Colloidal PbS and PbSeS Quantum Dot Sensitized Solar Cells Prepared by Electrophoretic Deposition

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Abstract:

Here we report the developement of quantum dot sensitized solar cells (QDSCs) using colloidal PbS and PbSeS QDs and polysulfide electrolyte for high photocurrents. QDSCs have been prepared in a novel sensitizing way employing electrophoretic deposition (EPD), and protecting the colloidal QDs from corrosive electrolyte with a CdS coating. EPD allows a rapid, uniform and effective sensitization with QDs, while the CdS coating stabilizes the electrode. The effect of electrophoretic deposition time and of colloidal QD size on cell efficiency is analyzed. Efficiencies as high as $2.1\pm0.2\%$ are reported.

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1. Introduction

The development of third generation solar cells overcoming the Shockley-Queisser efficiency limit for a single absorber, 31%, is one of the most fascinating challenges in the energy research field. In this aspect, semiconductor Quantum Dots (QDs) have shown extremely attractive properties for the development of solar cells overcoming the current limitations.² The demonstration of efficient multiple exciton generation (MEG) process in colloidal QDs, 3, 4 despite certain controversy, 5 has aroused a huge interest in the use of these materials in photovoltaic devices. This interest has been reinforced with the recent reports of absorbed photon-to-current efficiency (APCE) close to 200% and incident photon-to-current efficiency (IPCE) as high as 114%. These achievements are acquired by using QDs with IR absorption, PbS⁶ and PbSe. That the former case PbS QDs have been employed in a sensitized solar cell configuration.⁸ Electron-hole pairs, photogenerated and produced by impact ionization in a MEG process, in PbS colloidal QDs are quickly separated into two different media. Electrons are injected into flat TiO₂ single crystals while holes are regenerated by a polysulfide electrolyte. ⁶ Nanostructured TiO₂ electrodes, instead of flat electrodes, enhance dramatically light harvesting but two main problems have to be solved: i) the uniform sensitization with colloidal QDs of nanostructured electrode along all its thickness and ii) the development of a stable QDSC configuration with colloidal PbS QDs as sensitizers. We have addressed these problems preparing colloidal PbS and PbSeS quantum-dot sensitized solar cells (QDSCs) in a novel sensitizing way employing electrophoretic deposition (EPD) and protecting the colloidal QDs from corrosive electrolyte with a CdS coating. We have analyzed the effect of electrophoretic deposition time and QD size in the final solar cell performance, obtaining efficiencies as high as 2.1±0.2 %. These results represent a significant advance in the development of colloidal QDSCs with light absorption in the IR region. In addition, we discuss the role of QDs in the recombination process of the analyzed solar cells.

Electrophoretic deposition has been used for the deposition of TiO₂ nanoparticles in solar cell⁹ or photocatalytic¹⁰ applications. In addition, it is a method also employed to deposit colloidal QDs, especially of CdSe on different materials such Au,^{11, 12} patterned electrodes,¹³ stacked-cup carbon nanotubes,¹⁴ and polymer templates.¹⁵ Colloidal CdSe QDs have also been deposited by electrophoresis for

photovoltaic purposes. Electrophoretic deposition of CdSe-C60 was used for the preparation of composite films for solar energy generation. ¹⁶ Flexible QDSCs have been fabricated by using the electrophoretic deposition of CdSe QDs on ZnO nanorods, obtaining efficiencies of 0.98%. ¹⁷ Higher efficiencies, 1.7%, have been reported for TiO₂ nanostructured electrodes with a ZnS coating of the colloidal CdSe QDs. ¹⁸ But there is no report on the use of EPD of PbS or PbSeS QDs. Electrophoretic deposition presents a significant advantage over other deposition techniques for colloidal QDs, either as linker assisted ¹⁹⁻²¹ or direct adsorbed, ^{19, 21} because of its simplicity and short deposition time. While for electrophoretic deposition times as short as 2 h were sufficient for effective coating, ¹⁸ several hours or even days are needed with other techniques. ¹⁹⁻²¹

The use of PbS QDs in QDSCs has been significantly less than the utilization of CdSe QDs, in spite of the higher light harvesting potential of PbS QDs due to their tunable absorption in the IR range. This is largely due to the difficulty of finding an appropriate electrolyte for PbS in which it is stable. PbS is not stable neither with iodine nor polysulfide redox electrolytes. 22-24 Thus, most of the reports on PbS QDSCs are for all-solid devices. 23, 25-27 In the case of using a liquid electrolyte for hole transport in PbS QDSCs, the highest reported efficiency, 0.62%, has been reported using a Co redox electrolyte, ²⁸ at 1 sun and with PbS grown by the Successive Ionic Layer Absorption and Reaction (SILAR) method. We have shown that by employing the same deposition technique, stable QDSCs using polysulfide electrolyte can be obtained by coating the PbS QDs with CdS,²⁹ reporting a significant efficiency of 2.36% using nanostructured TiO₂ electrodes.³⁰ Similar efficiencies have been obtained using SnO₂ electrodes,³¹ and outstanding efficiencies of 3.82% have been obtained using TiO₂ photoanodes with hierarchical pore distribution,³² employing again in both cases the SILAR growth. But, the presynthesis of colloidal QDs allows the preparation of QDs with better defined properties than QD samples prepared by SILAR. Treatment of colloidal PbS/TiO2 cells using CdS grown by SILAR method has been successfully applied before in a depleted heterojunction solar cell configuration.³³ The ultrafast electron injection from PbS colloidal QDs into TiO2 as fast as 6.4 fs,34 points to the capability of extraction of charge generated by MEG. Thus the preparation of cells with colloidal QDs is extremely interesting.

2. Experimental Section

Colloidal QDs: PbSSe QDs with oleic acid capping were kindly provided by NANOCO, while PbS QDs were purchased from Evident Technologies. Both QDs were solved in toluene.

 TiO_2 photoanode Preparation: After cleaning the FTO glasses (Pilkington TEC 8 with 8 Ω^2 sheet resistance), a compact layer of TiO_2 was deposited on them by spray pyrolysis of titanium- (IV) bis(acetoacetonato) di(isopropanoxylate) followed by sintering at 450°C, in order to improve the electrical contact between the nanoparticles. TiO_2 photoanodes were prepared by "double-layer" screen-printing on FTO glass using two different TiO_2 pastes including a light-scattering layer on top of the transparent TiO_2 film. The transparent layer is formed by 20 nm TiO_2 nanoparticles (18NR-AO, Dyesol) and the opaque layer contains 300-400 nm TiO_2 Particles (WER4-O Dyesol). Finally, the resulting film was sintered again at 450 °C for 30 minutes. Total thickness of the photoanodes was $15\pm1~\mu m$, measured with a profilometer Dektack 6 from Veeco.

Electrophoretic Deposition of the QDs on the TiO2 Electrodes: QDs were diluted in toluene, with concentrations of $\sim 2.2 \cdot 10^{-6}$ M. Two TiO₂ FTO electrodes were immersed vertically in the QDs solution parallel to each other. The deposition area of the electrodes was about 0.25 cm² and the distance between them was adjusted at 1cm. A voltage of 200 V was applied during 5-90 min. QDs were deposited on both cathode and anode electrodes similar to previous reports. 18 Fresh layers at each deposition time were taken out from the electrophoretic cell, rinsed several times with toluene to wash off unbound QDs and subsequently rinsed with ethanol and dried at room temperature. After electrophoretic deposition colloidal QDs were coated with CdS layer grown by SILAR. The SILAR process has been carried out following the method recently described. Cd²⁺ ions have been deposited from an ethanolic 0.05 M solution of $Cd(NO_3)_2 \times 4H_2O$. The sulfide sources were a 0.05 M solutions of $Na_2S \times 9$ H₂O in methanol/water (50/50 V/V). A single SILAR cycle consisted of 1 minute dip-coating of the TiO₂ working electrode into the metal precursors and subsequently rinsed during one minute in ethanol. Subsequently sample is dipped into the sulfide solutions for one minute and rinsed in methanol/water (50/50 V/V) one more minute. This procedure constitutes a complete SILAR cycle. SILAR process has been carried out automatically using a robot designed by ISTest. All the analyzed cells in this work were coated with ZnS, by being alternately dipped into 0.1M Zn(CH₃COO)₂ and 0.1M Na₂S Milli-Q water solutions for 1 min/dip and subsequently rinsed with Milli-Q ultrapure water. Two SILAR cycles were employed for ZnS coating.

QDSC Preparation: Porous Cu_2S was used as counter-electrodes which was prepared by immersing brass in HCl solution at $70^{\circ}C$ for 5 min and subsequently dipping it into polysulfide solution for 10 min.¹⁹ The counter-electrode and a QD-sensitized electrode were assembled into sandwich type the using a scotch spacer (thickness 50 μ m) and with a droplet (10 μ l) of polysulfide electrolyte. Polysulfide electrolyte was composed of 1 M Na₂S, 1 M S, and 0.1 M NaOH solution in Milli-Q ultrapure water.

Photoanode and Solar Cell Characterization: The cross section morphology of the TiO₂-PbSeS electrode films was investigated using a field emission scanning electron microscope FE-SEM (ULTRA plus ZEISS FESEM). Energy-dispersive X-ray spectroscopy (Apollo X, Ametek® EDAX) was employed to map and determine the distribution of chemical elements. A Bruker AXS-D8 Advance X-ray diffractometer (XRD), using Cu Kα radiation, was used to analyze the structural properties of anodes before and after light sensitization. The optical absorption spectra of the photoanodes were recorded at 300-700 nm using a Cary 500 UV vis Varian photospectroscometer. The IPCE measurements were done using a 150 W Xe lamp coupled with a monochromator controlled by a computer; the photocurrent was measured using an optical power meter 70310 from Oriel Instruments, using a Si photodiode to calibrate the system. QDSCs were characterized by current-voltage and impedance spectroscopy using a 0.1256 cm²mask and no antireflective layer. These measurements were performed employing the PG-STAT30 potentiostat (Autolab) and solar simulator at AM1.5 G, where the light intensity was adjusted with an NREL calibrated Si solar cell with a KG-5 filter to one sun intensity (100 mW/cm²). For most of the conditions analyzed in this work more than one cell have been prepared, standard errors have been calculated for these conditions, and included in Tables 1 and 2. In few cases just a single cell was analyzed, in that cases errors are not provided. IS measurements were carried out in dark at different bias voltages with 10 mV AC perturbation over a frequency range of 400 kHz to 10 mHz.

3. Results and Discussion

QDSCs have been prepared in this work by electrophoretic deposition of PbS and PbSeS QDs. It has been shown that PbSeS QDs offer certain benefits with respect to PbS or PbSe QDs in depleted heterojunction solar cells.³⁵ Figure 1, shows a cross section of a PbSeS sensitized TiO₂ film prepared by EPD. The double layer structure of TiO₂ can be appreciated with a thicker TiO₂ transparent layer and a thinner top

scattering layer. Elementary mapping of Ti, O, Se, S and Pb at three different positions (i.e. sample depths) indicate that the deposition of colloidal PbSeS QDs was uniform along TiO_2 thickness, ruling out a preferential deposition on top layer. A rather continuous coating, with no inhomogeneities at nanoscale level, is detected by comparing high magnification SEM micrographs of samples before and after electrophoretic deposition (Figure S1). It is worth to mention that no effect of the electrophoretic deposition time, t_d , on the coating homogeneity was detected.

Solar cells prepared with photoanodes sensitized with PbS and PbSeS QDs show poor stability with polysulfide electrolyte. It has been shown that PbS is photocorroded in polysulfide electrolyte, ²³ and needs to be protected from direct contact with the electrolyte. This is accomplished in this work by coating of CdS layer, using SILAR technique, on top of PbSeS and PbS QDs deposited by electrophoresis. CdS coating has been demonstrated previously to be an efficient protection of PbS, with a significant enhancement of the solar cell efficiency and stability.²⁹ In this sense, we have used a CdS coating, deposited by SILAR, in order to protect the PbSeS and PbS QDs from the corrosive effect of polysulfide electrolyte, obtaining stable devices.

For photoanode sensitization with PbSeS 800 nm different deposition times (t_d) have been investigated. Hereafter, to distinguish among the different QD sizes analyzed after the QD type (PbS or PbSeS) we will add the wavelength of the first excitonic absorption peak. Figure 2a presents the absorption, in the allowed range of our experimental setup, of differently sensitized TiO₂ films: bare TiO₂ film, film sensitized just with 5 SILAR cycles of CdS, films sensitized with 800 nm PbSeS QDs plus 5 SILAR cycles of CdS at different deposition times. The absorption of the different samples has been extracted from their diffuse reflectance R and it is expressed in Kubelka-Munk units as F(R)=(1-R)²/2R. For the sensitized electrodes the absorption of TiO₂ substrate has been removed. The film sensitized just with CdS exhibits an absorption threshold at 550 nm. When PbSeS QDs are deposited and coated with CdS the absorption threshold red shifts causing light absorption in the red visible region to increase due to a higher colloidal QD loading with deposition time.

Figure 2b, shows the current-potential curves obtained for QDSCs using photoanodes with different t_d , the solar cell parameters corresponding to these cells can be found in Table 1. When colloidal PbSeS QDs are deposited before CdS, the photocurrent of the cells increases due to the higher light harvesting capability provided by PbSeS QDs, see Figure 2a. But, this is associated with a decrease in open circuit

voltage, V_{oc} , as the QD loading increases. It should be expected that the ligands are preserved in the electrophoretic deposition, although the photoinjection is still possible. Efficient photoinjection has been previously reported for devices using colloidal QDs. CdSe QDs capped with TOP directly adsorbed on TiO_2 showing an APCE rather high, ~90%, 36 and also colloidal QDS attached to TiO_2 using linker molecules present significant photocurrent. 19,21,37

The maximum performance in the analyzed cases has been obtained for t_d = 60 min. The origin of the decrease of V_{oc} can be understood by the analysis of impedance spectroscopy (EIS) data on the basis of the previously proposed models. 38, 39 Samples with different deposition time present the same chemical capacitance, see Supporting Information S2, indicating that the conduction band position and the density of states of TiO₂ are not affected by the QD loading. A clear trend in the recombination resistance is observed, Figure 2c. The recombination resistance is seen to decrease with t_d , indicating unambiguously that PbSeS QDs participate in the recombination process.⁴⁰ Recombination increases with the QD loading. PbSeS QDs are acting as recombination centers as it has been also observed recently for Sb₂S₃. 41, 42 The observation of this fact is decisive for the future optimization of the QDSCs. On the other hand, the reduction of recombination resistance due to increase in QD loading produces the observed decrease in V_{oc} , which adversely affect on the solar cell performance, see Table 1. Note that both PbSeS colloidal QDs and CdS coating contribute to the final light harvesting. PbSeS QDs are the responsible of light absorption for wavelengths lower than ~550 nm, while for wavelengths higher than ~550 nm both PbSeS QDs and CdS contribute to the light absorption, but with a higher part from CdS, see Figure 2a.

We have also analyzed the effect of QD size in the final solar cell performance using PbSeS and PbS QDs of different sizes keeping t_d constant, see Figure 3. As the first excitonic absorption peak shifts to the IR region, the light absorption in the visible region increases, Figure 3a. But the increase in the light harvesting capability does not translate into greater efficiency of QDSCs, or in an increase of the photocurrent, J_{sc} , see Figure 3b and Table 2. In fact, a systematic decrease of V_{oc} and J_{sc} is observed, with the highest efficiency obtained using PbS 743 nm QDs, i.e. the QDs with the smallest size (largest band gap). The relation between the wavelength of the first excitonic absortion peak and PbS QD size is described in Supporting Information S3, using data from reference 43 .

The decrease of solar cell performance with the increase of the size of QDs has two causes. On one hand, the recombination resistance depends on the QD size, see Figure 3d. The sample with PbS 743 nm presents the highest recombination resistance (lowest recombination rate). On the other hand, there is an especially interesting discrepancy between light absorption and incident photon to current efficiency (IPCE), Figure 3c. This discrepancy is clearly manifested for the biggest QDs, PbS 1427 nm. In this case, the sensitized photoanode presents strong light absorption in all the visible region, but practically null IPCE at wavelengths higher than 500 nm. Indicating that PbS is not contributing to the photocurrent. In this case only CdS light absorber is contributing to the photocurrent, as can be observed from the IPCE measurements. This result is in good agreement with the work of Hyun et al.⁴³ In that work it has been shown that PbS QDs with size bigger than 4.3 nm (wavelength of the first excitonic absorption peak: 1116 nm) cannot inject into TiO₂ conduction band (CB) as its conduction band is lower than the CB of TiO₂, as it is indicated schematically in Figure 3e. As the QD size decreases the band gap increases shifting the PbS CB to higher energies than the TiO₂ CB, allowing electron injection from PbS with small size into TiO₂. As the quantum confinement increases the energetic distance between both CBs increases too, enhancing the injection driving force and consequently the photocurrent.

Having shown that the recombination pathway is preferentially through PbS QDs, and also that depends on the QDs size, recombination in this QDSCs has to be related with QD traps. Note that for PbS 1427 nm QDs, that do not inject electrons into TiO₂, the cell performance is significantly lower than for the cell just with 5 CdS SILAR cycles, see Figure 3b. This implies that the PbS QDs act as recombination centers in all the analyzed cases even when they are not able to inject photoexcited electrons into TiO₂. On the other hand, PbSeS QDs present lower recombination resistance than PbS indicating a higher recombination rate than their PbS counterparts.

Additionally, for the QD size with the highest performance, PbS 743 nm, we have modified the number of CdS SILAR cycles obtaining an efficiency as high as 2.1±0.2% for 9 SILAR cycles (1.8 % for the sample just with 9 SILAR cycles of CdS), see Figure 3b and Table 2. Significantly this efficiency is very close to our previously reported efficiency of 2.21% for a PbS/CdS, both grown by SILAR and using the same TiO₂ electrode,²⁹ that conventionally produces solar cells with higher efficiencies than colloidal QDs.⁴⁴

4. Conclusions

In summary, we have sensitized nanostructured TiO₂ photoanodes with colloidal QDs of PbSeS and PbS with different sizes. We have shown that the electrophoretic deposition method can used advantageously for fast sensitization of the photoanode with these QDs. CdS coating, deposited by SILAR, protects the colloidal QDs stabilizing the solar cell performance. A clear effect between QD size and device performance is observed, obtaining better results for the smallest QDs, with efficiencies as high as 2.1±0.2%. In addition, we have shown unambiguously that QDs act as recombination centers in these QDSCs. There is plenty of room for the optimization of these devices by focusing in reducing recombination though the QD traps. The latter may be possible by improving control on the QD properties, further characterization and surface treatments seem thus to be crucial. As an example, PbSeS sensitized photoanodes were here characterized by X-ray diffraction and the presence of lead oxide (PbO) phase was detected, irrespectively of the t_d , (Supporting Information S4). Although the origin of oxidation and its final effect in solar cell performance is currently under investigation, this finding points out the wide room of improvement of present lead chalcogenide QDSCs.

Associated Content

Supporting Information. FE-SEM micrographs of cross sections of TiO₂ and TiO₂/PbSSe samples, Chemical Capacitance of the analyzed cells, Correlation between PbS QD size and wavelength of the first excitonic absorption peak, XRD Characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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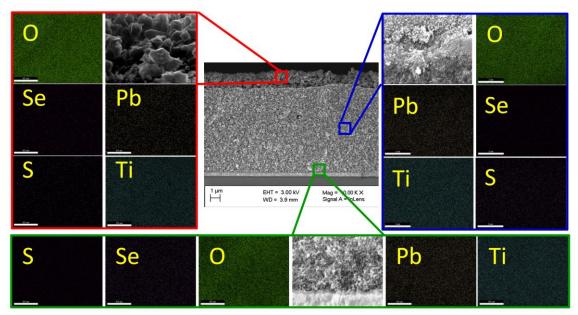


Figure 1. SEM analysis of a nanostructured TiO_2 sensitized with PbSeS QDs, t_d =60 min. The central picture of a photoanode cross section is surrounded by a magnified image and elemental maps of the three square boxes in the central picture. Elemental maps display Ti, O, Pb, Se and S spatial elemental distribution.

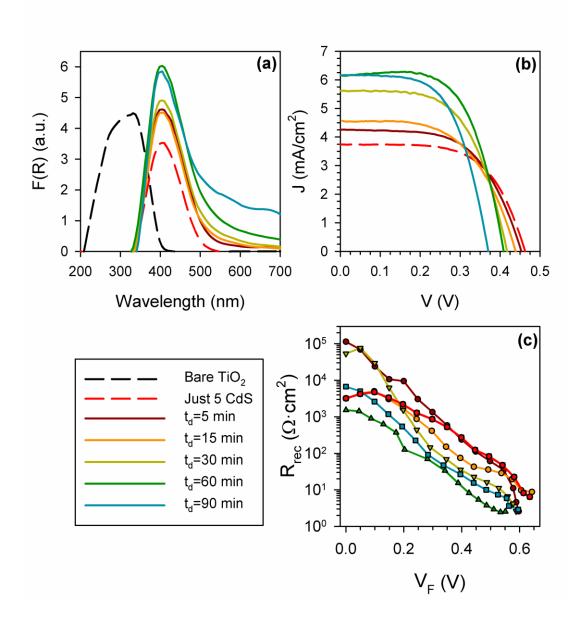


Figure 2. Effect of the electrophoretic deposition time, using 800 nm PbSeS QDs, in a) Kubelka-Munk plot of the diffuse reflectance spectra for bare TiO₂ film and TiO₂ sensitized just with 5 SILAR cycles of CdS and with 800 nm PbSeS QDs plus 5 SILAR cycles of CdS; in b) J-V curve and in c) recombination resistance.

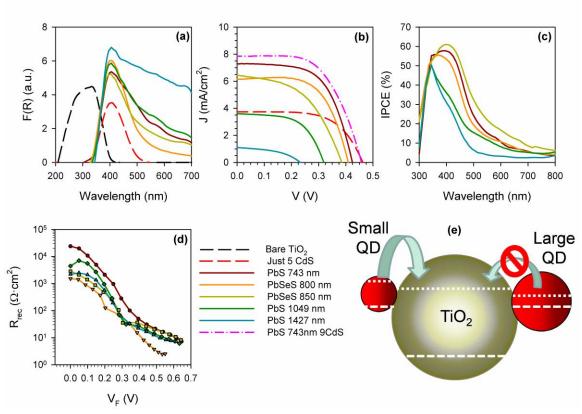


Figure 3. Effect of the QDs using the same electrophoretic deposition time, 60 min, in **a**) Kubelka-Munk plot of the diffuse reflectance spectra for bare TiO₂ film and TiO₂ sensitized just with 5 SILAR cycles of CdS and with 800 nm PbSeS QDs plus 5 SILAR cycles of CdS; in **b**) J-V curve; in **c**) IPCE; and in **d**) recombination resistance. **e**) Squeme of the relative alignment of the conduction band (dotted lines) of TiO₂ and PbS/PbSeS QDs depending on the QD size, relative Valence bands (dashed lines) are also included as reference.

Tables:

Table 1. Solar cell parameters of QDSCs prepared employing PbSeS 800 nm QDs and different electrophoresis deposition time. Open circuit voltage, V_{oc} , short circuit current, J_{sc} , fill factor, FF, and photovoltaic conversion efficiency, η .

PbSeS	V_{oc}	J_{sc}	FF	η
800	(V)	(mA/cm^2)		(%)
$nm^{[a]}$				
5CdS	0.46	3.7	0.62	1.07
5min	0.46 ± 0.04	4.3 ± 0.5	0.58 ± 0.03	1.14 ± 0.14
15min	0.440 ± 0.15	5±1	0.56 ± 0.01	1.1±0.3
30min	0.42 ± 0.2	5.6 ± 0.6	0.593 ± 0.005	1.4 ± 0.2
60min	0.41 ± 0.2	6.14 ± 0.5	0.63 ± 0.01	1.58±0.16
90min	0.37	6.2	0.60	1.36

[a] 5CdS is a sample prepared with no PbSeS QDs and just 5 SILAR cycles of CdS and 2 SILAR cycles of ZnS. The rest of the samples are identified by the PbSeS electrophoresis deposition time, in addition all these samples have also been coated with 5 SILAR cycles of CdS and 2 SILAR cycles of ZnS.

Table 2. Solar cell parameters of QDSCs prepared employing QDs of different type and size. All the samples present the same electrophoresis deposition time, 60 min, and CdS/ZnS coating, 5 and 2 SILAR cycles respectively, except the last one with 9 and 2 SILAR cycles. Sample prepared just with 9 SILAR cycles of CdS is included for comparison. Open circuit voltage, V_{oc} , short circuit current, J_{sc} , fill factor, FF, and photovoltaic conversion efficiency, η .

t_d =60 min	V_{oc}	J_{sc}	FF	η	
	(V)	(mA/cm^2)		(%)	
PbS 743 nm	0.425±0.15	7.3±0.7	0.61±0.03	1.9±0.2	
PbSeS 800nm	0.41 ± 0.2	6.14 ± 0.5	0.63 ± 0.01	1.58±0.16	
PbSeS 850nm	0.39	6.4	0.49	1.2	
PbS 1049nm	0.322±0.015	3.6 ± 0.8	0.584 ± 0.014	0.67 ± 0.14	
PbS 1427nm	0.234±0.010	1.09±0.12	0.46 ± 0.02	0.1235±0.0003	
PbS 743 nm	0.46±0.07	8±2	0.58±0.03	2.1±0.2	

9CdS					
9CdS	0.515	5.79	0.60	1.8	

TOC figure:

