Electronic Supplementary Information (ESI)

Mn doped quantum dots sensitized solar cells with power conversion efficiency exceeding 9%

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Ligand Exchange with Water-Soluble TGA.

The ligand exchange strategy can be achieved according to a literature method.[1] Typically, 2 mmol of TGA was dissolved in 1.0 mL of methanol, and the solution was then adjusted to pH 10-11 with NaOH (30% in water). The TGA–methanol solution was then added into the as prepared QDs solution (20.0 mL of CH_2Cl_2 containing 0.1 mmol of QDs in molecular unit) and stirred for about 2h until the complete reaction. Then 10.0 mL of deionized water was added into the reactor, and the stirring was continued for another 5 min, the TGA-capped water-soluble QDs was carried out for further purified by centrifugation and decantation with the addition of acetone, and the precipitate was re-dissolved in 1.5 mL deionized water. Finally, the PH of the TGA-capped CdSeTe (or Mn doped CdSeTe) QDs was adjusted to 11.0 for further use.

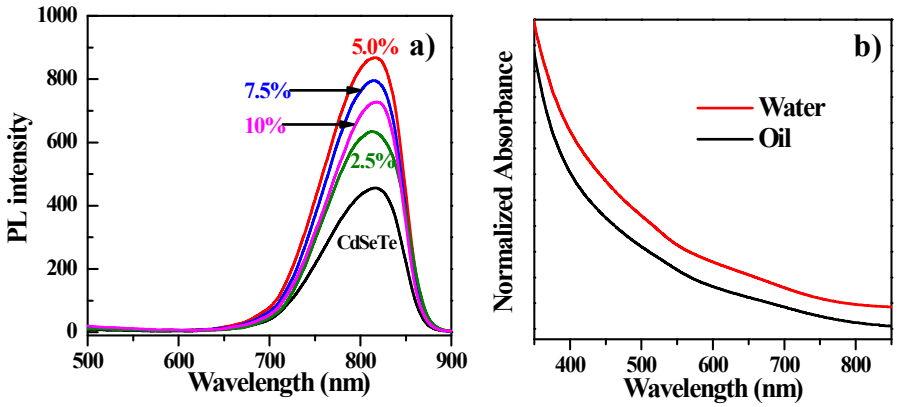

Figure S1. Absorption and PL emission spectra (λ_{ex} = 400 nm) of QD dispersions, respectively. (a) PL emission spectra (λ_{ex}= 400 nm) of CdSeTe and Mn:CdSeTe QDs corresponding to different nominal Mn contents in total cation component. (b) UV/Vis absorption spectra of Mn:CdSeTe QDs before (chloroform dispersion, black) and after phase transfer (aqueous dispersion, red).

Reference

[1] Yang, J. W.; Oshima, T.; Oshima, W.; Pan, Z. X.; Zhong, X. H.; Shen, Q. Influence of Linker Molecules on Interfacial Electron Transfer and Photovoltaic Performance of Quantum Dot Sensitized Solar Cells. *J. Mater. Chem. A* **2014**, *2*, 20882–20888

Table S1. Mn content in Mn:CdSeTe QD samples determined by ICP-AES and the corresponding nominal Mn concentration used in the synthesis of these samples.

Nominal Mn concentration relative to Cd (mol %)	Mn concentration relative to Cd determined by ICP-AES (mol %)
0	0
2.50	0.32
5.0	0.56
7.5	0.60
10	0.73

Table S2. Average photovoltaic parameters of 5 cells in parallel for Mn:CdSeTe/ZnS based QDSCs corresponding to the different concentration of Mn in QDs.

Mn initial molar concentration relative to Cd (mol %)	Mn content confirmed by ICP-AES (mol %)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
0	0	20.40	0.652	63.4	8.43±0.07
2.50	0.32	20.58	0.663	63.8	8.71±0.11
5.0	0.56	20.78	0.670	64.3	8.95±0.08
7.5	0.60	20.62	0.664	64.1	8.78±0.13
10	0.73	20.50	0.643	63.9	8.42±0.12

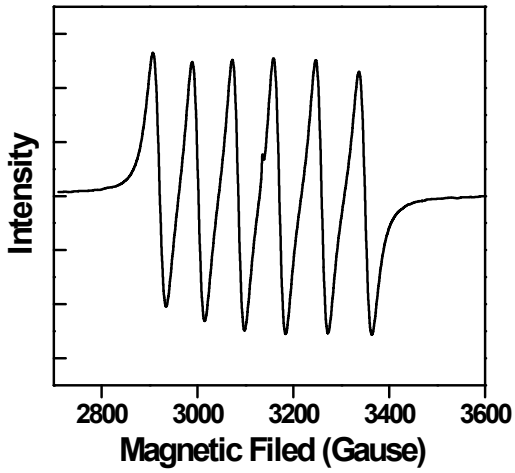

Figure S2. Continuous wave electron paramagnetic resonance (EPR) spectra of Mn:CdSeTe QDs at room temperature.

Table S3. The dependence of photovoltaic performance of Mn:QD/Mn:ZnS/SiO_2 QDSCs on the nominal Mn/Zn ratio in the ZnS passivation layer. Average photovoltaic parameters of 5 cells in parallel.

Mn/Zn (%)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
0	20.72	0.670	64.2	8.91±0.10
5.0	20.75	0.678	64.4	9.06±0.08
10.0	20.83	0.685	64.7	9.23±0.12
20.0	20.90	0.678	64.0	9.07±0.07
40.0	20.78	0.672	63.8	8.91±0.14

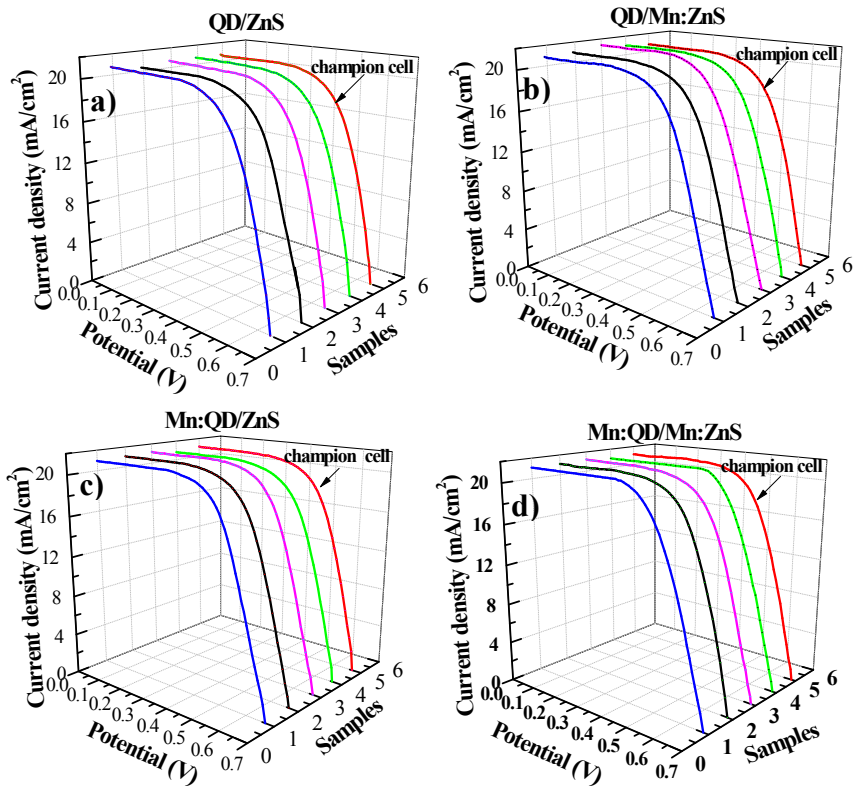

Figure S3. *J-V* curves of various solar cells (a) QD/ZnS, (b) QD/Mn:ZnS, (c) Mn:QD/ZnS and (d) Mn:QD/Mn:ZnS.

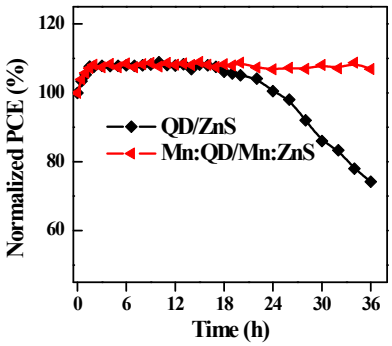

Figure S4. Cell efficiency normalized to the initial efficiency for samples with QD/ZnS and Mn:QD/Mn:ZnS based solar cells measured during 36 h period under continuous 1 sun illumination.

Table S4. Photovoltaic parameters derived from *J-V* measurement for various solar cells (Each group has 5 devices in parallel).

Electrode	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
QD/ZnS/SiO_2	20.32	0.655	63.0	8.39
	20.49	0.650	63.3	8.43
	20.46	0.654	63.9	8.55
	20.51	0.653	63.1	8.45
	20.36	0.651	63.4	8.40
QD/Mn:ZnS/SiO_2	20.52	0.667	63.8	8.73
	20.55	0.664	63.5	8.66
	20.60	0.668	64.1	8.82
	20.62	0.665	63.6	8.72
	20.56	0.668	63.3	8.69
Mn:QD/ZnS/SiO_2	20.73	0.669	64.4	8.93
	20.79	0.674	64.5	9.04
	20.64	0.668	64.2	8.85
	20.75	0.666	64.0	8.84
	20.68	0.672	63.9	8.88
Mn:QD/Mn:ZnS/SiO_2	20.88	0.687	65.5	9.40
	20.78	0.684	64.2	9.13
	20.91	0.680	64.5	9.17
	20.80	0.686	64.4	9.19
	20.75	0.689	64.9	9.28

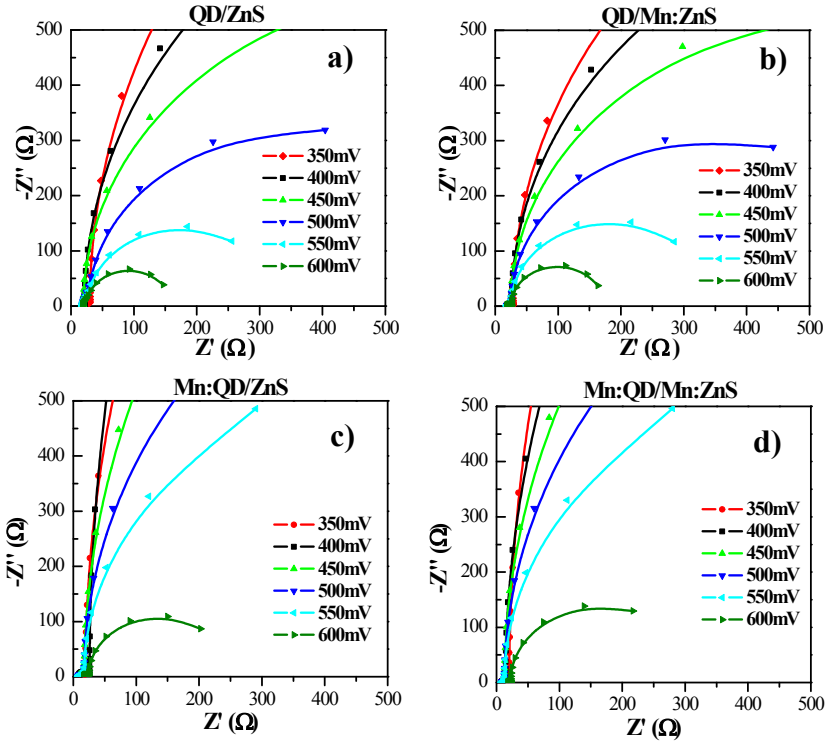

Figure S5. Nyquist curves under different bias voltages for QDSCs with different configurations: (a) QD/ZnS, (b) QD/Mn:ZnS, (c) Mn:QD/ZnS and (d) Mn:QD/Mn:ZnS.

Table S5. Impedance values at a –0.6 V forward bias for photoanodes subjected to different electrodes. Series resistance R_s, charge transfer resistance R_w, recombination resistance R_{rec}, and electron lifetime τ_n.

Electrode	R_s	R_w	R_{rec}	R_{rec} /R_w	τ_n
	Ω	Ω	Ω		s
QD/ZnS	19.62	26.89	101.5	3.8	0.45
QD/Mn:ZnS	19.83	33.15	128.1	3.9	0.60
Mn:QD/ZnS	20.15	29.51	209.3	7.1	0.88
Mn:QD/Mn: ZnS	20.02	35.03	278.7	8.0	1.46