Note

Synthesis of alkyl sulfonate/alcohol-protected $\gamma$-Fe$_2$O$_3$ nanocrystals with narrow size distributions

Junge Lu, a Jinda Fan, a Ruisong Xu, a Sujoy Roy, b Naushad Ali, b and Yong Gao a, *

a Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901-4409, USA
b Department of Physics, Southern Illinois University, Carbondale, IL 62901-4401, USA

Received 1 July 2002; accepted 20 November 2002

Abstract

Highly crystalline $\gamma$-Fe$_2$O$_3$ nanoparticles with narrow size distributions that are coated with 1-undecanesulfonic acid were synthesized via two distinct approaches using oxidation and site-exchange reactions. However, similar nanocrystals protected with 1-octanol could only be achieved via the site-exchange method, while the oxidation approach led to Fe$_2$O$_3$ nanoparticles of poor crystallinity and size uniformity. Our magnetization measurements confirmed the superparamagnetic nature of our Fe$_2$O$_3$ nanoparticle products and the effects of the coating materials on magnetization properties.

© 2003 Elsevier Science (USA). All rights reserved.

Keywords: Iron oxide; Nanoparticles; Oxidation; Site exchange; Coating

1. Introduction

In the nanoscale regiment, materials demonstrate unique size- and shape-dependent physical and chemical properties that are of technological importance and scientific research interest [1]. Below a critical size, magnetic Fe$_2$O$_3$ nanoparticles become single-domain and exhibit unique phenomena such as superparamagnetism, quantum tunneling of the magnetization, and unusually large coercivities [2], providing application potentials in information storage [3], refrigeration systems [4], bioprocessing [5], magnetic resonance imaging [6,7], controlled drug delivery [8] and ferrofluids [9]. However, very different physical properties, especially magnetic properties have been observed with materials having similar grain sizes but produced by distinct methods and therefore, possessing varied microstructures, such as different coatings, size uniformity, and crystallinity [10]. As a consequence, designing synthetic routes to achieve rigorous control of the microstructures of Fe$_2$O$_3$ nanoparticles, especially the coating, crystallinity, and size uniformity, is of particular importance for the applications of these magnetic nanomaterials.

Due to anisotropic dipolar attraction, Fe$_2$O$_3$ nanoparticles tend to aggregate into large clusters, causing the loss of the specific properties associated with single-domain nanostructures, and thus organic surfactant ligands are usually introduced to coat the Fe$_2$O$_3$ cores to prevent core aggregation. However, the introduction of the coatings could change the properties of the surfaces as well as those of the intrinsic cores, resulting in the alteration of the overall magnetization properties of the Fe$_2$O$_3$ nanoclusters [11]. For example, the functionality and chain length of the organic surfactants were found to decide the magnetization moment values of amorphous Fe$_2$O$_3$ and Fe nanoclusters [12,13]. On the other hand, the size uniformity and crystallinity of the Fe$_2$O$_3$ nanoparticles can influence the properties of Fe$_2$O$_3$ nanoparticles. Iron oxide has an amorphous form and four major polymorphs (alpha, beta, gamma, and epsilon). These Fe$_2$O$_3$ nanoparticles of different crystalline forms usually show great variations in their physical properties despite their similar sizes and shapes.

Although Fe$_2$O$_3$ nanoparticles of major forms have been investigated extensively [14–27], the syntheses of highly crystalline $\gamma$-Fe$_2$O$_3$ nanocrystallites with narrow size distributions were reported only in recent years [28–30]. Thermal transformations of iron-bearing materials in an oxidizing atmosphere and hydrolysis of iron salts represent two general approaches for the fabrication of Fe$_2$O$_3$ nanoparticles,
and the long-chain alkyl carboxylates are usually the surfactant of choice for protecting $\gamma$-Fe$_2$O$_3$ nanocrystals. As far as we know, the synthesis of highly crystalline and monodisperse $\gamma$-Fe$_2$O$_3$ nanoparticles protected with alkyl sulfonate/alcohol has not been reported. In the present paper, we would like to report our work on using the site-exchange and oxidation reactions for the synthesis of highly crystalline $\gamma$-Fe$_2$O$_3$ nanocrystals with narrow size distributions that are coated with 1-undecanesulfonic acid and 1-octanol, respectively. The products from those two methods were examined by the transmission electron microscopy (TEM), X-ray powder diffraction (XRD), SQUID magnetometry, $^1$H NMR, thin layer chromatography (TLC), and mass spectrometry (MS).

2. Experimental

2.1. Materials

1-Octanol, 1-undecanesulfonic acid, oleic acid, iron pentacarbonyl, and sodium cyanide were purchased from Acros Organics (Somerville, NJ) and used as received without further purification. Water was obtained from a Milli-Q reagent water system purchased from Millipore Corporation (Milford, MA).

2.2. Fabrication of $\gamma$-Fe$_2$O$_3$ nanocrystals (sulf-syn and alco-syn) and $\gamma$-Fe$_2$O$_3$-oleic acid via oxidation of iron pentacarbonyl

The procedure of Hyeon et al. [28] was modified. The mixture of iron pentacarbonyl (0.76 mmol) and organic ligands (2.28 mmol) in 5 ml of octyl ether was heated to reflux under Ar. The solution was gradually cooled to room temperature and trimethylamine oxide (2.28 mmol) in 5 ml of octyl ether was added to the above solution and the mixture was reheated to 130 $^\circ$C and then to reflux under Ar for about 1 h. The solution was cooled to room temperature again and ethanol was added. After centrifugation (15,000g, 30 min), precipitates of the final products were collected.

2.3. Synthesis of sulf-exch and alco-exch through site-exchange reactions

To a stirred solution of $\gamma$-Fe$_2$O$_3$ nanocrystals protected with oleic acid (10 µmol) that were synthesized in chloroform (15 ml) were added the exchanging organic ligands (1 mmol) at room temperature. After 12 h, acetonitrile (20 ml) was added to the above solution and the precipitates were collected via centrifugation (15,000g, 30 min). For the synthesis of alco-exch, the site-exchange reaction with 1-octanol was carried out in the aforementioned solution under reflux and the amount of alcohol was increased to 5 mmol.

2.4. NaCN etching of sulf-exch and alco-exch for $^1$H NMR analysis

Fe$_2$O$_3$ nanoparticles sulf-exch/alco-exch (20 mg) were dissolved in CH$_2$Cl$_2$ (40 ml) and treated with NaCN (2.1 mmol) in water (40 ml). After 12 h, the organic layer was separated, sequentially washed with 0.5 M HCl and NaCl aqueous solutions, and dried over anhydrous Na$_2$SO$_4$. The organic solvents were then removed in vacuo and the residues were analyzed by $^1$H NMR, TLC, and MS.

2.5. Instrumentation

$^1$H NMR data were obtained on a Varian VXR-300 system with an Oxford wide-bore magnet and the chemical shifts were reported in parts per million (ppm) downfield relative to tetramethylsilane using the residual proton resonance of solvents as the references: CDCl$_3$ 8 7.25; CD$_2$Cl$_2$ 8 5.32. TEM measurements were accomplished with a Hitachi H7100FA operating at an accelerating voltage of 75 or 100 kV. Fe$_2$O$_3$ nanoparticle specimens were deposited onto Formvar- and silicon-coated 200 mesh copper grids (Structure Probe, Inc.) and the edge of the grid touched to a filter paper to wick away most of the solvent. Images were either recorded on conventional photographic film or captured using a Gatan 789 digital camera. Magnification was calibrated using a MAG$^*$CAL high-resolution magnification standard accurate to 1 x 10$^{10}$ X. Magnetic measurements were performed on a SQUID magnetometer (Quantum Design MPMS-1). Magnetization measurements were made for powdered samples of nanoparticles in a gelatin capsule. The temperature was varied between 5 and 298 K according to zero-field cooling (ZFC) and field cooling (FC) procedures at 100 Oe for the magnetization versus temperature measurements, and the hysteretic loop was obtained in a magnetic field varying from +1 to −1 T. X-ray powder diffraction (XRD) patterns were obtained with graphite-monochromatized CuK$\alpha$ radiation in a Rigaku Miniflex diffractometer operated at 45 kV and 20 mA and the 2$\theta$ values were measured at 1$^\circ$/min at room temperature.

3. Results and discussion

Two different approaches were utilized for our synthesis of $\gamma$-Fe$_2$O$_3$ nanoparticles. In the first method [28], Fe(0) was treated with a mild oxidation reagent under Ar protection in the presence of large concentrations of the organic surfactant 1-octanol or 1-undecanesulfonic acid (Scheme 1a). The second approach employed a site-exchange reaction to replace the oleic acid molecules from the pre-formed $\gamma$-Fe$_2$O$_3$–oleic acid nanoclusters with alternative organic functionalities (Scheme 1b). The $\gamma$-Fe$_2$O$_3$–oleic acid nanoparticles are highly crystalline with a very narrow size distribution of 11±2 nm, and were synthesized by following the literature
Scheme 1. Schematic representation of the syntheses of Fe₂O₃ nanoparticles via (a) direct oxidation of Fe(0) in the presence of organic ligands R–X, and (b) place-exchanging R–X with Fe₂O₃–oleic acid pre-synthesized from the oxidation approach.

Protocols (Scheme 1a) [28] that are similar to the oxidation conditions used for the synthesis of sulf-syn and sulf-exch.

High-resolution TEM analyses reveal that the product via the direct oxidation method (Fig. 1a) has a very narrow size distribution of 11 ± 2 nm. However, under similar oxidation conditions, the product alco-syn (Fig. 1c) protected with 1-octanol is of poor size uniformity. Sulf-exch and alco-exch were synthesized from Fe₂O₃–oleic acid via the site-exchange reactions, and their TEM images (Figs. 1b and 1d) show that these two products have high crystallinity and narrow size distributions. The average core sizes of sulf-exch and alco-exch are about 11 nm, closely resembling that of the starting material γ-Fe₂O₃–oleic acid nanoparticles (not shown), suggesting that the site-exchange reaction does not alter the core dimension and size uniformity of the starting materials [31].

The X-ray powder diffraction patterns in Fig. 2 confirm the highly crystalline nature of sulf-syn, sulf-exch, and alco-exch, whose peaks match well with standard JCPDS γ-Fe₂O₃ reflections; however, alco-syn was found to have
The chemical identities of the organic surfactants in the four products were assessed by TLC, $^1$H NMR, and MS after NaN$_3$ etching of the Fe$_2$O$_3$ cores. The etching of Fe$_2$O$_3$ was carried out by treating Fe$_2$O$_3$ nanoparticles in methylene chloride with NaN$_3$ aqueous solutions. The organic ligands isolated from CH$_2$Cl$_2$ solutions were compared with authentic samples of 1-undecanesulfonic acid and 1-octanol using thin layer chromatography, and were further examined by $^1$H NMR and MS spectroscopy. 1-Undecanesulfonic acid was the only ligand extracted from sulf-syn, whereas a mixture of 1-octanol and its oxidized derivative octanoic acid were isolated from the product alco-syn. The unexpected isolation of octanoic acid from alco-syn was probably due to the presence of excessive oxidant trimethylamine oxide that could oxidize Fe(0) as well as the alcohol functionality, leading to the poor size uniformity and crystallinity of alco-syn.

Sulf-exch and alco-exch are the products from the site-exchange method, and the sole isolate 1-undecanesulfonic acid from sulf-exch reveals that oleic acid was completely replaced by alkyl sulfonate (100-fold in excess) in the site-exchange reaction. However, under similar conditions, a mixture of oleic acid and 1-octanol were isolated from alco-exch, suggesting that 1-octanol is a weaker binder to the Fe$_2$O$_3$ cores than 1-undecanesulfonic acid. The complete replacement of oleic acid from $\gamma$-Fe$_2$O$_3$–oleic acid nanoparticles could be achieved in the presence of a larger concentration of 1-octanol (500-fold in excess) at an elevated temperature (in refluxing chloroform).

Preliminary magnetization measurements of the magnetic moment versus applied magnetic field were performed on sulf-syn, sulf-exch, alco-syn, and alco-exch with a superconducting quantum interference device magnetometer (SQUID), and none of the four products showed hysteresis at room temperature. Figure 3 represents the magnetization versus applied field curves of sulf-exch and alco-exch at room temperature, revealing the lack of hysteresis of these two products. However, the magnetization values in

Fig. 2. XRD patterns of sulf-syn, sulf-exch, alco-syn, and alco-exch.

Table 1
The d values of samples sulf-syn, sulf-exch and alco-exch via XRD analysis and those of $\gamma$-Fe$_2$O$_3$ and Fe$_3$O$_4$ from the JCPDS database

<table>
<thead>
<tr>
<th>Sulf-syn</th>
<th>Sulf-exch</th>
<th>Alco-exch</th>
<th>Fe$_2$O$_3$ a</th>
<th>Fe$_3$O$_4$ b</th>
<th>hkI</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.9591</td>
<td>2.9577</td>
<td>2.9514</td>
<td>2.953</td>
<td>2.967</td>
<td>220</td>
</tr>
<tr>
<td>2.5267</td>
<td>2.5202</td>
<td>2.5173</td>
<td>2.5177</td>
<td>2.532</td>
<td>311</td>
</tr>
<tr>
<td>2.0914</td>
<td>2.0913</td>
<td>2.0871</td>
<td>2.0886</td>
<td>2.0993</td>
<td>400</td>
</tr>
<tr>
<td>2.0255</td>
<td>2.0248</td>
<td>2.0229</td>
<td>2.0255 n/a</td>
<td>410</td>
<td></td>
</tr>
<tr>
<td>1.7127</td>
<td>1.7125</td>
<td>1.7094</td>
<td>1.7045</td>
<td>1.7146</td>
<td>422</td>
</tr>
<tr>
<td>1.6129</td>
<td>1.6104</td>
<td>1.6077</td>
<td>1.6073</td>
<td>1.6158</td>
<td>511</td>
</tr>
<tr>
<td>1.4329</td>
<td>1.4487</td>
<td>1.4316</td>
<td>1.4758</td>
<td>1.4845</td>
<td>440</td>
</tr>
</tbody>
</table>

$\alpha$-Fe$_2$O$_3$ and Fe have distinctively different XRD patterns.

a JCPDS card number: 39-1346.
b JCPDS card number: 19-629.

poor crystallinity by its XRD pattern in Fig. 2. The d-spacing values of nanocrystallites sulf-syn, sulf-exch, and alco-exch were compared with those of standard $\gamma$-Fe$_2$O$_3$ (JCPDS card 39-1346) and Fe$_3$O$_4$ (JCPDS card 19-629) (Table 1), permitting the nature of the $\gamma$-Fe$_2$O$_3$ cores of these nanomaterials to be confirmed.

Fig. 3. Magnetization versus applied magnetic field for sulf-exch and alco-exch at room temperature (298 K). The external magnetic field is from +10,000 to −10,000 Oe. Inset: magnetization versus applied magnetic field for sulf-exch at 160 K.
that superparamagnetic Fe$_2$O$_3$ nanoparticles can become ferromagnetic if the measurements are carried out at a temperature below their blocking temperatures.

4. Conclusions

In this paper, highly crystalline $\gamma$-Fe$_2$O$_3$ nanocrystals with narrow size distributions that are coated with 1-undecanesulfonic acid and 1-octanol were synthesized via oxidation and/or site-exchange reactions. The site-exchange route can maintain the core dimension and size uniformity of the starting materials and, therefore, it is reasonable to assume that the combination of these two approaches could be utilized for the synthesis of highly crystalline and nanometer-sized $\gamma$-Fe$_2$O$_3$ particles coated with functionalities that are not easily accessible via the oxidation approach. In other word, sensitive coating chromophores could be introduced via site exchange onto the surfaces of highly crystalline and monodisperse $\gamma$-Fe$_2$O$_3$ nanoparticles that are pre-formed by the oxidation reaction. The introduction of coating materials onto the Fe$_2$O$_3$ nanoparticles could not only mutate the magnetic properties of these nanomaterials, but also provide a platform for the functionalization of the nanocluster surfaces, offering potential applications in areas such as magnetic drug delivery systems. All of these emphasize the importance of the research work in designing synthetic routes to control the microstructures of Fe$_2$O$_3$ nanoparticles.

Acknowledgments

This work was supported by SIU Materials Technology Center and the Office of Research Development and Administration. We thank Dr. Max Yen for helpful discussions and SIU microimaging analysis for TEM measurements of our samples. XRD and magnetization analyses were carried out in the Center for Microanalysis of Materials, University of Illinois, which is partially supported by the U.S. Department of Energy under Grant DEFG02-96-ER45439.

References