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Graphical abstract

# Systematic stacking of PbS/CdS/CdSe multi-layered quantum dots for the enhancement of solar cell efficiency by harvesting wide solar spectrum

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# Systematic stacking of PbS/CdS/CdSe multi-layered quantum dots for the enhancement of solar cell efficiency by harvesting wide solar spectrum

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#### Abstract

Fabrication of multi-layered quantum dot sensitized solar cells, especially q-dot solar cells that contain more than two layers of q-dots as light harvesting materials is a great challenge due to adverse effects exert by the of the q-dots in the outer-layers on the inner optimized q-dot layer. In this work, multi-bandgap q-dots of PbS (bandgap 1.16 eV), CdS (bandgap 2.01 eV) and CdSe (bandgap1.76 eV) are stacked in different combinations on the mesoporous TiO<sub>2</sub> layer to enhance the light harvesting ability. The problems associated with stacking of multi-layers of q-dots on the mesoporous TiO<sub>2</sub> layer were also investigated. The observed photovoltaic properties of multiband q-dot solar cells with different stacking configurations are then compared with the optical and electrical properties of multi-band gap quantum dots. The optimized three-layer PbS/CdS/CdSe q-dot solar cell showed a solar cell efficiency of 6.2% while two-layer q-dot solar cells fabricated with PbS/CdS and CdS/CdSe showed solar cell efficiencies of 5.8 and 4.2% respectively. The enhanced solar cell performance of three-layer PbS/CdS/CdSe q-dot solar cell is found to be mainly due to proper cascade stacking of three q-dot layers in photoanode that ensuing in enhanced charge transport as well as higher light harvesting.

Keywords: PbS/CdS, PbS/CdS/CdSe, light harvesting ability, quantum dots sensitized solar cell, multi-layered quantum dots, stacking of q-dots

#### Introduction

Quantum dot sensitized solar cells (QDSCs) are promising next-generation solar cells due to their characteristic features like tuneable band gap, high extinction coefficient, multiple exciton's generations, intrinsic dipole moment and ability to harvest the wide range of solar energy.[1-5] However, the efficiency of QDSCs is inferior to that of thin film and dye-sensitized solar cells (DSC) and the enhancement of solar cell performance of QDSCs has been hindered due to high charge recombination, surface defects and poor stability of QDSCs.[4] Despite their current modest solar cell performances, QDSCs are an important class of photovoltaic device that has a promising future owing to facile modification capability of their electrical, optical as well as physical properties to achieve higher solar cell efficiencies.[6-9] Structural configurations as well as working mechanism of both QDSCs and DSC are similar where they consist of photoanode, electrolyte and counter electrode.[10] The major difference in DSC and QDSC is that the former contains dye and the later contains q-dots as light harvesting materials. In DSCs, over 12 and 19.3 % efficiencies have been reported for organic dye sensitized materials [11] and perovskite sensitized materials respectively.[12] However, for QDSCs, the highest solar cell efficiency of over 9% has been reported for CdSe<sub>0.65</sub>Te<sub>0.35</sub> sensitized q-dots which is well below the theoretical efficiency limit of ~44% as well as the efficiency of liquid junction QDSCs.[13] The solar cell performance of QDSCs depends on several factors such as the electrocatalytic activity of the counter electrode, [14-16] redox properties of the electrolyte [17] and properties of Qdots.[18] Nevertheless, the inferior solar cell performance was mainly attributed to the very short charge carrier diffusion length due to abandon surface trap states (surface defects) in qdots.[18-23]

Though DSCs reported a record efficiency of 12%, further enhancement of efficiency of DSCs is hindered due to the complexity of synthesizing of new dye molecules that could

harvest wide solar spectrum. On the other hand, optical properties of Q-dots can be easily modified to capture the radiation from visible to infrared region and q-dots based solar cells have shown promising efficiency, especially in the IR region.[24-26] However, the major disadvantage of Q-dots that absorb near-IR region is their high charge recombination with the electrolyte yielding inferior device performance.[18, 26] Other problems associated with Qdots are their corrosion and stability and hence these properties should be considered when fabricating QDSCs. i.e. PbS nanoparticles have a narrow tuneable bandgap of 0.41 eV and due to its quantum confinement effect, PbS can be manipulated to absorb light over 1100 nm.[7, 21] The poor stability of PbS q-dots due to reaction with polysulfide electrolyte and atmospheric air, has been minimized by passivation of PbS q-dot with CdS.[18, 20]. Passivation of PbS with CdS leads to decrease in surface trap states and together with cosensitized characteristic nature of p-n junction, the PbS-CdS device enhanced the efficiency up to 5.7%.[18] Also it has been demonstrated that the methods of q-dots deposition greatly influence the solar cell performance of QDSC.[27] Fabrication of q-dot solar cells with the cascade of multiband gap of materials may further improve both light harvesting ability and as well as passivation effect. Hence, in this work, on top of the FTO/TiO<sub>2</sub> electron transport material, an inner PbS/CdS sensitized q-dots were deposited by Successive Ion Layer Deposition and Reaction methods (SILAR) and on top of the inner PbS/CdS Q-dot layers, the topmost CdSe q-dots were stacked by the same SILAR method to enhance the light harvesting as well as the passivation effect. The performance of such device and its properties were investigated with optical and electrochemical characterization.

#### Materials and methods

**Fabrication of TiO<sub>2</sub> mesoporous layer:** The TiO<sub>2</sub> photoanode was fabricated on FTO glass plates by sequential deposition of a compact TiO<sub>2</sub> layer and a mesoporous TiO<sub>2</sub> layer as described in our previous work.[16, 18] The TiO<sub>2</sub> compact layer was deposited on the

cleaned FTO glass plate by spin coating of a mixture containing titanium isopropoxide (0.177 ml, 97%, Fluka), diethanolamine (0.1 ml, 99%, Fluka) in butan-1-ol (1.822 ml, 99%, AnalaR) solution at 5000 rpm and the process was repeated three times and finally sintered at 500°C for 45 minutes. The TiO<sub>2</sub> mesoporous layer was fabricated on top of the compact TiO<sub>2</sub> layer with sequential deposition and sintering process with Dyesol TiO<sub>2</sub> (18-NRT, 20 nm average particle size) paste and with the TiO<sub>2</sub> paste prepared by modified Pichini method (TiO<sub>2</sub>Pichini1 and TiO<sub>2</sub>Pichini2). The detailed procedure of preparation of TiO<sub>2</sub>Pichini1 and TiO<sub>2</sub>Pichini2 methods are available in our previous publication.[18] Finally, TiO<sub>2</sub> photoanode treated with mixture of 40mM TiCl<sub>4</sub> and 0.4 mM MgCl<sub>2</sub> for thirty minutes and sintered at 450°C.

**Fabrication of Q-dots on top of TiO<sub>2</sub> photoanode:** The PbS, CdS and CdSe q-dots were deposited sequentially on top of the TiO<sub>2</sub> mesoporous layer by the SILAR method. Prior to deposition of q-dots on the TiO<sub>2</sub> surface, the prepared TiO<sub>2</sub> photoanode was immersed in solution-A [(3-mercaptoproponic acid (0.015M) and (0.03 M Na<sub>2</sub>S<sub>(aq)</sub>)] for 90 seconds followed by immersing in solution B [0.03 M Pb(Ac)<sub>2(aq)</sub> solution] for 90 seconds. For the full conversion of adsorbed Pb<sup>2+</sup> into PbS, the Pb<sup>2+</sup> adsorbed photoanode was dipped again in solution A for 90 seconds. The electrode was thoroughly washed with methanol in between every deposition and the process was repeated for three times. Likewise, for the deposition of CdS q-dots on PbS layer, the PbS coated TiO<sub>2</sub> photoanode was immersed into the 0.05 M Cd(Ac)<sub>2</sub> solution followed by immersing into the 0.05 M Na<sub>2</sub>S solution for 90 seconds and this step was repeated for three times to obtain a desired CdS layer thickness. Finally, on top of the CdS layer, the topmost CdSe q-dots were deposited by SILAR method. For the deposition of CdSe, the photoanode FTO/TiO<sub>2</sub>/PbS/CdS was immersed into the 0.1 M Cd(Ac)<sub>2</sub> and 0.1 M NaSeSO<sub>3</sub> solutions for four minutes and the process was repeated for six

cycles to optimize the CdSe layer thickness and in between the photoanode was thoroughly washed with distilled water. Finally, a ZnS over-layer was deposited on top of the FTO/TiO<sub>2</sub>/PbS/CdS/CdSe photoanode by immersing the photoanode into the 0.05 M Zn(Ac)<sub>2</sub> solution and 0.05 M Na<sub>2</sub>S solution consecutively for three times to get a thick ZnS layer. The photoanodes with different combinations of q-dots were labeled as follows: *A- PbS, B-CdS, C-CdSe, D-PbS/CdS, E-CdS/CdSe, F-PbS/CdSe, G-PbS/CdS/CdSe with a barrier layer.* 

**Preparation of NaSeSO<sub>3</sub> and polysulfide electrolyte:** To prepare NaSeSO<sub>3</sub> solution, 2.5 g of Na<sub>2</sub>SO<sub>3</sub> solution and 0.25 g selenium powder were mixed into the 12.5 ml water and refluxed at 70<sup>o</sup>C for six hours. Finally, 2.08 ml of resultant NaSeSO<sub>3</sub> solution was taken into a small bottle and diluted up to 5.00 ml by distilled water to prepare 0.1 M NaSeSO<sub>3</sub> solution. The electrolyte was prepared by mixing 2M Na<sub>2</sub>S, 2M S and 0.2M KCl in water: methanol mixture of 3: 7 ratio and stirred it for three hours in a closed vessel at 50<sup>o</sup>C.

To Fabrication device: assemble QDSC, of the the prepared the FTO/TiO<sub>2</sub>/PbS/CdS/CdSe photoanode was sandwiched with a Cu<sub>2</sub>S coated brass plate as the CE. The polysulfide liquid electrolyte was filled in the space in between the photoanode and the CE. To prepare Cu<sub>2</sub>S/brass CE, a brass plate was dipped into a 50 ml beaker containing 1.5 ml HCl and heated until all the HCl get evaporated and then the brass plate was washed thoroughly with distilled water and dried off. The Parafilm spacer with a hole was placed on top of the cleaned brass plate (treated with boiled HCl) and then the prepared polysulfide electrolyte was placed on the exposed area of the brass plate. The active area of the photovoltaic cell was  $0.159 \text{ cm}^2$ .

Characterization: Characterizations of fabricated photoanodes were performed by using xray diffraction (XRD) measurements, UV-visible spectroscopic measurements, Scanning Electron Microscopy (SEM) analysis, electrochemical impedance analysis (EIS), cyclic voltammetric analysis (CV) and dark current measurements. XRD analyses were performed by using powder diffraction (Siemens D5000 X-ray diffractometer with Cu K $\alpha$  radiation operating at 40 KV, scanning from  $2\theta = 20$  to 80°). Current-voltage (IV) characterization of the solar cell was done with Keithley 2400 source meter under one sun illumination using a solar simulator at AM1.5G (Newport AAA solar simulator at 100 mW/cm<sup>2</sup>). The intensity of light was calibrated with a standard Si-reference cell. External quantum efficiency (EQE) of the corresponding solar cell was recorded in the 300 - 1100 nm range by Bentham PVE300 unit with a TMc300 monochromator based IPCE with the Xenon arc lamp. Electrochemical impedance measurement was performed with Zahner Zannium universal electrochemical workstation equipped with a frequency response analyzer (Thalas) at 10 mV amplitude ac signal and in the frequency range from 0.1 Hz to 1MHz under dark and illumination conditions at 0.5 V to 0.1 V with 0.05 V intervals and at open circuit voltage respectively.[28] Cyclic voltammetric analysis and Mott-Schottky analysis were performed with three-component system in which platinum as the counter, Ag/AgCl (0.01M), saturated KCl as the reference electrode and FTO/TiO<sub>2</sub>/quantum dot photoanode as working electrode at 10 mV amplitude ac signal and 1KHz frequency. Cyclic-voltammetry measurements were performed at a scan rate of 50 mV.s<sup>-1</sup>.

### **Results and discussion**

In this work multi-band gap q-dots of PbS (bandgap 1.16 eV), CdS (bandgap 2.01 eV) and CdSe (bandgap 1.76 eV) were grown on the TiO<sub>2</sub> mesoporous layer. The crystalline

properties as well as surface morphology of q-dots were investigated by XRD, HRTEM and SEM are shown in Fig. S1, S2 and S3 respectively. In the three-layer system, crystalline CdSe (hexagonal), PbS (cubic) and CdS (cubic) nanoparticles were clearly identified by XRD diffraction patterns. In HRTEM image shown in Fig. S2, particles with the average diameter of 3.63 nm can be attributed to q-dots of CdS (111 crystalline plane with fringe width d=0.337 nm), PbS (111 crystalline plane with fringe width d=0.346 nm) and CdSe (100 crystalline plane with fringe width d=0.372 nm and 012 crystalline plan with fringe width d=0.255 nm). Additionally, bigger particles with fringe width of 0.352 nm were identified as TiO<sub>2</sub>. The measured TiO<sub>2</sub> layer thickness from the cross section SEM image of FTO/TiO<sub>2</sub>/PbS/CdS/CdSe is found to be ~15  $\mu$ m.

Photoanodes with different combinations of q-dots were fabricated with PbS, CdS and CdSe q-dot particles and the observed photovoltaic properties of multi-bandgap q-dot solar cells were then compared with the optical and electrical properties of multi-bandgap quantum dots. The absorption spectra of PbS, CdS and CdSe q-dots shown in Fig. 1a clearly indicate that q-dots of PbS, CdS and CdSe can harvest solar energy mainly in 600-1100 nm, 300-400 nm and 500-600 nm regions respectively. For comparison purpose, absorption spectra of multi-bandgap q-dots of PbS/CdS, PbS/CdSe, CdS/CdSe and PbS/CdS/CdSe are shown in Fig. 1b. As shown in Fig. 1, considering the optical properties of PbS, CdS and CdSe, a solar cell fabricated with these multi-bandgap q-dots in principle could harvest solar energy covering VU-Vis-IR regions of the solar spectrum. As shown in Fig. 1b, the stacked PbS/CdS/CdSe q-dots absorb light entirely from UV to IR regions and the combined absorption of stacked PbS/CdS/CdSe layer is found to be higher than that of individual absorptions of q-dots. When assembling multi-layered q-dots in an anode, especially deposition of three types of q-dots sequentially, it was noted that the q-dots deposition sequence and methods are very critical for solar cell performance where the new layer will

lead to improve or decrease the solar cell performance due to passivation or damage of the previous layer respectively. Although the combined PbS, CdS and CdSe absorber layer harvest light in the wide solar spectrum, to achieve the highest performance of the solar cell, alignments of quantum dot absorber layer should be arranged in a proper cascade manner for a facile electron flow towards mesoporous  $TiO_2$  from the cascade of q-dots. For proper assembling of q-dots in the anode, energy levels of q-dots were analysed by cyclic voltammetry.

Cyclic-voltammetry analyses of quantum dots were performed to determine the HOMO and LUMO levels (valence-band and conduction-band minimum, respectively) and extracted results were used to predict the energy levels of semiconductor. [29, 30] The CV spectra of PbS, CdS, CdSe are shown in Fig. 2a while in Fig. 2b, the CV spectra of PbS/CdS, CdS/CdSe and PbS/CdSe q-dots were given. Approximate energy level positions of HOMO, LUMO and bandgap of q-dots were extracted from the cyclic voltammetry analysis shown in Fig. 2 by using the equations (1) and (2). The energy levels of the conduction and valence band edges were calculated from the onset oxidation potential (Eox) and the onset reduction potential (Ered), respectively, according to the equation (1) and (2).

$$E_{LUMO} = -Ea = -e(E^{red} + 4.71) \,\mathrm{eV}$$
 (1)

$$E_{HOMO} = -Ec = -e(E^{ox} + 4.71) \,\mathrm{eV}$$
 (2)

i.e. in the case of PbS, it exhibits an oxidation process at about -0.841 V with a step onset of ca. -0.281 V and while the reduction process of PbS is observed at ~1.841 V with an onset at ~0.881 V corresponding to HOMO and LUMO levels of -4.429 eV and -5.591 eV respectively. The estimated CB and VB positions from the electrochemical measurements in the QD materials are given in Table 1.

To elucidate the solar cell performance of multilayered q-dots PbS/CdS/CdSe photoanode, PbS, CdS and CdSe q-dots were sequentially deposited on the TiO<sub>2</sub> mesoporous layer on the FTO glass plate and the current versus voltage (J-V) curves of QDSCs under one sun illumination was measured. For comparison purpose, we also studied the solar cell performance of individual and different combinations of q-dot photoanodes. J-V curves of QDSC fabricated with the individual PbS, CdS and CdSe q-dot are given in Fig. 3a and the solar cell performances of two-component PbS/CdS, PbS/CdSe, CdS/CdSe are given in Fig. 3b. In Fig. 3c, J-V curves of three component system containing PbS/CdS/CdSe with and without a MgO barrier layer are given and the estimated solar cell performance from J-V curves are given in Table 2. The corresponding IPCE curves of individual PbS, CdS, CdSe photoanode, two component PbS/CdS, PbS/CdSe, CdS/CdSe and PbS/CdS/CdSe with and without a barrier layer are shown in Fig. 3d, Fig. 3e and Fig. 3f respectively. From the J-V curves, the observed J<sub>sc</sub> values of photoanode fabricated either with PbS, CdS or CdSe q-dots were 10.14, 2.71 and 7.22 mA/cm<sup>2</sup> respectively while for the same,  $V_{oc}$  values of 279.5, 498.2 and 503.4 mV were observed respectively yielding solar cell efficiencies of 1.0, 0.87 and 2.46% for PbS, CdS and CdSe respectively. As shown in Fig.3b, Jsc was increased from 10.14 mA/cm<sup>2</sup> to 22.35 mA/cm<sup>2</sup> upon deposition of a CdS layer on PbS layer while deposition of a CdSe layer on top of the PbS layer resulted in the decrease in  $J_{sc}$  from 10.14 mA/cm<sup>2</sup> to 6.25 mA/cm<sup>2</sup>. However, when a CdSe layer was deposited on CdS layer, enhance in J<sub>sc</sub> from 2.71 mA/cm<sup>2</sup> to 13.42 mA/cm<sup>2</sup> was noted. Solar cell performance presented in Fig.3b for two-layer q-dot photoanode indicated that deposition of CdSe q-dots on the PbS qdots layer leading to deterioration of solar cell performance while it has a positive effect on the CdS layer. The negative effect or deterioration of solar cell performance upon deposition of CdSe q-dots on the PbS q-dot layer could be due to the conversion of PbS into PbSe by the reactive and corrosive Se<sup>2-</sup> ions of CdSe.[27] It is known that the PbSe q-dots are extremely

unstable under the atmospheric condition and a very short exposure of PbSe QDs to ambient air could result in their degradation leading to the generation of  $Se^{2-}$  ions. It has been reported the decrease in overall solar cell performance of q-dot solar cells due to the presence of  $Se^{2-}$  ions that makes short-paths and resulting in the increase in charge recombination leading to decrease in overall solar cell performance.[27] Hence, it can be assumed that due to the formation of  $Se^{2-}$  ions in PbS by the CdSe particcles may lead to higher charge recombination and hence resulting in lower Jsc of PbS/CdSe photoanode can be justified.

As given in Table 2, when a three component system containing q-dots of PbS/CdS/CdSe photoanode was fabricated by applying a thin CdSe layer on PbS/CdS layer, J<sub>sc</sub> of PbS/CdS/CdSe photoanode was decreased from 22.35 to 18.11 mA/cm<sup>2</sup> while the efficiency was decreased from 5.69 to 4.5%. As mentioned earlier, deposition of CdSe on PbS resulted in degradation of PbS q-dots that would lead to enhance in charge recombination and thereby decrease in J<sub>sc</sub>. As such, to minimize the formation of PbSe and decrease of the charge recombination in PbS/CdS/CdSe multi-band q-dot solar cell, a charge barrier layer was introduced on the mesoporous layer. The observed solar cell performance for PbS/CdS/CdSe photoanode with a barrier layer shown in Fig. 3c clearly indicate the increase in both  $J_{sc}$  (from 18.11 to 23.46  $mA/cm^2)$  and efficiency (from 4.5 to 6.24%) of PbS/CdS/CdSe photoanode after introducing a barrier layer. These results evidently indicate that the second q-dot layer can either enhance or decrease the solar cell performance especially CdSe has a negative effect on PbS while it has a positive effect on CdS. As shown in Fig. 3d, IPCE of individual photoanodes fabricated with CdS and CdSe clearly resemblance to the  $J_{sc}$  values shown in Fig. 3b and c. However, the external quantum efficiency results shown in Fig. 3d for PbS q-dots on TiO<sub>2</sub> is remarkably very low and very hard to match with the observed current density of PbS in Fig.3a which could be due to rapid

corrosion and instability of PbS when it contacts with the polysulfide electrolyte directly. Nevertheless, IPCE results shown in Fig. 3e for PbS/CdS (Fig. 3e-plot D) and CdS/CdSe (Fig. 3e-plot E) demonstrated the enhancement of IPCE values than the individual q-dots due to enhanced light harvesting as well as passivation effect. However, the IPCE values of the two-layer PbS/CdSe photoanode (Fig. 3e-plot F) are inferior to that of individual PbS or CdSe due to adverse effect of CdSe q-dots on PbS q-dots. On the other hand, three-layer q-dot photoanodes fabricated with PbS/CdS/CdSe with (Fig. 3f-plot H) and without (Fig. 3f-plot G) barrier layer showed enhanced IPCE values than the accumulated individual J<sub>sc</sub> values and more importantly as expected a three-layer q-dot cascade of PbS/CdS/CdSe can harvest solar energy from UV to IR regions.

The observed IV and IPCE results for different cascade arrangements of q-dots clearly demonstrated the importance of proper layering of q-dots in photoanode and hence the behavior of different q-dot layers on solar cell performance is vital to explain the observed solar cell performance of different combinations of q-dot layers in photoanode of QDSCs. Since, solar cell characterization under dark conditions is a widely used technique as it provides essential information necessary for the analysis of performance losses and device efficiency, IV and EIS of the PbS, CdS, CdSe, PbS/CdS, PbS/CdSe, PbS/CdS/CdSe photoanodes were investigated under dark conditions. [31] Dark IV measurements of individual PbS, CdS, CdSe q-dots and two-layer PbS/CdS, CdS/CdSe, PbS/CdSe q-dots on top of the TiO<sub>2</sub> photoanode are given in Fig. 4a and 4b respectively. While in Fig.4c, the dark IV of the three-layer q-dot system of PbS/CdS/CdSe with and without barrier layer is given. The Fig. 4c illustrates that the three component system (PbS/CdS/CdSe) shows lower leakage current and high rectification ratio with TiCl<sub>4</sub> and MgCl<sub>2</sub> treatments (Table 3). The rectification ratios were calculated by using ratios of forward and reverse dark current at 1.8V.[32] As given in Table 3, the three component system (PbS/CdS/CdSe) shows higher

rectification values (rectification values before and after the TiCl<sub>4</sub> and MgCl<sub>2</sub> treatment are 2.50 and 4.54 respectively) than the PbS/CdS binary system (rectification value of 2.44) and PbS quantum dots alone (rectification value of 1.99). High rectification values indicate the high charge career in only one direction at applied bias voltage and hence the enrichment of retention ratio would lead to higher efficiency of PbS/CdS/CdSe QDSSCs with TiCl<sub>4</sub> and MgCl<sub>2</sub> treatment.[32, 33]

Additionally, EIS of the PbS, CdS, CdSe, PbS/CdS, PbS/CdSe, PbS/CdS/CdSe solar cells were also investigated under dark and illumination conditions. Impedance measurements under the illumination condition of the individual PbS, CdS, CdSe q-dots, twolayer PbS/CdS, CdS/CdSe, PbS/CdSe q-dots and three-layer PbS/CdS/CdSe with and without barrier layer on top of TiO<sub>2</sub> photoanode are given in Fig. 5a, 5b and 5c respectively. The electrochemical impedance measurements shown in Figure 5 were measured by using Zenner-Zannium electrochemical workstation and corresponding curves were fitted with Zview software and under dark condition. In EIS plot, the first semi-circle in higher frequency region corresponds to charge transfer process of counter electrode and electrolyte and the second large semicircle adjacent to the first semi-circle of is regards with recombination resistance (Rk), charge transport resistance (Rct) at the QD-electrolyte interface and the chemical capacitance  $(C\mu)$  of the TiO2 layer. Third semi-circle in lower frequency region usually corresponds to Nernst diffusion which was not observed in this analysis.[34, 35] The variation and estimated charge recombination resistance ( $R_k$ ), charge transfer resistance ( $R_{ct}$ ), chemical capacitance ( $C_{\mu}$ ), electronic lifetime (T) and conductivity are shown in Figure 6a, 6b, 6c and 6d respectively and in Table 4.

The calculated  $R_k$ ,  $R_{ct}$ ,  $C_{\mu}$  and T values given in Table 4 indicate that the charge recombination resistance ( $R_k$ ) of PbS/CdS is the highest among the different q-dot cascade investigated on top of PbS q-dots. However, when a CdSe layer is introduced on both PbS

and PbS/CdS electrodes, a clear decrease in Rk is noted while an increase in Rct was noted upon a deposition of a CdSe layer on the CdS layer. These EIS results are in accordance with the observed solar cell performance of these q-dot photoanodes. i.e. the enhanced  $J_{sc}$  of PbS/CdS anode can be attributed to the increase in  $R_k$  value (less recombination) when a CdS layer is deposited on top of the PbS due to less charge recombination. Similarly, the observed decrease in Jsc of photoanodes of PbS/CdSe and PbS/CdS/CdSe upon applying a topmost CdSe layer to the anode could be due to higher charge recombination process (lower  $R_k$  values). The conclusions one could arrive from EIS results are that; (1) enhancement of charge recombination when a CdSe layer is deposited either on PbS or PbS/CdS resulting in lower J<sub>sc</sub> values; (2) decrease in charge transport resistance when a CdSe layer is deposited on CdS yielding higher J<sub>sc</sub>; (3) increase in charge recombination resistance when a CdS layer is deposited on PbS layer. These results are consistent with the  $J_{sc}$  variations observed with the different Q-dot assemblies shown in Fig.3 and could be explained as follows. In our previous results [18], enhancement in J<sub>sc</sub> upon coating of a CdS layer on PbS Q-dots was demonstrated and the observed higher J<sub>sc</sub> was assigned to the enhanced charge recombination resistance of PbS/CdS system due to passivation effect (elimination of trap states in PbS) of CdS on PbS.[18, 20] Additionally, in a recent publication, a detailed study was reported by Clark et.al [20] on the effect of CdS on PbS electrode in which they clearly demonstrated the passivation effect of CdS on PbS[18, 20] and hence enhance in Jsc upon coating of q-dot CdS layer on PbS q-dots. On the other hand, as mentioned earlier, the negative effect of the PbS/CdSe and PbS/CdS/CdSe can be understood based on the formation of PbSe and Se<sup>2-</sup> which leads to enhanced charge recombination and the charge recombination can be minimized by the introduction of a charge barrier layer in multi-layered PbS/CdS/CdSe cascade of q-dots. Additionally, the observed lower  $V_{oc}$  value of the photoanode PbS/CdS/CdSe with a MgO barrier layer (cell H) than that of CdSe and

CdS/CdSe photoanodes is anomalous. However, despite presence of a MgO barrier layer, the  $R_k$  value of PbS/CdS/CdSe is still lower than that of CdSe and CdS/CdSe indicating that short paths are not completely clogged-up by the MgO layer and hence lower  $V_{oc}$  can be justified. However we believe that a dense MgO barrier layer may enhance the  $V_{oc}$  of the PbS/CdS/CdSe photoanode.

The lifetime measurements of excited electrons were estimated by the open circuit voltage decay measurements with time. The  $V_{oc}$  decay curves are shown in Fig 7a (PbS, CdS, CdSe), Fig. 7b (PbS/CdS, CdS/CdSe, PbS/CdSe) and Fig. 7c (PbS/CdS/CdSe with and without a barrier layer). The estimated lifetimes of respective voltage decay curves of photoanodes are shown in Fig. d, e and f respectively. The electron lifetime of QDSCs was calculated by equation (3) where  $K_B$  is the Boltzmann constant (1.38x10<sup>-23</sup> J K<sup>-1</sup>), T is the absolute temperature, q is the elementary charge and  $dV_{oc}/dt$  is the gradient of the open circuit voltage decay measurements. A higher excited electron lifetime is an indication of effective transfer of excited electron, an enhanced  $J_{sc}$  can be expected from such q-dot materials as a result of diminish charge recombination.[36]

$$\tau = \left(\frac{K_B T}{q}\right) \left(\frac{d Voc}{dt}\right)^{-1} \tag{3}$$

As shown in Fig. 7d, the electron lifetime of PbS quantum dots is shorter than CdS or CdSe due to higher corrosion of PbS quantum dots by polysulfide electrolyte. As reported earlier,[18] after coating of CdS on PbS, an increase in electron lifetime is observed due to passivation of PbS by CdS (Fig. 7e-plot D). However, deposition of CdSe q-dots on PbS and PbS/CdS resulted in the decrease in electron lifetime (Fig. 7e-plot F and Fig. 7f-plot G) which agrees well with the observed  $J_{sc}$  as well as EIS measurements. Similarly, the comparison of electron lifetimes of PbS/CdS/CdSe with (Fig. 7f-plot H) and without (Fig. 7f-plot G) a barrier layer indicated an enhanced electron lifetime for PbS/CdS/CdSe with a

barrier layer strongly support that the MgO treatment prevents the charge recombination in PbS/CdS/CdSe q-dots due to inclusion of CdSe into the multilayered cascade photoanode.

Based on the solar cell performance of different cascade arrangements of q-dots and the energy levels derived for PbS, CdS and CdSe from voltammetry method and Mottthe best q-dot arrangement in the three-layer system was schematically Schottky methods, shown in Fig. 8. According to the estimated energy levels from electrochemical measurements and Mott-Schottky plots, the Femi levels of PbS, CdS and CdSe q-dots are situated at -0.003, -0.203 and -0.213 (vs NHE) respectively. Due to the lower flat-band potential of PbS/CdS with respect to CdS/CdSe, cascade alignments of q-dots were fabricated in the order of PbS/CdS/CdSe quantum dots that allow electron transfer and flow from CdSe to CdS and then PbS. As the flatband potential of TiCl<sub>4</sub> and MgCl<sub>2</sub> treated TiO<sub>2</sub> is situated at ~ +0.031 eV, the mesoporous  $TiO_2$  can collect and accommodates the excited electron efficiently from the cascade of q-dots. Hence, in the PbS/CdS/CdSe cascade structure, efficient charge collection can be expected due to proper alignment of energy band positions. It was noticed that a good barrier layer on the TiO<sub>2</sub> mesoporous layer is essential to avoid the back injection of electron from TiO<sub>2</sub> to quantum dots. By treating the mesoporous TiO<sub>2</sub> layer a strong charge barrier layer can be formed on the mesoporous TiO<sub>2</sub> layer with MgCl<sub>2</sub> which also leads to enhance the career density at the photoanode (charge density calculations of bare and treated TiO<sub>2</sub> were explained in the supporting information). While ZnS layer prevents the injection of excited electron from quantum dots to electrolyte.[37] Hence, based on the solar cell performance and the electrochemical measurements of different combinations of q-dot assemblies, it can be said that the less charge transfer resistance and wide solar light harvesting ability of PbS/CdS/CdSe quantum dot lead to better performance of the q-dots solar cell. Moreover, further research on reduction of recombination of PbS/CdS/CdSe quantum may boost the efficiency further.

# Conclusions

A three-layer photoanode consisting of q-dots of PbS, CdS and CdSe was successfully fabricated to harvest light from UV-Vis-IR regions of the solar spectrum. The enhanced solar cell performance of the three-layer PbS/CdS/CdSe arrangement of q-dot on mesoporous TiO<sub>2</sub> layer was found to be mainly due to higher light harvesting ability and enhanced charge transport ability of such cascade arrangement of three-layer arrangement. It was demonstrated that the q-dot deposition sequence and methods are very critical for solar cell performance especially deposition of CdSe q-dots on the PbS layer leads to deterioration of solar cell performance due to annihilation of PbS q-dot particles. A suitable charge recombination barrier layer is an essential component in assembling multilayer q-dot cascade photoanode in QDSC to minimize the charge recombination.

# **Declaration of interest**: none

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# **Table captions**

Table 1: The calculated cathodic, anodic peak onset potentials from cyclic voltammetry measurements and differences of cathodic, anodic peak onset of q-dots of *A*-*PbS*, *B*-*CdS*, *C*-*CdSe*, *D*-*PbS*/*CdS*, *E*-*CdS*/*CdSe*, *F*-*PbS*/*CdSe*, *G*-*PbS*/*CdS*/*CdSe*, *H*-*PbS*/*CdS*/*CdSe* with a barrier layer

Table 2: Solar cell performances of photoanode fabricated with A- PbS, B-CdS, C-CdSe, D-PbS/CdS, E-CdS/CdSe, F-PbS/CdSe, G- PbS/CdS/ CdSe, H-PbS/CdS/CdSe with a barrier layer

Table 3: Rectification values of photoanodes fabricated with *A- PbS, B-CdS, C-CdSe, D-PbS/CdS, E-CdS/CdSe, F-PbS/CdSe, G- PbS/CdS/ CdSe, H-PbS/CdS/CdSe with a barrier layer.* Rectification values obtain from dark current-voltage measurements at 1.8 V.

Table 4: Summary of electrochemical impedance (EIS) measurements of photoanodes fabricated with *A- PbS, B-CdS, C-CdSe, D-PbS/CdS, E-CdS/CdSe, F-PbS/CdSe, G-PbS/CdS/ CdSe, H-PbS/CdS/CdSe with a barrier layer* under one sun illumination. Where Rk, Rct, Cµ and T denotes recombination resistance, charge transport resistance, chemical capacitance and lifetime measurements obtain from EIS.

# **Figure captions**

Fig. 1: (a) UV-Visible absorbance spectrum of *A- PbS, B-CdS, C-CdSe, and* (b) UV-Visible absorbance spectrum of *D-PbS/CdS, E-CdS/CdSe, F-PbS/CdSe, G- PbS/CdS/ CdSe,* 

Fig 2: (a) Cyclic-voltammetry measurements of photoanodes fabricated with *A- PbS*, *B-CdS*, *C-CdSe*. The magnified inset images of anodic and cathodic onset of Fig. 2(a) denote as [a] and [b] respectively. (b) Cyclic-voltammetry measurements of photoanodes fabricated with *D-PbS/CdS*, *E-CdS/CdSe*, *F-PbS/CdSe*. The magnifiedinset images of anodic and cathodic onset of Fig. 2(b) denote as [c] and [d] respectively. Cyclic-voltammetry measurements were performed at scan rate of 50 mV.s<sup>-1</sup>.

Fig 3: (a) Current density-voltage curve of photoanodes fabricated with *A- PbS, B-CdS, C-CdSe,* (b) Current density-voltage curve of photoanodes fabricated with *D-PbS/CdS, E-CdS/CdSe, F-PbS/CdSe* and (c) Current density-voltage curve of photoanodes fabricated with *G- PbS/CdS/ CdSe, H-PbS/CdS/CdSe with a barrier layer.* Fig. (d), (e) and (f) are External quantum efficiency measurements of respective QDSCs of (a), (b) and (c) respectively

Fig 4: (a) Dark current-voltage measurements of photoanodes fabricated with *A- PbS, B-CdS, C-CdSe*(b) Dark current-voltage measurements of photoanodes fabricated with *D-PbS/CdS, E-CdS/CdSe, F-PbS/CdSe,* and (c) Dark current-voltage measurements of photoanodes fabricated with *G- PbS/CdS/CdSe, H-PbS/CdS/CdSe with a barrier layer.* 

Fig 5: (a) Dark electrochemical impedance measurements of photoanodes fabricated with *A*-*PbS, B-CdS, C-CdSe* (b) Dark current-voltage measurements of photoanodes fabricated with *D-PbS/CdS, E-CdS/CdSe, F-PbS/CdSe,* and (c) Dark current-voltage measurements of photoanodes fabricated with *G-PbS/CdS/CdSe, H-PbS/CdS/CdSe with a barrier layer.*.

Fig 6: (a) Charge recombination (Rk) (b) Capacitance(C $\mu$ ) (c) Lifetime derived from electrochemical impedance measurements (d) Conductivity measurements against applied voltage of QDSSCs of *A*- *PbS*, *B*-*CdS*, *C*-*CdSe* (b) Dark current-voltage measurements of photoanodes fabricated with *D*-*PbS/CdS*, *E*-*CdS/CdSe*, *F*-*PbS/CdSe*, and (c) Dark current-voltage measurements of photoanodes fabricated with *G*- *PbS/CdSe*, *H*-*PbS/CdS/CdSe* with a barrier layer. The measurements were done at dark condition with 0.159 cm<sup>2</sup> active area.

Fig 7: (a) open circuit voltage decay measurement of photoanodes fabricated with *A- PbS, B-CdS, C-CdSe,* (b) open circuit voltage decay measurement of photoanodes fabricated with *D-PbS/CdS, E-CdS/CdSe, F-PbS/CdSe,* and(c) open circuit voltage decay measurement of photoanodes fabricated with *G- PbS/CdS/CdSe, H-PbS/CdS/CdSe with a barrier layer.*(d), (e) and (f) are lifetime measurements of respective QDSSCs calculated from the Fig. 7(a), (b) and (c).

Fig 8: Energy level diagram of  $FTO/TiO_2/PbS/CdS/CdSe$  QDSCs. Position of energy level derived from cyclic voltammetry analysis. (a) Schematic diagram with energy level cascade arrangement of PbS/CdS/CdSe QDSSCs with TiCl<sub>4</sub> and MgCl<sub>2</sub> treated TiO<sub>2</sub>photoanode.

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Table 1:				
QDSCs	Cathode peak onset	Anode peak onset	Differences of	
	with respect to	with respect to	cathodic, anodic peak	
	Vacuum	Vacuum	onset	
	(V Vs Ag/ Ag <sup>+</sup> )	(V Vs Ag/ Ag <sup>+</sup> )	(V Vs Ag/ Ag <sup>+</sup> )	
А	-4.43	-5.59	1.16	
В	-4.31	-6.32	2.01	
С	-4.19	-5.95	1.76	
D	-4.39	-6.31	1.92	
Е	-4.31	-6.11	1.80	
F	-4.43	-5.83	1.40	
G	-4.47	-6.07	1.60	
Н	<mark>-4.43</mark>	1.40	1.68	

# Table 2:

Table 2.					3
QDSCs	Jsc(mA.cm <sup>-</sup>	Voc (mV)	FF	Ŋ(%)	
	<sup>2</sup> )		(%)		<i>Y</i>
Α	10.14	279.50	35.43	1.00	
В	2.71	498.20	64.43	0.87	
С	7.22	503.40	57.46	2.46	
D	22.35	499.00	51.05	5.69	
E	13.42	513.90	59.26	4.09	
F	6.25	363.40	56.18	1.50	
G	18.11	427.80	58.07	4.50	
Н	23.46	471.10	56.42	6.24	
	. (				

Table 3:

QDSCs	rectification values
A	1.99
В	4.51
С	2.72
D	2.44
Е	4.16
F	1.83

G	2.50
Н	4.54

Table 4:

QDSCs	Rk(Ω)	$Rct(\Omega)$	$C\mu(F.cm^{-2})$	Ţ(s)
A	26.47	0.18	0.005	0.022
В	154.3	0.20	0.019	0.472
C	157.6	0.15	0.020	0.491
D	34.96	0.12	0.018	0.102
E	38.69	0.02	0.010	0.059
F	21.81	0.17	0.013	0.046
G	21.99	0.10	0.014	0.047
Н	29.71	0.14	0.015	0.071



Figure 1



Figure 2



Figure 3







Figure 5







Highlights

- A three layer q-dot solar cell was fabricated with PbS/CdS/CdSe
- Solar cell performance of three layer system strongly depends on stacking order
- A charge recombination barrier layer plays a significant role in cell performance