

Comparison of Extra Electrons in Colloidal *n*-Type Al³⁺-Doped and Photochemically Reduced ZnO Nanocrystals

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Nanocrystal synthesis. Detailed descriptions of the syntheses of AZO¹ and ZnO^{2,3} NCs have been reported previously and are summarized here for completeness.

AZO nanocrystals: Solutions of (A) 1 mmol zinc stearate, 3 mmol oleic acid and 0.05, 0.1, 0.2 mmol aluminum acetylacetonate in 4 ml octadecene for a doping content of 1.8%, 2.5%, and 5.4% (as determined by ICP-AES analysis), respectively, and (B) 10 mmol 1,2-HDDIOL in 11 ml octadecene were degassed at 140 °C under argon for 1 h. The temperature of B was increased to 260 °C and A was rapidly injected. Following injection, the temperature dropped to 240 °C, where it was held for 5 h to allow NC growth. The resulting NCs were washed by precipitating with ethanol, collecting by centrifugation, and resuspending in hexane. On the third wash the NCs were suspended in 1:1 hexane/octane. To prepare dodecylamine-ligated AZO NCs, excess dodecylamine was added to the NC suspension and this solution was sonicated for 30 min. Following sonication, the NCs were washed twice by precipitation with ethanol and resuspension in toluene. This process was repeated a total of three times to ensure effective ligand exchange.

ZnO nanocrystals: A solution of 22 mmol tetramethylammonium hydroxide pentahydrate in 40 ml ethanol was added dropwise to a stirred solution of 13 mmol zinc acetate dihydrate in 135 ml dimethylsulfoxide at room temperature. NCs were grown for ~24 h, after which the reaction was stopped by precipitation with ~300 ml ethyl acetate. NCs were collected via centrifugation and resuspended in ethanol, followed by precipitation with heptane. The resulting pellet was suspended in ethanol and precipitated by adding dodecylamine that had been heated to 180 °C. The NCs were then collected via centrifugation and the resulting pellet was heated in

dodecylamine under N₂ at 180 °C for 20 min. These NCs were washed by 3 cycles of precipitation with ethanol, collection by centrifugation, and resuspension in toluene.

Physical Characterization. All electronic absorption and electron paramagnetic resonance (EPR) spectra were measured on colloidal suspensions at room temperature. Absorption spectra were measured using a Cary 500 spectrometer. EPR spectra were collected using a Bruker EMX X-band spectrometer with a SHQE resonator operating at 9.8 GHz. EPR *g* values were measured using diphenylpicrylhydrazyl (DPPH) as a reference. The ZnO TEM data were collected using a FEI Tecnai G2 F20 at the University of Washington Center for Nanotechnology User Facility. The AZO TEM data were collected using a JEOL 2100 microscope at LBNL.

Electron counting by titration with [FeCp*₂][BAR_F]. A 6 μM solution of dodecylamine-capped ZnO NCs in 2 ml toluene/THF (1:1) was prepared anaerobically. THF was used to aid the solubility of [FeCp*₂][BAR_F]. The NCs were charged by exposure to UV irradiation, and the NIR absorption was monitored periodically. Once the NIR absorption stopped changing, the NCs were considered to be charged to the maximum extent achievable with this photochemical method. To the maximally charged NCs, several 20 μl aliquots of 4.9 mM [FeCp*₂][BAR_F] in THF were added and the reduction of the NIR absorption was monitored. Figure S1a plots the absorption spectra of the uncharged NCs and maximally charged NCs with sequential additions of [FeCp*₂][BAR_F]. The NIR absorption decreases linearly in proportion to the added [FeCp*₂][BAR_F]. Figure S1b plots the difference in absorption between the charged and uncharged NCs at each stage of titration.

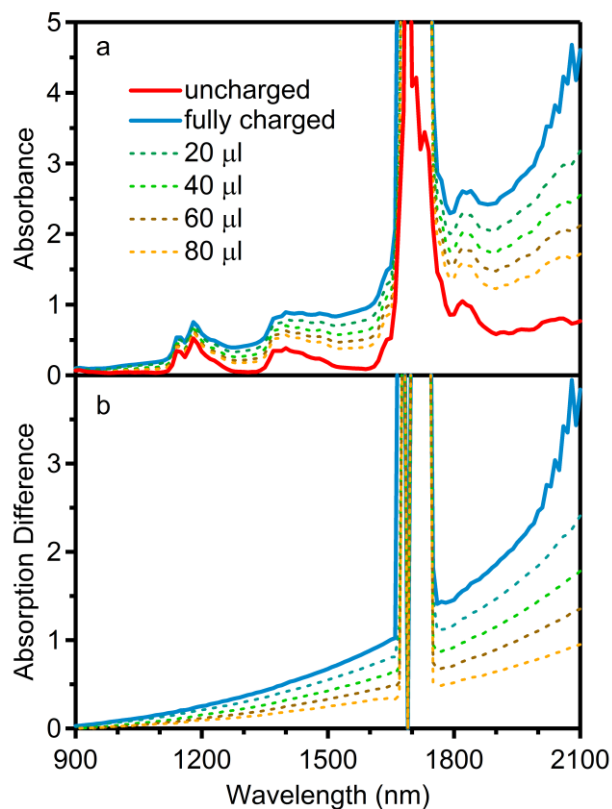


Figure S1. (a) NIR absorption spectra of uncharged ZnO NCs and charged ZnO NCs in 1:1 toluene/THF (6 μM) with titration of $[\text{FeCp}^*_2][\text{BAr}_\text{F}]$. (b) Difference in absorption between charged and uncharged NCs at each stage of titration.

To determine the equivalence point, the difference in absorption at various wavelengths was plotted as a function of added $[\text{FeCp}^*_2][\text{BAr}_\text{F}]$. This plot is shown in Figure S2a. The solid lines are linear fits to the data. From these fits, the points at which there is no difference in absorption (*i.e.*, the NCs are no longer charged) were determined and used to calculate the average number of electrons per NC ($e^-_{\text{CB/NC}}$). There is some scatter when the data are analyzed this way, so the the absorption differences integrated over low- and high-energy intervals were plotted (Figure S2b). The integrated intensities should be less sensitive to small baseline shifts and solvent peaks. Both data sets converge to the same crossing point of 48 $e^-_{\text{CB/NC}}$. The NCs were therefore concluded to contain an average of $\sim 48 e^-_{\text{CB}}$ each. This amount corresponds to an electron density of $9.2 \times 10^{19} \text{ cm}^{-3}$ for a spherical 10 nm NC.

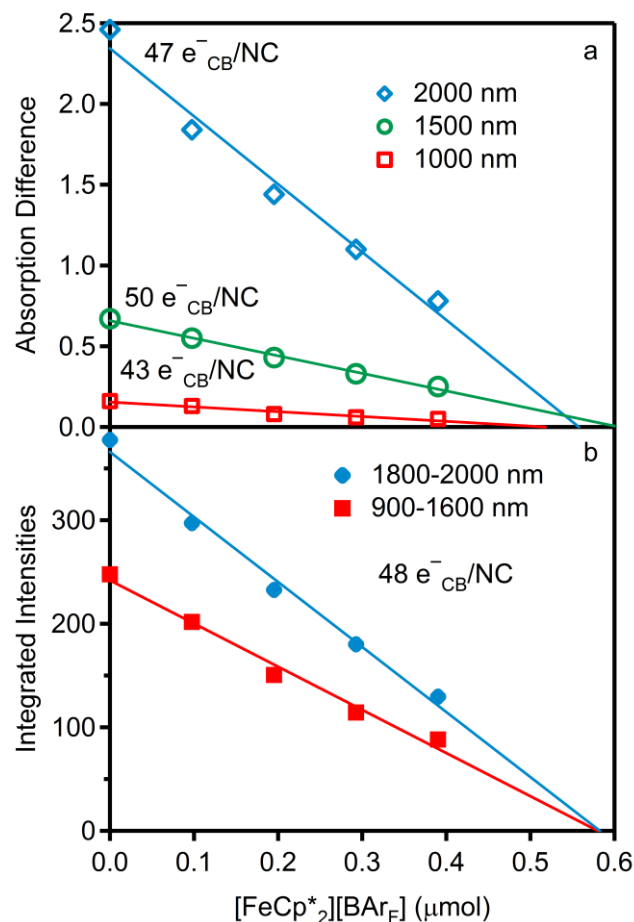


Figure S2. (a) Difference in absorption (from Figure S1b) at various wavelengths plotted as a function of mol $[\text{FeCp}^*_2][\text{BARF}]$ added. (b) Integrated absorption differences for two integration intervals, as a function of titration. The lines are fits to the data.

For the comparison with AZO by absorption and EPR spectroscopies presented in the manuscript, a 6 μM anaerobic solution of the same NCs in toluene was prepared. THF was not used in these experiments due to its incompatibility with room-temperature EPR experiments. The ZnO NCs were charged to an intermediate level such that the NIR absorption closely matched that of the AZO NCs (Fig. 2 of manuscript, referred to as the “highly charged” ZnO NCs). Figure S3a shows the NIR absorption spectrum of these uncharged and highly charged ZnO NCs. The difference compared to that of the highly charged NCs is shown in Figure S3b. The difference in absorption of the highly charged NCs is $\sim 2/3$ that of the maximally charged NCs, from which these highly charged NCs were determined to contain $32 e^-_{\text{CB}}/\text{NC}$ on average.

It is noted that this analysis assumes the same extinction coefficient for e^-_{CB} in toluene and in 1:1 toluene/THF.

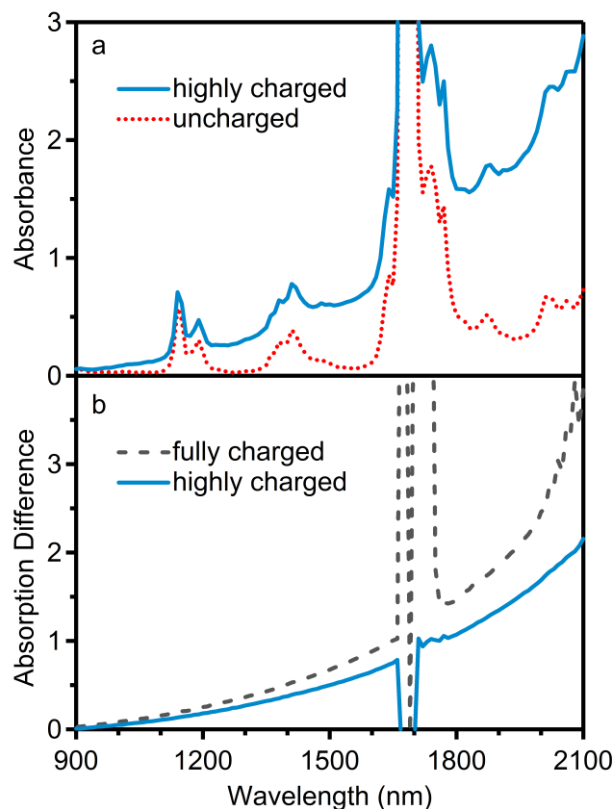


Figure S3. (a) NIR absorption spectra of uncharged and highly charged ZnO NCs in toluene (6 μ M). (b) Difference in absorption for maximally charged (taken from Fig. S1b) and highly charged ZnO NCs.

The titration of AZO NCs with $[\text{FeCp}^*_2][\text{BAR}_F]$ described in the main text (Fig. 3) was performed under the same conditions as the titration of charged ZnO NCs. Figure S4 shows the absorption spectrum of anaerobically prepared dodecylamine-capped 5.4% AZO NCs suspended in 1:1 toluene/THF and mixed with various amounts of $[\text{FeCp}^*_2][\text{BAR}_F]$. No loss of NIR absorption is observed upon addition of $[\text{FeCp}^*_2][\text{BAR}_F]$ to the NCs. As $[\text{FeCp}^*_2]$ is added, absorption from $[\text{FeCp}^*_2]^+$ appears with a maximum at ~ 780 nm. The immediate appearance of $[\text{FeCp}^*_2]^+$ absorption without loss of AZO NIR absorption indicates that no electrons are transferred from AZO to $[\text{FeCp}^*_2]^+$ (to form the colorless FeCp^*_2). To rule out slow electron-transfer kinetics, the final titration point (most $[\text{FeCp}^*_2][\text{BAR}_F]$) was monitored for 24 h but still showed no loss of NIR absorption.

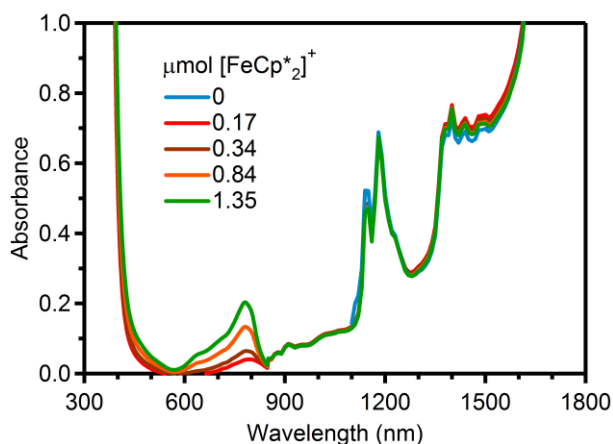


Figure S4. Electronic absorption spectra of 5.4% AZO NCs mixed with the various amounts of $[\text{FeCp}^*_2][\text{BAR}_F]$ indicated. Addition of $[\text{FeCp}^*_2]^+$ does not lead to decrease in AZO NIR absorption, but is accompanied by an increase in absorption of the $[\text{FeCp}^*_2]^+$ band centered at ~ 780 nm.

Comparison of reactivity toward MB^+ . Methylene blue (MB^+) undergoes facile two-electron proton-coupled reduction in the presence of electron donors to form the doubly reduced leuco methylene blue (LMB, eq S1a). LMB formation can be reversed upon reoxidation (eq S1b).⁴ By writing eq S1b, we do not intend to literally identify the fate of the reduced O_2 , which has not been investigated here. In contrast with the reactions with $[\text{FeCp}^*_2]^+$ described above, this reaction (like that with O_2 in air) involves proton-coupled electron transfer.



To illustrate the difference in reactivities of AZO and photochemically charged ZnO nanocrystals, samples of each were mixed with MB^+ under anaerobic conditions. MB^+ dissolved in ethanol was added to the NCs suspended in toluene. Figure S5a shows the absorption spectrum collected after anaerobic mixing of reduced ZnO NCs with excess MB^+ (solid line). Exposing this mixture to air increases the MB^+ absorption (circles), indicating formation of MB^+ via re-oxidation of LMB. LMB shows no absorption in this spectral range. Figure S5b shows the MB^+ absorption spectra obtained from the same experiment performed with AZO NCs. In this

case, exposing the reaction mixture to air does not increase the MB^+ absorption, indicating that no LMB was present and therefore that no electron transfer from the AZO NCs occurred. This experiment is solely intended to illustrate the reactivity difference, and no attempt was made to quantify the number of electrons in the photochemically charged ZnO using MB^+ as the acceptor as was done with $[\text{FeCp}^*_2][\text{BARF}]$ above.

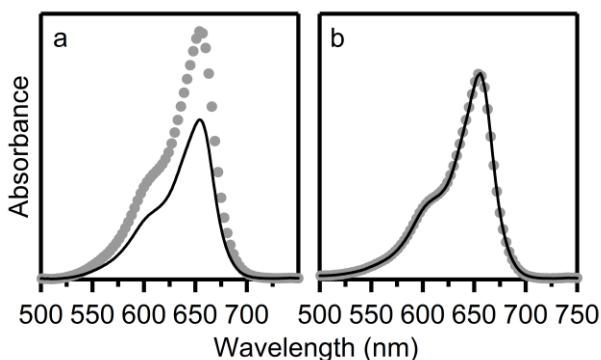


Figure S5. MB^+ absorption spectra (solid lines) collected after anaerobic mixing with (a) photochemically charged ZnO and (b) AZO NCs suspended in toluene. The gray circles show the absorption spectra of the same mixtures after exposure to air. LMB shows no absorption in this spectral range.

References

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