Published in final edited form as:

J Am Chem Soc. 2011 March 30; 133(12): 4228–4231. doi:10.1021/ja111143y.

Electron Transfer Between Colloidal ZnO Nanocrystals

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Abstract

Colloidal ZnO nanocrystals, capped with dodecylamine and dissolved in toluene, can be charged photochemically to give stable solutions in which electrons are present in the conduction bands of the nanocrystals. These conduction band electrons are readily monitored by EPR spectroscopy, with g^* values that correlate with the nanocrystal sizes. Mixing a solution of charged small nanocrystals with a solution of uncharged large nanocrystals, $e^-_{CB}:ZnO-S + ZnO-L$, causes changes in the EPR spectrum indicative of quantitative electron transfer from small to large nanocrystals. EPR spectra of the reverse reaction, $e^-_{CB}:ZnO-L + ZnO-S$, show that electrons do not transfer from large to small nanocrystals. Stopped-flow kinetic studies monitoring the change in the UV band edge absorption show that reactions of 50 μM nanocrystals are complete within the 5 ms mixing time of the instrument. Similar results are obtained for the reaction of charged nanocrystals with methyl viologen (MV^{2+}). These and related results indicate that the electron transfer reactions of these colloidal nanocrystals are quantitative and very rapid, despite the presence of ~ 1.5 nm long dodecylamine capping ligands. These soluble ZnO nanocrystals are thus well-defined redox reagents suitable for electron transfer studies involving semiconductor nanostructures.

Charge transfer reactions are critical to many applications of nanoscale materials, for instance in dye-sensitized solar cells.¹ Interfacial charge transfer is also key to heterogeneous photocatalysis and redox dissolution of minerals in the environment.² Although there has been a great deal of study of electron transfer (ET) involving nanocrystals,³ many aspects remain poorly understood. Zinc oxide (ZnO) has long attracted interest for its electronic, optical, and photochemical properties.⁴ It has also been used to develop a fundamental understanding of interfacial ET in electrochemical cells.⁵ Here, we describe ET reactions involving differently sized colloidal ZnO nanocrystals (quantum dots) that have been photochemically charged. Bimolecular ET between these nanocrystals is quantitative and very rapid. The driving force for ET derives from the greater quantum confinement of the electrons in the smaller nanocrystals. The rapid ET is surprising in light of the ~ 1.5 nm long dodecylamine capping ligands and the common observation of low conductivity in thin films of capped nanocrystals.⁶ These results show that the mixing of nanocrystals in solution is a valuable approach to probing interparticle redox chemistry.

The ZnO and Mn^{2+} -doped ZnO nanocrystals investigated here were prepared following reported methods⁷⁻⁹ and thereafter treated as molecular reagents. Their average sizes and size distributions were determined spectroscopically from the energies and shapes of the first excitonic absorption features.¹⁰ The concentrations of nanocrystals were determined from their average size and the total zinc concentration, measured by ICP-AES. As reported previously, UV irradiation creates reduced nanocrystals, $e^-_{CB}:ZnO$.¹¹ Charging can be

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Supporting Information Available: Experimental details and additional spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

monitored by the appearance of a strong EPR signal¹²⁻¹⁴ and the bleach of the absorption edge in the UV. The reduced nanocrystals are rapidly oxidized by air, so all manipulations were performed in a nitrogen-filled glove box and EPR spectra were taken in EPR tubes with PTFE valves. Under rigorously anaerobic conditions, the nanocrystals remain charged for weeks without measurable decay¹² and can thus be used as soluble reducing agents in toluene.

The studies reported here involved dodecylamine-capped ZnO nanocrystals of two different diameters (3.7 ± 0.2 nm and 6.0 ± 2.0 nm), termed **ZnO-S** and **ZnO-L** for small and large.⁹ Brief irradiation yields nanocrystal solutions that exhibit EPR resonances with $g^* = 1.967$ for $e^-_{CB}:ZnO-S$ and 1.963 for $e^-_{CB}:ZnO-L$ (Figure 1a; the signals at $g^* = 2.0037$ are from the external calibration standard DPPH [2,2-diphenyl-1-picrylhydrazyl radical]). The observed size dependence of the g^* values is one of the indications that the added electron is delocalized in the conduction band and not localized in a trap site, as previously discussed.¹²⁻¹⁴ For a given sample and with short irradiation times, g^* does not vary with charging time. This result indicates that the nanocrystals have fewer than one electron each on average ($\langle n_e \rangle < 1$).¹³

The size dependence of the $e^-_{CB}:ZnO$ EPR signal provides a direct way to monitor ET between nanocrystals. A 0.5 mL solution of small nanocrystals (1×10^{-4} M [moles of nanocrystals per liter]) was irradiated to form $e^-_{CB}:ZnO-S$ and an EPR spectrum was taken. This solution was then mixed with 0.5 mL of an equimolar solution of uncharged **ZnO-L**. The EPR spectrum of the mixed solution showed a signal at $g^* = 1.963$, characteristic of $e^-_{CB}:ZnO-L$, rather than the signal at $g^* = 1.967$ of the starting small nanocrystals (Figure 1b, dashed). This shift in g^* shows that the conduction band electrons have transferred from the small nanocrystals to the larger ones (Scheme 1). In the reverse direction, probed by mixing $e^-_{CB}:ZnO-L$ with **ZnO-S**, no change in g^* before and after mixing is observed (Figure 1c). This result shows that electrons do not transfer from large to small nanocrystals.

The driving force for ET from small to large nanocrystals comes from quantum confinement. The band gap is larger in the smaller particles, as is evident from the optical spectra, and the shifts in the individual valence and conduction bands (HOMO and LUMO) can be estimated from the Brus equation.^{15,16} The conduction band energy for **ZnO-S** is estimated to be 0.21 eV higher than that for **ZnO-L**.⁹ Assuming that this energy difference equals the difference in redox potentials, an equilibrium constant $K_{eq} = 10^{3.5}$ is predicted at room temperature, consistent with the experimental observation of complete transfer from small to large nanocrystals.¹⁷

Reduced nanocrystals have also been mixed with uncharged nanocrystals of the same size, from the same synthetic batch. EPR spectra of $e^-_{CB}:ZnO-S$ before and after mixing with an equal portion of uncharged **ZnO-S** show no shift in g^* . The same behavior is observed for $e^-_{CB}:ZnO-L + ZnO-L$. These results confirm that the shift in g^* in Figure 1b is due only to transfer of electrons from **ZnO-S** to **ZnO-L**, and not, for example, to a decrease in the average number of electrons per nanocrystal $\langle n_e \rangle$,¹³ to trap filling, or to some sort of aggregation behavior.

To quantitatively monitor the number of unpaired spins in a reaction, the double-integrated $e^-_{CB}:ZnO$ EPR intensities were compared with that of an internal capillary standard of 2,4,6-tri-*tert*-butylphenoxy radical ($tBu_3ArO^\bullet$).^{9,18} A portion of a **ZnO-L** solution was irradiated and the intensity of the $e^-_{CB}:ZnO$ EPR resonance was determined vs. the standard. An equal amount of the same **ZnO-L** solution that had not been charged was added to this EPR tube and another spectrum was recorded (Figure 1d). As found above, the g^* value did not shift. The double-integrated intensity of the EPR signal after mixing was found to be 48% of the

original intensity, the decrease resulting primarily from the two-fold dilution of the sample. After accounting for dilution, only ~4% of the original EPR intensity was lost upon mixing. (In Figures 1b-d, the intensities of the product spectra have been doubled to account for dilution.) In a similar experiment $e^-_{\text{CB}}\text{:ZnO-L}$ in toluene was mixed with an equal volume of a five times more dilute solution of ZnO-L in toluene, and again only a small (1%) decrease in intensity was observed after correction for dilution. These small decreases in EPR intensity likely result simply from losses associated with handling the dilute and highly air-sensitive solutions. These experiments show that ET occurs between $1S_e$ conduction band states with negligible loss to trap states. The role such electron traps might play in ZnO nanocrystal CB filling has been debated in recent literature.¹⁹

Another probe of ET is provided by Mn^{2+} -doped ZnO nanocrystals, which show a characteristic multiline EPR signal (hyperfine constant $A_{\text{iso}} \approx 74 \times 10^{-4} \text{ cm}^{-1}$, Figure 2a,b middle spectra).⁸ EPR spectra of reduced $\text{Mn}^{2+}\text{:ZnO}$ nanocrystals do not show a simple derivative signal such as in Figure 1; instead they show broadening of the Mn^{2+} multiline signal due to $e^-_{\text{CB}}\text{-Mn}^{2+}$ exchange coupling.^{12,20} A solution of uncharged $\text{Mn}^{2+}\text{:ZnO-L}$ (~0.7% Mn^{2+}) was mixed with a 10-fold excess of $e^-_{\text{CB}}\text{:ZnO-S}$. The EPR spectra of the reaction solution show loss of the sharp signal for the $e^-_{\text{CB}}\text{:ZnO-S}$ conduction band electron and a broadening of the Mn^{2+} fine structure (Figure 2a, lowest spectrum).⁹ To see significant broadening, an excess of $e^-_{\text{CB}}\text{:ZnO-S}$ was used and these nanocrystals were more extensively photochemically charged.⁹ The inverse reaction, mixing $e^-_{\text{CB}}\text{:ZnO-L}$ with $\text{Mn}^{2+}\text{:ZnO-S}$, gave an EPR spectrum with a superposition of the unbroadened Mn^{2+} multiplet and the sharp e^-_{CB} resonances (Figure 2b). These results support the conclusion that electrons readily transfer from small to large nanocrystals but not in the reverse direction.

The ET kinetics have been examined by optical spectroscopy using a stopped-flow apparatus.⁹ In initial experiments, methyl viologen dichloride (MV^{2+}) was used as the oxidant because its one-electron-reduced form, the radical cation $\text{MV}^{\bullet+}$, has a distinct absorbance at $\lambda_{\text{max}} = 609 \text{ nm}$ ²¹ that is well separated from the absorbances of ZnO and MV^{2+} . Toluene solutions of $e^-_{\text{CB}}\text{:ZnO-S}$ ($5 \times 10^{-5} \text{ M}$) were rapidly mixed with equimolar solutions of MV^{2+} in 4:1 toluene/ethanol. The first optical spectrum was obtained within 5 ms of mixing and already showed the strong characteristic 609 nm absorbance of $\text{MV}^{\bullet+}$ (Figure 3a). Subsequent spectra were almost identical, showing only slow decay of the $\text{MV}^{\bullet+}$ intensity over seconds, likely due to the presence of adventitious oxygen.²² This result demonstrates rapid ET from reduced ZnO to MV^{2+} to form $\text{MV}^{\bullet+}$.

Using the same stopped-flow apparatus, $5 \times 10^{-5} \text{ M}$ solutions of $e^-_{\text{CB}}\text{:ZnO-S}$ were rapidly mixed with an equivalent amount of ZnO-L . Again, the optical spectra were essentially constant from the first spectrum ~5 ms after mixing. The resulting spectrum is shown as the solid black line in Figure 3b. The dashed black line shows the spectrum anticipated for the $e^-_{\text{CB}}\text{:ZnO-S} + \text{ZnO-L}$ mixture had no reaction occurred, obtained by mathematically adding the separately measured spectra of these two solutions. The absorbance change upon mixing is small but the difference spectrum (red, bottom) clearly shows a bleach at the band edge ~375 nm that is consistent with ET from small to large nanocrystals.

In both the reactions of $e^-_{\text{CB}}\text{:ZnO-S}$ with methyl viologen and of $e^-_{\text{CB}}\text{:ZnO-S}$ with ZnO-L , the optical spectra show complete reaction of the 50 μM solutions within 5 ms. Assuming second-order kinetics, this implies bimolecular rate constants $>10^7 \text{ M}^{-1} \text{ s}^{-1}$. These are remarkably high rate constants, within three orders of magnitude of the diffusion limit.⁹ Very rapid electron transfer between nanocrystals is surprising because each particle is capped by ~1.5 nm-long dodecylamine ligands. If the capping groups form a ~3 nm dielectric tunnel barrier for interparticle ET, the highest possible rate constant would be ~10

$\text{M}^{-1} \text{s}^{-1}$, when $\Delta G^\circ = -\lambda$ and taking $k^0 = 10^{14} \text{s}^{-1}$ and $\beta = 1 \text{\AA}^{-1}$.²³ This kind of barrier has been invoked to explain the low conductivities of thin films of capped semiconducting nanoparticles.⁶ Closer approach of the ZnO nanocrystals may be possible because of incomplete capping, or due to interpenetration of the dodecylamine chains from different particles. Indeed, ligand interdigitation has been proposed to explain rapid interparticle ET in films of thiolate-capped gold clusters.²⁴ A rate constant of $10^7 \text{M}^{-1} \text{s}^{-1}$ could be consistent with a 1.5 nm particle separation, but just barely.

In conclusion, EPR and optical spectra demonstrate rapid electron transfer (ET) between colloidal dodecylamine-capped ZnO nanocrystals in toluene. Electrons in the conduction bands of $3.7 \pm 0.2 \text{ nm}$ diameter nanocrystals readily transfer to the conduction bands of $6.0 \pm 2.0 \text{ nm}$ diameter nanocrystals, but no transfer occurs in the opposite direction. The quantitative ET from small to large nanocrystals is consistent with the band-edge energies anticipated from the Brus equation.¹⁵ Integration of the EPR spectra shows that ET is quantitative, and that there are no significant EPR-silent trap states. Stopped-flow optical experiments indicate that ET occurs very rapidly, with apparent bimolecular rate constants of $>10^7 \text{M}^{-1} \text{s}^{-1}$. This simple and direct method of mixing charged nanocrystals in solution thus provides new insights into nanoscale ET processes. Experiments using this approach are underway to probe the roles of capping ligands, counterions, solvent, and the number of electrons per nanocrystal in interparticle electron transfer reactions.

Supplementary Material

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Acknowledgments

We are grateful to the University of Washington for financial support to J.M.M., R.H., and K.M.W., and to the US National Science Foundation (CHE 0628252-CRC) for support for D.R.G. and K.M.W. EPR instrumentation support was provided by the Center for Ecogenetics and Environmental Health UW Center grant no. P30 ES07033 from the National Institute of Environmental Health Sciences. We thank Drs. Stefan T. Ochsenbein and Kevin R. Kittilstved for helpful discussions.

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Figure 1. EPR spectra at 298 K of $e^-_{CB}:ZnO$ nanocrystals in toluene (a) Spectra of $e^-_{CB}:ZnO-S$ (dashed line) and $e^-_{CB}:ZnO-L$ (solid), with DPPH external standard, showing the size dependence of g^* . (b) Spectra of $e^-_{CB}:ZnO-S$ (dashed) and the reaction mixture $e^-_{CB}:ZnO-S + ZnO-L$ (solid), showing the transfer of electrons to **ZnO-L**. (c) Spectra of $e^-_{CB}:ZnO-L$ (dashed) and mixed $e^-_{CB}:ZnO-L + ZnO-S$ (solid), showing no transfer of electrons. (d) Spectra of $e^-_{CB}:ZnO-L$ (dashed) and mixed $e^-_{CB}:ZnO-L + ZnO-L$ (solid), with a capillary of $tBu_3ArO^\bullet$ as a standard, showing negligible loss of EPR intensity upon mixing. In (b) – (d), the intensities of the spectra of the mixed solutions have been doubled to account for dilution.

Figure 2.

EPR spectra of: (a) $e^-_{\text{CB}}\text{:ZnO-S}$ (top, red), uncharged $\text{Mn}^{2+}\text{:ZnO-L}$ (middle, blue) and mixed $e^-_{\text{CB}}\text{:ZnO-S} + \text{Mn}^{2+}\text{:ZnO-L}$ (bottom, black); (b) $e^-_{\text{CB}}\text{:ZnO-L}$ (top, red), uncharged $\text{Mn}^{2+}\text{:ZnO-S}$ (middle, blue) and mixed uncharged $\text{Mn}^{2+}\text{:ZnO-S} + e^-_{\text{CB}}\text{:ZnO-L}$ (bottom, black); the sharp signal for $e^-_{\text{CB}}\text{:ZnO-L}$ is unchanged.

Figure 3.

(a) Selected optical spectra for the reaction between $5 \times 10^{-5} \text{ M } \text{MV}^{2+}$ and $e^{-}_{\text{CB}}\text{:ZnO}$. The top spectrum is obtained within 5 ms after mixing; the subsequent spectra are at intervals of 150 ms. (b) The experimental spectrum of $e^{-}_{\text{CB}}\text{:ZnO-S} + \text{ZnO-L}$ in toluene 5 ms after mixing (solid black line), compared with the sum of the separate spectra for $e^{-}_{\text{CB}}\text{:ZnO-S}$ and ZnO-L (corrected for dilution, dashed black line). The difference spectrum, 'experimental' – 'calculated' showing the band edge bleach (red line). *Inset:* Experimental absorbance at 375 nm vs. time (and a linear fit, solid line); the dashed line indicates A_{375} calculated for a hypothetical unreacted mixture of $e^{-}_{\text{CB}}\text{:ZnO-S} + \text{ZnO-L}$.

Scheme 1.