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Effect of Protons on the Redox Chemistry of Colloidal Zinc Oxide Nanocrystals

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Supporting Information

ABSTRACT: Electron transfer (ET) reactions of colloidal 3−5 nm diameter ZnO nanocrystals (NCs) with molecular reagents are explored in aprotic solvents. Addition of an excess of the one-electron reductant Cp^*_2Co (Cp^* = pentamethylcyclopentadienyl) gives NCs that are reduced by up to 1−3 electrons per NC. Protons can be added stoichiometrically to the NCs by either a photoreduction/oxidation sequence or by addition of acid. The added protons facilitate the reduction of the ZnO NCs. In the presence of acid, NC reduction by Cp^*_2Co can be increased to over 15 electrons per NC. The weaker reductant Cp^*_2Cr transfers electrons only to ZnO NCs in the presence of protons. $Cp^*_2M^+$ counterions are much less effective than protons at stabilizing reduced NCs. With excess Cp^*_2Co or Cp^*_2Cr, the extent of reduction increases roughly linearly with the number of protons added. Some of the challenges in understanding these results are discussed.

The energetics of the conduction and valence bands (CB and VB) are critical determinants of semiconductor properties ranging from chemical- and photocatalysis to charge injection in dye-sensitized solar cells. Zinc oxide (ZnO), in both bulk and nanocrystalline forms, has long attracted interest for these and other applications,[1] and has been used to develop fundamental understanding of interfacial ET.[2] Band energies in ZnO (as well as many other materials) shift with pH or proton activity of contacting solutions, with a linear "Nernstian" decline of ~60 meV per pH unit.[3] ZnO nanocrystal (NC) films have higher differential capacitances when exposed to protic (aqueous) vs aprotic solutions, also indicating that protons play an important role.[4] This study examines how addition of stoichiometric protons affects the electron transfer chemistry of colloidal ZnO NCs.

ZnO NCs with average diameters (d) between 3 and 5 nm were synthesized by a wet chemical method described previously,[5] washed with ethanol, capped with dodecylamine (DDA), and stored in toluene (ca. 4×10^{-4} M NCs).[6] UV irradiation of ZnO NCs in the absence of oxygen generates reduced NCs[7] that are stable for weeks and are blue in color.[8] Photoreduction occurs with concomitant oxidation of ethanol under these conditions to form acetaldehyde, which condenses with one of the many DDA molecules in the NC solution to form the corresponding imine (eq 1; R = $C_{12}H_{25}$).[9,10] Extended photolysis generates reduced NCs with an average of more than one electron per NC ($n_{e-} > 1$), as determined spectroscopically or by titration.[7d,8b] Reaction of the reduced NCs with the $1e^-/1H^+$ acceptor 2,4,6-tri-*tert*-butylphenoxyl radical (${}^t\mathrm{Bu}_3\mathrm{ArO}^\bullet$) regenerates the original ZnO NCs and ${}^t\mathrm{Bu}_3\mathrm{ArOH}$ (eq 2).[10] In contrast, oxidation by the e^- acceptor decamethylferrocenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate $[Cp^*_2Fe^+][BAr^F_4{}^-]$ generates NCs with n_{e-} more protons than the original ZnO NCs (eq 3).

$$\mathrm{ZnO} + h\nu + {}^1/_2\,\mathrm{EtOH} + {}^1/_2\,\mathrm{H_2NR} \rightarrow \mathrm{ZnO{:}}e^-\text{-}\mathrm{H^+} + {}^1/_2\,\mathrm{CH_3CH{=}NR} + {}^1/_2\,\mathrm{H_2O} \qquad (1)$$

$$\mathrm{ZnO{:}}e^-\text{-}\mathrm{H^+} + {}^t\mathrm{Bu_3ArO}^\bullet \rightarrow \mathrm{ZnO} + {}^t\mathrm{Bu_3ArOH} \qquad (2)$$

$$\mathrm{ZnO{:}}e^-\text{-}\mathrm{H^+} + [\mathrm{Cp^*{}_2Fe^+}][\mathrm{BAr^F{}_4{}^-}] \rightarrow \mathrm{ZnO\text{-}H^+}[\mathrm{BAr^F{}_4{}^-}] + \mathrm{Cp^*{}_2Fe} \qquad (3)$$

This report describes the addition of protons and reductants to colloidal ZnO NCs in aprotic toluene/THF solutions (50/50 v/v, unless otherwise noted, to allow solubility of all reagents). Addition of the strong reductant Cp^*_2Co ($E^{\circ\prime}$ = −1.91 V vs Fc/Fc^+ in MeCN[11]) resulted in ZnO NC reduction (eq 4) as indicated by appearance of the characteristic EPR signal[8b] at $g \approx 1.96$ and broad IR absorption band[7c,e] that tails deeply into the visible[8b] (the high energy portion of which is shown in Figure 1a). This procedure generates $\mathrm{ZnO{:}}e^-$ with $Cp^*_2Co^+$ counterions rather than the protons that come from

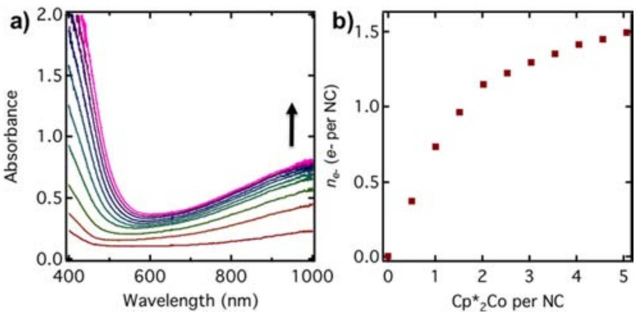

Figure 1. Absorption spectra of the chemical reduction of ZnO NCs in toluene (4.3×10^{-4} M, d = 3.6 nm) by 10 μL aliquots of Cp^*_2Co in toluene (0.5 equiv each addition). (a) Absorbance changes with each aliquot; at long wavelengths due to $\mathrm{ZnO{:}}e^-$ (see arrow) and below 500 nm due to excess Cp^*_2Co. (b) Average e^-/NC (n_{e-}) (from A(850)) vs equivalents of Cp^*_2Co.

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photochemical reduction (eq 1). With a large excess of Cp^*_2Co, a maximum absorbance is reached, suggesting an equilibrium-limited process.

The n_{e-} for the chemically reduced NCs can be estimated using the extinction coefficient (ε) of $1000 \pm 200\ M^{-1}\ cm^{-1}/e^-$ at 850 nm previously determined for photocharged NCs.[10] Parallel EPR and optical studies suggest that this $\varepsilon(850)$ is valid for the chemically reduced NCs as well. For photoreduced $ZnO{:}e^-\text{-}H^+$ NCs, the EPR g values correlate with both the $A(850)$ and n_{e-} from titrations,[8b,10] yielding a simple relationship between g and $A(850)$. The chemically reduced and protonated NCs described here follow this same $g/A(850)$ relationship (Supporting Information Figure S6), which supports the use of the same ε.

Using the $\varepsilon(850)$, the spectra in Figure 1 indicate a maximum n_{e-} of ~1.5. However, this value is different for each batch of NCs (max n_{e-} = 1−3). Addition of excess $[Cp^*_2Fe^+][BAr^F{}_4{}^-]$ to these solutions regenerates the starting NCs. No reduction of ZnO NCs was observed with an excess of the weaker metallocene reducing agents Cp_2Co (Cp = cylcopentadienyl) or Cp^*_2Cr.[12]

$$ZnO + Cp^*_2Co \rightleftarrows ZnO{:}e^-[Cp^*_2Co^+] \qquad (4)$$

To investigate the effect of protons, a single solution of ZnO NCs was photoreduced and then split into two separate cuvettes. The reduced NCs were completely oxidized using $[Cp^*_2Fe^+][BAr^F{}_4{}^-]$ or ${}^tBu_3ArO^\bullet$ to yield $ZnO\text{-}H^+[BAr^F{}_4{}^-]$ (eq 3) and ZnO NCs (eq 2). The two different products have identical UV−vis spectra and are both EPR silent.[12] However, they have different redox properties. Addition of Cp^*_2Cr to the NCs oxidized by ${}^tBu_3ArO^\bullet$ shows no reaction, as expected because this reagent removed both the proton and the electron. In contrast, addition of Cp^*_2Cr to $ZnO\text{-}H^+[BAr^F{}_4{}^-]$ yields reduced NCs (Figure 2, Scheme 1a). This shows that the presence of only a few extra protons per NC substantially affects their redox properties.[13]

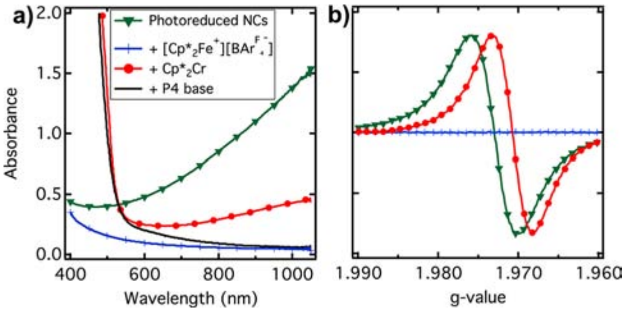
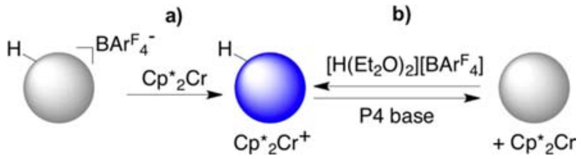


Figure 2. (a) Photochemically reduced ZnO NCs with n_{e-} = 3.7 (3×10^{-4} M, d = 3.7 nm, green ▼), oxidized with 4.5 equiv $[Cp^*_2Fe^+][BAr^F{}_4{}^-]$ (blue +), then reduced again by 31 equiv Cp^*_2Cr (red ●), n_{e-} = 1.2. Subsequent addition of P4-^{t}Bu base forms uncharged NCs and Cp^*_2Cr (black —). (b) EPR spectra of ZnO NCs (3×10^{-4} M, d = 3.9 nm) after photocharging (green ▼) then oxidation with $[Cp^*_2Fe^+][BAr^F{}_4{}^-]$ (blue +), and recharging with Cp^*_2Cr (red ●, normalized to the peak height of green ▼).

Addition of the strong base P4-^{t}Bu phosphazene[14] to the $ZnO\text{-}H^+[BAr^F{}_4{}^-] + Cp^*_2Cr$ reaction mixture deprotonated the NCs, as observed by ${}^{31}P$ NMR spectroscopy,[12] and shifted the equilibrium completely back to the starting reagents ZnO and Cp^*_2Cr (Scheme 1b). No reduction of the NCs by Cp^*_2Cr has been observed in the presence of the base.

Scheme 1. Reduction of ZnO NCs by Cp^*_2Cr Modulated by Protons



Protonated ZnO NCs can also be generated using the strong acid $[H(Et_2O)_2{}^+][BAr^F{}_4{}^-]$. We presume that this initially protonates a few of the ca. 10^2 DDA molecules per NC present in the solution, and the same effects are observed when protonated dodecylamine ($[H(DDA)^+][BAr^F{}_4{}^-]$) is used instead of the stronger acid. Addition of Cp^*_2Cr to a solution of acidified NCs forms reduced NCs (Scheme 1b). This contrasts with the lack of reaction between Cp^*_2Cr and unprotonated NCs. These results confirm the key role played by protons.

Using the acid $[H(Et_2O)_2{}^+][BAr^F{}_4{}^-]$ as a proton source enabled a systematic study of the effect of each proton on the redox chemistry of the NCs. Adding aliquots of Cp^*_2Cr to a solution already containing NCs and 10 equiv of acid resulted in an equilibrium-determined reduction of the NCs (Figure 3a). This result is similar to the chemical reduction with Cp^*_2Co in Figure 1. In contrast, the opposite experiment involving acid addition to a NC solution containing 10 equiv Cp^*_2Cr gave a roughly linearly increasing n_{e-} (Figure 3b). For a given solution composition, the same n_{e-} was obtained independent of the order of addition of acid and reductant, but the paths to that point are not identical. In sum, each addition of protons allows for more reduction of the NCs by Cp^*_2Cr.

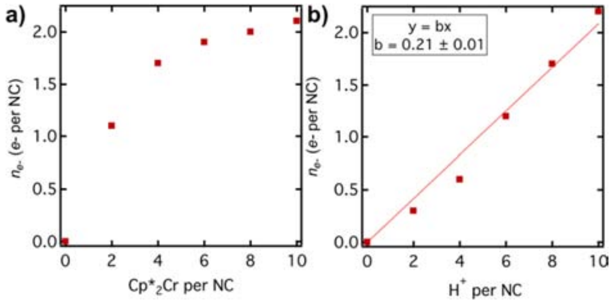


Figure 3. Chemical reduction of ZnO NCs (2.5×10^{-4} M, d = 3.7 nm) using Cp^*_2Cr and the acid $[H(Et_2O)_2{}^+][BAr^F{}_4{}^-]$. (a) Addition of $5 \times 10\ \mu L$ aliquots of Cp^*_2Cr (~2 equiv each) into a solution of ZnO NCs with 10 equiv acid. (b) Addition of $5 \times 10\ \mu L$ aliquots of acid (~2 equiv each) into a solution of ZnO NCs with 10 equiv Cp^*_2Cr.

The same trends were observed with the stronger reducing agent Cp^*_2Co. After a solution of NCs was initially reduced with 20 equiv Cp^*_2Co to $n_{e-} \approx 1.4$, addition of $[H(Et_2O)_2{}^+][BAr^F{}_4{}^-]$ caused a roughly linear increase in n_{e-} up to at least 15 e^-/NC (Figure 4). This is substantially more reduction than can be achieved for the same NCs by the photochemical process of eq 1 (n_{e-}(max) ≈ 6[8b]).

The above reactions are summarized in the proton-coupled electron transfer (PCET) square scheme in Scheme 2. The facilitation of reduction by stoichiometric protons is qualitatively consistent with the effect of pH on metal-oxide band-edge energies. However, the traditional ~60 meV/pH

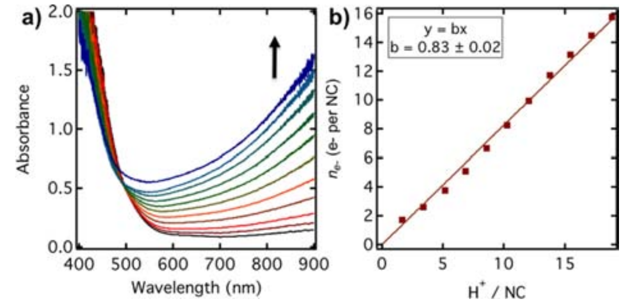
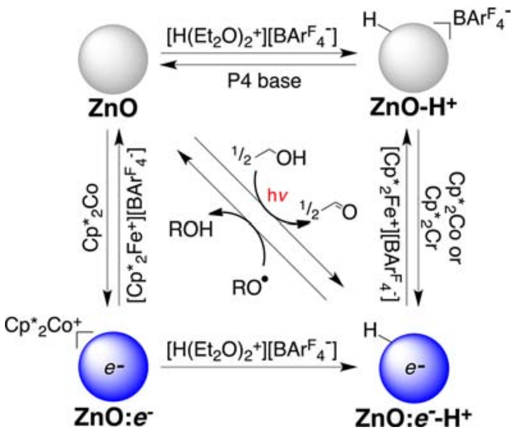


Figure 4. (a) Absorption spectra of ZnO NCs (1×10^{-4} M, $d = 4.3$ nm) with 20 equiv Cp^*_2Co (bottom black trace), then with 10 μL (1.7 equiv each) aliquots of $[H(Et_2O)_2^+][BAr^F_4{}^-]$ in THF. After ~20 equiv of acid, the NCs precipitated. (b) Plot of n_{e-} vs equivalents of acid.

Scheme 2. Reactions Interconverting Reduced and Protonated ZnO NCs



linear relationship for band-edge energies seems to suggest a 1:1 e^-/H^+ stoichiometry via the Nernst equation,[3,15] but for $Cp^*_2Cr/[H(Et_2O)_2^+][BAr^F_4{}^-]$ titrations a much smaller e^-/H^+ ratio is observed (Figure 3).

Thus the ZnO NCs are more extensively reduced with H^+ as a counterion compared to oxidized metallocene as the counterion. These results indicate that the coupling between H^+ and the NC is significant. The protonated NCs are drawn with an H^+ on the surface (i.e., a surface hydroxide), but the extra proton could be present as an intercalated H^+. A $ZnO{:}e^-{-}H^+$ NC with an intercalated H^+ would be related to the much-discussed hydrogen (atom)-doped bulk ZnO.[16] While further studies will examine this structural issue, the results reported here show that a few protons associated with the NCs strongly affect their reactivity.

Moreover, one striking result is that the difference in n_{e-}(max) obtained using Cp^*_2Co vs Cp^*_2Cr is much smaller than would be expected from the difference in their reduction potentials. Cp^*_2Co is a 400 mV stronger reductant than Cp^*_2Cr, from cyclic voltammetry in THF/toluene mixtures (Supporting Information Figure S2). This difference should result in a $>10^6$ difference in the equilibrium constants for NC reduction (59 mV = 10 × in K_{eq} from $\ln K_{eq} = -nFE°/RT$). However, using a common batch of acidified NCs, Cp^*_2Co injects only an average of roughly three times more electrons than Cp^*_2Cr (Supporting Information Figure S8). This observation may be related to the phenomenon of Fermi level pinning observed at some semiconductor/liquid interfaces.[17]

In conclusion, the addition of few protons strongly affects the redox chemistry of dodecylamine-capped ZnO nanocrystals in toluene/THF solutions. Protons can be added to the NCs in a stoichiometric fashion, either by addition of acid or by photochemical charging followed by oxidation. Cp^*_2Cr reduces the ZnO NCs only when protons are added, and the extent of NC reduction by Cp^*_2Co is greatly enhanced by added protons. This use of stoichiometric proton and reductant titrations is a powerful approach to study the factors underlying the redox properties of these free-standing colloidal NCs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental methods, optical/near-IR and EPR spectra, and electrochemical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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