The dependence of Ni-Fe bioxide composites nanoparticles on the FeCl₂ solution used

Yueqiang Lin, Jian Li*, Lihua Lin, Xiaodong Liu, Longlong Chen and Jun Fu

Abstract

Background: Ni₂O₃-γ-Fe₂O₃ composite nanoparticles coated with a layer of 2FeCl₃·5H₂O can be prepared by co-precipitation and processing in FeCl₂ solution. Using vibrating sample magnetometer (VSM), X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) diffraction techniques, the dependence of the preparation on the concentration of the FeCl₂ treatment solution is revealed.

Results: The magnetization of the as-prepared products varied non-monotonically as the FeCl₂ concentration increased from 0.020 M to 1.000 M. The Experimental results show that for the composite nanoparticles, the size of the γ-Fe₂O₃ phase is constant at about 8 nm, the Ni₂O₃ phase decreased and the 2FeCl₃·5H₂O phase increased with increasing concentration of FeCl₂ solution. The magnetization of the as-prepared products mainly results from the γ-Fe₂O₃ core, and the competition between the reduction of the Ni₂O₃ phase with the increase of the 2FeCl₃·5H₂O phase resulted in the apparent magnetization varying non-monotonically.

Conclusions: When the concentration of FeCl₂ treatment solution did not exceed 0.100 M, the products are spherical nanoparticles of size about 11 nm; their magnetization increased monotonically with increasing the concentration of FeCl₂ solution due to the decreasing proportion of Ni₂O₃ phase.

Keywords: Composite, Nanoparticles, FeCl₂ solution, Concentration

Introduction

Magnetic nanoparticles with diameters less than 100 nm have attracted increasing interest as particles in this size range may allow investigation of fundamental aspects of magnetic ordering phenomena in magnetic materials with reduced dimensions and could lead to new technological applications [1-5]. Studies of magnetic nanoparticles have focused on the development of novel synthetic methods [5]. A nanocomposite is a material composed of two or more phases, one of which has a grain size of less than 100 nm. The combination of different physical or chemical properties may give rise to completely new materials [6,7]. It has been demonstrated that the formation of a passive coating of an inert material on the surface of iron oxide nanoparticles can help to improve their chemical stability and prevent their aggregation in liquids [8-11]. Recently, composite nanoparticles based on magnetic iron oxide have been prepared [12-16]. Such magnetic nanocomposites have applications ranging from ferrofluids to separation science and technology [17].

In previous work, we described a method to prepare magnetic nanoparticles using a chemically induced transition[15,16,18,19] and Ni-Fe bioxide composite nanoparticles were prepared using this method. In the preparation, a precursor consisting of FeOOH wrapped in Ni(OH)₂ was synthesized by the well-known co-precipitation method. Then, using heat treatment in 0.25 M FeCl₂ solution at 100°C, a transition took place in which in addition to the Ni(OH)₂ partially dissolving, the FeOOH/Ni(OH)₂ precursor was transformed into γ-Fe₂O₃/ Ni₂O₃ composite nanoparticles coated with FeCl₃[15]. The Ni₂O₃ is weakly ferromagnetic [16] and the FeCl₃ is paramagnetic. Experiments have shown that such Ni-Fe bioxide composite nanoparticles are very suitable for the synthesis of ferrofluids [20]. This chemically induced transition using FeCl₂ solution may provide a new route for the preparation of oxide nanoparticles. In the present work, we have investigated the characteristics of Ni-Fe bioxide composite nanoparticles as a function of the concentration of FeCl₂ treatment solution.
Experimental
Preparation
The preparation of the Ni-Fe bixide composite nanoparticles was divided into two steps. Firstly, the precursor based on FeOOH wrapped with Ni(OH)₂ was synthesized using the co-precipitation method, which has been described in detail elsewhere [15,21]. The second step was to add the precursor to FeCl₂ solution, using concentrations of 0.025 M, 0.050 M, 0.075 M, 0.100 M, 0.125 M, 0.250 M, 0.500 M, 0.750 M and 1.000 M, to obtain 400ml of the mixed solution. Then this solution was heated to boiling point for 30 min in atmosphere; the nanoparticles precipitated gradually after the heating had stopped. Finally, these particles were dehydrated with acetone and allowed to dry naturally.

Characterization
A series of Ni-Fe oxide composite nanoparticles was prepared by a chemically induced transition involving FeCl₂ solution. The dependence on the concentration of the FeCl₂ solution was investigated by measuring the specific magnetization curves of the samples at room temperature using a vibrating sample magnetometer (VSM, HH-15, applied field up to 10⁴ Oe).

The samples were prepared using FeCl₂ solutions 0.025 M, 0.075 M, 0.100 M, 0.125 M and 0.500 M, which were named samples (1), (2), (3), (4) and (5), respectively. In addition to the magnetic measurements, their crystal structures, morphology and chemical composition were analyzed by X-ray diffraction (XRD, XD-2, Cu Kα radiation), transmission electron microscopy (TEM, JEM-2100F, at 100 kV) and X-ray photoelectron spectroscopy (XPS, Thermo ESCA250, Mg target).

Results and analysis
Figure 1 shows the specific magnetization curves of the samples. Clearly, all samples exhibited ferromagnetic features, with their specific magnetization varying non-monotonically with the concentration of FeCl₂ solution. At first, the magnetization strengthened as the FeCl₂ concentration increased from 0.025 M to 0.100 M, then the magnetization weakened as the concentration increased from 0.100 M to 1.000 M.

Figure 1 Specific magnetization curves for the samples.

Figure 2 XRD patterns for the samples.
The XRD patterns of the samples are shown in Figure 2. The results show that these samples contain mainly γ-Fe₂O₃ with a trace of Ni₂O₃ and 2FeCl₃·5H₂O, as indicated by the arrows A, B, C and D for Ni₂O₃, and by arrows A₀, B₀ and C₀ for 2FeCl₃·5H₂O. For the ferrite nanoparticles, the grain sizes dₐ can be estimated from the half-maximum width of the (311) diffraction peak β using Scherrer’s formula [22], dₐ=Kλ/βcosθ, where K is a constant 0.89, λ is the X-ray wavelength (Cu Kα=0.1542 nm) and θ is the Bragg diffraction angle of the (311) plane. The calculated results gave about the same value 8 nm for the γ-Fe₂O₃ grains in all the samples. In addition, comparing the intensity ratios of the A peak of Ni₂O₃(d=0.2800 nm) with the C' peak of 2FeCl₃·5H₂O (d=0.2980 nm) show that the proportion of Ni₂O₃ was reduced and 2FeCl₃·5H₂O increased as the concentration of the FeCl₂ solution increased.

TEM observations of the samples are shown in Figure 3. These results show that the particles in samples (1), (2), (3) and (4) are nearly spherical, with an average particles size d_p of about 11 nm, but in sample (5) there are a few rod-shaped particles (shown in the insert) in addition to the spherical particles. Clearly, the size of the spherical particles in sample (5) is less than those of samples (1), (2), (3) and (4), and is about 8 nm. High-resolution TEM results reveal that the particles have core-shell structure, as Figure 4 shown.

XPS measurements confirmed that there were Fe, O, Ni and Cl in the samples as illustrated in Figure 5.
analysis of the binding energies in the spectra, it can be deduced that the samples consisted of $\gamma$-Fe$_2$O$_3$, Ni$_2$O$_3$ and FeCl$_3$. The binding energy data are listed in Table 1. A quantitative analysis shows that for samples (1), (2), (3) and (4), the ratio Ni:Cl decreased in that order, the ratio Fe:Ni clearly increased and the ratio Fe:Cl increased slightly. For sample (5), the ratio Fe:Cl was clearly lower than that for sample (4), along with the ratio Ni:Cl. The ratio Fe:Ni was, however, higher. The complete data are listed in Table 2. In conclusion, it can be determined that for all the samples, the proportion of Ni$_2$O$_3$ phase decreased and FeCl$_3$ phase increased as the concentration of FeCl$_3$ solution increased. This also agrees with the XRD results.

Discussion

The results show that in the preparation of Ni-Fe bioxide nanoparticles, when the concentration of FeCl$_2$ solutions were less than 0.5 M, the samples (1), (2), (3) and (4) were single spherical particles consisting of a $\gamma$-Fe$_2$O$_3$ core, Ni$_2$O$_3$ outside the core and with an outermost layer of 2FeCl$_3$·5H$_2$O. However, when the concentration reached 0.5 M, sample (5) formed rod-shaped particles together with spherical particles than smaller those of samples (1), (2), (3) and (4).

For samples (1), (2), (3) and (4), the results of both XRD analysis and TEM observations indicated that the $\gamma$-Fe$_2$O$_3$ grain size and the size of the complete particles remain about constant. However, the XPS results showed that the proportion of Ni$_2$O$_3$ decreased and FeCl$_3$ increased smoothly. This suggests that over the XPS detection range $d_x$ determined by the mean free paths of the electrons detected [23,24] and which is about 3 nm, the volume fraction of the $\gamma$-Fe$_2$O$_3$ phase remained constant (i.e. diameter of $\gamma$-Fe$_2$O$_3$ core $d_c$ can be regarded as constant), as did the sum of the volume fractions of Ni$_2$O$_3$ and 2FeCl$_3$·5H$_2$O, whose detection ranges are $d_{Ni}$ and $d_{Cl}$, respectively. So, from samples (1) to (4), the reduction of Ni species and the increase of Cl species in the XPS results corresponds to the variation of the volume fraction, a thinning of the Ni$_2$O$_3$ layer and a thickening of the 2FeCl$_3$·5H$_2$O layer. This is also in agreement with the clear increase of the Fe:Ni ratio and the slight increase of the Fe:Cl ratio as the concentration of FeCl$_2$ solution increases. Since samples (1), (2), (3) and (4) consist of spherical particles and the measured XPS depth $d_x$ is greater than the combined thickness of Ni$_2$O$_3$ ($d_{Ni}$) and FeCl$_3$ ($d_{Cl}$), as shown in Figure 6, the measured atomic ratio between Ni and Cl species Ni/Cl allows the molar ratio between Ni$_2$O$_3$ and FeCl$_3$ to be deduced as Ni$_2$O$_3$/FeCl$_3$=1.5 Ni/Cl. The results are also listed in Table 2.

For sample (5), the results from both the XRD analysis and TEM observations show that the $\gamma$-Fe$_2$O$_3$ grain size is the same and the particles size is less than the samples (1), (2), (3) and (4), and the both sizes are about the same. Since there is much less Ni species than Fe, it is concluded that the spherical particles could consist of a $\gamma$-Fe$_2$O$_3$ core and a Ni$_2$O$_3$ surface layer. The average particle size depends mainly on the $\gamma$-Fe$_2$O$_3$ phase, and the rod-shaped particles may consist of crystals of 2FeCl$_3$·5H$_2$O. This is also in agreement with the Fe:Cl ratio for samples (1) to (4) which shows a decrease rather than an increase.

In summary, as the concentration of FeCl$_2$ solution used for the chemically induced transition increases, the samples retain a constant $\gamma$-Fe$_2$O$_3$ composition but the proportion of Ni$_2$O$_3$ is reduced and that of 2FeCl$_3$·5H$_2$O increases. Clearly, the non-monotonic variation of the specific magnetization of the samples as a function of FeCl$_2$ concentration can be attributed to the phase changes. These can be formulated as follows.

The specific magnetization of the samples $\sigma$ can be described as

$$\sigma = \sigma_{m,\gamma} + \sigma_{m,Ni} \sigma_{Ni} + \sigma_{m,Cl} \sigma_{Cl}$$

(1)

where $\sigma_{m,\gamma}$, $\sigma_{Ni}$ and $\sigma_{Cl}$ are specific magnetizations, and $\sigma_{m,\gamma}$, $\sigma_{m, Ni}$ and $\sigma_{m, Cl}$ are the mass fractions of the $\gamma$-Fe$_2$O$_3$, Ni$_2$O$_3$ and 2FeCl$_3$·5H$_2$O phases, respectively. According to the definition of the mass fraction, the relationship between $\sigma_{m,\gamma}$, $\sigma_{m, Ni}$ and $\sigma_{m, Cl}$ is $\sigma_{m,\gamma} + \sigma_{m, Ni} + \sigma_{m, Cl} = 1$. So, formula (1) can be written as

$$\sigma = \sigma_{\gamma} - \left[ \sigma_{m,\gamma} (\sigma_{\gamma} - \sigma_{Ni}) + \sigma_{m,Cl} (\sigma_{\gamma} - \sigma_{Cl}) \right]$$

(2)
Figure 5 XPS results: Fe2p(a), O1s(b), Ni2p(c) and Cl1s(d).
In addition, the $\phi_{m,Ni}$ and $\phi_{m,Cl}$ can be described as follows

$$\phi_{m,Ni} = \frac{\rho_{Ni}}{\rho_{Ni} - \rho_{Cl} + [\phi_{v,Ni}(\rho_{v} - \rho_{Cl})] + \phi_{v,Ni}}$$

$$\phi_{m,Cl} = \frac{\rho_{Cl}}{\rho_{Ni} - \rho_{Cl} + [\phi_{v,Cl}(\rho_{v} - \rho_{Ni})] + \phi_{v,Cl}}$$

where $\rho_{v}$, $\rho_{Ni}$, and $\rho_{Cl}$ are the densities, and $\phi_{v,Ni}$ and $\phi_{v,Cl}$ are the volume fractions of $\gamma$-Fe$_2$O$_3$, Ni$_2$O$_3$, and 2FeCl$_3$·5H$_2$O, respectively, and $\phi_{v,Ni} + \phi_{v,Cl} = 1$. From the experimental results, it is clear that $\phi_{v}$ can be regarded as constant for all the samples. Thus, it can be determined from equation (3) that the variations of $\phi_{v,Ni}$ and $\phi_{v,Cl}$ depend on $\phi_{v,Ni}$ and $\phi_{v,Cl}$, respectively. In addition, the $\gamma$-Fe$_2$O$_3$ is ferrimagnetic, Ni$_2$O$_3$ is weakly magnetic, and 2FeCl$_3$·5H$_2$O is paramagnetic, so that the magnetization of the samples depends mainly on the $\gamma$-Fe$_2$O$_3$ phase. Therefore, since $\phi_{m,Ni}(\sigma_{v,Cl}) >> \phi_{m,Cl}(\sigma_{v,Ni})$, equation (2) can be written as

$$\sigma \equiv \sigma_{v} - [\phi_{m,Ni}(\sigma_{v,Cl})]$$

So, for concentrations of FeCl$_2$ solution below 0.100 M, as the concentration increases from 0.025 to 0.100 M, the $\phi_{m,Ni}$ (or $\phi_{v,Ni}$) decreases gradually, so that $\sigma$ increases. As long as $\phi_{m,Ni}(\sigma_{v,Cl}) < \phi_{m,Cl}(\sigma_{v,Cl})$, formula (2) can be written as

$$\sigma \equiv \sigma_{v} - [\phi_{m,Ni}(\sigma_{v,Cl})]$$

Therefore, for FeCl$_2$ solutions above 0.100 M, as the concentration increases from 0.100 to 1.000 M, the values of $\phi_{m,Cl}$ (or $\phi_{v,Cl}$) increase so that $\sigma$ is reduced. In addition, it can be deduced that when the concentration of FeCl$_2$ solution is about 0.100 M, corresponding to sample(3), perhaps $\phi_{m,Ni}(\sigma_{v,Cl}) < \phi_{m,Cl}(\sigma_{v,Cl})$, i.e. $\phi_{m,Ni}/\phi_{m,Cl} < (\sigma_{v,Cl})/(\sigma_{v,Cl})$, so the specific magnetization $\sigma$ has its maximum value.

**Conclusion**

Using a chemically induced transition, Ni$_2$O$_3$, $\gamma$-Fe$_2$O$_3$, bixide composite nanoparticles can be prepared using FeCl$_2$ solutions with different concentrations. Using a number of characterization tools, such as VSM, XRD, TEM, and XPS, the dependence of the samples on the concentration of the FeCl$_2$ solution has been revealed. When the FeCl$_2$ concentration was less than 0.500 M, the samples consisted of spherical Ni$_2$O$_3$, $\gamma$-Fe$_2$O$_3$ particles, about 11 nm diameter, coated with 2FeCl$_3$·5H$_2$O. When the FeCl$_2$ concentration was 0.500 M, the product consisted of both Ni$_2$O$_3$, $\gamma$-Fe$_2$O$_3$ spherical particles, of about 8 nm size, and 2FeCl$_3$·5H$_2$O rod-shaped particles. Nevertheless, the size of the $\gamma$-Fe$_2$O$_3$ grains was about the same for all samples. Significantly, the magnetization of the samples exhibited a non-monotonic variation although the ratio between the Ni and Cl species decreased monotonically with the increasing concentration of the FeCl$_2$ solution. It was noticed that samples prepared using FeCl$_2$ solutions with concentrations

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**Table 1 Binding energy data for the elements of the samples from XPS(eV)**

|       | Fe2p$_{3/2}$ | O1s   | Ni2p$_{3/2}$ | Cl2p  |
|-------|-------------|-------|-------------|-------|
| (1)   | 710.30      | 530.04 | 854.93      | 197.66|
| (2)   | 710.66      | 530.13 | 855.10      | 197.73|
| (3)   | 710.36      | 530.11 | 854.96      | 198.08|
| (4)   | 710.43      | 530.04 | 855.04      | 197.95|
| (5)   | 710.86      | 530.34 | 855.66      | 198.35|

**Table 2 The atomic percentages of Fe, O, Ni and Cl from XPS measurement and the molar ratio of Ni2O3/FeCl3**

|       | Fe | O  | Ni | Cl | Fe : Ni : Cl | Ni2O3/FeCl3 |
|-------|----|----|----|----|--------------|-------------|
| (1)   | 13.79 | 72.50 | 5.15 | 1.02 | 0.62 : 0.37 | 1.0/0.40    |
| (2)   | 15.48 | 74.94 | 5.88 | 4.58 | 1.38 : 0.30 | 1.0/0.53    |
| (3)   | 19.21 | 71.06 | 4.15 | 5.58 | 1.02 : 0.29 | 1.0/0.59    |
| (4)   | 16.74 | 75.45 | 3.11 | 4.70 | 1.09 : 0.28 | 1.0/1.02    |
| (5)   | 18.71 | 67.21 | 1.84 | 12.25 | 1.01 : 0.65 |             |
0.025 M 0.075 M, 0.100 M and 0.125 M, have the same size particles, about 11 nm, and same size of γ-Fe₂O₃ grains, about 8 nm. Therefore, it is deduced that the variation of the apparent magnetization has resulted from the competition between the reduced Ni₂O₃ phase and increasing 2FeCl₂·5H₂O. When the concentration of FeCl₂ solution does not exceed 0.100 M, the magnetization of the samples increases with increasing concentration since the rate of reduction of Ni₂O₃ is larger than the increase of 2FeCl₂·5H₂O. When the FeCl₂ concentration exceeds 0.100 M, the magnetization of the samples weakens since the increase of 2FeCl₂·5H₂O is now larger than the decrease of Ni₂O₃. Therefore, it can be concluded that using the chemically induced transition method to prepare Ni-Fe bioxide composite nanoparticles, as long as the concentration of the FeCl₂ solution does not exceed 0.100 M, the thickness of both Ni₂O₃ and 2FeCl₂·5H₂O layers can be controlled and the γ-Fe₂O₃ core size remains constant. As a result, magnetic nanoparticles with a fixed size of about 11nm but different magnetization can be obtained.

Competing interests
Non-financial competing interests.

Authors’ contributions
All authors contributed equally to this work. All authors read and approved the final manuscript.

Acknowledgements
Financial support for this work was provided by the National Science Foundation of China (No.11074205).

Received: 26 July 2012 Accepted: 12 October 2012 Published: 30 October 2012

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