

## Electronic Supplementary Information for:

### Electron trapping on Fe<sup>3+</sup> sites in photodoped ZnO colloidal nanocrystals

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#### Experimental methods

1% of colloidal Fe doped ZnO nanocrystals were prepared using previous method.<sup>1</sup> Briefly, 0.01 cation mol fraction of Fe(OAc)<sub>2</sub> was added to 2.5 mmol of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O dissolved in 25 mL DMSO. 1.7 equivalents of tetramethylammonium hydroxide was dissolved in 7.7 mL of ethanol was added dropwise into Zn precursor under vigorous magnetic stirring to initiate nucleation and growth. After 5 h of growth, the nanocrystals were precipitated with ethyl acetate, resuspended in heptane and washed with ethanol. The final particle size was controlled by heating the nanocrystal in dodecylamine at 180 °C for different time. For medium size, quantum-confined Fe doped ZnO QDs the heating time was 15min and for larger Fe doped ZnO NCs the heating time was 2h. After reaching the final size, nanocrystals were precipitated and washed with ethanol. The particles were dried under vacuum for 2 h, transferred to the glove box and suspended in degassed hexanes with 5% ethanol as the hole quencher.

Photodoping was performed by placing the sample in an air-tight vial and irradiating with the light from either a 75 W or 1000 W Xe lamp for different times. The particle concentration is controlled to provide appropriate optical densities for both the band gap (pathlength = 0.05 mm) and ligand to metal charge transfer (pathlength = 1 cm). For each charging, the vial was took out from glove box with air tight cap and charged for different time. After each charging, the vial was put back in the glove box and the sample was transferred to the air-tight 1-cm cuvette (1.5 mL), demountable KBr cell with 0.05-mm pathlength, and air-tight EPR tube (0.4 mL). The band gap absorption, localized surface plasmon resonance (LSPR), LMCT transition and room-temperature EPR were collected within 10 minutes after sample transfer. Electronic absorption spectra were collected using on a Varian Cary 50. MIR spectra were collected on a Varian 670 FT spectrometer equipped with a KBr beam splitter and DLaTGS detector. EPR spectra were collected on a Bruker Elexsys E-500 at X-band. Mössbauer spectra were collected in the Mineral Spectroscopy Laboratory at Mount Holyoke College using a WEB Research Co. model WT302 spectrometer and a source of ~60 mCi <sup>57</sup>Co on 5% Fe-doped ZnO powders dispersed in matrix of sugar.

## Results

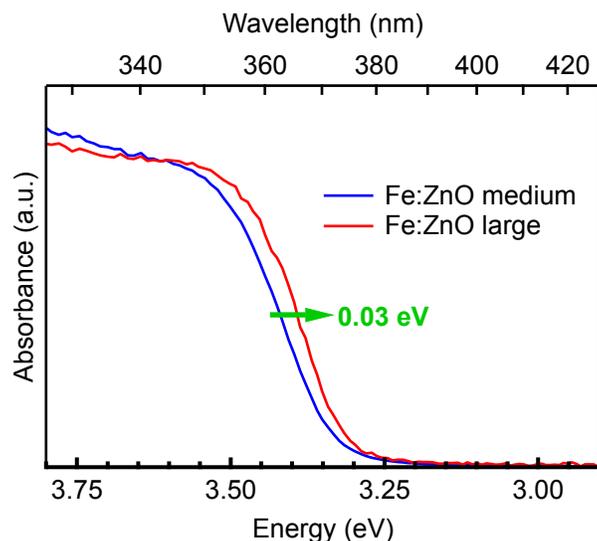


Figure S1. Electronic absorption spectra of the band gap transition of nominally 1% Fe-doped ZnO medium (blue) and large (red) colloidal nanocrystals. The energy at half-height is 0.03 eV redshifted in the larger nanocrystals.

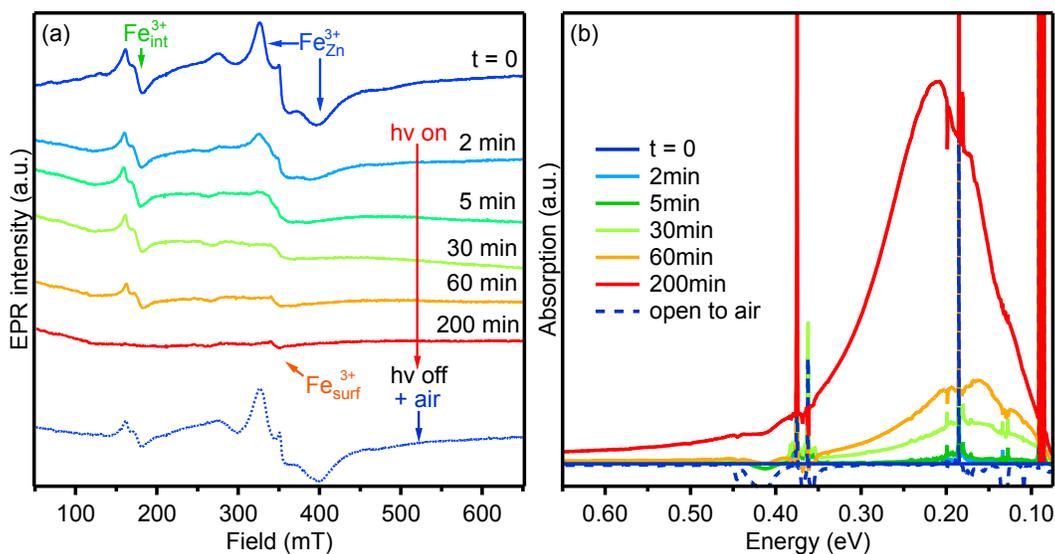


Figure S2. (a) EPR and (b) MIR spectra of nominally 1% Fe-doped ZnO QDs ( $\bar{r} \geq 3.2$  nm) as a function of photodoping with a 1000 W Xe lamp instead of the 75 W Xe lamp used for the smaller QDs shown in Figure 1 of the main text. The appearance of the LSPR in the MIR occurs *before* all the Fe<sup>3+</sup> has disappeared by EPR spectroscopy confirming the coexistence of Fe<sup>3+</sup> and conduction band electrons in these unconfined Fe-doped ZnO QDs. With increasing irradiation times, the LSPR blueshifts in agreement with previous photodoping studies of ZnO QDs.<sup>2</sup>

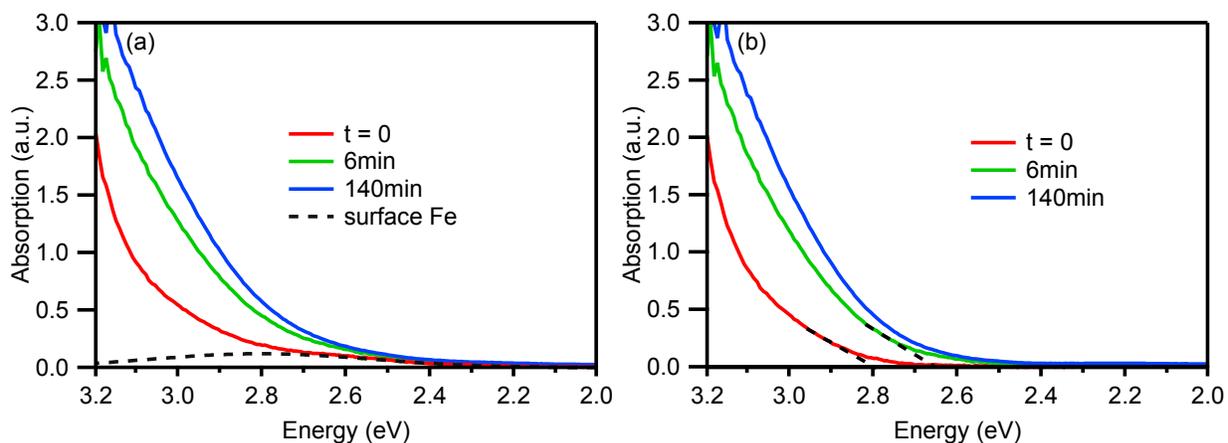


Figure S3. (a) Absorption spectra of the LMCT transition of 1% Fe-doped ZnO ( $\bar{r} = 2.8$  nm) at different photodoping times after subtracting the absorption spectrum of pure ZnO with the same concentration and size. The contribution from surface Fe does not change during photodoping as shown in the EPR spectra in Figure S1. We therefore estimated a broad absorption from this surface Fe<sup>3+</sup> (shown as a dashed line) and subtracted it from the absorption spectra shown in (a). The resulting corrected absorption spectra is shown in (b). The thresholds of LMCT transitions involving the different Fe species are estimated at  $LFe_{Zn}^{3+CT} = 2.8$  eV,  $LFe_{Zn}^{2+CT} = 2.65$  eV, respectively.

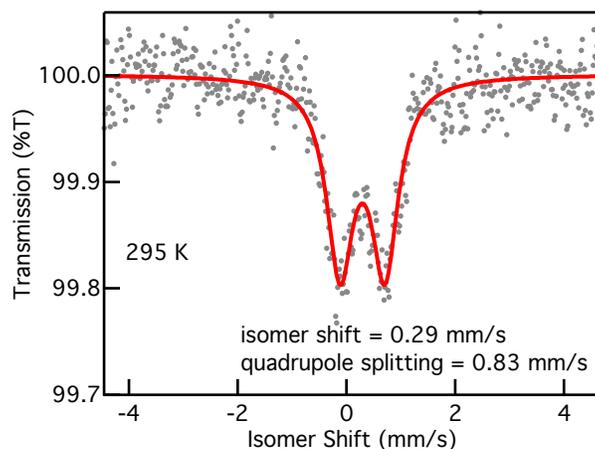


Figure S4. Room temperature Mössbauer spectra of 5% Fe-doped ZnO QD powders dispersed in a sugar mixture. The fit to the spectra was performed using a double-Lorentzian lineshape with the widths of the two Lorentzian bands fixed. The experimental isomer shift and quadrupole splitting are in agreement with previously reported room temperature spectra of Fe<sup>3+</sup> in ZnO.<sup>3</sup>

## References

- 1 D. M. Zhou and K. R. Kittilstved, *J. Mater. Chem. C*, 2015, **3**, 4352-4358.
- 2 A. M. Schimpf, C. E. Gunthardt, J. D. Rinehart, J. M. Mayer and D. R. Gamelin, *J. Am. Chem. Soc.*, 2013, **135**, 16569-16577.
- 3 G. Y. Ahn, S.-I. Park, I.-B. Shim and C. S. Kim, *J. Magn. Magn. Mater.*, 2004, **282**, 166-169.