Supporting Online Material for

Low-Field Magnetic Separation of Monodisperse Fe₃O₄ Nanocrystals


*To whom correspondence should be addressed. E-mail: colvin@rice.edu

Published 10 November 2006, Science 314, 964 (2006)
DOI: 10.1126/science.1131475

This PDF file includes:

Figs. S1 to S5
Table S1
References
**Figure S1.** (A – B) TEM micrographs showing arrays of highly monodisperse Fe₃O₄ NCs. The materials were synthesized from the high temperature (320°C) decomposition of finely ground Fe(O)OH (0.178 g.) in oleic acid (2.26 g.) using 1-octadecene (5.00 g.) as a solvent (1). Contrast differences in the images reflect the crystalline nature of the NCs and their random orientations with respect to the electron beam. Panel A shows particles of average diameter 12 ± 1.0 nm while panel B samples are 4.0 ± 0.3 nm. The smaller sizes are synthesized by Sun’s method (2) which refluxes at 265°C a mixture of 2 mmoles of Fe(acac)₃, 10 mmoles of 1,2-hexadecanediol, 6 mmoles of oleic acid, 6 mmoles of oleylamine and diphenyl ether (solvent) under nitrogen. (C) Normalized magnetization (magnetization/maximum magnetization) vs. applied field (Oe) for two representative samples, 16 nm and 4.0 nm NCs. These samples have no magnetic moment unless an external field is applied; as expected, the larger size reaches its saturation magnetization at lower field than the smaller size. (D) A schematic of an
oleic acid coated magnetite NC [circles are iron (black), oxygen (red) and carbon (blue) - hydrogens were omitted for clarity]. The surface coating adds about 3.6 nm to the core diameter in defining the hydrodynamic diameter. Inset shows an expansion of the magnetization data near zero field (-100 Oe to 100 Oe). Both of these materials show no residual magnetization at zero applied field.

Fig. S2. Sample Library. Representative transmission electron micrographs of all materials used in this work are shown along with the histogram of their diameters. In this work, the average size as found from counting over 1000 nanoparticles is reported. For
these values we used two significant figures which was the error imposed by the sampling error for a population of $N = 1000$.

**Fig. S3.** Cryogenic transmission electron microscopy of iron oxide nanoparticle suspensions. Panels A and B show cryogenic TEM images of magnetic nanocrystal suspensions before magnetic separation. For these experiments water solutions of iron oxide nanocrystals were flash frozen to produce a thin film of amorphous ice, and this specimen was imaged using a JEOL-200 equipped with a cryogenic sample stage. This technique is widely used in structural biology and the freezing process has been shown to preserve the room temperature solution state structure of complex biomolecules (3, 4). Panel A shows Igepal CO 630 ® coated nanoparticles similar to those used for arsenic experiments. This particular image is displayed because it contains many nanoparticles and the solution is necessarily much more concentrated suspension than that used in this work. These nanoparticles are not fused crystallites nor do they show any indication of large-scale (e.g. > 100 nm) clustering. Panel B shows a similar sample which has been stabilized with a thicker amphiphilic polymer coating that is also water soluble.
Nanoparticles are well separated in this image and show no evidence of interparticle interactions. Both types of nanoparticles exhibit similar low gradient magnetic separations.

**Fig. S4.** Dynamic light scattering (DLS) of iron oxide nanocrystal suspensions. Above are DLS data collected on dilute suspensions of iron oxide nanocrystals using a Malvern Zetasizer Nano ZS machine; a column graph fit was used to calculate the nanoparticle size. Panels A, B and C show similar results for 4.0, 8.0 and 16 nm iron
oxide cores; light scattering finds average particle sizes range from 10 to 20 nm. These results are quite good considering the semi-quantitative nature of DLS when applied to nanoscale systems. Most critically for this work is the complete absence of any aggregates in suspension (e.g. no DLS signals for larger sizes). This is consistent with cryogenic TEM images that show no hard aggregation of these materials.

**Fig. S5.** Powder x-ray diffraction data for 4.0 and 6.0 nm Fe₃O₄ Nanocrystals from a Rigaku D/Max Ultima II. Black plot corresponds to 4.0 nm diameter iron oxide and red plot to 6.0 nm. The organge lines represent the theoretical diffraction pattern for a magnetite crystal from Jade ® software’s library for crystals. For bigger sizes of nanocrystals please refer to Yu et. al (1).
<table>
<thead>
<tr>
<th>Particle Size (nm)</th>
<th>As(V) or As(III)</th>
<th>Freundlich Slope, $K_F$ (µg$^{(1-N)}$L$^N$/Kg)</th>
<th>Freundlich Exponent, $N$</th>
<th>Residual As Concentration (µg/L)</th>
<th>% Removal</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>As (III)</td>
<td>4.62E5</td>
<td>0.56</td>
<td>3.9</td>
<td>99.2</td>
<td>0.982</td>
</tr>
<tr>
<td>20</td>
<td>As (III)</td>
<td>1.30E5</td>
<td>0.51</td>
<td>45.3</td>
<td>90.9</td>
<td>0.991</td>
</tr>
<tr>
<td>300</td>
<td>As (III)</td>
<td>3.09E3</td>
<td>0.74</td>
<td>375.7</td>
<td>24.9</td>
<td>0.999</td>
</tr>
<tr>
<td>12</td>
<td>As (V)</td>
<td>2.25E5</td>
<td>0.72</td>
<td>7.8</td>
<td>98.4</td>
<td>0.990</td>
</tr>
<tr>
<td>20</td>
<td>As (V)</td>
<td>2.83E5</td>
<td>0.43</td>
<td>17.3</td>
<td>96.5</td>
<td>0.997</td>
</tr>
<tr>
<td>300</td>
<td>As (V)</td>
<td>4.46E4</td>
<td>0.32</td>
<td>354.1</td>
<td>29.2</td>
<td>0.978</td>
</tr>
</tbody>
</table>

**Table S1.** The Freundlich isotherms are curve fitted parameters with adsorption data at 0 - 500 µg/L aqueous concentration using the Freundlich equation, $q = K_F C^N$, and the correlation coefficients of the adsorption data to the Freundlich equation are listed in Column 7.

**References**