Electronic Supplementary Information

Davydov Splitting in Cadmium Vacancy Emission, Ferromagnetism and Photosensitivity in Manganese incorporated CdS nanocrystals

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ESI. Table 1: Average particle size for SLS/BD and SLS/PD assisted Mn^{2+}-CdS nanocrystals from XRD measurement using Debye-Scherer formula.

System	Average particle size (nm)	
	SLS/BD	SLS/PD
CdS	9.0	12.5
0.1% Mn^{2+}-CdS	9.2	13.5
0.5% Mn^{2+}-CdS	9.0	12.0
1% Mn^{2+}-CdS	10.5	14.5
5% Mn^{2+}-CdS	10.0	14.0

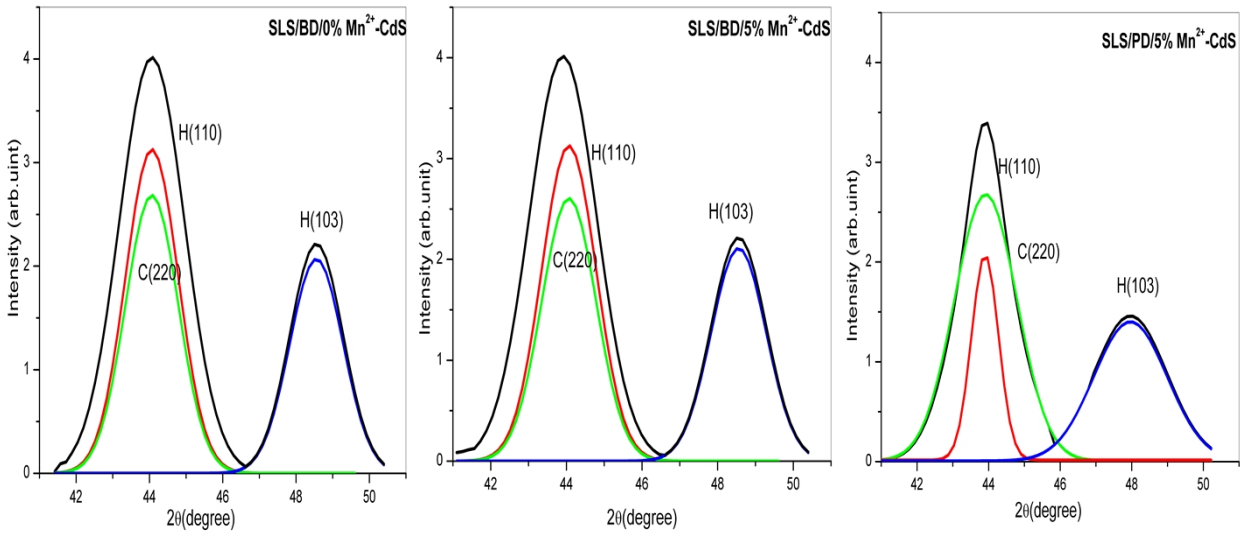
Deconvolution of XRD pattern using Short and Steward Method

The quantitative percentage of cubic or hexagonal phase in a given system of Mn^{2+}/CdS can be calculated from the following equation which was earlier proposed by Short and Steword.[23]

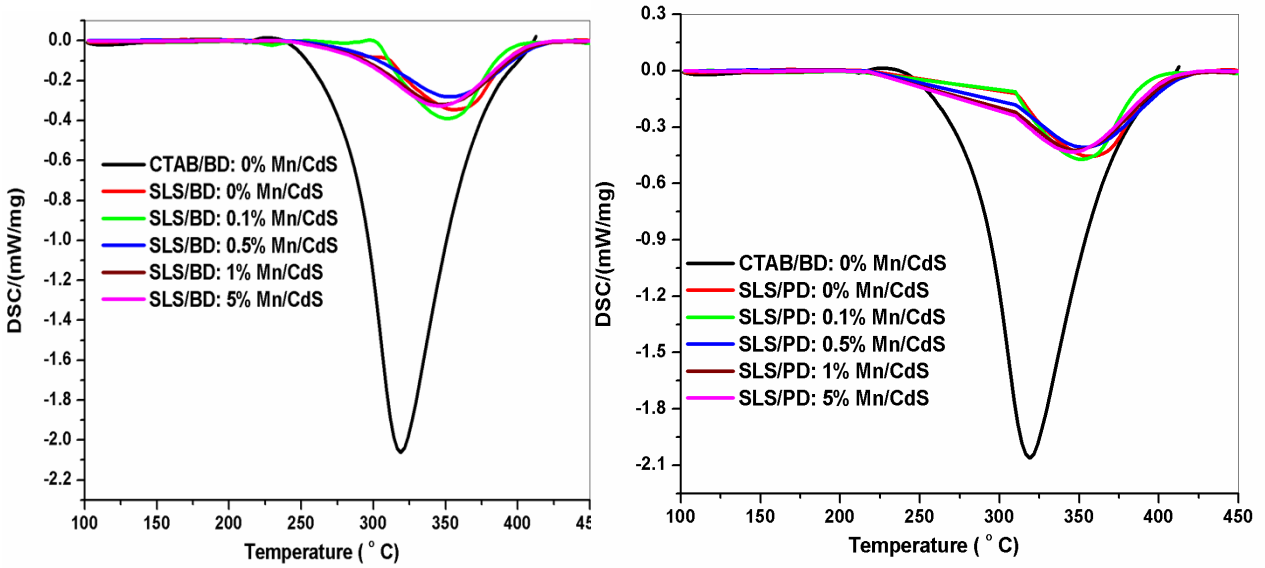
$$H = \frac{1.96R}{0.96R + 1} \qquad (1)$$

where R is the ratio of the integrated intensities of the cubic and hexagonal components measured in the ranges 2θ = 46.75-48.75˚ (peak H (103)) and 2θ = 42.75-44.75˚ (peak H (110) or C (220)). A careful deconvolution of the XRD patterns of all Mn^{2+} added samples was performed in order to get the ratio of cubic *vs* hexagonal as defined in equation (1). The resulting values are

summarized in Table 1. While the peak around 2θ ≈ 42-45° accounts for both hexagonal (110) and cubic (220), the peak at 48.2° (in our work) corresponds to pure hexagonal phase (103). The deconvolution profile for SLS/BD and SLS/PD samples are shown below (ESI Fig. 1)



ESI Fig. 1. Deconvolution of XRD pattern for SLS/BD assisted CdS (left) and 5% Mn^{2+}-CdS (middle) and SLS/PD assisted Mn^{2+}-CdS (right) nanocrystals

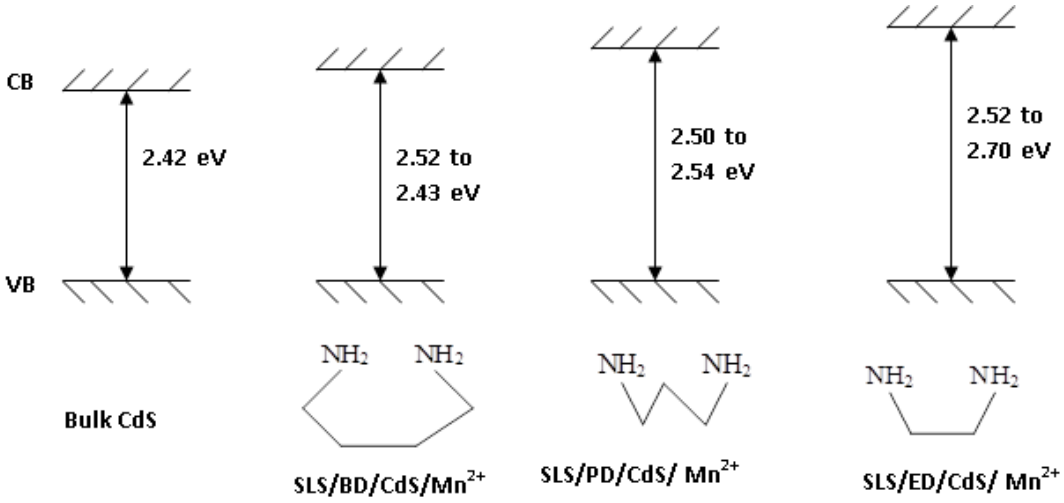


ESI Fig. 2: DSC profile for (a) SLS/BD and (b) SLS/PD assisted various concentrations of manganese doped CdS nanocrystal. CTAB/BD assisted 0% Mn^{2+}/CdS nanocrystals taking as a reference due to its pure cubic nature.

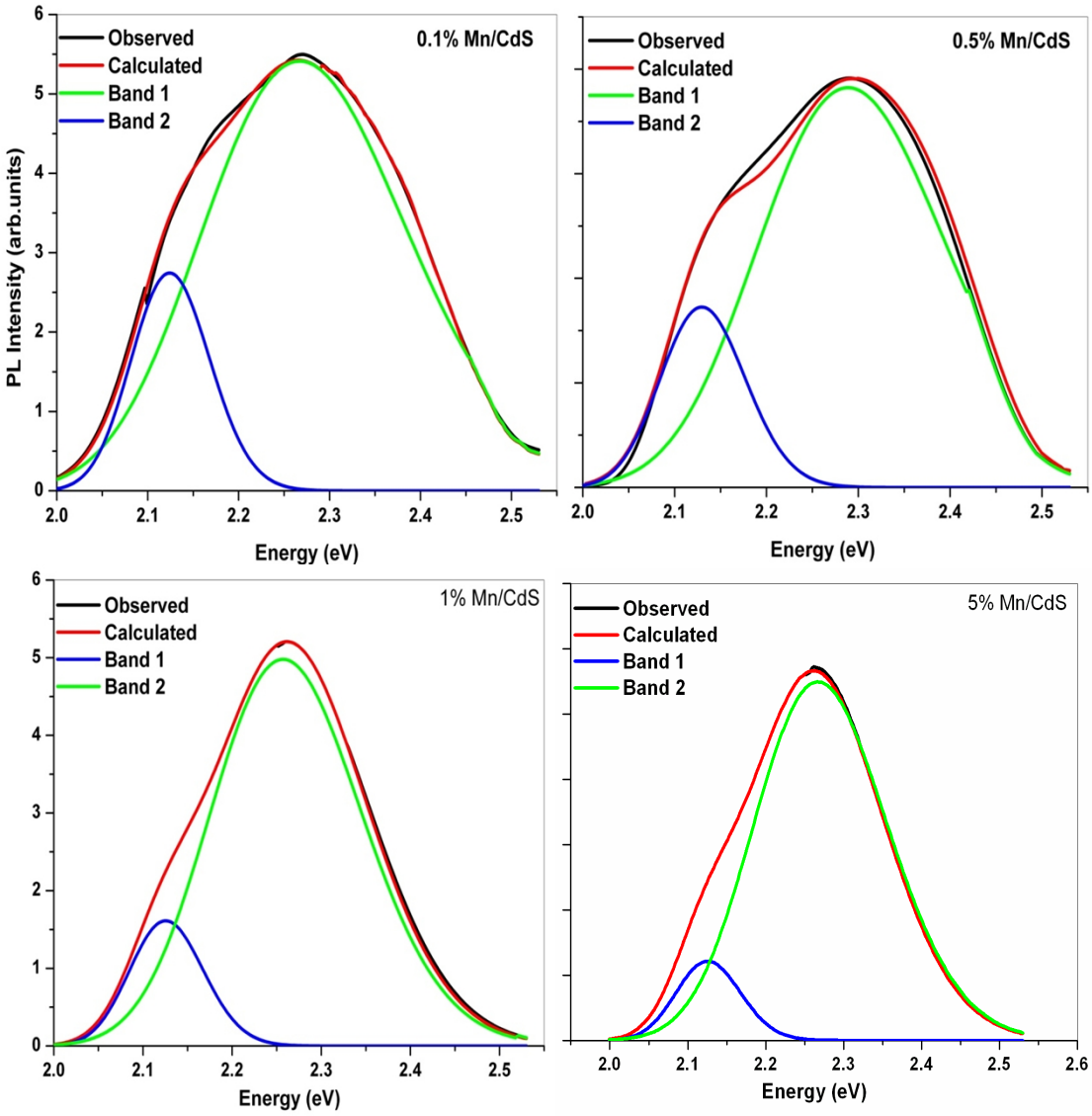
ESI. Table 2: A comparison of percentages of cubic and hexagonal components in SLS/BD/n%Mn^{2+}/CdS calculated from XRD (Short and Steward method) and DSC measurements.

System	Area of the curve	% of cubic	% of hexagonal
CTAB/BD/0%Mn^{2+}-CdS	128.1	100	0
SLS/BD/0% Mn^{2+}-CdS	24.8	19.4(19.0*)	80.6(81.0*)
SLS/BD/0.1% Mn^{2+}-CdS	23.7	18.5(18.2*)	81.5(81.8*)
SLS/BD/0.5% Mn^{2+}-CdS	24.1	18.8(18.5*)	81.2(81.5*)
SLS/BD/1% Mn^{2+}-CdS	24.3	19.0(18.7*)	81.0(81.3*)
SLS/BD/5% Mn^{2+}-CdS	24.3	19.0(18.7*)	81.0(81.3*)

*denotes result from XRD data



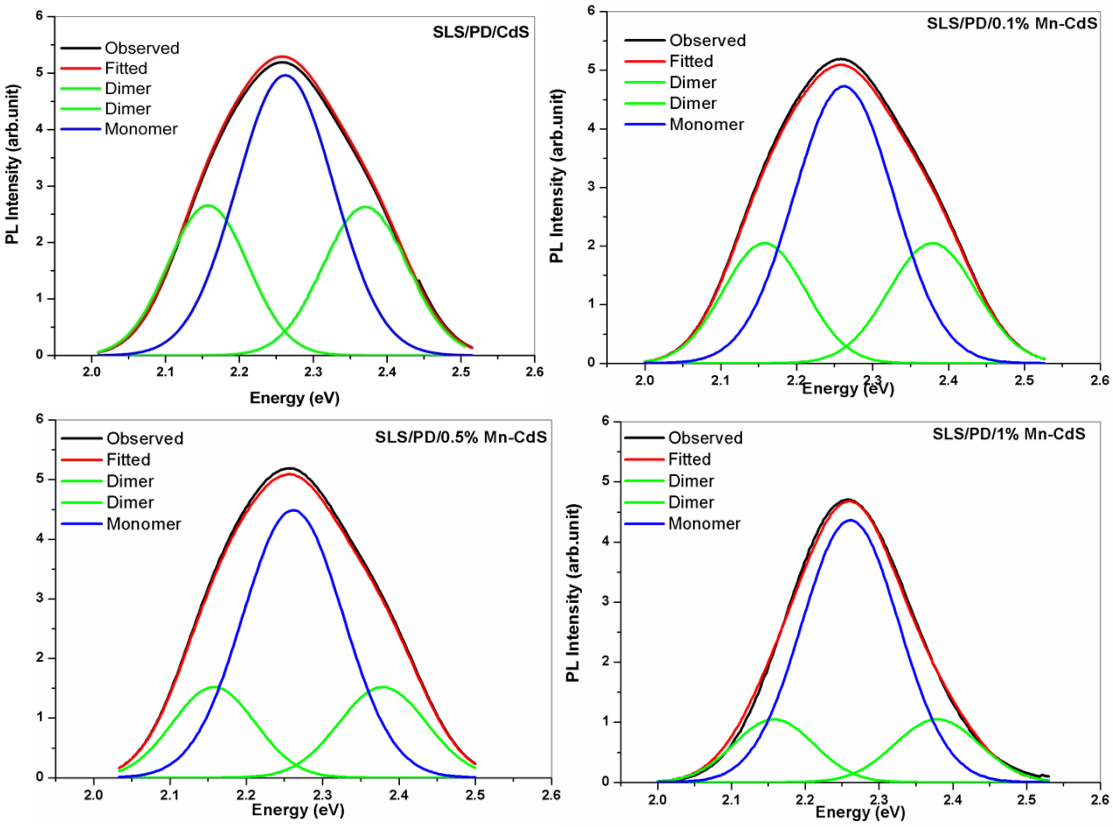
ESI. Fig. 3. Comparison of band gap energies for ligand chain length dependent CdS/Mn^{2+}



ESI Fig. 4: PL deconvolution energy profile for SLS/PD assisted CdS/Mn^{2+} nanocrystals for various concentrations of Mn^{2+} .

ESI Table 3: PL deconvolution energy values for V_{Cd} and Mn d-d emissions for 0.1% to 5% manganese doped CdS nanocrystals assisted by SLS/PD medium.

System	Peak position (eV)	Peak width (cm^{-1})	Peak amplitude (a.u)	Peak intensity (a.u)
Pure CdS V_{Cd}	2.26	2005	5.55	5564
0.1% V_{Cd}	2.27	2001	5.45	5453
Mn^{2+}	2.13	570	2.7	770
0.5% V_{Cd}	2.26	1998	5.4	5395
Mn^{2+}	2.13	570	2.4	684
1% V_{Cd}	2.25	1821	5.3	4826
Mn^{2+}	2.13	568	1.6	454
5% V_{Cd}	2.26	1734	5.1	4422
Mn^{2+}	2.13	568	1.1	312



ESI Fig. 5. Photoluminescence deconvolution of cadmium vacancies (V_{Cd}) for SLS/PD assisted manganese incorporated CdS nanocrystals.

ESI Table 4.Deconvolution of photoluminescence energy values of cadmium vacancies (V_{Cd}) emission in SLS/PD assisted Mn/CdS nanocrystals showing Davydov Spliting.

SLS/PD assisted Mn^{2+}-CdS	**Peak position (eV)**	**Peak width (cm^{-1})**	**Peak amplitude (a.u)**	**Peak intensity (a.u)**
Pure CdS V_{Cd}				
Monomer	2.26	1733	5.0	4333
Dimer	2.379	1334	2.6	1734
	2.149			
0.1% Mn/CdS V_{Cd}				
Monomer	2.26	1733	4.75	4116
Dimer	2.379	1334	2.1	1401
	2.149			
0.5% Mn/CdS V_{Cd}				
Monomer	2.26	1733	4.5	3899
Dimer	2.379	1334	1.52	1014
	2.149			
1% Mn/CdS V_{Cd}				
Monomer	2.26	1733	4.3	3726
Dimer	2.379	1334	1.1	734
	2.149			

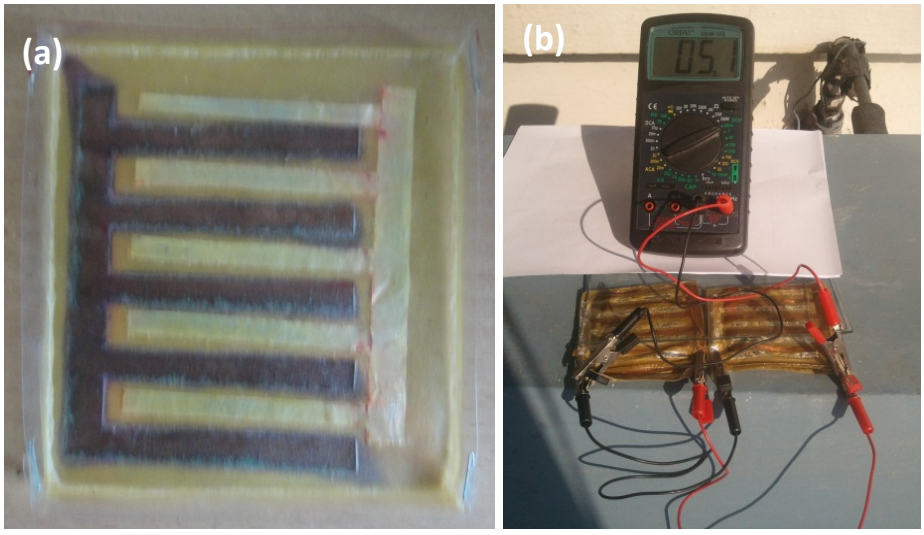
Dimer energy separation = 0.23 eV

Synthesis of CNP:

Cotton wicks were put in a 50ml capacity earthenware pot containing 40 ml of 'sesamum Indicum' oil. On litting the wicks the smoke emanates with soot which was collected from the bottom spherical surface of the earthenware pot. Collection of the soot was achieved by the use of stainless steel scalpel and stored separately.

CNP and CdS based heterostructures

Different concentrations of undoped CdS nanoparticles with 5mg of CNP were manually and homogeneously mixed and analyzed for their best photovolaic performance and decided on using 5 mg of CdS (undoped CdS assisted by SLS/BD) nanoparticles for further experimentation. The same concentration is also fixed for 5% Mn/CdS samples of SLS/BD and SLS/PD origin;. The films were cast using 1 g of polyurethane solution by slow stirring using magnetc stirrer (100rpm). In a typical experiment 1 g of polyurethane in 25 ml of tetrahydrofuran (THF) solvent were taken and heated at 60°C. The polyurethane solution was then mixed with a fixed concenrations (5 mg of each) of CNP and separately CNP + CdS/ 0% and 5% Mn^{2+} nanoparticles of SLS/BD and SLS/PD origin using Ultra Turrax (T-25 basic, 1KA werke). The air bubbles were removed my using vacuum pump and were poured in to a glass tray with dimension of measuring 7.5 x 8.5cm, which has the anode (Aluminum) and cathode (Copper) were placed as shown in the ESI Fig. 6 with the distance gap of 3mm interval among the material and they were air dried at room temperature at 30-35 ºC and stored.



ESI Fig. 6. (a) SLS/BD assisted CdS nanocrystals and CNP heterostructure based panel and (b) experimental set up for voltage measurement.