Role of Mn^{2+} in Doped Quantum Dot Solar Cell

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ABSTRACT

In recent times, Mn doped quantum dot sensitized solar cells have shown a lot of interest as it provides a different strategy to improve the photovoltaic performances. In this work, we have systematically studied the effect of Mn^{2+} dopant concentration on the photovoltaic performances of CdS based QDSCs. The open circuit potential increases systematically with increase in Mn^{2+} dopant concentration. The efficiency of the solar cell increases from 1.63 % to 2.53 % from undoped to 7.5 % doped CdS. The role of Mn^{2+} in enhancing the photovoltaic performances was further probed by open circuit voltage decay and the energy levels were studied using transient absorption spectroscopy. Both spin and orbital forbidden Mn *d-d* transition ($^4\text{T}_1 - ^6\text{A}_1$) helps in reducing the recombination inside the solar cell, which improves the overall photovoltaic performances.

1. INTRODUCTION

Quantum dots (QDs) possess versatile properties like easy tunability of bandgap through size control[1] and composition,[2, 3] high absorption coefficient,[4] multiple exciton generation[5] and possibility of hot electron transfer,[6] thus making them an ideal building block to capture and convert solar energy. Quantum dot based solar cells have emerged as a potential candidate for the next generation solar cells.[7-18] Quantum dots have been used in both depleted heterojunction[13-18] and sensitized solar cell configurations.[7-12] A power conversion efficiency of 8.5 % have been achieved from depleted heterojunction configuration.[16] Quantum dot sensitized solar cells (QDSSC) based on liquid redox electrolyte has achieved a maximum efficiency of 5.6 % with unprecedented photocurrent of 30 mA/cm^2 . [12] Recently, Bisquert and coworkers have shown liquid junction solar cell with an efficiency of 7.0% from a Cd and Pb free QDSSC using core/shell $\text{CuInS}_2/\text{ZnS}$ QDs.[19] The basic structure and working principle of QDSSCs is very similar to its previous analogue, dye sensitized solar cells (DSSCs).[20] Upon illumination, QDs attached to mesoporous TiO_2 films, injects electrons to the conduction band (CB) of TiO_2 . The electron gets transported to the conducting electrode through the TiO_2 network. In a regenerative liquid junction QDSCs, holes from the valence band (VB) of QD are transferred to the counter electrode by a redox couple. In spite of possessing

several advantages of QDs and promise of unprecedentedly high photocurrent, QDSSCs still exhibit lower power conversion efficiencies compared to DSSCs and organo lead halide perovskites,[21] mainly due to poor open circuit potential.

The intrinsically low open circuit potential of QDSSCs is due to the highly negative redox potential of the popularly used polysulfide electrolyte. Alternative redox couples *e.g.*, Co(II)-Co(III) complex [22] or solid state hole conductor *e.g.*, spiro-OMeTAD,[23] CuSCN,[24, 25] P3HT,[26] CuI[27] *etc.* have been explored to overcome the limitation of polysulfide electrolyte. Apart from the electrolyte or solid state hole conductor, the electron-hole recombination within the solar cell also deteriorates the open circuit potential.[28] Several attempts have been made to address the charge recombination in QDSSC. A commonly practiced method to prevent the scavenging of electrons from QD or TiO₂ by the electrolyte, is to passivate the QDs attached to TiO₂ by coating higher band gap semiconductor like ZnS. [29-32] Significant decreases in charge recombination have been achieved by employing a thin compact layer of TiO₂ between the mesoporous TiO₂ and FTO electrode.[33] Few reports have also shown that a thin barrier layer of Al₂O₃[34] and MgO[35] helps in filling up the surface states as well decrease the charge recombination. While most of the reported methods modify the surface of the working electrode, Chi *et al.* have shown that by proper alignment of band levels in TiO₂/CdS/CdSe, it is possible to increase the electron injection and decrease the recombination.[36, 37]

There have also been few attempts made to enhance the photovoltage by altering the energy levels of the QDs. Zaban and coworkers have used molecular dipole of the passivating ligand around the QDs to alter their electronic structure in a way to enhance the open circuit potential of QDSSCs.[38, 39] Recently, Buhbhut *et al.* have shown the effect of photoinduced dipole moment of type-II QDs in enhancing the open circuit potential.[40] In our previous work,[41] we have introduced Mn²⁺ doping in CdS and CdS/CdSe QDs to enhance the open circuit potential of QDSSC. A power conversion efficiency of 5.4% was achieved from Mn²⁺ doped CdS/CdSe QDSSC. We have proposed that the long lifetime ($\sim$ few hundreds of μ s) of *d-d* transitions in Mn²⁺ decreases the electron-hole recombination within the QD thus increasing the open circuit potential.

In this work, we report a systematic study of Mn²⁺ doping on photovoltaic performances of

CdS based sensitized solar cells grown by successive ionic layer adsorption and reaction (SILAR) method. In spite of being a relatively high bandgap material, we have chosen CdS due to its easy, ambient condition and reproducible bench top experiments. We have doped four different concentrations of Mn^{2+} and have studied absorption as well as photovoltaic performances. Open circuit photovoltage decay gives us insight of the role of Mn^{2+} , which have further verified with transient absorption spectroscopy. The solar cells reported here do not possess high efficiency but it helps us in understanding the role of doping and the concept can be applied to other systems as well to make high efficiency solar cells.

2. EXPERIMENTAL

2.1 Preparation of the mesoporous TiO_2 . The mesoporous TiO_2 active layer was prepared by previously reported method.[22, 32, 42] In brief, fluorine doped tin oxide (FTO) coated glasses (TEC 8 glasses from Pilkington) were washed for half an hour with soap solution under sonication followed by another 10 minutes wash in ethanol. A compact layer of TiO_2 was deposited on the FTO glass by treating these in 40 mM TiCl_4 solution at 70 °C for 30 min and washing with water and ethanol respectively. A TiO_2 paste (Solaronix Ti-Nanoxide T/SP, average size ~ 20 nm) was doctor bladed on the FTO and dried at room temperature for 30 min followed by drying for another 1 h at 80 °C. The dried TiO_2 films were annealed at 500 °C for another 1 h. Another layer of TiO_2 , (JGC Catalysts and Chemicals Ltd., PST-400C, average size ~ 400 nm) served as scattering layer, was also doctor bladed on top of the active TiO_2 and dried and annealed in a similar way. A final TiCl_4 treatment was performed before the sensitization to further increase the surface area of the mesoporous electrode.

2.2 Sensitization of the working electrode. The sensitizations of the TiO_2 working electrodes were done by successive ionic layer adsorption and reaction (SILAR) method. Stock solutions of Cd^{2+} and S^{2-} were prepared from 0.1 M $\text{Cd}(\text{NO}_3)_2$ in methanol and 0.1 M Na_2S were prepared in 1:1 methanol and water solution respectively. The SILAR process was performed by soaking the working electrodes in the cation and anion solutions for 1 min each solution. The working electrode was washed with methanol and dried with air in between each step. A total of 10 cycles of SILAR process was done in all the cases.

2.3 Characterization. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was used to determine the actual concentrations of Mn in different CdS films. The concentrations determined from ICP-AES are mentioned in Table 1. The absorption spectra of the sensitized electrodes were collected using double-beam Shimadzu 3101 PC spectrometer in diffuse reflectance mode. The TEM micrographs were collected using FEI Titan 80 – 300 electron microscope operating at a voltage of 300 kV. A working electrode with mesoporous TiO₂ only was used as blank. Incident photon to charge carrier conversion efficiency (IPCE) was measured using a Newport QE/IPCE system. A standard Si cell with known calibration was used as a reference. A monochromator and filter wheel was used to select wavelengths and prevent secondary reflections. The scans were recorded from 350 nm to 750 nm with a step size of 10 nm. The current was allowed to equilibrate at each point measured for 10 s.

The counter electrodes of Cu₂S-reduced graphene oxide (RGO) were prepared similarly as reported earlier in the literature.[43] The polysulfide electrolyte was prepared by dissolving 1 M Na₂S and 1 M S was dissolved in water. The QDSC were assembled in sandwich fashion with parafilm as spacer. Photovoltaic measurements were performed using a PARStat 2263 (Princeton Applied Research) potentiostat. The illumination source was a 300 W Xe lamp (Oriel) with a global AM1.5 filter. A calibrated Si photodiode was used to adjust the light intensity to be 100 mW/cm² (1 sun intensity).

Transient Absorption Spectroscopy measurements were performed using a Clark-MXR-2010 laser system combined with a Helios transient absorption detection system from Ultrafast Systems.[44] The samples were prepared by growing both doped and undoped CdS on TiO₂ and SiO₂ films on glass slides. The films were placed in specially designed spectrophotometric cells and were kept under vacuum for 1 h before the time-resolved transient absorption experiments to prevent oxidation of sample under the intense laser light.

3. RESULTS AND DISCUSSION

We have prepared four different concentration of Mn²⁺ dopant in CdS by varying the concentration of manganese acetate in cadmium nitrate in methanol. The actual dopant concentration in the CdS QDs was determined from Inductively Coupled Plasma-Atomic

Emission Spectroscopy (ICP-AES) as mentioned in Table 1. The actual Mn content is less compared to the nominal concentration. For 1 % dopant concentration, we have found only 0.3 % Mn in the QDs. With the increase in dopant concentration, the actual concentration of Mn in CdS QDs has increased to a maximum of 0.8 % for 7.5 % nominal concentration. Earlier reports[45-48] have shown that higher concentration of doping in nanocrystals cannot be achieved easily. It was suggested that Mn^{2+} ions inside the quantum dot lattice is energetically unfavorable thus preferred to be ejected out from the nanocrystal, commonly known as self purification.

The absorption spectra of the undoped and Mn^{2+} doped CdS sensitized TiO_2 electrodes are shown in Figure 1A. The broad absorption spectra indicate the heterogeneity in the size distribution of the CdS QDs. Interestingly, with increase in Mn^{2+} doping concentration in CdS, the band edge systematically shifts towards higher wavelength. The average band gaps of these samples are mentioned in Table 1. For the undoped CdS, the band gap was calculated to be 2.6 eV, which is higher than the bulk band gap 2.3 eV for CdS. With increase in Mn dopant concentration, the band gap decreased to 2.4 eV for 7.5 % dopant. Malik *et al.* have earlier reported[49] similar red shifts in absorption spectra of CdS QDs with Mn doping, synthesized by hot injection method. Few other transition metal ion doped II-VI semiconductor system also show similar red shifts.[50] The photographs of the sensitized electrodes are shown in Figure 1B. The color of the electrodes systematically changed from light orange for undoped CdS towards dark orange for 7.5 % Mn^{2+} doped CdS. Representative TEM micrographs of undoped CdS and 5 % Mn doped CdS are shown in Figure 1C and 1D, respectively. The average particle size is ~ 5 nm for both cases.

Figure 2 shows the photoaction spectra of the electrodes sensitized with undoped and Mn^{2+} doped CdS QDs. The incident photocurrent to charge carrier conversion efficiency (IPCE) or external quantum efficiency (EQE) was determined by measuring the photocurrent of the working electrodes at different monochromatic excitations. The IPCE spectra are very similar to the absorption spectra as shown earlier in Figure 1A. The maximum IPCE values for all the samples were around 65-70 %. The IPCE spectra for doped CdS were red shifted with respect to undoped CdS as observed for the UV-visible absorption spectra.

The J - V characteristics of the QDSCs sensitized with undoped and Mn^{2+} doped CdS are shown in Figure 3. The active area of the working electrode was kept with in $0.18 - 0.25 \text{ cm}^2$. The photovoltaic parameters, short circuit potential (J_{SC}), open circuit potential (V_{OC}), fill factor (FF) and total power conversion efficiencies (η) for different QDSCs are summarized in Table 1. The J_{SC} increases from 7.16 mA/cm^2 for undoped CdS to 9.35 mA/cm^2 for 3% Mn^{2+} doped CdS. Further increase in Mn^{2+} in CdS rather decreases the J_{SC} to 8.93 mA/cm^2 for 7.5 % dopant concentration. However, it is interesting to note that the V_{OC} increases consistently Mn doping. The V_{OC} for undoped CdS was observed to be 0.497 V , which had increased by $\sim 90 \text{ mV}$ with 5% Mn^{2+} doping in CdS. Further increase in doping concentration did not increase the open circuit potential. The effect of Mn^{2+} doping in CdS was observed in both J_{SC} and V_{OC} , which had increased the overall power conversion efficiency from 1.63% for undoped CdS to 2.53% for 7.5% Mn^{2+} doped CdS.

To understand the increase in V_{OC} , we have recorded the open circuit voltage decay (OCVD) for both undoped and doped CdS QDSCs as shown in Figure 4. Analysis of OCVD at open circuit condition is a simple procedure to obtain electron recombination lifetime.[51] The experiments were performed by monitoring the V_{OC} with time, initially under illumination, as shown by the shaded yellow region on the left hand side of the figure. At 120 sec, the illumination was switched off while monitoring the change in V_{OC} with time. For undoped CdS, the $t_{1/2}^{decay}$ (time taken to decay the V_{OC} 1/e times of its original values measured under illumination) is found to be 12 s. The $t_{1/2}^{decay}$ had increased with doping of Mn in CdS to a maximum of 116 s for 5% dopant concentration. Further increase in dopant concentration to 7.5% decreases the $t_{1/2}^{decay}$ to 98 s.

The V_{OC} is directly related to the recombination inside the solar cell. The recombination can occur through several pathways – via the semiconductor CB - VB recombination or via TiO_2 /semiconductor heterojunction recombination. Another major pathway for recombination is possible through the electrolyte.[52, 53] In this particular case, we have changed only the recombination path of between CB and VB, and TiO_2 and CdS heterojunction by doping Mn in CdS, while the electrolyte has been kept same. With an assumption that Mn doping does not affect the recombination with the electrolyte, the change in $t_{1/2}^{decay}$ measured from OCVD can be

Schematic 1: Schematic model of electron and hole recombination between TiO₂/CdS heterojunction

explained using Schematic 1. Upon shining light of sufficient energy on CdS/TiO₂ system, an electron-hole pair forms in CdS as denoted by CdS(e+h)/TiO₂. The rate of the electron-hole pair generation, k_f^1 , is directly proportional to the intensity of the incident light. The electron and hole can undergo recombination with a rate of k_b^1 via several possible pathways.[51, 54, 55] The electron will also be injected to the conduction band of TiO₂ and the hole will be scavenged by the S²⁻ electrolyte and will change to S_n²⁻ (rate constant k_f^2). Simplistically, we can consider only k_f^1 and k_b^1 are responsible to determine the V_{OC} for a given system with specific electrolyte. If the incident illumination is switched off, there will be no production of the electron and hole pair, thus k_f^1 will be 0 and k_b^1 will decrease the V_{OC} . In other words, after switching off the illumination, the decay rate in the open circuit potential measures the recombination inside the cell. From the increase in $t_{1/2}^{decay}$ with increase in dopant concentrations, it is clear that Mn doping decreases the recombination in doped CdS, which is responsible for the higher V_{OC} .

It was earlier reported that Mn²⁺ doping in CdS creates states in the mid band gap region due to atomic *d* orbitals of Mn (⁴T₁ and ⁶A₁) as shown schematically in Figure 6. However, the transition between these two energy levels (⁴T₁ - ⁶A₁) is both spin and orbital forbidden, which makes the recombination slow. Thus electron stays for a longer time at Mn *d*-states and then gets injected to TiO₂ as shown schematically in Figure 5.

We have further probed the relative energy position of the quantum dots (both undoped and Mn doped CdS) from where the electron gets injected to the TiO₂ conduction band by monitoring the electron injection rate by transient absorption spectroscopy as reported earlier for CdSe,[56-59] CuInS₂[60] *etc.* In brief, we have recorded the transient absorption spectra using 387 nm laser pulse excitation of both the undoped and Mn (5 %) doped CdS grown in SiO₂ and TiO₂ substrates by SILAR method. The transient absorption spectra recorded immediately after the laser pulse excitation of the QDs attached to both SiO₂ and TiO₂ exhibit similar features,

suggesting the electronic transitions remain unperturbed by the nature of the substrate. The absorption-time profile of bleaching recovery to SiO₂ and TiO₂ substrates are shown in Figure 6. We have observed for both undoped and doped CdS QDs, the ground state bleach recovery is faster for TiO₂ substrates, suggesting an additional deactivation pathway for QDs attached to TiO₂.

As discussed in earlier studies,[32, 59, 60] the bleaching recovery occurs with a range of heterogeneous reactions but can be fitted with a biexponential function. In case of QDs attached to SiO₂, the possibility of electron injection from QD to SiO₂ is negligible as it is energetically unfavorable due to high band gap of SiO₂. If we assume the faster ground state bleach recovery is entirely due to the electron injection to TiO₂, we can determine the electron injection rate (k_{ET}) as shown below in equation 2.

$$k_{ET} = \frac{1}{t(TiO_2)} - \frac{1}{t(SiO_2)} \quad \text{Equation 2}$$

where $t(TiO_2)$ and $t(SiO_2)$ are the average lifetimes of the bleaching recovery of QD/TiO₂ and QD/SiO₂ films.

The electron injection (k_{ET}) rate was calculated to be $7.0 \times 10^{10} \text{ s}^{-1}$ and $3.9 \times 10^{10} \text{ s}^{-1}$ for undoped and 5% Mn doped CdS, respectively. As shown earlier by Tvrđy *et al.*, the electron injection rate depends on the difference between the two energy levels involved in electron transfer process.[59] In these cases, the recipient energy level is the conduction band of TiO₂. However, the donor level is different for undoped and Mn doped CdS – conduction band of CdS and ⁴T₁ state for Mn doped CdS. The slower electron injection for Mn doped CdS compared to undoped CdS further supports our explanation that electrons first transferred to Mn *d* energy level from the conduction band of CdS and then get injected to TiO₂ conduction band.

4. CONCLUSION

The role of Mn²⁺ in CdS based quantum dot sensitized solar cells has been studied in this work. The spin and orbital forbidden *d-d* transition of Mn²⁺ decreases the recombination within the quantum dots. The long lifetime of the photoexcited electron eventually improves the short

circuit current and the open circuit potential by raising the Fermi energy at higher negative potential. This study also suggests that other dopants responsible in slower recombination in quantum dots can be successfully applied for sensitized or colloidal quantum dot solar cells to make high efficiency solar cells.

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TABLE AND FIGURE CAPTIONS

Table 1. Concentration of Mn as determined from ICP-AES and photovoltaics parameters of undoped and Mn^{2+} doped CdS QDSCs

Figure 1. (A) Absorption spectra and (B) photographs of Mn^{2+} doped CdS with different doping concentration - (a) undoped, (b) 1 %, (c) 3 %, (d) 5 % and (e) 7.5 %. (Absorption spectra for undoped and 7.5 % Mn doped CdS are taken from reference 41, Copyright 2012 American Chemical Society). TEM micrographs of (C) undoped CdS and (D) 5 % Mn doped CdS on mesoporous TiO_2 . A few particles are highlighted with yellow arrows. The scale bar in both the micrographs is 20 nm.

Figure 2. IPCE spectra for Mn^{2+} doped CdS with different doping concentration – (a) undoped, (b) 1%, (c) 3%, (d) 5% and (e) 7.5%. (Data for undoped and 7.5 % Mn doped CdS are taken from reference 41, Copyright 2012 American Chemical Society)

Figure 3. J - V characteristics of different working electrodes measured under AM 1.5 global filter of 100 mW/cm^2 intensity sunlight: (a) undoped CdS, (b) 1%, (c) 3%, (d) 5% and (e) 7.5% Mn^{2+} doped CdS. (Cu_2S -RGO was used as counter electrode and aqueous $1\text{M S}^{2-}/1\text{M S}$ as electrolyte). Data for undoped and 7.5 % Mn doped CdS are taken from reference 41. (Copyright 2012 American Chemical Society)

Figure 4. Open circuit voltage decay of (a) undoped CdS, (b) 1%, (c) 3%, (d) 5% and (e) 7.5% Mn^{2+} doped CdS. (Cu_2S -RGO was used as counter electrode and aqueous $1\text{M S}^{2-}/1\text{M S}$ as electrolyte). The left side yellow shaded region shows when the illumination was kept on and it was switched off at 120 s. The life time of the V_{OC} decay was found to be 12 s, 24 s, 44 s, 116 s and 98 s for undoped, 1%, 3%, 5% and 7.5% Mn^{2+} doped CdS respectively.

Figure 5. Schematic representation of the energy diagram of Mn-doped-CdS. The electron from the conduction band of CdS transfers to Mn d state ($^4\text{T}_1$) within a few ps, but the Mn d - d transition has lifetime in range of several hundreds of μs due to spin and orbitally forbidden transition.

Figure 6. Transient absorption kinetics traces of the excitonic decay of (A) undoped CdS and (B) 5% Mn doped CdS QDs. The black and red traces correspond to the QDs attached to TiO_2 and SiO_2 substrate, respectively. Decays are monitored at 490 nm and 492 nm for undoped and doped CdS, respectively.

Table 1. Concentration of Mn as determined from ICP-AES and photovoltaics parameters of undoped and Mn²⁺ doped CdS QDSCs

Sample	Mn (%) (determined from ICP-AES)	Band gap (eV)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)	$t_{1/2}$ (s)
CdS	-	2.61	7.16	0.497	0.46	1.63	12
1 % Mn ²⁺ - CdS	0.3	2.53	8.70	0.534	0.47	2.16	24
3 % Mn ²⁺ - CdS	0.5	2.43	9.35	0.549	0.47	2.42	44
5 % Mn ²⁺ - CdS	0.6	2.36	9.08	0.584	0.46	2.45	116
7.5 % Mn ²⁺ - CdS	0.8	2.40	8.93	0.584	0.49	2.53	98

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6