Supplementary Information

Exploring the effect of manganese in lead sulfide quantum dot

sensitized solar cell to enhance the photovoltaic performance

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From XPS analysis (Fig.S1) the successful doping of Mn over PbS/CdS/CdSe/ZnS can be confirmed. XPS was measured to know the composition and chemical bond configuration of elements present in Mn-d-PbS/CdS/CdSe/ZnS. Fig. S1(i) and S1(ii) shows the binding energy peaks at 653.9eV for Mn $2p_{1/2}$ and 137.8 eV for Pb $4f_{7/2}$ which is well in agreement with the previous reports. ^[1,2] The XPS clearly detects and confirms the presence of Mn, whereas the Mn peak is not detected in the XRD pattern.



Fig.S1 XPS survey of 10 % Mn-doped PbS/CdS/CdSe/ZnS films; inset shows the (i) Mn and (ii) Pb binding energy peaks.

From the band gap, the possible electron transfer mechanism in the photo-anode is expected using the previous reports ^[3, 4] and schematically depicted in Fig. S2. In Mn doped PbS sensitized solar cells, the low band gap of bulk PbS shows an inability of electron transfer to the conduction band of the semiconductor photo-anode i.e., the conduction band position of PbS is

much lower than that of semiconductor. But in case of PbS quantum confinement the conduction band of PbS tend to an upshift, allowing the fast electron into the semiconductor photo-anode. ^[5-7] Furthermore, the band position of bulk PbS, CdS and CdSe shows a type-I band structure, when the materials were brought into direct contact, the band edges reorganize due to Fermi level alignment and forms a type-II band structure. ^[8-10]Apart from this, the consecutive CdS/CdSe passivation layers over Mn doped PbS can also favor more stability against the polysulfide electrolyte.



Fig. S2 Schematic representation of the energy band gap alignment of Mn-doped PbS/ CdS/CdSe/ZnS sensitised TiO₂ films

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