Supporting Information for: Control over Fe³⁺ speciation in colloidal ZnO nanocrystals

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Fig. S1 Histograms from TEM particle analysis as a function of Fe³⁺:ZnO growth times for samples shown in Figure 4: (a) 1 min 30 sec (b) 20 min (c) 5h. Overview TEM images are shown in the right panel.



Fig. S2 Powder X-ray diffraction patterns of 0.15% (bottom) and 2.0% (top) Fe:ZnO. The vertical lines with varying intensity are the reflections from bulk wurtzite ZnO (ICSD #82028). The asterisk (*) above the (102), (2-10) and (103) reflections denote that these peaks were fit to a Gaussian function and used in the Scherrer equation to determine the average grain size and deviation for the two samples. EPR spectra of these two samples were shown in Figure 2 of the text. Powder X-ray diffraction is less sensitive than EPR spectroscopy to minute secondary phases considering the nominal concentration of Fe(OAc)₂ added to the Zn(OAc)₂.

In situ absorption spectroscopy during growth:

The absorption spectrum of Fe:ZnO QDs in the band gap region was monitored¹ *in situ* as a function of growth time after ZnO nucleation was initiated by the addition of 1.7 equiv of TMAOH. Figure S3 shows a broad feature at 3.5 eV in the absorption spectrum of Fe(OAc)₂ and Zn(ac)₂ in DMSO prior to adding TMAOH. This absorption band is tentatively assigned to the LMCT transition of pseudo-octahedral Fe²⁺, Fe³⁺, or basic Fe(III) acetate, [Fe₃O(OAc)₆(H₂O)₃]OAc in solution. After addition of TMAOH the 3.5 eV band decreases in intensity with increasing growth time and disappears after 90 s. Concomitantly, the ZnO first exciton gains intensity and redshifts in energy with increasing growth time. The growth dependence is consistent with nucleation and growth of a pure ZnO core followed by adsorption and incorporation of Fe³⁺.



Fig. S3 Absorption spectra of 0.5% Fe:ZnO before (black solid line) and after TMAOH addition at various reaction times (dashed lines), and ZnO after 90 s of TMAOH addition (red solid line, shaded under curve).



Fig. S4 Effect of varying the magnitude of *E*-strain on the simulated EPR spectrum ($\Delta D = 184 \times 10^{-4}$ cm⁻¹).

Table S1 Spin-Hamiltonian parameters used in the EasySpin simulations. Units on *D*, *E*, *a* and *F* are 10^{-4} cm⁻¹.

Sample	8	line width	$D(\Delta D)$	$E(\Delta E)$	а	F	ref.
Exp	2.0062	30 G	-594 (184)	0 (184)	41	4	this work
Single crystal ^a	2.0062	n/a	-594 (0)	0 (0)	41	4	[2]

^{*a*}The line width for the simulation shown in Figure 3a is 30 G.



Fig. S5 Zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility of 2% Fe³⁺:ZnO nanocrystals. The magnetic field strength for the FC curve and susceptibility measurement was 100 Oe. Although somewhat noisy as higher temperatures, the ZFC and FC susceptibility curves are superimposable, especially at lower temperatures. The mass is for the total mass of Fe:ZnO in the sample.



Fig. S6 Electronic absorption (left panel) and FTIR spectra (right panel) of Fe^{3+} :ZnO with Fe mol percent of 0, 0.15%, 0.78% and 2.0% suspended in hexanes. The IR region shows only features of the surface ligand (dodecylamine). The UV-Vis and FTIR spectra were collected using a demountable cell on the same samples. In other words, the sample pathlength and concentration was the same for both measurements. Note the change in the energy scale for the two panels.

Supporting Information References:

- 1 P. Dagtepe, V. Chikan, J. Jasinski and V. J. Leppert, *J Phys Chem C*, 2007, **111**, 14977-14983.
- 2 W. M. Walsh and L. W. Rupp, *Phys. Rev.*, 1962, **126**, 952-955.