Synthesis of Magnetite Nanorods from the Reduction of Iron Oxy-Hydroxide with Hydrazine

Menuka Adhikari, Elena Echeverria, Gabrielle Risica, David N. McIlroy, Michael Nippe, and Yolanda Vasquez*

ABSTRACT: Nanowires and nanorods of magnetite (Fe₃O₄) are of interest due to their varied biological applications but most importantly for their use as magnetic resonance imaging contrast agents. One-dimensional (1D) structures of magnetite, however, are more challenging to synthesize because the surface energy favors the formation of isotropic structures. Synthetic protocols can be dichotomous, producing either the 1D structure or the magnetite phase but not both. Here, superparamagnetic Fe₃O₄ nanorods were prepared in solution by the reduction of iron oxy-hydroxide (β-FeOOH) nanoneedles with hydrazine (N₂H₄). The amount of hydrazine and the reaction time affected the phase and morphology of the resulting iron oxide nanoparticles. One-dimensional nanostructures of Fe₃O₄ could be produced consistently from various aspect ratios of β-FeOOH nanoneedles, although the length of the template was not retained. Fe₃O₄ nanorods were characterized by transmission electron microscopy, X-ray powder diffraction, X-ray photoelectron spectroscopy, and SQUID magnetometry.

1. INTRODUCTION

Iron oxide nanoparticles have been widely explored for numerous applications from magnetic storage devices¹−³ to gas sensors,⁴,⁵ in water treatment,⁶ and broadly in biomedical applications.⁷−¹⁴ Among the various shapes of magnetite (Fe₃O₄) nanoparticles, anisotropic nanostructures such as wires and rods have drawn remarkable attention due to the considerable influence of the one-dimensional (1D) structure on their physicochemical properties.¹⁵−¹⁸ For instance, the elongated Fe₃O₄ nanostructures (nanowires and nanorods) have shown to be efficient as magnetic resonance imaging contrast agents,⁷,¹⁹,²⁰ exhibit enhanced heating efficiency,²⁰,²¹ have prolonged retention time at the tumor site,²² better performance in Li-ion batteries as an anode by accommodatign the volume expansion of active materials,²²,²³ and increased specific attachment to their target during drug delivery as compared to spherical nanoparticles.²⁴ However, 1D Fe₃O₄ nanoparticles are more challenging to synthesize because the surface energy favors the formation of isotropic spherical structures.²⁵ Several protocols have been reported for the synthesis of spherical Fe₃O₄ nanoparticles,²⁵−³¹ while fewer reports of nanorods are available in the literature due to the difficulty in growing a 1D structure from a material with a highly symmetric cubic crystal structure.³²−³⁴ Hydrothermal/solvothermal techniques³⁵,³⁶,³⁹,⁴⁰−⁴² and the high-temperature heating of an organometallic precursor [Fe(CO)₅, Fe(acac)₅, etc.] in solution³⁸−⁴⁰ are the most explored methods for the preparation of iron oxide nanorods. However, the use of high-pressure reaction vessels (autoclaves) at high temperatures are associated not only with safety hazards but also the inability to monitor the ongoing reaction. Similarly, high-temperature-based methods cause the aggregation and sintering of nanoparticles which results in the loss of the desired characteristic properties of the nanostructures.⁴³ One of the more successful solution-based strategies used to synthesize 1D structures of Fe₃O₄ is the reduction of the iron oxy-hydroxide (FeOOH) polymorph.¹⁷,¹⁸,³⁴,⁴³ However, a challenging aspect of this method is controlling the rod-shaped morphology of the final product due to aggregation and coalescence of the template.³⁷,⁴⁴ Some reports have shown that when efforts were made to maintain the rod-shaped morphology, a mixture of iron oxides such as α-FeOOH, α-Fe₂O₃ were formed along with Fe₃O₄.¹⁷,¹⁸ Therefore, it remains a challenge to synthesize 1D Fe₃O₄ nanostructures with considerable control over shape, size, and phase purity using reduction reactions in solution. Toward this end, we decided to add to the current literature on using hydrazine as a reducing agent to generate Fe₃O₄ nanorods utilizing different aspect ratios (ARs) of β-FeOOH nanoneedles.³⁴,⁴⁵ We explored alternative methods employing oleylamine as a reducing agent and found those not to be reproducible.⁷,³⁹,⁴³

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Herein, we report both phase and shape-controlled chemical transformation of β-FeOOH nanoneedles to superparamagnetic Fe3O4 nanorods. We found that larger amounts of hydrazine led to the loss of the elongated morphology of the final product accompanied by the formation of a mixture of Fe3O4 and γ-Fe2O3. At lower concentrations of hydrazine, the 1D morphology of Fe3O4 was retained in the reduction step. As mentioned above, the Fe3O4 nanostructures were evaluated by superconducting quantum interference device (SQUID) magnetometry and were found to be superparamagnetic and exhibited the Verwey transition.

2. RESULTS AND DISCUSSION

2.1. Synthesis of β-FeOOH Nanoneedles. β-FeOOH nanoneedles were synthesized using poly(ethyleneimine) (PEI) (MW = 750,000) as a surface capping agent and characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS).1,7,46 PEI is a positively charged ligand that remains protonated in solution and limits unidirectional growth because it adsorbs onto the (200) planes of β-FeOOH nanoneedles.1,7,47,48 Consistent with previous reports, higher concentrations of PEI yielded shorter nanoneedles.7 Nanoneedles of ARs 8.0, 7.0, 6.0, 5.7, 5.5, and 4.0 could be synthesized by varying the final concentration of PEI (Figure 1a–f), as described in the Experimental Section. The longest nanoneedles (l = 200 μm, w = 30 μm) were obtained in the absence of the capping agent (Figure S2). Figure 1c (inset) shows a high magnification TEM image of lattice fringes with d-spacing = 0.26 nm, which corresponds to the (200) planes of β-FeOOH nanoneedles.1,7,47,48

2.2. Synthesis of Fe3O4 Nanorods. It has been reported in the literature that oleylamine can reduce β-FeOOH to magnetite;1,7,17,47 however, we were unable to reproduce these results and chose to use hydrazine as a reducing agent instead.32,45,52 The reduction reactions were studied with β-FeOOH nanoneedles of AR 8.0. The amount of hydrazine in the reaction was varied (6.3, 7.6, 8.9, 10.1, 10.8, and 11.4 mmol)
and complete phase transformation from $\beta$-FeOOH to Fe$_3$O$_4$ was observed at a hydrazine concentration of 10.8 mmol. XRD data shown in Figure 2b are consistent with the cubic phase of iron oxide, Fe$_3$O$_4$ (Fd$\bar{3}$m), JCPD file no. 00-019-0629. Presence of diffraction peaks at 20$\theta$ angles of 30, 35.4, 43, 53.3, 56.9, and 62.5$\theta$ from the (220), (311), (400), (422), (511), and (440) planes confirm the conversion to Fe$_3$O$_4$. The diffraction peak at 44.4$\theta$ is consistent with Fe$_2$H$_4$O$_4$ (JCPD 00-008-0093), which could be due to a small amount of iron oxide hydrate in the crystal lattice of Fe$_3$O$_4$ during the phase transformation. Conversion to the magnetite phase was dependent on the concentration of OH$^-$ ions.45 The standard reduction potential ($E^\circ$) of Fe$_3$H$_6^+$/$N_2H_5^+$ vs standard hydrogen electrode (SHE) is lower than that of Fe$^{2+}$/Fe$^{3+}$ (+0.77 V vs SHE), which results in the reduction of Fe$^{3+}$ ions in the crystal lattice of Fe$_3$O$_4$ during the phase transformation.

Hydrazine hydrolyzes to form N$_2$H$_5^+$ (hydrazinium ion) and OH$^-$ ions.45 The reduction mechanism of hydrazine can be affected by the iron oxide surface and the pH of the solution ($E^\circ$ = +1.15 V, basic medium).55,56 This may cause the reoxidation of adsorbed Fe$^{2+}$ ions and lead to the formation of $\gamma$-Fe$_3$O$_4$ even at higher concentrations of hydrazine.

Figure 4. XRD patterns of the different phases of iron oxide nanorods generated as a function of the amount of hydrazine used in the reduction of $\beta$-FeOOH. $\beta$-FeOOH, space group I4/m, JCPD card no. 34-1266; Fe$_3$O$_4$, space group Fd$\bar{3}$m, JCPD card no. 00-019-0629; and $\gamma$-Fe$_3$O$_4$, space group P4$_1$32, JCPD card no. 00-039-1346.

The transformation from $\beta$-FeOOH to Fe$_3$O$_4$ was studied as a function of time (1, 2, 4, 6, 8, and 12 h). The temperature (90 °C) and the amounts of hydrazine (10.8 mmol) and $\beta$-FeOOH (0.02 g) remained constant. TEM images show that the resulting particles maintain a 1D morphology after the evolution of N$_2$ gas from the surface and/or by the quick outward diffusion of iron ions through the $\beta$-FeOOH surface as observed in the nanoscale Kirkendall effect57,58 and galvanic replacement reactions (Figures S4 and S5).59,60

Figure 5. TEM images of nanoparticles resulting from the reduction of $\beta$-FeOOH nanoneedles with varying amounts of anhydrous hydrazine: (a) 6.3, (b) 7.6, (c) 8.9, (d) 10.1, (e) 10.8, and (f) 11.4 mmol.

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larger ARs (8.0, 7.0, and 6.0) of β-FeOOH nanoneedles were reduced. Figure S7 represents the effect of the initial AR on the size distribution of the resulting Fe₃O₄ nanorods. The length of nanorods increased by 25–30% as compared to their respective template materials (β-FeOOH nanoneedles) in all samples. The number of long wires (≥180 nm) increased and triangular shaped nanoparticles started to appear when small ARs (5.7, 5.5, and 4.0) of β-FeOOH nanoneedles were used as a precursor for the reduction. Figure S8 shows the pie chart for the shape distribution of the resulting nanoparticles. Decreasing the AR of the template led to samples with a greater composition of triangles and wires. TEM images of triangular particles (Figure S9) reveal that the d-spacing of 0.30 nm matches with the (220) plane of the cubic phase of Fe₃O₄. The adsorbed –NH₂ group on the lateral site of nanorods can hinder the growth in the [100] direction and hence lead to an increase in the growth of other facets to form triangular-shaped nanoparticles. XRD data (Figure S10) of nanoparticles resulting from the reduction of different ARs of β-FeOOH (from AR 8.0 to 4.0) matched with the cubic phase of Fe₃O₄ [JCPD card no. 00-019-0629]. The diffraction peaks arising from (220), (311), (400), (422), (511), and (440) planes at 2θ angles of 30, 35.4, 43, 53.3, 56.9, and 62.5° were observed in all samples. This indicates the phase transformation is consistent even though the AR was not retained. As mentioned before, the diffraction peak at 44.4° (corresponding to iron oxide hydrate) appeared for the samples obtained on the reduction of β-FeOOH samples of ARs ranging from 5.7 to 8.0. To further confirm the formation of the Fe₃O₄ phase, powder samples (obtained by reduction of β-FeOOH nanoneedles of AR 8.0) were investigated by XPS. Figure 9 represents the core level Fe 2p spectrum showing peaks at 711.3 eV (Fe 2p₃/2) and 724.2 eV (Fe 2p₁/2) without the satellite peak around 720 eV. The peak positions are consistent with the reported Fe 2p photoelectron peaks of Fe₃O₄ in the literature. No other peaks or shoulders were observed from other phases of iron oxides.

### 2.4. Magnetic Properties.

Figure 10a,b show temperature-dependent zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves for β-FeOOH nanoneedles and Fe₃O₄ nanorods (made using an AR 8.0 template) in an applied field of 100 Oe. The β-FeOOH nanoneedles are antiferromagnetic as demonstrated by the magnetic susceptibility (χ) versus temperature (T) curve typical of antiferromagnets shown in Figure 10a. A maximum blocking temperature of 14 K was observed in the ZFC curve. A slight inflection point was observed at about 45 K on the FC curve (inset, Figure 10a) which indicates the antiferromagnetic ordering temperature, Tₘ. The value of Tₘ for β-FeOOH nanorods is lower than the bulk (270–299 K) and is usually attributed to the finite size and surface properties of materials. At the nanoscale, the size, shape, and synthetic procedure of nanomaterials can affect the ordering temperature. The ZFC magnetization versus temperature curve (Figure 10b) of Fe₃O₄ shows a change in magnetization at 120 K, which is called a Verwey transition. This is due to the structural change from cubic to monoclinic phase that occurs around 120 K and which is characteristic of stoichiometrically pure magnetite nanorods. Small defects in stoichiometry and poor crystallinity would lead to the disappearance of Verwey transition. Figure 10c represents the hysteresis curve of β-FeOOH nanorods which shows the linear dependence of magnetization (M) with the applied field without reaching

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**Figure 6.** TEM images of Fe₃O₄ nanorods from the reaction of 0.02 g of β-FeOOH with 10.8 mmol of hydrazine as a function of time: (a) 1, (b) 2, (c) 4, (d) 6, (e) 8, and (f) 12 h.

**Figure 7.** XRD patterns of the reaction progress of β-FeOOH with 10.8 mmol of hydrazine as a function of time. [Fe₃O₄ space group Fd3m, JCPD card no. 00-019-0629].

Larger particles and long nanowires observed at reaction times ≥8 h likely result from the dissolution of smaller particles and growth of larger particles as explained by the Ostwald ripening crystal growth mechanism.

### 2.3. Effect of AR.

The reduction reaction was attempted with several ARs of β-FeOOH nanoneedles to determine if the sizes of the particles would affect the phase of iron oxide formed. Also, we were interested in determining whether the AR of the template could be maintained upon reduction to generate reproducible ARs of Fe₃O₄. Six ARs of β-FeOOH ranging from 8.0 to 4.0 were studied using the optimum reaction parameters determined above: 10.8 mmol of hydrazine, 0.02 g of FeOOH, and a 6 h reaction time. Figure 8 shows TEM images of the 1D nanoparticles generated when...
saturation,\textsuperscript{66,67} which is expected in typical antiferromagnetic materials.\textsuperscript{43}

Figure 10d shows hysteresis curves for Fe\textsubscript{3}O\textsubscript{4} nanorods at different temperatures (10, 150, and 300 K). The magnetization value reached the saturation point without noticeable coercivity and remanence at 300 K which is characteristic of the superparamagnetic nature of Fe\textsubscript{3}O\textsubscript{4} nanorods.\textsuperscript{7,4} A saturation magnetization ($M_s$) value of \(~21\) emu/g was estimated for this sample, which is low when compared to the bulk material \(~92\) emu/g.\textsuperscript{11} A lower value of $M_s$ has been reported for anisotropic Fe\textsubscript{3}O\textsubscript{4} nanostructures even when a single Fe\textsubscript{3}O\textsubscript{4} phase was the final product.\textsuperscript{75}−\textsuperscript{77} This $M_s$ value is in agreement with the commercially available contrast agent ferumoxytol (carboxymethyl-dextran-coated iron oxide) with an $M_s$ value of \(~23.6\) emu/g\textsuperscript{78} and oleylamine-stabilized Fe\textsubscript{3}O\textsubscript{4} nanorods with an $M_s$ value of \(~22.5\) emu/g.\textsuperscript{43} The smaller $M_s$ value of magnetite nanorods has been reported by others too.\textsuperscript{43,65,75−77} This may be due to the presence of shape anisotropy,\textsuperscript{76} the organic dead layer (stabilizer) on the surface of nanorods,\textsuperscript{69} or randomly oriented surface spins.\textsuperscript{79} [We did not measure the exact amount of organic material on the surface]. The randomly oriented Fe\textsubscript{3}O\textsubscript{4} nanorods and wires may have different easy magnetic axes which can be magnetized in a different direction.\textsuperscript{76,79} Thus, non-collinear spins present on the surface could be the reason for the low $M_s$ value. Surface defects can also lead to the pinning of magnetic domains which could lead to a significantly decreased saturation magnetization (the surfaces of our particles are porous).\textsuperscript{76,79} Also, the existence of canted Fe\textsubscript{3}O\textsubscript{4} nanorods/wires could be responsible for a lower value of $M_s$.\textsuperscript{79,80} Therefore, a more detailed study would need to be undertaken to understand the magnetism of these structures to probe specifically what leads to the lower $M_s$ value.

3. CONCLUSIONS

In summary, we report a simple and cost-effective protocol for the preparation of Fe\textsubscript{3}O\textsubscript{4} nanorods. A noteworthy aspect of this synthetic method is the reproducibility of the chemical transformation from antiferromagnetic $\beta$-FeOOH to superparamagnetic, 1D Fe\textsubscript{3}O\textsubscript{4} nanostructures when hydrazine is used as the reducing agent. The reaction time has a considerable effect on the morphology of the final sample, producing larger nanoparticles along with long wires at longer
reaction times (≥8 h). The amount of hydrazine added was found to be crucial to produce a single-phase iron oxide, and the formation of two phases (Fe₃O₄ and γ-Fe₂O₃) was observed with a greater amount of hydrazine (>10.8 mmol). While more work is needed to generate controllable lengths of 1D nanostructures, the hydrazine method has been shown to consistently produce 1D structures of magnetite.

4. EXPERIMENTAL SECTION

4.1. Materials. Ferric chloride hexahydrate (FeCl₃·6H₂O, ≥98%), a 50% (w/v) PEI solution (MW 750,000), and anhydrous hydrazine (N₂H₄·98%) were purchased from Sigma-Aldrich (St. Louis, MO). Anhydrous ethyl alcohol 200 proof (absolute, ACS/USP grade) was purchased from Pharmco (Brookfield, CT). TEM Cu grids (carbon-coated, 200 mesh) were purchased from Electron Microscopy Sciences (Hatfield, PA).

4.2. Synthesis of Iron Oxy-Hydroxide (β-FeOOH) Nanoneedles. Iron oxyhydroxide nanoneedles were synthesized using an existing preparation method from the literature with minor modifications. In a 500 mL three-necked round bottom flask fitted with a condenser, solid FeCl₃·6H₂O (5.4 g, 20.0 mmol) was dissolved in 100 mL of deionized (DI) water (18.2 Ω/cm) under ambient conditions. A 33.3% v/v PEI stock solution was prepared by dissolving 20 mL of PEI in DI water to make a 60 mL solution. Different volumes of the stock solution were added to the reaction flask using a micropipette to control the sizes of the resulting β-FeOOH nanoneedles. The length of the nanoneedles could be tuned from approximately 15–85 nm by decreasing the concentration of PEI from 10.0 to 1.0 mg/mL in the reaction mixture. The following volumes of the PEI stock solution were added: 600 µL, 900 µL, 1.20 mL, 1.50 mL, 3.00 mL, and 5.00 mL for a final concentration of PEI of 1.0, 1.5, 2.0, 2.5, 5.0, and 10.0 mg/mL in the final reaction mixture. [Note that the volume of the stock solution of PEI was added directly to the 100 mL reaction mixture and not adjusted to a total volume of 100 mL]. The resulting solution was stirred (400 rpm) using a Teflon-coated magnetic stir bar at 80 °C in an oil bath for 2 h. The brownish-yellow precipitate was collected by centrifugation at 8000 rpm for 15 min, washed with ethanol five times, and dried in a vacuum desiccator (Nalgene) overnight. The dried sample was stored in a polypropylene centrifuge tube sealed with parafilm. The average lengths of β-FeOOH nanoneedles were 87 ± 15, 56 ± 9, 42 ± 7, 28.4 ± 4, 22 ± 4, and 16 ± 3 nm with widths of 11 ± 3, 8.4 ± 2, 7.0 ± 2, 5.0 ± 1, 4.0 ± 1, and 3.4 ± 1 nm for 1.0, 1.5, 2.0, 2.5, 5.0, and 10.0 mg/mL of PEI solution, respectively (see histograms of particles in Figure S1).

4.3. Synthesis of Fe₃O₄ Nanorods. Hydrazine was used to reduce β-FeOOH to Fe₃O₄. In a typical reaction, 0.02 g of β-FeOOH powder was dissolved in DI water in a 50 mL single-necked round底部 flask with a septum and degassed with Ar-filled balloons for 1 h in a sonicator to remove dissolved oxygen. Then, the solution was transferred to a three-necked round bottom flask fitted with a condenser using a syringe under inert atmosphere (Ar). Anhydrous hydrazine was added drop by drop under a continuous flow of argon gas via syringe while stirring at 400 rpm at a temperature of 90 °C for 6 h. The black precipitate, indicative of Fe₃O₄, was separated by centrifugation (7000 rpm, 10 min) and washed with DI water five times followed by drying in a vacuum desiccator. The amount of hydrazine was varied from 6.3 to 11.4 mmol.

Constant amounts of hydrazine (10.8 mmol) and β-FeOOH (0.02 g) were used when the reaction time was varied from 1 to 12 h.

4.4. Characterization. The morphology and size distribution of the particles were analyzed using a JEOL JEM 2100 transmission electron microscope operating at an accelerating voltage of 200 kV and a beam current of 102 μA. The samples for TEM were prepared by casting a dilute solution of nanoparticles in DI water on a Cu TEM grid (carbon-coated, square mesh, 200) and dried under vacuum. The crystalline phase of the iron oxide nanoparticles was analyzed using a Rigaku Smart lab X-ray diffractometer with a Cu Kz radiation source (λ = 1.54 Å). The wide-scan angle was varied from 5 to 90° (2θ) at a scan rate of 1°/min. XPS measurements were performed at room temperature in an ultra-high vacuum chamber with a base pressure of 7.6 × 10⁻¹⁰ Torr. XPS spectra were acquired with the Al Kz emission line (hv = 1486.6 eV) from a dual-anode X-ray source (Physical Electronics XR 04-548) operated at 400 W, an incident angle of 54.7°, and normal emission. The photoelectrons were collected and analyzed with an Omicrometer EA 125 hemispherical electron energy analyzer with a resolution of 25 meV. The magnetic properties of the nanoparticles were probed using a Quantum Design MPMS3 SQUID magnetometer. Samples for magnetic characterization were prepared from nanoparticle material, that was ground and suspended in an eicosane matrix, by melting in a hot water bath at 42 °C until a uniform material was formed, and flame sealed under vacuum in high-purity NMR tubes. The temperature dependence of the magnetic properties of Fe₃O₄ and β-FeOOH were measured under 100 Oe applied magnetic field at a temperature range of 2–300 K. Both FC and ZFC direct current (dc) susceptibility measurements were taken. Data obtained through dc susceptibility measurements was corrected for the diamagnetism of both eicosane and metal centers. Variable field magnetization studies were also conducted at 300, 150, and 10 K at a 4 mT s⁻¹ scan rate.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02928.

Size distribution histograms, TEM images of porous iron oxide nanoparticles, XRD and XPS of iron oxides nanoparticles, and pie-chart of shape distribution of magnetite nanoparticles (PDF)

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Author Contributions
M.A. performed the synthetic experiments and analyzed the data. E.E. and D.N.M. designed and performed XPS experiments. G.R. and M.N. performed and performed SQUID magnetometry experiments. Y.V. designed and supervised the research. M.A. and Y.V. wrote the manuscript. All authors reviewed and revised the manuscript.

Notes
The authors declare no competing financial interest.

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