Ultrafast Electron and Energy Transfer in Dye-Sensitized Iron Oxide and Oxyhydroxide Nanoparticles

-- SUPPLEMENTARY TABLE and FIGURES
Table S1. Summary of experimental determinations of the flatband potential, $E_{fb}$, for hematite and titanium dioxide in aqueous solution at a pH value close to the point of zero surface charge.

<table>
<thead>
<tr>
<th>References</th>
<th>Sample</th>
<th>pH</th>
<th>$E_{fb}$ (V vs SHE)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hematite</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quinn et al., (1976)</td>
<td>Single crystal</td>
<td>8.6</td>
<td>-0.168</td>
<td>Mott-Schottky</td>
</tr>
<tr>
<td>Kennedy &amp; Frese (1978)</td>
<td>Polycrystalline electrode</td>
<td>8.9</td>
<td>-0.098</td>
<td>Mott-Schottky</td>
</tr>
<tr>
<td>Dimitrijevic et al., (1984)</td>
<td>72-nm diameter colloids</td>
<td>8.6</td>
<td>-0.28</td>
<td>Radiolysis and MV$^+/MV^{2+}$ redox equilibrium</td>
</tr>
<tr>
<td>Khan et al., (1999)</td>
<td>Nanocrystal electrode</td>
<td>9*</td>
<td>-0.184</td>
<td>Mott-Schottky</td>
</tr>
<tr>
<td>Bjökestén et al., 1994</td>
<td>Nanocrystal electrode</td>
<td>9*</td>
<td>-0.18</td>
<td>Detection of Burstein shift</td>
</tr>
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<td><strong>Titanium dioxide</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bolts &amp; Wrighton (1976)</td>
<td>Single crystal</td>
<td>6</td>
<td>-0.6</td>
<td>Mott-Schottky</td>
</tr>
<tr>
<td>Dimitrijevic et al., (1984)</td>
<td>10-nm diameter colloids</td>
<td>6*</td>
<td>-0.52</td>
<td>Radiolysis and MV$^+/MV^{2+}$ redox equilibrium</td>
</tr>
<tr>
<td>Rothenberger et al., (1992)</td>
<td>Nanocrystal electrode</td>
<td>6*</td>
<td>-0.56</td>
<td>Optical absorbance</td>
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</tbody>
</table>

Footnotes: *For pH values indicated by an asterisk, the measured $E_{fb}$ potential was not performed at the given pH value, but was calculated assuming a Nernstian shift of 0.059 V per pH unit.

References cited in Table S1.


Nanoparticle Synthesis

All chemicals, used as received, were ACS reagent grade or better. Water was $>18.1\, \text{M}\Omega\, \text{cm}$ resistivity. Solution pH was adjusted by addition of HCl or NaOH as needed.

**Maghemite Nanoparticles.** Nanoparticles of magnetite were prepared by co-precipitation of Fe(II) and Fe(III) under anaerobic conditions ([37]). A freshly prepared solution (3 mL) containing FeCl$_2$ (0.99 M), Fe(NO$_3$)$_3$ (1.92 M), and NaNO$_3$ (3.0 M) was slowly added to 40 mL of 6 M NaNO$_3$, maintaining a pH of 12 ± 0.1 by the addition of ~6 M NaOH under auto-titrator control (Mettler Toledo T70), resulting in the immediate precipitation of a black solid. This magnetic solid was immediately oxidized in its mother liquor to maghemite by heating to 60 °C and gently bubbling pure O$_2$(g) through the suspension for 48 h. Particle suspensions were subsequently centrifuged, decanted, and rinsed with water 3–4 times, and finally re-suspended in a pH 4 solution before use.

**Ferrihydrite Nanoparticles.** Nanoparticles of ferrihydrite were prepared by precipitation of Fe(III) under anaerobic conditions. A freshly prepared solution (3 mL) containing FeCl$_3$ (3.1 M) and NaNO$_3$ (3.0 M) was slowly added to 40 mL of 6 M NaNO$_3$, maintaining a pH of 12 ± 0.1 by the addition of ~6 M NaOH under auto-titrator control (Mettler Toledo T70), resulting in the immediate precipitation of a brown solid. Immediately following, the reaction mixture was neutralized to pH ~7 by addition of 1 M HCl, and subsequently dialyzed (in air) against ultrapure H$_2$O.

**Hematite Nanoparticles.** Nanoparticles of hematite were prepared by use of a two-step precipitation process ([38]). First a solution of 200 mL filtered FeCl$_3$ (2.0 M) with 200 mL of NaOH (5.94 M) was aged in a closed Pyrex bottle at 100 °C for 44 hrs. The sediment was washed with distilled water and freeze-dried, then ball milled with HNO$_3$ (0.01 M), dispersed by ultrasonic treatment, and centrifuged. The supernatant liquid was used as a seed-solution. To a new solution of 100 mL filtered FeCl$_3$ (2.0 M) with 100 mL of NaOH (4.8 M) and 100 mL of Na$_2$SO$_4$ (0.12 M), 100 mL of the seed solution (~25 mM) was added. The solution was aged at 100 °C for 42 hrs, and the resulting nanoparticle sample was washed in several steps with NH$_3$ (1.0 M), NaNO$_3$ (0.5 M), and a 1:1 water/methanol mixture.
**Figure S1.** Ground state UV-vis absorption spectra for uncoated and 2',7'-dichlorofluorescein (DCF) nanoparticles.
Figure S2. Small-angle X-ray scattering (SAXS) analyses. A The background-subtracted SAXS data for suspension of uncoated 6-line ferrhydrite nanoparticles is consistent with a dispersion of charge stabilized nanoparticles with a mean radius of 2.0 nm (Gilbert et al., 2007). B The background-subtracted SAXS data for a solution containing ferric iron complexed by 2’,7’-dichlorofluorescein (Fe-DCF) reveals only noise, indicating the absence of precipitated particles.


Note: All other nanoparticle samples could not be analyzed by SAXS for particle size due to aggregation.
Figure S3. Pump power dependence of the transient absorption signal from 2’,7-dichlorofluorescein (DCF) sensitized iron oxide and oxyhydroxide nanoparticles at a probe wavelength of 450 nm and a delay of 1.3 ps. Hm = hematite, M = maghemite, 6LF = six-line ferrihydrite, 2LF = two-line ferrihydrite.
**Figure S4.** Results of global analyses for all samples. 

- **a)** DCF-coated hematite (Hm).
- **b)** DCF-coated maghemite (M).
- **c)** DCF-coated 6-line ferrihydrite (6LF).
- **d)** DCF-coated 2-line ferrihydrite (2LF).
- **d)** A cluster compound composed of DCF bound to dissolved iron(III). A 1-ps temporal offset has been added to the time axes for plotting on a logarithmic scale.
Figure S5. The intensity of the excited state absorption (ESA) observed at 605-nm for DCF-sensitized 6-line ferrihydrite (6LF) is dependent on the amount of dye bound to the nanoparticles. **a)** Ground state UV-vis spectra for two samples of 6LF sensitized with identical iron oxide concentration but with different quantities of dye. **b)** Comparison of the ESA for the two samples shows greater ESA for the higher dye loading.
Figure S6. Calculated excited-state population dynamics (top) and associated kinetics (bottom) for three scenarios for dye relaxation pathways. a) Charge-transfer only. b) Energy-transfer only. c) Both charge- and energy-transfer. The charge- and energy transfer rates were chosen so that the lifetime of the dye excited state, $S_0$, is the same in all cases. With regard to the transient spectra, the most important distinction between charge- and energy-transfer is that the latter regenerates the dye ground state, leading to the loss of the ground-state bleach signal.
Figure S7. Comparison of the oxygen K-edge X-ray near-edge absorption structure (XANES) spectra for bulk references of hematite and maghemite and one sample of 6-line ferrihydrite nanoparticles. The vertical dashed line is the approximate position of the energy position for electron transfer from the dye excited state.