCl₃ and Fe, support the opinion.

In the FeCl₂ solution process, since the Ni(OH)₂ partially dissolved, the FeCl₃ was absorbed, the Fe nanoparticles are formed, and the ratio of Fe to Ni in derived nanoparticles is larger than in the precursor for both EDX and XPS. In combination with the XRD results, it is further concluded that the amount of FeCl₃ will increase with the concentration of FeCl₂ solution in the hydrothermal process. The reaction (3) shows that the increasing amount of Fe is only a half of that of FeCl₃, so that the affection of the FeCl₃ increasing could be more obvious than the Fe increasing with the concentration of FeCl₂ solution. This is in agreement with the magnetization measured by VSM since FeCl₃ is paramagnetic, and its magnetization is less than the ferrimagnetic γ-Fe₂O₃ or weakly magnetic Ni₂O₃ (see the inset in Figure 1).

According to the data in Table 2(d), it can be known that if all the Cl is from FeCl₃, the content of Fe should be larger than 72.51 which is three times that of Cl. But, in fact the content of Fe is only 65.37 as shown in Table 2(d). Thus, it is judged that FeCl₂ could exist in the outer layer and increase with the concentration of the processing solution. Therefore, for the surface layer outside the magnetic γ-Fe₂O₃/Ni₂O₃, the exact description should be as FeCl₃ (FeCl₂). The FeCl₃ (FeCl₂) surface is a chemically passive and nonmagnetic (paramagnetic) coating. Thus, the chemical stability of the particles is improved and their aggregation is prevented, a phenomenon similar to the effect of silica coating on the surface of iron oxide nanoparticles [10–12]. And the content of FeCl₃ (FeCl₂) in the composite particles increased with the concentration of FeCl₂ solution in the hydrothermal process, so the magnetization of the particles lessened accordingly. The saturation magnetizations of the as-prepared composite nanoparticles (57.4~62.2 emu/g) are close to the ones of the nanocrystalline γ-Fe₂O₃ particles prepared by generally

hydrothermal synthesis (52.78~72.87 emu/g) [13]. Using the particles prepared in 1 M FeCl₂ solution, ionic ferrofluids [14] have been synthesized and the ferrofluid particles observed by TEM, as shown in Figure 4. It can be seen that these ferrofluid particles were well dispersed. Also, experiments have shown that such ferrofluids based on γ -Fe₂O₃/Ni₂O₃/FeCl₃(FeCl₂) nanoparticles exhibited greater optical transmission than the ones based on γ -Fe₂O₃ nanoparticles. This could be very interesting for the field of magneto-optical effects and will be investigated further.

5. Conclusions

Using a coprecipitation method, a precursor of amorphous composite in which FeOOH is coated with Ni(OH)₂, has been produced. Using a hydrothermal process in FeCl₂ solution, a transition is induced to form γ -Fe₂O₃/Ni₂O₃/FeCl₃(FeCl₂) composite nanoparticles about 10 nm in diameter besides little amount of Fe nanoparticles. The magnetizations of γ -Fe₂O₃, Ni₂O₃, and FeCl₃(FeCl₂) are different. Accordingly, these composite nanoparticles show a gradient of magnetization from core to shell. In many cases, a passivating coating can be applied to avoid agglomeration (important for ferrofluids) [2]. Therefore, such composite nanoparticles could be particularly suitable for the synthesis of ferrofluids. In the hydrothermal process, the formation of the inert FeCl₃(FeCl₂) surface immediately follows the formation of the particles themselves, in situ and in the identical FeCl₂ medium. This contrasts with the coating method, in which the coating is added to as-prepared particles and the possibility of aggregation of the particles exists before coating, that is, the so-called preaggregation [15]. Therefore, the degree of dispersion of the particles prepared by this hydrothermal process in FeCl₂ solution may be better than for particles coated using inert materials. The transition role from hydroxyl composite to oxide composite in FeCl₂ solution could provide to a route to prepare oxide composite nanoparticles if any species in the precursor is insoluble or only slightly soluble in water.

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