Supporting Information

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Superparamagnetic Magnetite Colloidal Nanocrystal Clusters
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Chemicals:
Diethylene glycol (reagent grade), ethyl alcohol (denatured), and sodium hydroxide (98.8%) were purchased from Fisher Scientific. Iron (III) chloride anhydrous (98%) was purchased from Riedel-de Haën, German. Poly (acrylic acid) (MW=1,800) was obtained from Sigma-Aldrich. All chemicals were directly used as received without further treatment.

Characterization:
Morphology and size distribution of the products were characterized using a Tecnai T12 transmission electron microscope (TEM). High-resolution TEM (HRTEM) images were obtained using a Tecnai G2 S-Twin electron microscope operated at 200 kV. The aqueous CNC dispersions were cast onto a carbon-coated copper grid, followed by evaporation under vacuum at room temperature. Electron diffraction (ED) pattern was also acquired on the TEM.

Crystal structures were measured on a Bruker D8 Advance X-ray Diffractometer (XRD) with a CuKα radiation (λ=1.5418Å). The data were collected from 2θ=20-70° at a scan rate of 0.02° per step and 1.5s per point. Debye-Scherrer formula $D_{hkl}=\frac{k\lambda}{\beta \cos \theta}$ was used to estimate an average crystallite size from the XRD patterns, where $D_{hkl}$ is the size in the axis parallel to the $(hkl)$ plane, $k$ is a constant with a typical value of 0.89 for spherical particle, $\lambda$ is the wavelength of radiation, $\beta$ is the full width at half maximum (FWHM) in radians, and $\theta$ is the position of the maximum of diffraction.

The magnetite crystal phase of CNCs was confirmed by X-ray Absorption Spectroscopy (XAS) measurements performed at beamline 7.0 of Advanced Light Source, Lawrence Berkeley National Laboratory. The measurements were performed at room temperature, with a base pressure in the experimental
chamber lower than $5 \times 10^{-9}$ mbar. XAS spectra were obtained by measuring both the total electron yield (TEY) and fluorescence yield (FY) from the sample as a function of the incoming photon energy. All spectra were normalized to the photocurrent from a clean gold mesh introduced into the beam.

Magnetic property measurements were performed using a Quantum Design MPMS XL-7 Superconducting Quantum Interference Device (SQUID). The magnetic moment $M$ was measured as function of applied magnetic field $H$ at room temperature and low temperature. The optical dark-field images of CNC dispersion on a glass substrate were observed through a Zeiss Imager A1m Optical Microscope and recorded by a Cannon Digital Camera.

**X-ray Absorption Spectroscopy of CNCs:**

XAS spectroscopy was used to identify the crystal phase of the products since magnetite ($\text{Fe}_3\text{O}_4$) and maghemite ($\gamma$-$\text{Fe}_2\text{O}_3$) have very similar XRD patterns. The splitting of the $L_3$ peak (705-710 eV) and the varying ratio of the two peaks at the $L_2$ edge (719-725) are two important features to distinguish $\text{Fe}_3\text{O}_4$, $\gamma$-$\text{Fe}_2\text{O}_3$, and $\alpha$-$\text{Fe}_2\text{O}_3$. Figure S-1 shows the Fe L-edge x-ray absorption of CNCs. The splitting of peak A and B was measured to be 1.12 eV, which is close to results of $\text{Fe}_3\text{O}_4$ reported in the literature (1.2 eV for $\text{Fe}_3\text{O}_4$, 1.4 eV for $\gamma$-$\text{Fe}_2\text{O}_3$, 1.6 eV for $\alpha$-$\text{Fe}_2\text{O}_3$, S. A. Krasnikov et al. Mater. Sci. Eng. B 2004, 109, 207). Peak C at the $L_2$ edge is higher than peak D, also supporting the CNCs to be $\text{Fe}_3\text{O}_4$ in composition (S. Sun et al. JACS, 2004, 126, 273).

![Figure S-1 XAS spectra at the Fe L-edge of magnetite CNCs.](image)
Magnetic Moment of CNCs:

The magnetic moment of an individual grain ($\mu$) can be determined by the Langevin paramagnetic function: $M(x) = N\mu(\coth x - (1/x))$, where $x = \mu H/k_B T$, $N$ is the number of grains, $H$ is the applied field, $k_B$ is the Boltzmann’s constant, and $T$ is the absolute temperature. In this experiment, $T$ is 300K. We let $\mu = m\mu_B$ and $A = N\mu$ ($\mu_B$ is the Bohr magneton; $m$ and $A$ are constants to be determined). Fitting the data of $M(x)$ and $H$ into the Langevin function, two constants $A$ and $m$ were determined, as shown in Table S-1. Finally the magnetic moment per grain can be simply calculated using $\mu = m\mu_B$.

For 8nm nanodots, single particle magnetic moment equals to that of single grain. For CNCs, single cluster magnetic moment is the sum of that of all inclusive grains. The grain size was calculated by using the Debye-Scherrer formula, and the number of grains inside each cluster was estimated by $(D_{\text{cluster}}/D_{\text{grain}})^3$. Finally, the magnetic moment per cluster was calculated for each sample and listed in Table S-1.

Table S-1. Magnetization of the magnetite CNCs and the referential nanodots.

<table>
<thead>
<tr>
<th>Size (nm)</th>
<th>A</th>
<th>m</th>
<th>Magnetization per grain (emu)</th>
<th>Grain size (nm)</th>
<th>Magnetization per cluster (emu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>21.33</td>
<td>9110</td>
<td>8.44871E-17</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>53</td>
<td>30.84</td>
<td>21537</td>
<td>1.99736E-16</td>
<td>9.73</td>
<td>3.22809E-14</td>
</tr>
<tr>
<td>93</td>
<td>57.24</td>
<td>21508</td>
<td>1.99467E-16</td>
<td>9.65</td>
<td>1.78541E-13</td>
</tr>
<tr>
<td>174</td>
<td>64.17</td>
<td>18541</td>
<td>1.71951E-16</td>
<td>10.83</td>
<td>7.13127E-13</td>
</tr>
</tbody>
</table>
Figure S-2. The magnetization of individual grains was obtained by fitting the data into the Langevin paramagnetic function for dots of 8 nm (a) and CNCs of 53 nm (b), 93 nm (c), and 174 nm (d).