Preparation of γ-Fe₂O₃/ZnFe₂O₄ nanoparticles by enhancement of surface modification with NaOH

Longlong Chen¹, Jian Li¹*, Yueqiang Lin¹, Xiaodong Liu¹, Junming Li¹, Xiaomin Gong¹ and Decai Li²

Abstract

**Background:** During liquid-phase synthesis of γ-Fe₂O₃ nanoparticles by chemically induced transition in FeCl₂ solution, enhancement of surface modification by adding ZnCl₂ was attempted by using NaOH. By using transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, energy-dispersive X-ray spectrometry, and vibrating sample magnetometry, the dependence of the synthesis on the amount of additional NaOH was studied.

**Results:** The experimental results show that the surface of the γ-Fe₂O₃ nanoparticles could be modified by adding ZnCl₂ to form composite nanoparticles with γ-Fe₂O₃/ZnFe₂O₄ ferrite core coated with Zn(OH)₂ and adsorbed FeCl₂, and that modification could be enhanced by adding NaOH.

**Conclusions:** In the experimental conditions, when the concentration of additional NaOH was below 0.70 M, the amounts of ZnFe₂O₄ and Zn(OH)₂ phases increased slightly and that of adsorbed FeCl₂ was unchanged. When the concentration of NaOH exceeded 0.70 M, the amount of FeCl₂, ZnFe₂O₄, and Zn(OH)₂ increased.

**Keywords:** Nanoparticles, Composite, Surface modification, γ-Fe₂O₃, ZnFe₂O₄

Introduction

Nanoparticles are typically defined as solids that are less than 100 nm in all three dimensions. Many physical phenomena in both organic and inorganic materials have natural length scales between 1 and 100 nm (10⁻⁷ to 10⁻⁵ atoms) [1,2]. A nanocomposite is a material composed of two or more phases with at least one phase with nanometer dimensions. Due to combination of different physical or chemical properties, composite nanoparticles may lead to completely novel materials [3]. For example, the type and geometric arrangement of surface coating on a magnetic core determine the overall size of a nanocomposite colloid and play a significant role in its biological fate in biomedical applications [4].

Magnetic nanoparticles are an important class of functional materials that have attracted increasing interest in terms of their science and their technological applications [5]. Studies on ferromagnetic (FM)–antiferromagnetic (AFM) exchange interactions in systems of fine composite particle have led to interesting applications in improving the performance of permanent magnetic materials or in exceeding the superparamagnetic limit in magnetic recording media [6]. Studies on magnetic nanoparticles have focused on the development of novel technologies for their synthesis. Liquid-phase synthesis is still one of the most commonly used methods to obtain inorganic nanoparticles [7]. Many studies have shown that surface modification, which provides additional functionality to nanoparticles, is easily accomplished after or during synthesis [1]. Recently, we proposed a new method to produce magnetic nanoparticles. This method involves chemically induced transition in which γ-Fe₂O₃-based nanoparticles are prepared by processing a precursor based on iron oxide hydroxide and/or metal hydroxide in FeCl₂ solution [8-10]. In this method, γ-Fe₂O₃ nanoparticles can be prepared by using an amorphous coating of FeOOH and Mg(OH)₂, as described in the following equation [10]:

\[
2\text{FeOOH} + \text{Mg(OH)}_2 \xrightarrow{\text{FeCl}_2 \text{ solution (heating)}} \gamma\text{-Fe}_2\text{O}_3 \downarrow + \text{H}_2\text{O} + \text{Mg}^{2+} + 2\text{OH}^- 
\]

In another study, surface modification of the particles was undertaken during synthesis by adding ZnCl₂ to the FeCl₂ solution to prepare γ-Fe₂O₃/ZnFe₂O₄ composite nanoparticles [11]. Experimental results show that when the concentration of ZnCl₂ in solution did not exceed...
2 M (50 mL), γ-Fe$_2$O$_3$/ZnFe$_2$O$_4$ bixode nanoparticles coated with FeCl$_3$·6H$_2$O could be prepared. Generally, alkaline solution could assist the precipitation reaction. In the present work, we attempted to enhance the surface modification by adding NaOH to the processing solution. The morphology, crystal structure, surface and bulk chemical composition, and magnetization of the as-prepared products were characterized. The structure of the particles was proposed and the role of NaOH was revealed.

**Experimental Preparation**

Preparation of the nanoparticles could be divided into two steps. First, the precursor based on amorphous FeOOH and Mg(OH)$_2$ was synthesized by coprecipitation of FeCl$_3$ and Mg(NO$_3$)$_2$, as described in detail elsewhere [10]. In the second step, the precursor was added to 400 mL of 0.25 M FeCl$_3$ solution, and the resulting mixture was heated to boiling for 20 min. Afterward, a mixture of 50 mL of 1 M ZnCl$_2$ solution and 20 mL NaOH solution at a specific concentration was added to the boiling FeCl$_3$ solution, and the resulting mixture was boiled continuously for 10 min. Subsequently, the mixture was allowed to cool to room temperature, and the as-prepared particles were allowed to settle. The NaOH concentrations used for the preparation were 0.35, 0.70, 1.40, and 2.10 M, corresponding to the as-prepared samples (1), (2), (3), and (4), respectively. For comparison, modified particles were prepared without adding NaOH (sample (0)).

**Characterization**

The morphology of the particles in the samples was observed by transmission electron microscopy (TEM, Philips Tecnai 10), and their crystal structure was analyzed by X-ray diffraction (XRD, XD-2). The chemical species were measured using X-ray photoelectron spectroscopy (XPS, XSAM 800), and energy-dispersive X-ray spectroscopy (EDX, Genesis) equipped in scanning electron microscopy (SEM, Quanta-200). The magnetization was measured by using a vibrating sample magnetometer (VSM, HH-15).

**Results and analysis**

TEM images of the samples are shown in Figure 1. It can be seen that sample (0) consisted of nearly spherical nanoparticles. Statistical analysis showed that the size of the particles fit a log-normal distribution, with the median diameter $d_{50}$ about 9.78 nm and the standard deviation $\ln d_{50} = 0.28$. Samples (1) – (4) images indicated that these samples consisted of irregular flake particles and nearly spherical particles, whose sizes are clearly larger than size of sample (0). This shows that NaOH can stimulate aggregation of the initial particles to grow into larger particles via oriented attachment [12].

XRD results (Figure 2) reveal that the samples contained mainly γ-Fe$_2$O$_3$ and traces of ZnFe$_2$O$_4$ and Zn(OH)$_2$, but no ZnCl$_2$.

XPS measurements show that O, Fe, Zn, and Cl but no Mg and Na species were present in the samples, as illustrated in Figure 3. Therefore, the samples consisted of Fe$_2$O$_3$, ZnFe$_2$O$_4$, Zn(OH)$_2$, and FeCl$_3$. Binding energy data are listed in Table 1. As a comparison, the binding energy data of ZnCl$_2$ [13] are listed also in Table 1. Obviously, the data of measured deviate from data of ZnCl$_2$. Quantitative analysis, whose relative error are less that 1 %, shows that relative to sample (0) this ratio of Fe to Cl keeps almost invariant for low NaOH concentrations (up to 0.70 M) – samples (1) and (2), but it increase with NaOH concentrations above that level – sample (3) and (4). Alternatively, to use the same criteria used for the ratio of Fe to Zn of samples, (1) ≈ (2) < (3) < (4). Complete data are listed in Table 2.

The results of EDX measurements of all samples confirm the same chemical species as those detected by XPS. Results of quantitative analysis, whose relative error are less in 2 %, are listed in Table 3. Evidently, the Fe:Cl and Fe:Zn ratios show the same trends for the samples as those observed with XPS. Figure 4 shows the specific magnetization curves of the samples. All samples showed distinct FM behavior. Their specific saturation values $\sigma_s$ were deduced by plotting $\sigma$ vs. $1/H$ in the high-field region [14]. These values were found to be 52.29, 53.63, 58.29, 55.09, and 47.15 emu/g for samples (0), (1), (2), (3), and (4), respectively. Magnetization of samples (0) and (1) were nearly the same, that of sample (2) was the strongest, and the magnetization weakened gradually from samples (2) to sample (4).

**Discussion**

The experimental results and analysis above indicate that all of the samples were composed of γ-Fe$_2$O$_3$, ZnFe$_2$O$_4$, Zn(OH)$_2$ and FeCl$_3$, and no ZnCl$_2$. The experimental results show that the ratios of Fe to Cl and Fe to Zn obtained by XPS were less than those obtained by EDX spectrometry, and the ratio of Cl to Zn obtained by XPS agree with that obtained by EDX spectrometry (see Tables 2 and 3). Since the EDX spectrometry measurements are acquired at micrometer depths whereas XPS data are obtained from the surface layer of nanometer thickness [15,16], the experimental results suggest that the core of the particles is essentially γ-Fe$_2$O$_3$ and the coating layers are Zn and Cl based.

XRD results show the presence of ZnFe$_2$O$_4$ and Zn(OH)$_2$ phases in addition to the γ-Fe$_2$O$_3$ phase, but no clear FeCl$_3$ crystal phase. These results therefore suggest that the layer of adsorbed FeCl$_3$ was very thin and amorphous. Therefore,
the structure of the composite nanoparticles consisted of four parts, namely, a $\gamma$-$\text{Fe}_2\text{O}_3$ core, external shells of $\text{ZnFe}_2\text{O}_4$ and $\text{Zn(OH)}_2$, and an outermost layer of adsorbed $\text{FeCl}_3$. A schematic model of this structure is shown in Figure 5. Accordingly, the formation of the composite nanoparticles can be described as follows.

When the FeOOH/Mg(OH)$_2$ precursor was thermally treated with $\text{FeCl}_2$ solution, Mg(OH)$_2$ was dissolved, an amorphous FeOOH species was transformed into $\gamma$-$\text{Fe}_2\text{O}_3$ crystallites, and $\text{Fe}^{2+}$ was oxidized to $\text{Fe}^{3+}$. While adding $\text{ZnCl}_2$ to the solution, a precipitation reaction took place on the $\gamma$-$\text{Fe}_2\text{O}_3$ crystallites, which can be described as follows:

$$x[\text{Fe}^{3+} + 3\text{OH}^-] + y[\text{Zn}^{2+} + 2\text{OH}^-] \rightarrow [\text{Fe(OH)}_3]_x[\text{Zn(OH)}_2]_y$$

If $y/x > 1/2$, then

$$[\text{Fe(OH)}_3]_x[\text{Zn(OH)}_2]_y \rightarrow [\text{ZnFe}_2\text{O}_4]_{x/2}[\text{Zn(OH)}_2]_{y-x/2} + 2x\text{H}_2\text{O}$$

Thus, ZnFe$_2$O$_4$ grew epitaxially on the $\gamma$-$\text{Fe}_2\text{O}_3$ crystallites and some Zn(OH)$_2$ outside of the ZnFe$_2$O$_4$ layer was preserved. Clearly, additional NaOH enhanced the reaction so that $x$ and $y$ increased with increasing NaOH content. In addition, $\text{Fe}^{3+}$ and Cl$^-$ in the liquid phase were adsorbed and were subsequently converted to composite nanoparticles coated with $\text{FeCl}_3$. Experimental results show that with increasing NaOH content, the amount of phases based on Zn increased. When the NaOH concentration was lower than 0.70 M, the $\text{FeCl}_3$ phase was nearly unchanged since the Fe: Cl ratio is almost invariant (Table 2); thus, only when the NaOH...
concentration exceeded 0.70 M did the amount of FeCl$_3$ increase clearly with NaOH concentration due to increasing amount of Cl. This means that the value of $x$ in equation (2) increased with NaOH concentration at low NaOH concentrations, i.e., the amount of ZnFe$_2$O$_4$ phase increased clearly with NaOH concentration when the NaOH concentration did not exceed 0.70 M, but it increased slightly with NaOH concentration when the NaOH concentration was >0.70 M. As the results in Table 2 show a consistent increase of the Zn: Fe ratio with increasing NaOH concentration, it can be judged that Zn(OH)$_2$ increased slightly under low NaOH concentration (<0.70 M) and did clearly under high NaOH concentration (>0.70 M). According to the relation between the specific magnetization and NaOH content, the action of additional NaOH can be discussed further as follows.

The magnetization exhibited stepwise distribution, being strongest in the innermost region of the composite nanoparticle: Zn(OH)$_2$/FeCl$_3$ < ZnFe$_2$O$_4$ < γ-Fe$_2$O$_3$. The specific magnetization of the composite nanoparticle system $\sigma$ can be described as follows:

$$\sigma = \phi_{\gamma-Fe} \sigma_{\gamma-Fe} + \phi_{ZnFe₂O₄} \sigma_{ZnFe₂O₄} + \phi_{Zn(OH)₂} \sigma_{Zn(OH)₂} + \phi_{FeCl₃} \sigma_{FeCl₃}$$

(4)

where $\phi_{\gamma-Fe}$, $\phi_{ZnFe₂O₄}$, $\phi_{Zn(OH)₂}$ and $\phi_{FeCl₃}$ are mass fractions; $\sigma_{\gamma-Fe}$, $\sigma_{ZnFe₂O₄}$, $\sigma_{Zn(OH)₂}$ and $\sigma_{FeCl₃}$ are the specific magnetizations for the γ-Fe$_2$O$_3$, ZnFe$_2$O$_4$, Zn(OH)$_2$, and FeCl$_3$ phases, respectively. $\sigma_{\gamma-Fe} > \sigma_{ZnFe₂O₄} > \sigma_{Zn(OH)₂} (= \sigma_{FeCl₃})$ since nanoscale ZnFe$_2$O$_4$ could be weakly ferromagnetic [17], and Zn(OH)$_2$ and FeCl$_3$ are paramagnetic. Considering as well that $\phi_{\gamma-Fe} + \phi_{Zn-Fe} + \phi_{Zn} + \phi_{Cl} = 1$, equation (4) can be written as

$$\sigma = \phi_{\gamma-Fe} (\sigma_{\gamma-Fe} - \sigma_{Zn-Fe}) - \phi_{Zn}(\sigma_{\gamma-Fe} - \sigma_{Zn}) - \phi_{Cl}(\sigma_{\gamma-Fe} - \sigma_{Cl})$$

(5)

Qualitatively, the variation of the specific magnetization $\Delta \sigma$ can be described as follows:

$$\Delta \sigma = -\Delta \phi_{Zn-Fe} (\sigma_{\gamma-Fe} - \sigma_{Zn-Fe}) - \Delta \phi_{Zn}(\sigma_{\gamma-Fe} - \sigma_{Zn}) - \Delta \phi_{Cl}(\sigma_{\gamma-Fe} - \sigma_{Cl})$$

(6)

The mass fraction of every phase should be directly proportional to the molar ratio. The mass fraction is

![Figure 2 XRD patterns of the samples prepared without NaOH (0) and with increasing NaOH concentrations: 0.35 (1), 0.70 (2), 1.40 (3) and 2.10 M (4). Crystallographic indexes (hkl), (h0l), as well as A, B, C, D, and E correspond to the γ-Fe$_2$O$_3$ (PDF #39-1346), ZnFe$_2$O$_4$ (PDF #22-1012), and Zn(OH)$_2$ (PDF #20-1435) phases, respectively.](Image)

![Figure 3 XPS spectra of the samples prepared without NaOH (0) and with increasing NaOH concentrations: 0.35 (1), 0.70 (2), 1.40 (3) and 2.10 M (4).](Image)

![Table 1 Binding energy data from XPS (eV) for samples prepared without NaOH (0) and with increasing NaOH concentrations: 0.35 (1), 0.70 (2), 1.40 (3) and 2.10 M (4).](Table)

|          | O1s  | Fe2p$_{3/2}$ | Zn2p$_{3/2}$ | Cl2p |
|----------|------|--------------|--------------|------|
| 0        | 529.90 | 710.44       | 1021.15      | 198.07 |
| 1        | 529.94 | 710.71       | 1021.40      | 198.19 |
| 2        | 529.93 | 710.88       | 1021.17      | 198.10 |
| 3        | 529.84 | 710.79       | 1021.16      | 198.13 |
| 4        | 530.08 | 710.98       | 1021.20      | 198.28 |
| Fe$_2$O$_3$ | 530.00 | 710.70       |              |      |
| ZnFe$_2$O$_4$ | 530.84 | 710.95       | 1020.86      |      |
| Zn(OH)$_2$ | 531.35 |              | 1022.30      |      |
| FeCl$_3$  | 571.10 |              | 198.70       |      |
| ZnCl$_2$  | 1022.50 |              | 198.85       |      |

Note: (a) The data are taken from Ref. [17].
(b) The data are from Ref. [17].
(c) The data are from Ref. [17].

The data are taken from the Handbook of X-ray photoelectron.
defined as $\phi = m_i / \Sigma m_p$, where $m_i$ represents $m_{\gamma\text{-Fe}}$, $m_{\gamma\text{-FeO}}$, $m_{\gamma\text{FeO}_2\gamma}$ and $m_{\gamma\text{Fe(OH)}_2}$, which are the masses of $\gamma\text{-FeO}_3$, $\gamma\text{Fe}_2\text{O}_4$, $\gamma\text{Fe(OH)}_2$, and $\gamma\text{FeCl}_3$ phases in the sample, respectively. In the modification to this equation, the mass of the $\gamma\text{-FeO}_3$ phase $m_{\gamma\text{Fe}}$ may be treated as constant. Thus, when $m_{\gamma\text{Cl}}$ was nearly constant under low amounts of additional 0.70 M NaOH, $\phi_{\gamma\text{Cl}}$ decreased as $m_{\gamma\text{FeO}}$, and $m_{\gamma\text{Fe}}$ increased. As a consequence, when $\Sigma m_i$ increased at low amounts of NaOH, $\Delta\phi_{\gamma\text{Cl}}$ was negative since $m_{\gamma\text{Cl}}$ was unchanged, i.e., $-\Delta\phi_{\gamma\text{Cl}} > 0$; thus, equation (6) can be written as

$$
\Delta\sigma = -\Delta\phi_{\gamma\text{FeO}}(\sigma_{\gamma\text{FeO}} - \sigma_{\gamma\text{FeO}_2\gamma}) - \Delta\phi_{\gamma\text{Cl}}(\sigma_{\gamma\text{Cl}} - \sigma_{\gamma\text{Cl}}) + |\Delta\phi_{\gamma\text{Cl}}|(\sigma_{\gamma\text{Fe}} - \sigma_{\gamma\text{Cl}})
$$

(7)

Equation (7) shows that increment of the mass fraction of the $\gamma\text{Fe}_2\text{O}_4$ and $\gamma\text{Fe(OH)}_2$ phases lowered the value of $\sigma$, whereas a decrement in the mass fraction of the $\gamma\text{FeCl}_3$ phase increased it. For sample (1), $x$ and $y$ in the precipitation reaction described by equation (2) increased slightly compared with those for sample (0); hence, $\Delta\phi_{\gamma\text{FeO}}$, $\Delta\phi_{\gamma\text{FeO}_2\gamma}$, and $\Delta\phi_{\gamma\text{Cl}}$ were very small compared with their counterparts for sample (0). Therefore, $\sigma$ of sample (1) was about the same as that of sample (0). For sample (2), $x$ and $y$ in the precipitation reaction increased, but the increment of $x$ could be larger than $y$. Thus, it can be judged from equation (3) that the increment in molar content $x/2$ of the $\gamma\text{Fe}_2\text{O}_4$ phase would be larger than that of the $\gamma\text{Fe(OH)}_2$ phase $(y - x/2)$, i.e., $\Delta\phi_{\gamma\text{FeO}} > \Delta\phi_{\gamma\text{FeO}_2\gamma}$. Since $\sigma_{\gamma\text{Fe}} - \sigma_{\gamma\text{FeO}_2\gamma} < \sigma_{\gamma\text{Fe}} - \sigma_{\gamma\text{Cl}} (= \sigma_{\gamma\text{Fe}} - \sigma_{\gamma\text{Cl}})$ and $|\Delta\phi_{\gamma\text{Cl}}|$ is proportional to $\Delta\phi_{\gamma\text{Fe}} + |\Delta\phi_{\gamma\text{FeO}}| \Delta\phi_{\gamma\text{Cl}}$ ($\sigma_{\gamma\text{Fe}} - \sigma_{\gamma\text{Cl}} > \Delta\phi_{\gamma\text{Fe}}(\sigma_{\gamma\text{Fe}} - \sigma_{\gamma\text{Cl}}) + \Delta\phi_{\gamma\text{Cl}}(\sigma_{\gamma\text{Fe}} - \sigma_{\gamma\text{Cl}})$). Consequently, the $\sigma$ value of sample (2) was greater than those for samples (0) and (1).

When the concentration of additional NaOH exceeded 0.70 M, the amount of $\gamma\text{FeCl}_3$ phase increased with the NaOH content. Therefore, the variation of $\sigma$ should be described as follows:

$$
\Delta\sigma = -\Delta\phi_{\gamma\text{FeO}}(\sigma_{\gamma\text{FeO}} - \sigma_{\gamma\text{FeO}_2\gamma}) - \Delta\phi_{\gamma\text{Cl}}(\sigma_{\gamma\text{Cl}} - \sigma_{\gamma\text{Cl}}) + \Delta\phi_{\gamma\text{Cl}}(\sigma_{\gamma\text{Cl}} - \sigma_{\gamma\text{Cl}})
$$

(8)

Therefore, the $\sigma$ weakened in the order of samples (2) to (4).

---

**Table 2 Atomic percentages of O, Fe, Cl, and Zn from XPS measurements for samples prepared without NaOH (0) and with increasing NaOH concentrations: 0.35 (1), 0.70 (2), 1.40 (3) and 2.10 M (4)**

|       | O   | Fe   | Zn   | Cl   | FeZnCl | ClZn |
|-------|-----|------|------|------|--------|------|
| 0     | 71.43 | 25.16 | 0.61 | 2.80 | 1.0024:0.111 | 1.022 |
| 1     | 72.36 | 23.69 | 1.36 | 2.59 | 1.0057:0.109 | 1.052 |
| 2     | 69.60 | 25.05 | 2.65 | 2.70 | 1.0108:0.106 | 1.102 |
| 3     | 68.01 | 22.89 | 5.91 | 3.19 | 1.0258:0.139 | 1.186 |
| 4     | 68.06 | 20.90 | 7.82 | 3.22 | 1.0374:0.154 | 1.243 |

**Table 3 Atomic percentages of O, Fe, Cl, and Zn from EDX spectrometry measurements for samples prepared without NaOH (0) and with increasing NaOH concentrations: 0.35 (1), 0.70 (2), 1.40 (3) and 2.10 M (4)**

|       | O   | Fe   | Zn   | Cl   | FeZnCl | ClZn |
|-------|-----|------|------|------|--------|------|
| 0     | 55.75 | 42.15 | 0.48 | 1.62 | 1.0011:0.038 | 1.029 |
| 1     | 57.85 | 39.97 | 0.60 | 1.58 | 1.0015:0.040 | 1.038 |
| 2     | 55.41 | 41.36 | 1.70 | 1.53 | 1.0041:0.037 | 1.111 |
| 3     | 55.57 | 39.63 | 3.15 | 1.65 | 1.0079:0.042 | 1.188 |
| 4     | 53.56 | 39.51 | 4.86 | 2.07 | 1.0123:0.053 | 1.232 |

**Figure 4 Specific magnetization curves of the samples prepared without NaOH (0) and with increasing NaOH concentrations: 0.35 (1), 0.70 (2), 1.40 (3) and 2.10 M (4).**

**Figure 5 Schematic diagram of the particle structure.** $d_p$ is the diameter of the composite particle, $d_y$ is the diameter of the $\gamma\text{Fe}_3\text{O}_4$ core, and $d_z$ is the depth detected by XPS.
Conclusions
During liquid-phase synthesis of γ-Fe₂O₃ nanoparticles from precursor composed of amorphous FeOOH and Mg(OH)₂ by chemically induced transition in FeCl₃ solution, Mg(OH)₂ dissolved, FeOOH transformed into γ-Fe₂O₃ nanocrystallites, and Fe²⁺ was oxidized partially into Fe³⁺. The surface of the particles could be modified by adding ZnCl₂ to form γ-Fe₂O₃/ZnFe₂O₄ composite nanoparticles coated with Zn(OH)₂ and adsorbed FeCl₃. Such composite nanoparticles exhibited stepwise distribution of magnetization from inner to outer regions. Thus, they could be easily dispersed in carrier liquid to form excellent ferrofluids [18]. Experimental results indicate that when the amount of ZnCl₂ solution was constant (1 M, 50 mL), the modification could be enhanced by addition of NaOH. When the concentration of additional NaOH was below 0.70 M, the amount of FeCl₃ adsorbed was unchanged, but that of ZnFe₂O₄ and Zn(OH)₂ increased slightly, increasing the magnetization of the products. When the concentration of additional NaOH exceeded 0.70 M, the amount of adsorbed FeCl₃ and ZnFe₂O₄ and Zn(OH)₂ phases increased, and the specific magnetization of the as-prepared products weakened with increasing amount of NaOH. These results show that surface modification during synthesis of the composite nanoparticles γ-Fe₂O₃/ZnFe₂O₄ coated with Zn(OH)₂ and FeCl₃ could be enhanced by additional NaOH to obtain various proportions of phases in the composite particles. This route could be an interesting route for preparing magnetic composite nanoparticles with novel properties. It could potentially be used to prepare other composite nanoparticles based on γ-Fe₂O₃. In this regard, it will be investigated further.

Competing interests
The authors declare that they have no competing interests.

Authors’ contributions
LC carried out characteristical studies of the nanoparticles, participated in the sequence alignment and drafted the manuscript. JL conceived of the study, and participated in its design and coordination and help to draft the manuscript. YL carried out the preparation of samples. XL carried out the measurements of both VSM and XRD. JL carried out the analysis of both EDX and XPS results. XG performed the analysis of TEM results. DL participated in the design of the study. All authors read and approval the final manuscript.

Acknowledgments
Financial support for this work was provided by the National Science Foundation of P.R. China (No. 51375039 and 11074205).

Author details
1School of Physical Science & Technology, Southwest University, Chongqing 400715, People’s Republic of China. 2School of Mechanical & Control Engineering, Beijing Jiaotong University, Beijing 100044, People’s Republic of China.

Received: 11 March 2014 Accepted: 16 June 2014 Published: 24 June 2014

References
1. Willard MA, Kuthara LK, Carpenter EE, Calvin S, Harris VG: Chemically prepared magnetic nanoparticles. Int Mater Rev 2004, 49:125–170.
2. Murray CB, Kagan CR, Bawendi MG: Synthesis and characterization of monodisperse nanocrystals and close-packed nanocrystal assemblies. Annu Rev Mater 2000, 30:545–610.
3. Szabó DV, Vollath D: Nanocomposites from coated nanoparticles. Adv Mater 1999, 11:1313–1316.
4. Reddy LH, Arias JL, Nicolas J, Couvreur P: Magnetic nanoparticles: design and characterization, toxicity and biocompatibility, pharmaceutical and biomedical applications. Chem Rev 2012, 112:5818–5878.
5. Sun SH: Recent advances in chemical synthesis, self-assembly, and applications of FePt nanoparticles. Adv Mater 2005, 18:403–403.
6. Nogué J, Sort J, Langlais V, Skumryev V, Suriñach S, Muñoz JS, Baró MD: Exchange bias in nanostructures. Phys Rep 2005, 422:65–117.
7. Cushing BL, Kolesnichenko VL, O’Connor CJ: Recent advances in the liquid-phase syntheses of inorganic nanoparticles. Chem Rev 2004, 104:3983–3946.
8. Zhang QM, Li J, Lin YQ, Liu XD, Mao H: The preparation and characterization of Ni-Fe biodioque composite nanoparticles. J Alloy Compd 2010, 508:396–399.
9. Miao H, Li J, Lin Y, Liu X, Zhang Q, Fu J: Characterization of γ-Fe₂O₃ nanoparticles prepared by transformation of o-FeOOH. Chin Sci Bull 2011, 56:2385–2388.
10. Wen BC, Li J, Lin YQ, Liu XD, Fu J, Miao H, Zhang QM: A novel preparation method γ-Fe₂O₃ nanoparticles and their characterization. Mater Chem Phys 2011, 128:35–38.
11. Chen LL, Li J, Lin YQ, Liu XD, Lin LH, Li DC: Surface modification and characterization of γ-Fe₂O₃ nanoparticles synthesized by chemically-induced transition. Mater Chem Phys 2013, 141:828–834.
12. Narayanaswamy A, Xu HF, Pradhan N, Peng XG: Crystalline nanoflowers with different chemical compositions and physical properties grown by limited ligand protection. Angew Chem Int Ed 2006, 45:5361–5364.
13. Seals R, Alexander R, Taylor LT, Dillard JG: Core electron binding energy study of group IIIb-VIIa compounds. Inorg Chem 1973, 12:2485–2487.
14. Arulmugan R, Vaidyanathan G, Senthilkumar S, Jeyadevan C: Co-Zn ferrite nanoparticles for ferrofluid preparation: Study on magnetic properties. Physica B 2005, 363:225–231.
15. Tanuma S, Powell CJ, Penn DR: Calculations of Electron Inelastic Mean Free Paths III. Data for 15 Inorganic Compounds over the 50-2000 eV Range. Surf Interface Anal 1991, 17:927–939.
16. Smořák-Slufovič I, Vlkošová B, Bartík Z, Haslettl T: Bimetalllic (Ag)Au nanoparticles prepared by the seed growth method: Two-dimensional assembling, characterization by energy dispersive X-ray analysis, X-ray photoelectron spectroscopy, and surface enhanced Raman spectroscopy, and proposed mechanism of growth. Langmuir 2004, 20:3407–3415.
17. Li J, Wang AR, Lin YQ, Liu XD, Fu J, Lin LH: A study of ZnFe₂O₄ nanoparticles modified by ferric nitrate. J Magn Magn Mater 2013, 330:96–100.
18. Lin LH, Li J, Fu J, Lin YQ, Liu XD: Preparation, magnetization, and microstructure of ionic ferrofluids based on γ-Fe₂O₃/NiO₂ composite nanoparticles. Mater Chem Phys 2012, 134:407–411.

doi:10.1186/1752-153X-4-80
Cite this article as: Chen et al.: Preparation of γ-Fe₂O₃/ZnFe₂O₄ nanoparticles by enhancement of surface modification with NaOH. Chemistry Central Journal 2014 8:40.