Research Article

**Cu(I) Modification during $\gamma$-Fe$_2$O$_3$ Nanoparticles Synthesis and Subsequent Characterization**

Hong Mao, 1 Xiaoyan Qiu, 1 Decai Li, 2 Yueqiang Lin, 1 Xiaodong Liu, 1 and Jian Li 1

1School of Physical Science and Technology, Southwest University, Chongqing 400715, China
2School of Mechanical and Control Engineering, Beijing Jiaotong University, Beijing 100044, China

Correspondence should be addressed to Jian Li; aizhong@swu.edu.cn

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During the synthesis of the $\gamma$-Fe$_2$O$_3$ nanoparticles via the chemically induced transition method, Cu(I) modification has been attempted by adding CuCl/NaOH to the treatment solution. The experimental results showed that, under the condition of a NaOH content equal to 0.04 moles, when the content of CuCl is as low as $1.25 \times 10^{-3}$ or $2.50 \times 10^{-3}$ moles, the products are single $\gamma$-Fe$_2$O$_3$/Cu(II)FeO$_3$/FeCl$_3$·6H$_2$O composite nanoparticles, whereas when the content of CuCl is higher, $5 \times 10^{-2}$ moles, the product is a mixture consisting of $\gamma$-Fe$_2$O$_3$/Cu(I)FeO$_3$/FeCl$_3$·6H$_2$O nanoparticles and Cu(II)/(OH)Cl nanoparticles. For the $\gamma$-Fe$_2$O$_3$/Cu(I)FeO$_3$/FeCl$_3$·6H$_2$O composite nanoparticles, the Cu(I)FeO$_3$ interface layer is not thick enough to form one unit cell, but it can modify the formation of a FeCl$_3$·6H$_2$O surface layer and the effective magnetization of the $\gamma$-Fe$_2$O$_3$ core.

1. Introduction

By definition, nanomaterials have one or more dimensions in the nanometer scale range (<100 nm) and consequently show novel properties when compared to bulk materials [1]. A nanocomposite is a material composed of two or more phases. Nanoparticles are typically defined as solids measuring less than 100 nm in all the three dimensions; composite nanoparticles are generally coatings in which the combination of different physical and chemical properties may lead to completely novel materials with modified properties [1, 2]. Significant research effort has shown that the surface modification of the particles can be easily accomplished in postsynthesis steps or during the synthesis, thereby providing the nanoparticles with additional functionalities [3]. Magnetic nanoparticles constitute an important class of functional materials and can be categorized, based on single or multiple materials, into simple and core/shell— or composite—nanoparticles, which are gaining increasing interest because of their novel properties and the numerous applications in many diverse fields [3–5]. Composite magnetic iron oxide nanoparticles have applications ranging from ferrofluids to separation science and technology [6–8].

Studies on nanoparticles have focused on the development of simple and effective methods for fabricating nanomaterials with controlled size and morphology and hence tailoring their properties [9]. Liquid-phase synthesis is often used to prepare inorganic nanoparticles [10]; the conventional aqueous synthesis of the $\gamma$-Fe$_2$O$_3$ particles involves three or more steps [11, 12]. We have proposed a method to synthesize $\gamma$-Fe$_2$O$_3$ nanoparticles by thermally treating the FeOOH/Mg(OH)$_2$ precursor in FeCl$_3$ treating solution [13, 14]. Through this method, known as chemically induced transition (CIT) method, FeOOH species were transformed into $\gamma$-Fe$_2$O$_3$ nanocrystallites by dehydration and Mg(OH)$_2$ was dissolved to assist the precipitation of the nanoparticles. Besides, the Fe$^{2+}$ ions in the FeCl$_3$ solution were oxidized to Fe$^{3+}$ to form a FeCl$_3$·6H$_2$O coating on the $\gamma$-Fe$_2$O$_3$ nanocrystallites [14]. During the synthesis of the $\gamma$-Fe$_2$O$_3$ nanoparticles, the surface modification was performed by adding a salt solution composed of metal ions with a valency of two, such as Zn(II)Cl$_2$ [15, 16] and Co(II)(NO$_3$)$_2$ [17], to fabricate Zn(II)Fe$_2$O$_3$ and Co(II)Fe$_2$O$_4$ epitaxial layers, respectively, on the $\gamma$-Fe$_2$O$_3$ crystallites. Additional NaOH can enhance these modifications to produce more ZnFe$_2$O$_4$ or CoFe$_2$O$_4$. In this work, a surface modification
using metal ions with a valency of one is attempted by
adding Cu(I)Cl/NaOH to the FeCl2 treating solution, and
the as-prepared products were characterized using multiple
techniques. Accordingly, the features of the Cu(I)-modified γ-Fe2O3 nanoparticles were investigated.

2. Materials and Methods

2.1. Chemicals. Ferric chloride (FeCl3), magnesium nitrate
(Mg(NO3)2), ferrous chloride (FeCl2), cuprous chloride
(CuCl), and sodium hydroxide (NaOH) were of analytical
grade, and all other chemicals were used as received without
further purification. Distilled water was used throughout the
experiments.

2.2. Preparation. The preparation of Cu(I)-modified γ-Fe2O3
nanoparticles by the so-called chemically induced transi-
tion method can be divided into two steps. First, the
FeOOH/Mg(OH)2 precursor was synthesized by coprecip-
titation, as described in detail elsewhere [13]. Second, 5 g
of the precursor was added to a boiling FeCl3 treating
solution (0.25 M, 400 mL) and kept boiling under reflux for
20 min. Then, both CuCl solution (50 mL), with a varying
concentration, and NaOH solution (2 M, 20 mL) were added
simultaneously to the solution, and the resulting mixture
was boiled continuously for 10 min. After cooling naturally
to room temperature, the products precipitated from the
solution; subsequently, they were washed with acetone and
allowed to dry. The concentrations of the CuCl solutions were
0.025, 0.050, and 1.000 M, corresponding to samples (1), (2),
and (3), respectively. For comparison, unmodified particles
were also prepared by adding the precursor to the FeCl2
solution and boiling for 30 min, producing sample (0).

2.3. Characterization. The bulk chemical compositions of
the as-prepared products were obtained by energy dispersive
X-ray spectroscopy (EDS, Quanta-200). The morphologies
were observed by transmission electron microscopy (TEM,
G20ST). The crystal properties were analyzed by high-
resolution TEM (HRTEM, JEM-2100F) and X-ray diffrac-
tometry (XRD, D/Max-RC). The surface chemical composi-
tions were determined by X-ray photoelectron spectroscopy
(XPS, ESCALAB250Xi). The specific magnetization curves
were measured at room temperature by vibrating sample
magnetometry (VSM, HH-15).

3. Results and Discussion

3.1. Results. The EDS measurements revealed that samples
(1), (2), and (3) contained not only O, Fe, and Cl and no
Mg or Na—as sample (0)—but also Cu. Figure 1 shows the
EDS spectra. The atomic percentages of the Fe, Cl, and Cu
elements (a2 values), listed in Table 1, show that the amount of
Cu increases from sample (1) to sample (3).

Typical TEM images are shown in Figure 2. All the
samples are made of approximately spherical nanoparticles
involving hexagonal particles. The size of the nanoparticles
for both samples (1) and (2) is clearly larger than that of the
unmodified sample (0). Additionally, sample (3) contained
two kinds of particles, larger size and smaller size, as the
arrows marked with “A” and “B,” respectively, indicate.

The HRTEM revealed these particles to be small crystal-
lites. Figure 3 is a typical HRTEM image of sample (2), which
shows that the interlaced lattice fringes of two sets of planes
have the same spacing of approximately 0.29 nm. As shown
by the XRD spectra in Figure 4, the modified samples can be
divided into two types, with samples (1) and (2) belonging
to the same type and sample (3) showing notable differences.
Similar to the unmodified sample (0), samples (1) and (2)
predominantly possess a ferrite-like spinel structure with the
features of γ-Fe2O3 (JCPDS card number 39-1346). Sample
(3) clearly contained γ-Fe2O3 and Cu(II)(OH)Cl (JCPDS
card number 23-1063).

For samples (1), (2), and (3), the XPS results confirmed
the presence of the same chemical elements as determined by
EDS. The quantitative results for the Fe, Cl, and Cu elements
are listed in Table 1. Figure 5 shows the O 1s, Fe 2p, Cl 2p,
and Cu 2p spectra for samples (1) to (3). Similar to the
XRD results, the XPS spectra can also be divided into two
categories and are analyzed as follows.

Both samples (1) and (2) have the same XPS spectral
structure. Their O 1s spectra exhibited two peaks: the P1 peak
at approximately 529.5 eV can be attributed to Fe2O3, and the
P2 peak at approximately 532.2 eV is due to molecular H2O
[19]. The Cl 2p3/2 peak at approximately 198.7 eV corresponds
to Cl 2p3/2 in FeCl3 (199 eV), which is in good agreement with
the probable presence of FeCl3·6H2O, as unmodified sample
[14]. Thus, the Fe 2p3/2 peak at ~711.2 eV resulted from both

![Figure 1: Energy dispersive X-ray spectroscopy (EDS) spectra of samples (0), (1), (2), and (3).](image-url)
Table 1: Atomic percentages of Fe, Cl, and Cu from energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) measurements for samples (1), (2), and (3).

<table>
<thead>
<tr>
<th>Sample</th>
<th>EDS</th>
<th>XPS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>Cl</td>
</tr>
<tr>
<td>(0)</td>
<td>97.28</td>
<td>2.72</td>
</tr>
<tr>
<td>(1)</td>
<td>95.19</td>
<td>4.04</td>
</tr>
<tr>
<td>(2)</td>
<td>94.73</td>
<td>3.93</td>
</tr>
<tr>
<td>(3)</td>
<td>60.99</td>
<td>19.03</td>
</tr>
</tbody>
</table>

Figure 2: Typical transmission electron microscopy (TEM) images of samples (0), (1), (2), and (3).

The Cu 2p_{3/2} peak at ~932.0 eV clearly corresponds to Cu(I)FeO_2 (Cu 2p_{3/2} peaks at ~932.6 eV), rather than Cu(II)FeO_2 (Cu 2p_{3/2} peaks at ~933.7 eV) [20]. The binding energy data of both samples (1) and (2) are listed in Table 2(a). For sample (3), the O 1s and Fe 2p_{3/2} spectra are similar to those of samples (1) and (2). The Cl 2p spectrum exhibited two peaks, and the P1 peak (198.59 eV) could correspond to FeCl_3. Therefore, the Fe-containing compounds in sample (3) also consisted of both γ-Fe_2O_3 and FeCl_3. The spectrum of Cu 2p of sample (3) has a more complicated structure than the spectra of both samples (1) and (2). It is known that the filled 3d shell of Cu^{+} could prevent the ligand-metal charge transfer shake-up transition from occurring, so that one major difference between Cu(I) oxide and Cu(II) oxide is the satellite structure on the high energy side of the copper core lined in Cu(II) oxide [20]. The XRD analysis clearly determined that sample (3) contained Cu(OH)Cl; thus, besides the P0 peak corresponding to the Cu peaks present in samples (1) and (2) and attributed to Cu 2p_{3/2} in CuFeO_2, the P0' peak could originate from Cu 2p_{3/2} in CuFeO_3 and other peaks could result from Cu(OH)Cl. The Cu spectrum of sample (3) shows a pronounced shake-up satellite (SAT) structure, which is similar to the structure of Cu 2p in CuCl_2 [18]. Furthermore, as the Cl 2p spectrum of CuCl_3 has two distinguishable Cl 2p_{1/2} and Cl 2p_{3/2} peaks [18], the spectrum of Cu(OH)Cl could contain a contribution from both Cl 2p_{1/2} and Cl 2p_{3/2}, explaining the two peaks exhibited by the Cl spectrum of sample (3). The binding
Table 2: Binding energies (eV) from X-ray photoelectron spectroscopy (XPS) spectra for samples (1), (2), and (3).

<table>
<thead>
<tr>
<th></th>
<th>O 1s</th>
<th>Fe 2p_{3/2}</th>
<th>Cl 2p_{3/2}</th>
<th>Cu 2p_{1/2}</th>
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<tr>
<td><strong>(a) For samples (1) and (2)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample (1)</td>
<td>529.79 (P1); 532.39 (P2)</td>
<td>711.39</td>
<td>198.59</td>
<td>932.09</td>
</tr>
<tr>
<td>Sample (2)</td>
<td>529.29 (P1); 532.09 (P2)</td>
<td>711.09</td>
<td>198.79</td>
<td>931.99</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>529.6</td>
<td></td>
<td>710.7</td>
<td></td>
</tr>
<tr>
<td>CuFeO₂</td>
<td>?</td>
<td></td>
<td></td>
<td>932.6</td>
</tr>
<tr>
<td>FeCl₃</td>
<td></td>
<td></td>
<td>711.3</td>
<td>199.0</td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
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<td></td>
<td>532.8</td>
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<tr>
<th></th>
<th>O 1s</th>
<th>Fe 2p_{3/2}</th>
<th>Cl 2p_{3/2}</th>
<th>Cu 2p_{1/2}</th>
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<td><strong>(b) For sample (3)</strong></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Sample (3)</td>
<td>530.09 (P1); 532.49 (P2)</td>
<td>711.19</td>
<td>198.59 (P1)</td>
<td>932.59 (P0)</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>529.6</td>
<td></td>
<td>710.7</td>
<td></td>
</tr>
<tr>
<td>CuFeO₂</td>
<td>?</td>
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<td>932.6</td>
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<tr>
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<td>H₂O</td>
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<td>532.8</td>
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<thead>
<tr>
<th></th>
<th>Cl 2p_{3/2}</th>
<th>Cl 2p_{3/2}</th>
<th>Cu 2p_{1/2}</th>
<th>STA</th>
<th>Cu 2p_{1/2}</th>
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<tr>
<td>Sample (3)</td>
<td>198.59 (P1)</td>
<td>200.09 (P2)</td>
<td>934.59 (P1)</td>
<td>943.50 (P2)</td>
<td>954.49 (P3)</td>
<td>962.50 (P4)</td>
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<tr>
<td>Cu(OH)Cl</td>
<td>Δ</td>
<td>Δ</td>
<td>Δ</td>
<td>Δ</td>
<td>Δ</td>
<td>Δ</td>
</tr>
<tr>
<td>CuCl₃</td>
<td>199.1</td>
<td>200.7</td>
<td>935.7</td>
<td>943.2</td>
<td>955.3</td>
<td>964.0</td>
</tr>
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Note: standard data for Fe₂O₃, CuFeO₂, FeCl₃, and H₂O from the NIST X-ray Photoelectron Spectroscopy Database at http://www.nist.gov, in which no O 1s, Fe 2p_{3/2}, and Cu 2p_{1/2} data for CuFeO₂ and no Cu(OH)Cl data were provided. Standard data for CuCl₂ from [18]. The binding energy of both O 1s and Fe 2p_{3/2} for CuFe₂O could not be determined in the present investigation.

3.2. Discussion. According to the experimental results, every sample modified by CuCl/NaOH contained same γ-Fe₂O₃ phase as the unmodified sample (0). Also, the modified samples have Cu-containing compounds. This result indicates that the precursor first transformed into γ-Fe₂O₃ crystals in the FeCl₂ treating solution and, then, following the addition of CuCl/NaOH, the Cu-containing compounds were formed. Under an additional specific content of NaOH equal to 4 × 10⁻² moles (20 mL, 2 M), the composition of the as-prepared products depended on the content of additional CuCl. For lower contents of CuCl—1.25 × 10⁻¹ moles (50 mL, 0.025 M) and 2.50 × 10⁻¹ moles (50 mL, 0.050 M), that is, samples (1) and (2), respectively—the Cu-containing compound is Cu(I)FeO₂, whereas when the content of CuCl is higher—5.00 × 10⁻² moles (50 mL, 1.000 M), that is, sample (3)—the product exhibits two different Cu-containing compounds: Cu(I)FeO₂ and Cu(II)(OH)Cl. These results reveal that, by adding CuCl/Na(OH) to the treating solution, the oxidation of the Cu⁺ ions and the formation of the Cu-containing compounds could depend on the concentration of CuCl under a certain content of NaOH. At low CuCl concentration, all the Cu⁺ ions formed Cu(I)FeO₂ and no Cu(II) compound was created, whereas, at higher CuCl concentration, part of the Cu⁺ ions formed Cu(I)FeO₂, and the remaining Cu⁺ ions were oxidized to Cu²⁺ ions to produce Cu(II)(OH)Cl. The formation of Cu(OH)Cl rather than CuFe₂O₄ could be due to a reason similar to that behind the formation of Cu₂(OH)₃NO₃, where Cu²⁺ does not coprecipitate with Fe³⁺ as the pH of the reaction is too low [22].

Figure 3: High-resolution transmission electron microscopy (HRTEM) image of a particle from sample (2).
For the unmodified sample (0), it is known that FeCl$_3$·6H$_2$O forms on the γ-Fe$_2$O$_3$ crystallites [14]. XPS results revealed the presence of FeCl$_3$·6H$_2$O in the modified samples (1), (2), and (3). For both samples (1) and (2), based on the γ-Fe$_2$O$_3$, Cu(I)FeO$_2$, and FeCl$_3$·6H$_2$O phases, the nanoparticles contained γ-Fe$_2$O$_3$ and FeCl$_3$·6H$_2$O, as confirmed by the lattice fringes of the two sets of planes observed in the HRTEM images, which precisely correspond to the (220) plane of γ-Fe$_2$O$_3$ (spacing of 0.2953 nm) and (002) plane of FeCl$_3$·6H$_2$O (spacing of 0.2927 nm), respectively. The Cu(I)FeO$_2$ could be an intermediate layer formed between the γ-Fe$_2$O$_3$ core and the FeCl$_3$·6H$_2$O surface layer, as the ratio of Cu to Cl obtained from the XPS measurement is lower than that obtained from the EDS measurement. As a consequence, a schematic model of the particle structure of both samples (1) and (2) is shown in Figure 7. This inference can be explained as follows.

Notably, the collection depth of the signal in the EDS analysis largely exceeds the dimensions of the nanoparticles, whereas the signal collection depth in the XPS experiment is ∼3λ, where λ = 1.24 nm and 1.51 nm for Fe 2p and Cu 2p electrons, respectively [23, 24]. After statistical analysis [25], the TEM results revealed that the size of the particles of both samples (1) and (2) followed a lognormal distribution similar to that of sample (0). Their median diameter $d_\text{m}$ and standard deviation ln $\sigma_\text{m}$ are listed in Table 3. Consequently, the average size of the particles $\langle d \rangle$ is calculated by the formula $\langle d \rangle = \exp[\ln d_\text{m} + 0.5\ln^2 \sigma_\text{m}]$ [25], and the results show the size of samples (1) and (2) larger than 11 nm, as also listed in Table 3. Thus, for the nanoparticles in samples (1) and (2), the EDS results reflected the average ratio of the elements in the nanoparticles, whereas the XPS results reflected the ratio of the elements near the nanoparticle surface. Therefore, for the nanoparticles having a multiple layer structure, as shown in Figure 7, as the depth of the XPS detection is smaller than the radius of the particles (as $\langle d \rangle/2$), the ratio of the elements in the internal layer to the elements in the outer layer, from XPS measurement, is lower than the average ratio in the total nanoparticle measured by EDS. For samples (1) and (2), the experimental results (see Table 1) show that the ratio of Cu to Cl from XPS measurements is far lower than that obtained from EDS measurements. Accordingly, for samples (1) and (2), the Cu(I)FeO$_2$ grows between the γ-Fe$_2$O$_3$ core and the FeCl$_3$·6H$_2$O surface layer to form γ-Fe$_2$O$_3$/Cu(I)FeO$_2$/FeCl$_3$·6H$_2$O composite nanoparticles.

Furthermore, sample (3) exhibited strong diffraction peaks of Cu(II)(OH)Cl in the XRD spectra. Therefore, sample (3) is a mixture of γ-Fe$_2$O$_3$/Cu(I)FeO$_2$/FeCl$_3$·6H$_2$O nanoparticles and Cu(II)(OH)Cl nanoparticles, which may correspond to the larger and smaller particles, respectively, observed in the TEM image.

![Figure 4: X-ray diffractometry (XRD) spectra of samples (0), (1), (2), and (3).](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$d_\text{m}$ (nm)</th>
<th>ln $\sigma_\text{m}$</th>
<th>$\langle d \rangle$ (nm)</th>
</tr>
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<tr>
<td>(0)</td>
<td>10.24</td>
<td>0.36</td>
<td>10.93</td>
</tr>
<tr>
<td>(1)</td>
<td>11.64</td>
<td>0.29</td>
<td>12.14</td>
</tr>
<tr>
<td>(2)</td>
<td>11.03</td>
<td>0.28</td>
<td>11.47</td>
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</table>
Figure 5: X-ray photoelectron spectroscopy (XPS) spectra of samples (1), (2), and (3), showing O 1s, Fe 2p$_{3/2}$, Cl 2p, and Cu 2p.

For sample (0), based on γ-Fe$_2$O$_3$/FeCl$_3$·6H$_2$O nanoparticles, and samples (1) and (2), based on γ-Fe$_2$O$_3$/Cu(I)FeO$_2$/FeCl$_3$·6H$_2$O nanoparticles, the molar percentages of the γ-Fe$_2$O$_3$ phase, y$_\gamma$, Cu(I)FeO$_2$ phase, y$_{Cu-Fe}$, and FeCl$_3$·6H$_2$O phase, y$_{Fe-Cl}$, can be estimated by

$$y_\gamma = \frac{(a_{Fe} - a_{Cu} - a_{Cl}/3)/2 + a_{Cu} a_{Cl}/3}{(a_{Fe} - a_{Cu} - a_{Cl}/3)/2 + a_{Cu} a_{Cl}/3} \times 100,$$

$$y_{Cu-Fe} = \frac{a_{Cu}}{(a_{Fe} - a_{Cu} - a_{Cl}/3)/2 + a_{Cu} a_{Cl}/3} \times 100,$$

$$y_{Cl-Fe} = \frac{a_{Cl}/3}{(a_{Fe} - a_{Cu} - a_{Cl}/3)/2 + a_{Cu} a_{Cl}/3} \times 100,$$

where $a_{Fe}$, $a_{Cu}$, and $a_{Cl}$ are the atomic percentages of Fe, Cu, and Cl, respectively, and $a_{Cu}$ is equal to zero for sample (0).

Thus, the molar percentages of every phase in samples (0), (1), and (2) can be obtained from the values of $a_{Fe}$, $a_{Cu}$, and $a_{Cl}$ as measured by EDS (see Table 1). As a consequence, the mass percentages of these phases can be derived from

$$z_i = \frac{y_i A_i}{\sum y_i A_i} \times 100,$$

where $y_i$ is the molar percentage and $A_i$ is the molar mass of the $i$ phase. Accordingly, the mass percentages of each phase in samples (0), (1), and (2) were calculated from the values of $y_i$ and the molar masses of γ-Fe$_2$O$_3$, Cu(I)FeO$_2$, and FeCl$_3$·6H$_2$O. The values of both $y_i$ and $z_i$ are listed in Table 4.
Table 4: Molar percentages \( y_i \) and mass percentages \( z_i \) of the phases for samples (0), (1), and (2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( y_i ) (%)</th>
<th>( z_i ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0)</td>
<td>98.15</td>
<td>1.85</td>
</tr>
<tr>
<td>(1)</td>
<td>96.56</td>
<td>1.58</td>
</tr>
<tr>
<td>(2)</td>
<td>94.56</td>
<td>2.75</td>
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</table>

Table 5: Volume percentages \( \phi_i \), average density (g/cm\(^3\)) \( \langle \rho \rangle \), and saturation magnetization (emu/cm\(^3\)) \( M_s \) for samples (0), (1), and (2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \gamma\text{-Fe}_2\text{O}_3 )</th>
<th>( \text{Cu(I)FeO}_2 )</th>
<th>( \text{FeCl}_3\cdot6\text{H}_2\text{O} )</th>
<th>( \langle \rho \rangle )</th>
<th>( M_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0)</td>
<td>92.19</td>
<td>1.24</td>
<td>7.81</td>
<td>4.66</td>
<td>268.93</td>
</tr>
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<td>(1)</td>
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<td>11.41</td>
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<tr>
<td>(2)</td>
<td>86.72</td>
<td>2.16</td>
<td>11.11</td>
<td>4.57</td>
<td>328.13</td>
</tr>
</tbody>
</table>

For samples (1) and (2), the specific magnetization \( \sigma \) can be described by

\[
\sigma = \left( \frac{x_{\gamma}\sigma_{\gamma} + x_{\text{Cu-Fe}}\sigma_{\text{Cu-Fe}} + x_{\text{FeCl}}\sigma_{\text{FeCl}}}{100} \right),
\]

where \( \sigma_{\gamma} \), \( \sigma_{\text{Cu-Fe}} \), and \( \sigma_{\text{FeCl}} \) are the specific magnetization of the \( \gamma\text{-Fe}_2\text{O}_3 \), Cu(I)FeO\(_2\), and FeCl\(_3\)·6H\(_2\)O phase, respectively, and \( x_i/100 \) is the mass fraction of the \( i \) phase. As \( \gamma\text{-Fe}_2\text{O}_3 \) and Cu(I)FeO\(_2\) are ferrimagnetic and FeCl\(_3\)·6H\(_2\)O is paramagnetic, the specific magnetization of both samples (1) and (2) results mainly from the mass percentages of the ferrimagnetic phase, \( x_f = x_\gamma + x_{\text{Cu-Fe}} \). From the results listed in Table 4, \( x_f = 95.40 \) for sample (1) and \( x_f = 95.52 \) for sample (2). Thus, the specific magnetization of sample (1) is slightly less than that of sample (2). In addition, sample (3) contained Cu(II)(OH)Cl particles, so the specific magnetization of sample (3) is lower than that of both samples (1) and (2).

The magnetization (moment per unit volume) \( M \) is an important parameter used to characterize magnetic materials. For a particle system, the magnetization can be obtained generally from \( M = \sigma \cdot \rho \), where \( \sigma \) is the specific magnetization (moment per unit mass) and \( \rho \) is the density of the material. For composite nanoparticles containing many phases with different densities, the density of the particles should be taken as the average density \( \langle \rho \rangle \), which can be derived from

\[
\langle \rho \rangle = \frac{\sum \phi_i \rho_i}{100},
\]

where \( \phi_i \) is volume percentage and \( \rho_i \) is density of the \( i \) phase. The \( \phi_i \) can be described as

\[
\phi_i = \frac{x_i/\rho_i}{\sum x_i/\rho_i} \times 100.
\]

Accordingly, the volume percentages \( \phi_i \) of the \( \gamma\text{-Fe}_2\text{O}_3 \), Cu(I)FeO\(_2\), and FeCl\(_3\)·6H\(_2\)O phases in samples (0), (1), and (2) can be calculated, and the average density \( \langle \rho \rangle \) for every sample can be derived. Therefore, the saturation magnetization \( M_s = \sigma_s \cdot \langle \rho \rangle \) can be obtained. These results, \( \phi_i, \langle \rho \rangle, \) and \( M_s \) for samples (0), (1), and (2), are listed in Table 5.

For samples (1) and (2), the amount of Cu(I)FeO\(_2\) listed in Table 5 is so small that the thickness of the Cu(I)FeO\(_2\) is generally from \( M = \sigma \cdot \rho \), where \( \sigma \) is the specific magnetization (moment per unit mass) and \( \rho \) is the density of the material. For composite nanoparticles containing many phases with different densities, the density of the particles should be taken as the average density \( \langle \rho \rangle \), which can be derived from

\[
\langle \rho \rangle = \frac{\sum \phi_i \rho_i}{100},
\]

where \( \phi_i \) is volume percentage and \( \rho_i \) is density of the \( i \) phase. The \( \phi_i \) can be described as

\[
\phi_i = \frac{x_i/\rho_i}{\sum x_i/\rho_i} \times 100.
\]

Accordingly, the volume percentages \( \phi_i \) of the \( \gamma\text{-Fe}_2\text{O}_3 \), Cu(I)FeO\(_2\), and FeCl\(_3\)·6H\(_2\)O phases in samples (0), (1), and (2) can be calculated, and the average density \( \langle \rho \rangle \) for every sample can be derived. Therefore, the saturation magnetization \( M_s = \sigma_s \cdot \langle \rho \rangle \) can be obtained. These results, \( \phi_i, \langle \rho \rangle, \) and \( M_s \) for samples (0), (1), and (2), are listed in Table 5.

For samples (1) and (2), the amount of Cu(I)FeO\(_2\) listed in Table 5 is so small that the thickness of the Cu(I)FeO\(_2\) is...
in the $\gamma$-Fe$_2$O$_3$/Cu(I)FeOCl/FeCl$_3$⋅6H$_2$O nanoparticles is no more than one unit cell, and Cu(I) is not in the same state as in bulk Cu(I)FeOCl; this case is similar to that of $\gamma$-Fe$_2$O$_3$ nanoparticles having CoFe$_2$O$_4$ layer less thick than one unit cell [26]. The presence of Cu(I)FeOCl could modify the formation of FeCl$_3$⋅6H$_2$O and make the FeCl$_3$⋅6H$_2$O layer assume a three-dimensional (3D) oriented arrangement [27], so as to have a certain crystalized orientation relatively to the $\gamma$-Fe$_2$O$_3$ crystallites. Therefore, both $\gamma$-Fe$_2$O$_3$ and FeCl$_3$⋅6H$_2$O are identified in the HRTEM stripe images showing the two sets of planes. Also, the saturation magnetization of both the modified samples (1) and (2) is higher than that of the unmodified sample (0), although the ferrite volume percentages of the formers are lower than that of the latter. It is known that the spins close to the surface to be pinned by surfactant molecules, which cause anomalously large magnetic anisotropy, would result in the less apparent saturation magnetization of nanoparticles than that of the bulk [28]. Accordingly, it is judged that the Cu(I)FeOCl thin layer in the $\gamma$-Fe$_2$O$_3$/Cu(I)FeOCl/FeCl$_3$⋅6H$_2$O nanoparticles may modify the magnetically silent “dead layer” [29], which existed at the interface between the $\gamma$-Fe$_2$O$_3$ and FeCl$_3$⋅6H$_2$O phases of the $\gamma$-Fe$_2$O$_3$/FeCl$_3$⋅6H$_2$O nanoparticles of the unmodified sample (0) and did not provide any contribution to the effective magnetization.

4. Conclusions

When the FeOOH/Mg(OH)$_2$ precursor was thermally treated in FeCl$_3$ solution, the Mg(OH)$_2$ dissolved, FeOOH transformed into $\gamma$-Fe$_2$O$_3$ nanocrystallites, and Fe$^{3+}$ in the FeCl$_3$ treating solution was simultaneously oxidized to Fe$^{2+}$. The nanocrystallites absorbed Fe$^{3+}$ and Cl$^-$ to form $\gamma$-Fe$_2$O$_3$/FeCl$_3$⋅6H$_2$O nanoparticles, in which the $\gamma$-Fe$_2$O$_3$ core was coated with the FeCl$_3$⋅6H$_2$O layer. By adding Cu(I)Cl/NaOH to the FeCl$_3$ solution during the synthesis, the compositions of the as-prepared products can be modified. For a certain content of NaOH, 0.04 moles, using a low content of Cu(I)Cl (1.25 $\times$ 10$^{-3}$ moles or 2.50 $\times$ 10$^{-3}$ moles), single Cu(I) modified composite nanoparticles can be prepared. The structure of such composite nanoparticles can be described as $\gamma$-Fe$_2$O$_3$/Cu(I)FeOCl/FeCl$_3$⋅6H$_2$O and consisted of three parts as follows: $\gamma$-Fe$_2$O$_3$ core, a Cu(I)FeOCl intermediate layer, and an outermost FeCl$_3$⋅6H$_2$O layer. For a higher content of CuCl, 5 $\times$ 10$^{-2}$ moles, Cu$^+$ was partially oxidized to Cu$^{2+}$, and the as-prepared product was a mixture of $\gamma$-Fe$_2$O$_3$/Cu(I)FeOCl/FeCl$_3$⋅6H$_2$O nanoparticles and Cu(I)OHCl nanoparticles. The Cl and Cu spectra of Cu(OH)Cl measured by XPS have the same structure as those of CuCl$_2$, and the binding energies of Cl 2p$_{3/2}$, Cl 2p$_{1/2}$, Cu 2p$_{3/2}$, and Cu 2p$_{1/2}$ for the Cu(OH)Cl compound are approximately 198.6, 200.1, 934.6, and 954.5 eV, respectively.

For the $\gamma$-Fe$_2$O$_3$/Cu(I)FeOCl/FeCl$_3$⋅6H$_2$O composite nanoparticles, the average thickness of the Cu(I)FeOCl layer is not enough to form one unit cell, and Cu(I) is not in the same state in bulk Cu(I)FeOCl. The experimental results show that the Cu(I)FeOCl intermediate layer could modify the formation of the FeCl$_3$⋅6H$_2$O layer to stimulate a 3D oriented attachment of the layer relatively to the $\gamma$-Fe$_2$O$_3$ crystallites; it may also modify the magnetic “dead layer” between the $\gamma$-Fe$_2$O$_3$ core and FeCl$_3$⋅6H$_2$O surface layer to enhance the effective magnetization. Besides having high magnetization, such nanoparticles have an inert FeCl$_3$⋅6H$_2$O surface; therefore they could possess a relatively good chemical stability and can be used directly to synthesize ionic ferrofluids without ferric nitric treatment as the Massart method [30].

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References


