Supporting Information

Unusually Slow Electron Cooling to Charge Transfer State in Gradient CdTeSe Alloy Nanocrystal Mediated Through Mn Atom

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1) Materials:

Cadmium oxide (CdO, Aldrich), Manganese acetate (Aldrich), oleic acid (OA, Aldrich), trioctylphosphine (TOP, Aldrich, 90%), 1- octadecene (ODE, Aldrich), Selenium shot (Se, 99.99%) (Aldrich) and tellurium tellur (Te, 99.9%, Aldrich) were used to prepare Mn doped CdSe, CdTe NC and Mn doped CdTeSe alloy NC. AR grade chloroform and methanol were used for precipitation.

## 2) Synthesis of undoped and Mn doped CdTeSe gradient alloy NC:

Oleic-capped Cd-based NCs were synthesized after modifying previously reported method of high-temperature reaction in non-coordinating solvent octadecene (ODE).[1] In a three neck round bottom flask 1mmol CdO was taken and oleic acid (1mL) was added into it which acts as capping agent in high boiling octadecene solvent and allow the mixture to heat at ~200°C in inert atmosphere for complete dissolution for 20mins. Simultaneously TOP-Te and TOP-Se solution were prepared by dissolving 0.5mmol of each Te and Se in TOP (in octadecene solvent) and heat to ~200°C and 70°C respectively till complete dissolution. Hot TOP-Se solution was then added to TOP-Te solution. Now the reaction temperature of Cd-oleate was raised to 250°C and the mixture of TOP-Se and TOP-Te were injected at once for gradient alloying. The reaction mixture was allowed to keep at that temperature for 10mins to complete the alloying. The reaction was quenched by adding methanol to it once the temperature lies below 100°C and re-dissolved in chloroform. The washing of the alloy nanocrystal was carried out twice.

Synthesis of Mn doped CdTeSe alloy NC also carried out in a similar way after adding Mn acetate (1%) to CdO precursor initially in the reaction vessel.

Mn doped CdSe and Mn doped CdTe NCs were synthesized in a similar way where in the Cd/Mn mixture either TOP-Se or TOP-Te was injected respectively.

3) High resolution Transmission Electron Microscope Measurements:

High-resolution TEM (HRTEM) measurements were carried out using a JEOL–JEM-2010 UHR instrument operated at an acceleration voltage of 200 kV with a lattice image resolution of 0.14 nm. Mn-CdSe NC and Mn-CdSeTe alloy NC have dissolved in chloroform to take TEM image. A drop of sample is added to the TEM grid (200 Mesh Size Holey Carbon coated Cu Grid). The sample on the grid is heated in oven for 1/2 h at 40ºC to remove the excess chloroform. Particle size of Mn-CdSe determined to be ~ 2.8 nm and spherical in shape whereas for Mn-doped CdTeSe the average size of particle is ~3nm.
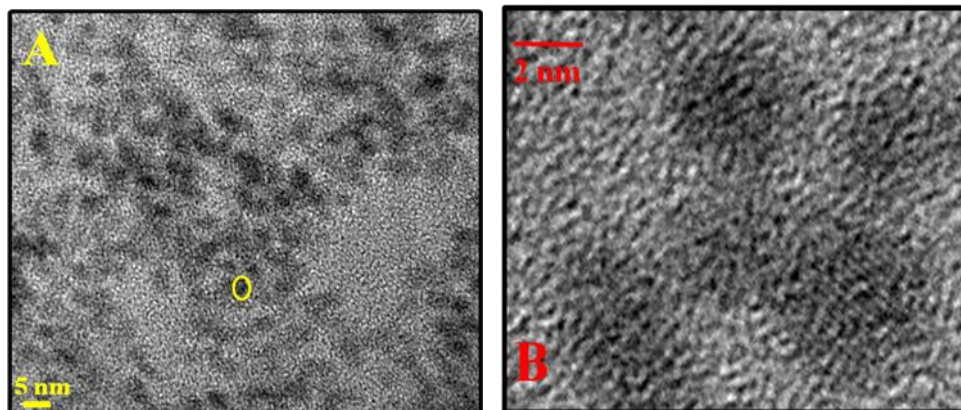

SI Figure 1: HRTEM images of (A) Mn doped CdSe NC and (B) Mn doped CdTeSe NC.

4) Electron Paramagnetic Resonance (EPR) Measurements

To detect the presence of Mn atom in Mn-CdSe and Mn-CdTeSe NC, 9.5 GHz Bruker ESP-300 spectrometer (X-band frequency) was used for EPR measurements. Experimental results clearly indicate that Mn resonance is splitted into six lines due to hyperfine coupling of five unpaired electrons in Mn for either of the NC.

The hyperfine constant (A) is calculated by taking the difference between two splitted lines which is determined to be ~93 Gauss for Mn-CdSe and ~95 Gauss for Mn-CdTeSe NC.
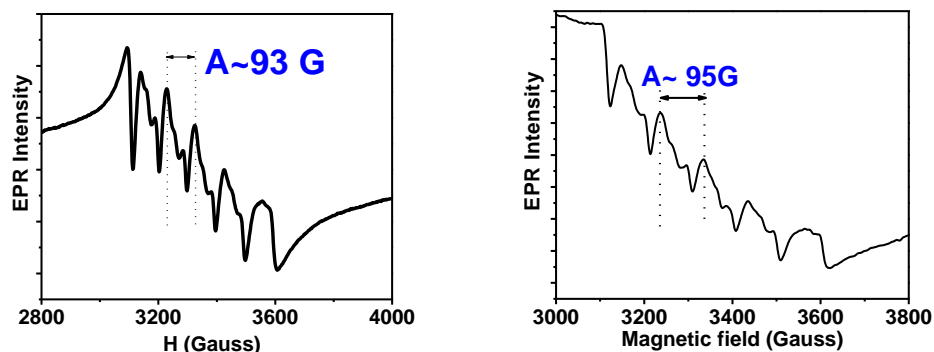
SI Figure 2: EPR spectrum of Mn-CdSe (Left) and Mn-CdTeSe (Right) NC.

5) Steady state optical absorption and emission studies undoped and Mn-doped CdSe, CdTe, and CdTeSe alloy NCs:

SI Figure 3 compares the steady state optical absorption and emission spectra of undoped (SI Figure 3A) and Mn-doped (SI Figure 3B) CdSe (trace a and a′), CdTeSe (b and b′) and CdTe (trace c and c′) NCs. Different excitonic absorption have been observed in the UV-vis spectra of all the undoped and Mn-doped NCs. Exciton absorption due to $1S_{3/2}$-$1S_e$ transition (1S exciton) appears at 520nm, 685nm and 675nm for undoped CdSe, CdTeSe and CdTe NCs where as
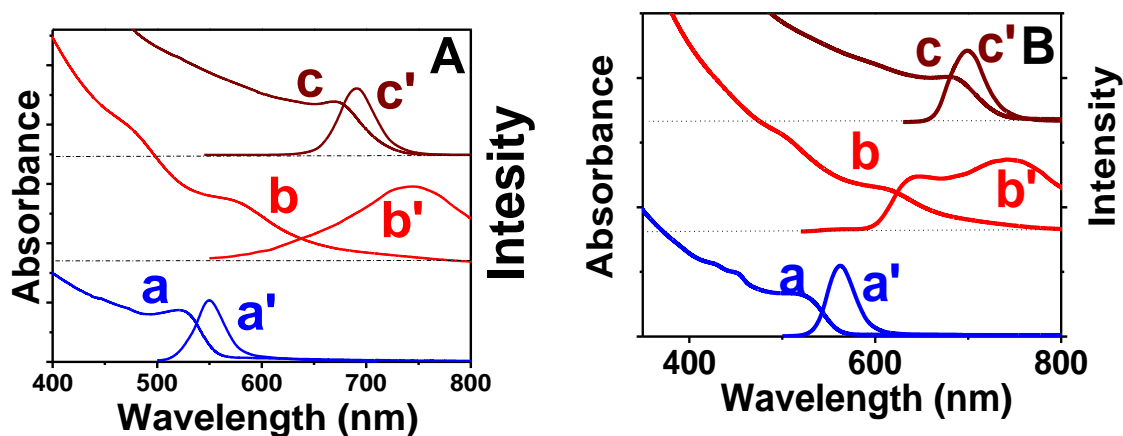

SI Figure 3: (A) Steady state optical absorption and emission spectrum of (a, a') CdSe, (b, b') CdTeSe and (c, c') CdTe quantum dots respectively. (B) Steady state optical absorption and emission spectrum of (a, a') Mn-doped CdSe, (b, b') Mn-doped CdTeSe and (c, c') Mn doped CdTe quantum dots respectively.

525nm, 615nm and 680nm for Mn-doped CdSe, CdSeTe and CdTe NCs respectively. Although UV-vis spectra shows both undoped and Mn-doped CdSe and Mn-doped CdTe absorbs up to 580nm and 750nm respectively, undoped and Mn-doped CdTeSe alloy NC absorbs beyond 800nm. Steady state emission spectra after exciting the 1S exciton, shows sharp band edge emission for undoped CdSe (550nm) and CdTe (693nm) whereas CdTeSe alloy shows broad emission peaking at 740nm having a blue tail (described in the main manuscript). Similarly Mn-doped CdSe (563nm) and Mn-doped CdTe (700nm) show sharp band edge emission whereas Mn-doped CdSTe shows broad dual emission (details described in the main text). No Mn PL has observed in any of the doped NCs which have been explained in the main manuscript. It is to be noted that both absorption and emission spectra (band edge) of undoped and Mn-doped alloy lies in between their constituent NCs.

## 6) Delayed Photoluminescence Studies

To confirm that luminescence at 560 nm for Mn-doped CdSe QD is purely due to excitonic emission, we have carried out the delayed photoluminescence spectrum after giving a delay of 100μs. It is clearly seen for Mn-doped CdSe QD material (SI Figure 4) that there is no luminescence after 100μs delay which ensure there is no admixture of Mn emission to the 560nm emission. PL decay trace starting from 100μs upto 20 ms has been carried out and shown in the inset of the Figure below.
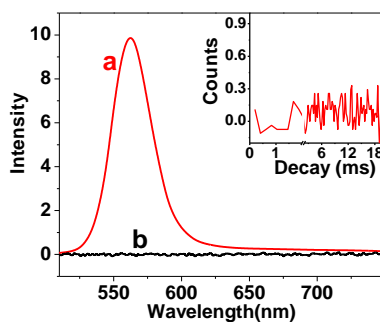
SI Figure 4: Photoluminescence (PL) spectrum of Mn-doped CdSe at a) 0 μs delay and b) 100 μs delay. (Inset) Long time (up to 20 ms) PL decay measurement.

7) Time resolved emission decay of undoped and Mn doped CdSeTe NC

To understand the existence of dual emission in CdTeSe and Mn-CdTeSe NC we have carried out time resolved emission measurement at both the emission peak positions. The emission lifetime at band edge position (610nm) for CdTeSe NC cab be fitted tri-exponentially with time constants 0.2 ns (60.5%), 2.3 ns (24%) and 17.5 ns (15.5%) with average lifetime of 14 ns. At CT position (740nm) the tri-exponential time constants are 0.64 ns (48.8%), 3.7 ns (21.5%) and 21.5 ns (29.7%) with average lifetime of 19ns. However for Mn-CdTeSe NC the emission lifetime at band edge position (630nm) cab be fitted bi-exponentially with time constants 3.96 ns (45.8%) and 34.95 ns (54.2%) with average lifetime of 21 ns. On the other hand at CT position (740nm) the bi-exponential time constants of each component increases and found to be 6.55 ns (41.4%) and 73.46 ns (58.6%) with average lifetime of 46ns. The higher emission lifetime for CT state is due to higher charge separation in the CT state.
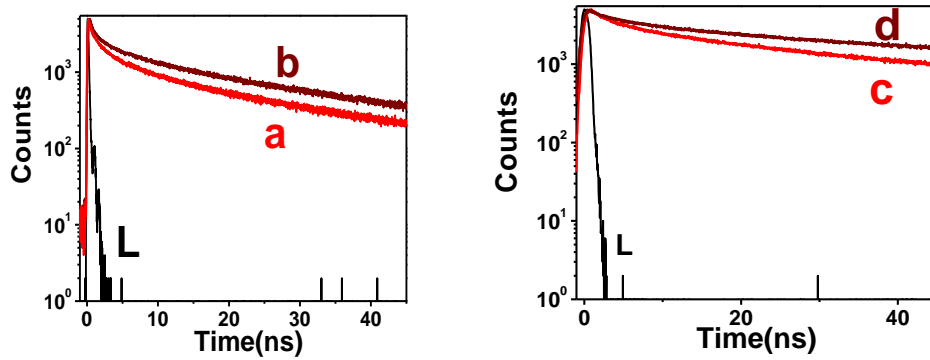
SI Figure 5: Time resolved emission decay trace of (Left) CdTeSe alloy at (a) 610nm, (b) 740nm, and (Right) for Mn-CdTeSe alloy NC at (c) 640nm and (d) 750nm after 490nm laser excitation. L stands for lamp profile of 490nm laser excitation source.

8) Electron Transfer reaction following Marcus theory:[2-5]

The ground state simple harmonic potential was used for Marcus theory analysis which can be expressed as: $G_{GS} = \frac{1}{2} K x^2$

Absorption and emission spectrum are de-convoluted to give band edge and CT state respectively. Below table shows the required parameters for Marcus theory analysis of Mn-CdSeTe NC.

	A_{CdTe}	A_{CT}	E_{CdTe}^{max}	E_{CT}^{max}	λ_{CdTe}	λ_{CT}	ΔG°_{CdTe}	a_{CdTe}	ΔG°_{CT}	a_{CT}
Mn-CdSeTe (K=2)	611.7nm 2.03eV	730nm 1.7eV	640nm 1.94eV	745nm 1.67eV	0.045eV	0.015eV	1.985eV	0.21	1.685eV	0.12

λ_{CdTe} and λ_{CT} have been calculated using the relation, $\lambda_{CdTe/CT} = \frac{1}{2} \Delta \nu$, where $\Delta \nu$ is stokes shift.
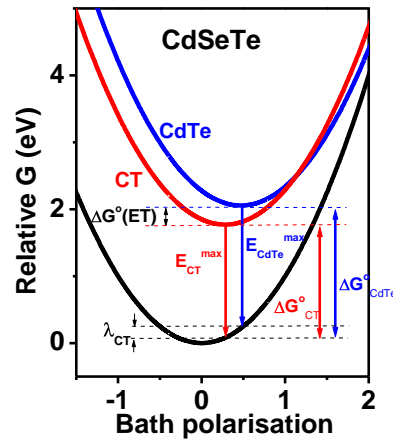
Again, $\Delta G^\circ_{CdTe/CT} = A_{CdTe/CT} - \lambda_{CdTe/CT}$

Therefore for Mn-CdSeTe, $\Delta G^\circ_{ET} = \Delta G^\circ_{CdTe} - \Delta G^\circ_{CT}$

$= 0.3$ eV

And $\lambda_{CT} = 0.015$eV

a_{CdTe} and a_{CT} were calculated using, $a = (2\lambda/K)^{1/2}$

SI Figure 6: Potential energy diagram of ground state, photo excited CdTe and CT dominated state using Marcus analysis for CdSeTe alloy NC respectively.

Similarly, for CdSeTe NC Marcus analysis has been carried out.

	A_{CdTe}	A_{CT}	E_{CdTe}^{max}	E_{CT}^{max}	λ_{CdTe}	λ_{CT}	ΔG°_{CdTe}	a_{CdTe}	ΔG°_{CT}	a_{CT}
CdSeTe (K=2)	586nm 2.11eV	675nm 1.83eV	620nm 2.0eV	743nm 1.67eV	0.055eV	0.08eV	2.055eV	0.23	1.75eV	0.28

$\Delta G^\circ_{ET} = 2.055 - 1.75 = 0.3$ eV and $\lambda_{CT} = 0.08$ eV.

9) Femtosecond Transient Absorption Spectrometer:

Ultrafast transient absorption measurements were carried out in femtosecond (0.1 ps-4 ns) transient absorption (TA) spectrometer which is based on multi-pass Ti: sapphire laser system (CDP, Moscow, 800 nm, <100 fs, 1.2 mJ/pulse, and 1 kHz repetition rate) and Excipro pump-probe spectrometer (CDP, Moscow). Briefly the pulses of 40 fs duration and 4 nJ energy per pulse at 800 nm obtained from a self-mode-locked Ti-Sapphire laser oscillator (Tissa 50, CDP, Moscow, Russia) were amplified in a multi-pass amplifier pumped by a 20W DPSS laser (Jade-II, Thales Laser, France) to generate 40 fs laser pulses of about 1.2 mJ energy at a repetition rate of 1 kHz. Pump pulse at 400 nm were generated by frequency doubling of the 800 nm pulse at a β-barium borate (BBO) crystal. The spectrometer is coupled with Multi channel detector head, with two 1024-pixels linear image sensors, 200 -1000 nm spectral response (10% of peak), up to 1 kHz readout rep rate. To generate visible probe pulses, about 1 μJ of the 800 nm beam is focused onto a 1.5 mm thick sapphire window. An imaging spectrometer is adapted to the detector head and connected to a computer via serial port with visible grating 300 –1100 nm spectral range which has 206 nm detection ranges. The pump beam diameter at the sample is ~350 μm, corresponding to an excitation density of 0.28 μJ/cm^2. A white light continuum (from 450 to 850 nm) was generated by attenuating and focusing ~10 μJ of the 800 nm pulse into a sapphire window and splitting into a probe and reference beam. The probe beam was focused with an Al parabolic reflector onto the sample (with a beam diameter of 150 μm at the sample). The instrument response function (IRF) for 400 nm excitation was obtained by fitting the rise time of the bleach of sodium salt of *meso* tetrakis (4 sulfonatophenyl) porphyrin (TPPS) at 710 nm and found to be 120 fs. The <N> (jσ) was maintained <1 to prevent multiexciton formation due to higher pump intensity. For all spectroscopy measurements, the samples were kept in a 1 mm cuvette and the experimental solutions were circulated to avoid sample bleaching during the course of the experiment. The data analysis and fitting at individual wavelengths were carried out by Lab-View program.[6]

10) Femtosecond Transient Absorption study of Mn-CdSe and Mn-CdTe NC:

SI Figure 7A, B depicts transient absorption spectrum of Mn-doped CdSe and Mn-doped CdTe NCs at 500fs to 1ns time delay. 1S excitonic bleach below 580nm region has been observed for

Mn/CdSe NC. In addition negligible positive absorption in the region 580-720nm has observed. On the contrary the TA spectrum of Mn/CdTe, in addition to one sharp bleach at 690nm (due to 1S exciton) shows another hump at 590nm which may attribute due to 1P exciton bleach. The bleach recovery kinetics at 1S bleach maxima position for both the NCs (in undoped and Mn-doped form) is shown in SI Figure 8. The multi-exponential fitted time constants are summarized in SI Table 1. The electron cooling time to conduction band edge for Mn-CdSe and Mn-CdTe has found to be 0.5ps and 2ps respectively as monitored by bleach growth kinetics.
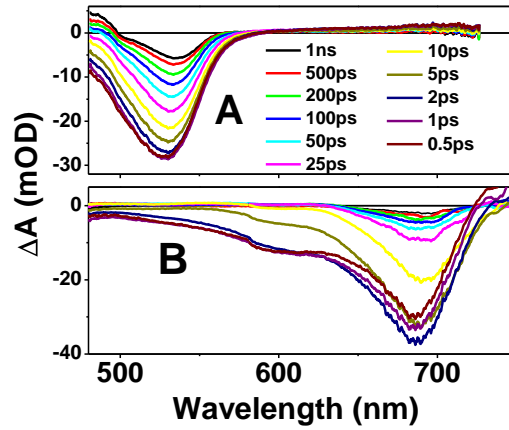
SI Figure 7: Ultrafast transient absorption spectrum of (A) Mn-doped CdSe and (B) Mn-doped CdTe NCs after 400nm laser excitation at different time delay.
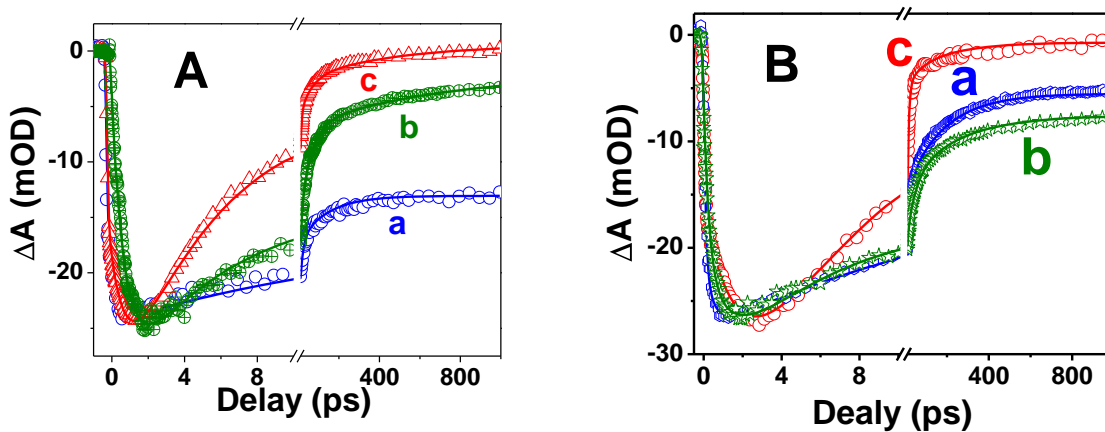

SI Figure 8: Bleach recovery dynamics of (A) undoped (a) CdSe (at 525), (b) CdTeSe (at 590 nm) and (c) CdTe (at 675 nm) NCs; B) Mn-doped (a) CdSe (at 530), (b) CdTeSe (at 615 nm) and (c) CdTe (at 680 nm) NCs at 1S excitonic position after 400nm laser excitation.

SI Table 1: Comparison of transient bleach recovery parameters at different wavelengths for undoped and Mn-doped NCs after 400nm laser excitation.

		Growth (Cooling) Dynamics		Recovery (Trapping/Recombination) Dynamics		
		τ_{g1} (%)	τ_{g2} (%)	τ_1 (%)	τ_2 (%)	τ_3 (%)
CdSe	525nm	0.1ps (90%)	0.6 ps (10%)	14 ps (32.8%)	140 ps (11.2%)	> 1 ns (56%)
Mn-CdSe	530nm	0.1ps (72%)	0.6ps (28%)	15ps (56%)	180ps (23%)	>1ns (21%)
CdTe	675nm	0.1 ps (65%)	1ps (35%)	5ps (78%)	55ps (21%)	>1ns (1%)
Mn-CdTe	680nm	0.1ps (60%)	2ps (40%)	7ps (81%)	60ps (13%)	>1ns (6%)

11) Ultrafast Transient Absorption spectrum of undoped and Mn doped CdTeSe alloy NCs:
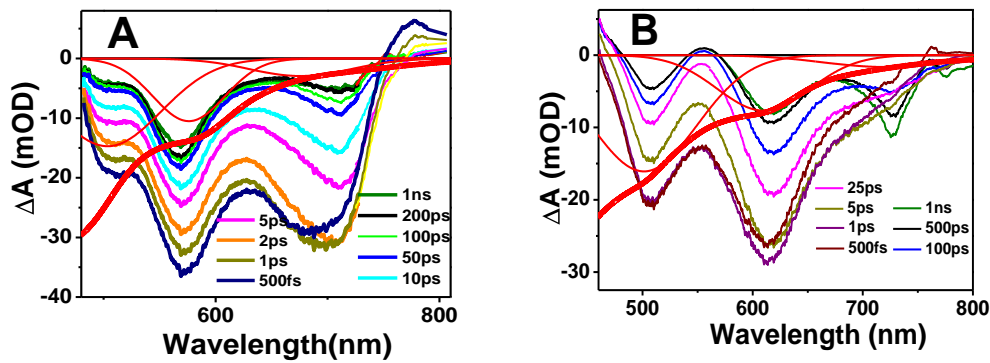
SI Figure 9: The overlaid inverted linear absorption spectra (along with de-convoluted spectra) to ultrafast transient absorption spectrum of (A) undoped and (B) Mn-doped CdTeSe alloy NCs

after 400nm laser excitation at different time delay. The thick red line indicates inverted linear absorption spectra and thin red lines are corresponding de-convoluted absorption spectrum.

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