Supporting Information:

Electrical Detection of Quantum Dot Hot Electrons Generated *via* a Mn^{2+}-Enhanced Auger Process

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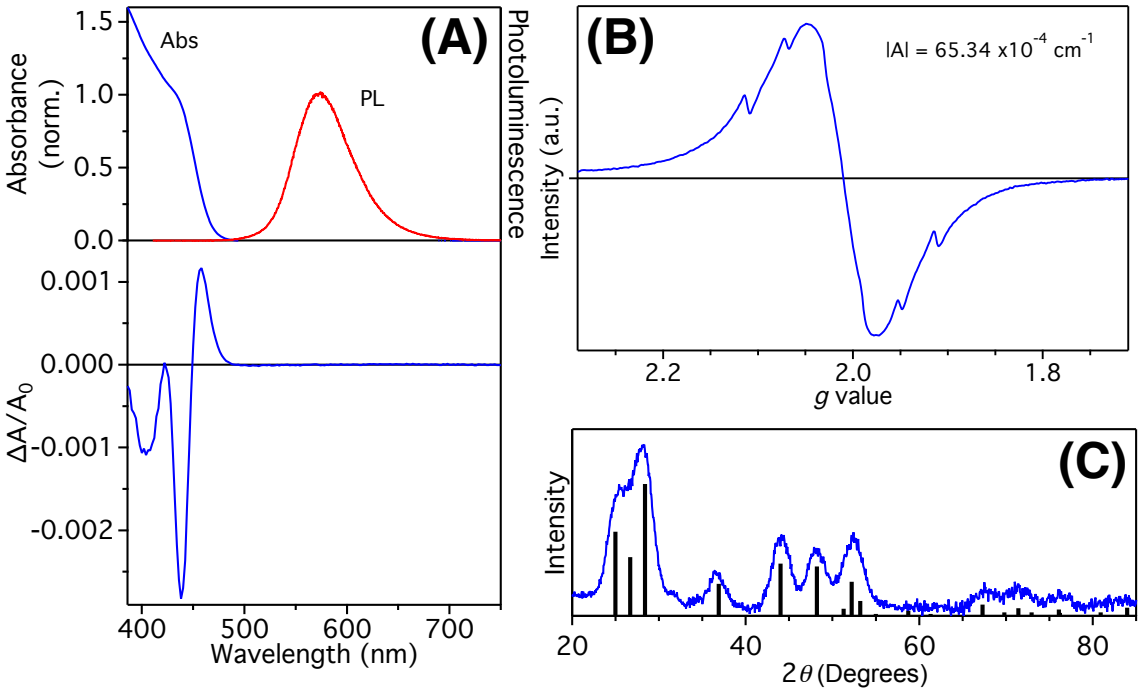

Figure S1. General characterization of $Cd_{0.9}Mn_{0.1}S$/ZnS core/shell QDs by room-temperature electronic absorption (**A**; top, left), photoluminescence (**A**; top, right), magnetic circular dichroism (MCD) at 1.5 T (**A**; bottom), EPR (**B**), and XRD (**C**). The bandgap is at 443 nm, corresponding to a QD diameter of 5.0 nm.[1] The PL is centered at 575 nm, consistent with the $^4T_1$-$^6A_1$ ligand-field transition of Mn^{2+}. The MCD shows inversion of the first excitonic Zeeman splitting, caused by *sp-d* exchange of the dopant with the CdS lattice.[2-3] The hyperfine splitting observed in the EPR spectrum is consistent with Mn^{2+} in a tetrahedral sulfide environment.[4] The XRD pattern is consistent with wurtzite CdS (black bars).

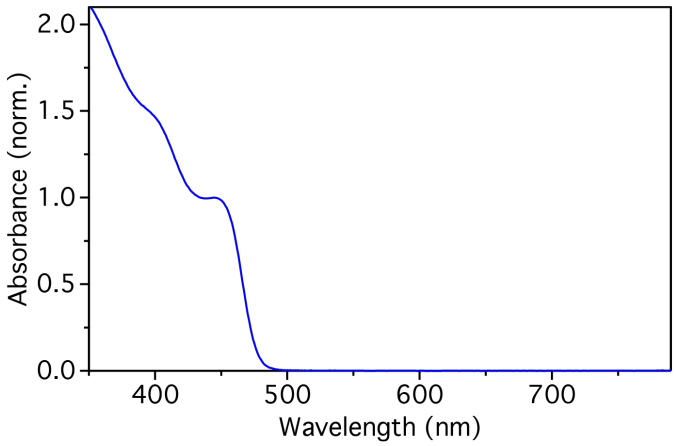

Figure S2. Room-temperature electronic absorption spectrum of undoped CdS/ZnS core/shell QDs used in the control device. The bandgap is at 453 nm, corresponding to a QD diameter of 5.4 nm.[1]

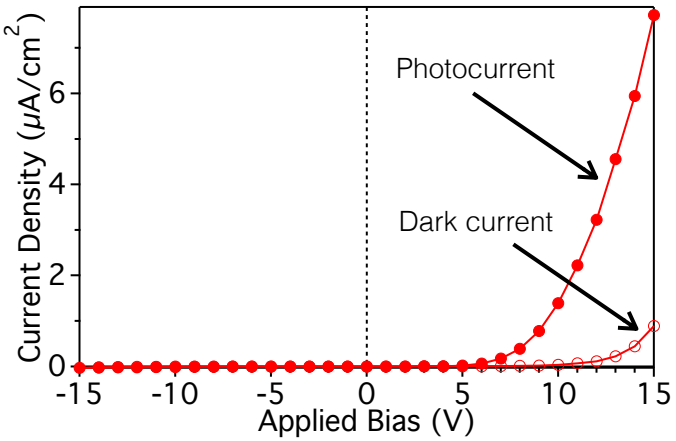

Figure S3. *J-V* characteristics at 300 K for the Mn^{2+}-doped multilayer device. The device acts as a rectifier, with current only flowing under positive bias. Under 0.12 μW/cm^2 illumination with a 405 nm laser diode, the photocurrent (closed circles) turns on at lower voltages than the dark current (open circles). The power-normalized difference between the photo- and dark current densities plotted here yields the responsivity plotted in Figure 2B of the main text.

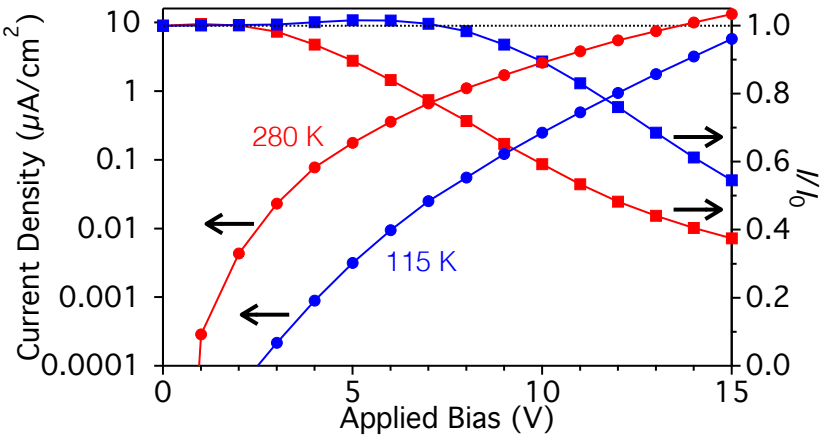

Figure S4. Voltage dependence of photocurrent density and PL in the Mn^{2+}-doped multilayer device, measured at 115 K (blue) and 280 K (red). At the higher temperature, the onset voltage is lower for both photocurrent and PL quenching. Note the log scale of the photocurrent densities.

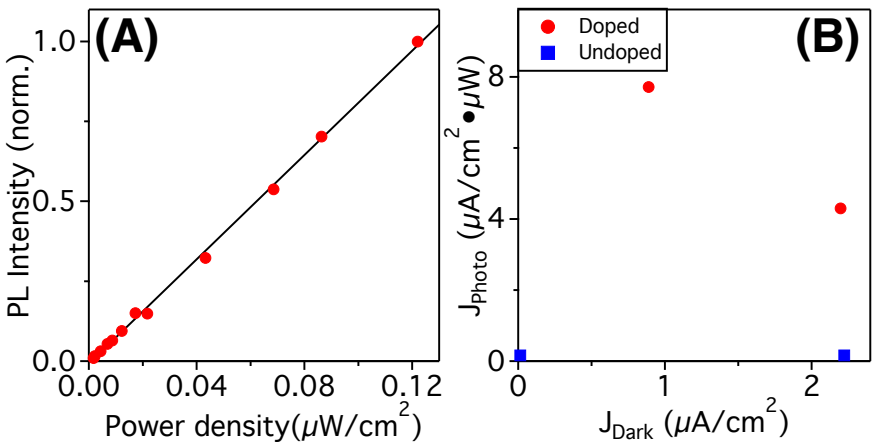

Figure S5. (A) PL intensity of the Mn^{2+}-doped multilayer device plotted vs excitation power (405 nm) over three orders of magnitude. The black line is a linear best-fit to the data. **(B)** Photocurrent density (normalized to excitation power) and dark current density (normalized to the same mask area as the photocurrent measurements) for different $Cd_{1-x}Mn_xS$ (red circles) and CdS (blue squares) multilayer devices, each measured at +15 V. The presence of Mn^{2+} increases the photocurrent relative to undoped devices. There is no detectable correlation between photocurrent and dark current, with or without Mn^{2+}.

Additional Methods Description

QD Characterization. Room-temperature electronic absorption spectra were collected for colloidal toluene suspensions of nanocrystals in 0.1 cm path length cuvettes using a Cary 500 spectrophotometer (Varian). Room-temperature magnetic circular dichroism (MCD) spectra were collected on colloidal toluene suspensions of nanocrystals in a 0.1 cm path length cuvette placed in a 1.5 T electromagnet oriented in the Faraday configuration. MCD spectra were collected using an Aviv 40DS spectropolarimeter. The differential absorption collected in the MCD experiment is reported as $\Delta A = A_L - A_R$, where A_L and A_R refer to the absorption of left and right circularly polarized photons in the sign convention of Piepho and Schatz.[3, 5] CW EPR experiments were performed on colloidal toluene suspensions of nanocrystals using an X-band Bruker EMX spectrometer. XRD data were collected from evaporated nanocrystal films on glass slides using a Bruker D8 Discover spectrometer at the University of Washington (UW) NanoTech User Facility.

Device fabrication. Ethanol and 1,7-heptanediamine (HDA) were purchased from Sigma-Aldrich. Zinc Sulfide (ZnS; 99.99%) was purchased from Kurt J. Lesker Company. Indium tin oxide (ITO) substrates were scrubbed with detergent solution (2 vol % Micro-90, International Products Corp., in purified deionized water), followed by sonication in deionized water, acetone, and isopropanol for 20 min each. The ITO substrates were then cleaned by air plasma treatment for 10 min. QD films were fabricated in inert atmosphere using a layer-by-layer spin-coating method.[6] QD films were fabricated from a solution of Mn^{2+}:CdS/ZnS core/shell QDs or undoped CdS/ZnS core/shell QDs in toluene (20 mg/mL) and a solution of the cross-linker 1,7-heptanediamine in anhydrous ethanol (0.5 v/v%). Each layer-by-layer deposition consisted of five steps: (1) A volume of 50 μL of QD solution was dropped onto the substrate and spin-coated at 1500 rpm for 60 seconds; (2) The QD film was transferred to a hot plate and annealed at 80 ºC for 2 min; (3) The QD film was then immersed in a solution of HDA at 80 ºC for 2 min to replace the long-chained oleylamine (OLA) ligands with HDA cross-linker; (4) The QD film was dried and annealed on the hot plate at 80 ºC for 1 min; (5) Residual OLA and HDA ligands on the QD film were subsequently removed by spin-coating twice with anhydrous ethanol. This layer-by-layer deposition was repeated 3 times to obtain a smooth QD film.

References

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