Pulsed voltage deposited lead selenide thin film as efficient counter electrode for quantum-dot-sensitized solar cells

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Abstract Lead selenide (PbSe) thin films were deposited on fluorine doped tin oxide (FTO) glass by a facile one-step pulse voltage electrodeposition method, and used as counter electrode (CE) in CdS/CdSe quantum dot-sensitized solar cell (QDSSCs). A power conversion efficiency of 4.67% is received for the CdS/CdSe co-sensitized solar cells, which is much better than that of 2.39% received using Pt CEs. The enhanced performance is attributed to the extended absorption in the near infrared region, superior electrocatalytic activity and *p*-type conductivity with a reflection of the incident light at the back electrode in addition. The physical and chemical properties were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), energy-dispersive spectroscopy (EDS), reflectance spectra, electrochemical impedance spectroscopy (EIS) and Tafel polarization measurements. The present work provides a facile pathway to an efficient CE in the QDSSCs.

Keywords Lead selenide thin films; pulse voltage electrodeposition; counter electrode; quantum dot sensitized solar cells

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1. Introduction

The counter electrodes (CEs) in quantum dot sensitized solar cells (QDSSCs) are not well developed as their counterparts in dye cells [1-5]. In QDSSCs, sulfide/polysulfide redox couple is commonly used instead of iodine/iodide electrolyte to stabilize the quantum dots and improve the cell performance. In this circumstance, the traditional Pt CE is not compatible to polysulfide electrolytes due to the chemisorb of sulfur species on the Pt surface and induction of poisoning effect, which result in low photocurrent density and fill factor [6-7]. Compared with Pt, metal sulfides such as cobalt sulfide (CoS) [1], cobalt disulfide (CoS₂) [2], iron sulfide (FeS) [8], nickel sulfide (NiS) [9], lead sulfide (PbS) [3], cuprous sulfide (Cu₂S) [4,5], copper sulfide (CuS) [10], Cu₂ZnSnS₄ [11], Cu₂ZnSnSe₄ [12] and Cu₂ZnSn(S_{1-x}Se_x)₄ [13] have been reported as more effective CE materials to replace Pt. Among them, Cu₂S exhibits the best electrocatalytic activities toward polysulfide reduction up to now. However, Cu₂S CEs are mechanical and chemical instable, which result in the poisoning of photoanode [12, 14]. Stability and electronic conductivity of the Cu₂S-based CE can be improved by combining carbon [15] and reduced graphene oxide [7, 16]. Nevertheless, because of the complexity of manufacture process and rigorous synthesis condition, these CEs are still unsuitable for the large-scale industrial production. Some issues including high overpotential for polysulfide reduction at the counter electrode and large internal resistance, which lead to low open circuit voltage, short circuit current density and poor fill factor, are still unsolved [17]. Therefore, it remains a challenge to find a stable and efficient CE with a facile preparation process at low production cost.

Photoactive materials, especially *p*-type narrow band gap semiconductors, are identified as a promising CE candidate for efficient QDSSCs nowadays [3, 18]. On one hand, the narrow band gap characteristics of CE harvest the residual red to infra-red light penetrating the photoanode to generate extra photoelectron, and facilitate electron injection to the electrolyte to achieve a higher short-circuit photocurrent (J_{sc}) and fill factor. On the other hand, the *p*-type conductivity of CE can form a tandem junction between the CE and the anode, which increases the photovoltage. Zaban *et al* reported that a tandem solar cell consisting of the *p*-type CdS CE, *n*-type CdSe photoanode and polysulfide electrolytes exhibits photovoltage (V_{oc}) of 816 mV, which is the highest reported V_{oc} to date for QD based photoelectrochemical cells [18]. Teng *et al* achieved a power conversion efficiency of 4.7% for CuInS₂/CdS/ZnS QDSSCs using the photoactive *p*-type PbS as the CE, which is more than 15% greater than that of a cell assembled with the highly electrocatalytically active copper sulfide [3]. Among various narrow band-gap semiconductors, PbSe is a *p*-type direct band-gap semiconductor with a band gap of ~0.26 eV in air [19]. Furthermore, it also **does**

not form many crystal defects. With its high carrier mobility, low production cost and easily scalable large batch synthesis [20], PbSe is thus usually used as light absorber due to strong quantum confinement and enhanced multiple exciton generation [21]. However, the electrocatalytic activity of PbSe has not drawn enough attention.

In this paper, *p*-type PbSe thin films were successfully deposited on fluorine doped tin oxide (FTO) glass substrate by a facile one-step pulse voltage electrodeposition method. The highly reproducible PbSe thin films are compact, stable, and highly reflective, which was characterized by XRD, SEM, TEM, EDS, and reflection spectroscopy. The electronic and catalytic activities were evaluated by EIS, Tafel and potentiostatic current-voltage polarization curves. When the PbSe thin films were used as CE in CdS/CdSe QDSSCs, all cell parameters including short-circuit current density, open-circuit voltage, and fill factors are all higher than that for Pt CE cells, resulting in an improved power conversion efficiency of 4.67%. IPCE curve suggests enhanced conversion efficiency with better catalytic activity at the CE. These results are coincidence with each other and those received by electrochemical impedance spectroscopy, suggesting that pulse voltage electrodeposited *p*-type PbSe is a promising candidate as CE in QDSSCs.

2. Experimental Section

2.1. Materials

All reagents, including lead acetate ($\text{Pb}(\text{OAc})_2$), ethylenediaminetetraacetic acid disodium salt (Na_2EDTA), selenium powder (Se), sodium sulfite (Na_2SO_3), sodium sulfide nonahydrate ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$), cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$), sulfur sublimed (S), zinc acetate dihydrate ($\text{Zn}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$), chloroplatinic acid (H_2PtCl_6), isopropanol ($(\text{CH}_3)_2\text{CHOH}$), sodium hydroxide (NaOH), methanol (CH_3OH), and absolute ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) were analytical grade, purchased from Sinopharm Chemical Reagent Co., and used without further purification. P25 was purchased from Germany Degussa Co. Fluorine doped tin oxide (FTO) glass ($7\ \Omega/\square$) and hot-melt gaskets were purchased from WuHan GEAO company.

2.2 Electrodeposition of PbSe CE

Pulse voltage electrodeposition in a two-electrode system with a constant current of 5 A at room temperature was carried out to prepare the PbSe CE on a Maynuo M8811 DC source meter. In this process, the FTO glass was used as the working electrode and a graphite rod was used as the counter electrode. The distance between two electrodes was kept at 1 cm. The electrolyte for the electrodeposition of PbSe was an aqueous solution composed of $\text{Pb}(\text{OAc})_2$, Na_2EDTA , and Na_2SeSO_3 . In a typical process, 0.02 M $\text{Pb}(\text{OAc})_2$ and 0.04 M Na_2EDTA was mixed to make a 30 ml of white turbid solution under magnetic stirring. Then, the white

turbid solution turned to a colorless transparent solution by adjusting the pH of the solution to 7.5-8.0 with 10 M NaOH solution. The appearance of the colorless transparent solution indicated that Na₂EDTA reacted with Pb(OAc)₂ to form a PbEDTA complex, which in order to prevent the spontaneous precipitation of Pb²⁺ as Pb(OH)₂ [22-24]. After being stirred for 20 min, 20 ml of 0.02 M Na₂SeSO₃ aqueous solution (prepared by refluxing Se powder (0.3 M) and Na₂SO₃ (0.6 M) in distilled water at 70°C for 7 h) was added into the above solution with a constant stirring for another 20 min. In the experiment, the deposition voltage is the key to obtain high quality PbSe CE. The deposition voltage used in the present work was 3 V, which was the lowest voltage to form PbSe. Under the voltage of 3 V, the reductions of Pb²⁺ to Pb and SeSO₃²⁻ to Se could be simultaneous on the surface of the FTO glass substrate, which resulted in the formation of PbSe, due to a solid-state reaction between Pb and Se [25,26]. If the voltage is higher than 3 V, the reduction rate of Pb²⁺ to Pb and SeSO₃²⁻ to Se too fast to form a compact layer of PbSe on the FTO glass substrate. Finally, PbSe film would fall off from the FTO glass substrate in several seconds. Hence, the PbSe was electrodeposited at room temperature using a 3 V of pulse voltage with the 0.4 s on-time and 0.1 s off-time for 5 s. The experimental setup scheme is depicted in Fig. 1. After deposition, the PbSe CE was rinsed successively with distilled water, ethanol, and then dried in the open air. For comparison, Pt CE was prepared by spraying 5mM H₂PtCl₆ isopropanol solution onto FTO glass substrate, followed by sintering at 380°C for 30 min. This process was repeated three times.

2.3 Fabrication of CdS/CdSe sensitized photoanodes

Microporous TiO₂ films were prepared by spin coating of TiO₂ paste (Degussa P25) on FTO glass substrate, followed by sintering at 450°C for 30 min. The as-prepared TiO₂ films were sensitized with CdS/CdSe QDs by the successive ionic layer adsorption and reaction (SILAR) method. Firstly, the TiO₂ films were immersed in a solution containing 0.1 M Cd(NO₃)₂·4H₂O in methanol for 1 min. Then, the films were immersed in a methanol-water mixture (1:1 by volume) which contains 0.1 M Na₂S·9H₂O for 1 min. The films were thoroughly rinsed with methanol to remove the excess precursor after each immersion. The same procedure was repeated 5 times to form CdS sensitized TiO₂ electrodes. For CdSe QDs deposition, 5 cycles of TiO₂/CdS electrodes were immersed in a solution containing 0.1 M Cd(NO₃)₂·4H₂O in methanol for 10 min. Subsequently, the electrodes were immersed in 0.02 M Na₂SeSO₃ aqueous solution at 50°C for 20 min. The electrodes were thoroughly rinsed with pure solvent to remove the excess precursor after each immersion. The same procedure was repeated 7 times to form CdSe sensitized electrodes. Finally, the CdS/CdSe cosensitized electrodes were coated with ZnS passivation layer by twice dipping

alternately into $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.1 M) and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (0.1 M) aqueous solutions for 1 min.

2.4. Fabrication and measurement of QDSSCs

The polysulfide electrolyte (1 M Na_2S , 1M S and 0.1 M NaOH aqueous solution) was sandwiched between the CdS/CdSe sensitized photoanode and the PbSe or Pt CE to give the cell, which was separated by using a silicone spacer (thickness: 50 μm). The area of the cell was 0.28 cm^2 . The current-voltage characteristics were monitored and recorded by a source meter (Keithly 2400) under an irradiation of simulated solar light (AM 1.5G, 100mW/ cm^2).

2.5 Characterization

The phase and purity of the as-prepared PbSe CE were characterized by X-ray diffraction (XRD) with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The morphology and composition of PbSe CE were examined by Philips-FEI Quanta 200 scanning electron microscope (SEM) combined with energy-dispersive spectroscopy (EDS). Transmission electron microscopy (TEM) images were taken on a JEOL JEM-2010 high resolution transmission electron microscopy. The reflectance spectra of counter electrodes were measured on a Perkin-Elmer Lambda 950 ultraviolet visible-near infrared (UV-vis-NIR) spectrophotometer. The IPCE was measured as a function of wavelength from 300 to 800 nm by using CROWNTech Q-test station 500TI. Electrochemical impedance spectroscopy (EIS) and Tafel polarization measurements were conducted in a symmetrical dummy cell fabricated with two identical CEs using a CHI 660D electrochemical workstation (Shanghai, China). **The detailed procedure for the fabrication of the symmetric dummy cell is as follow: one electrode (PbSe or Pt) was masked with a 3 M double-sided bonding tapes with a circular hollow of 6.0 mm in diameter. Then, one drop (50 μL) of polysulfide electrolyte was pipetted onto the electrode surface. Finally, the other identical electrode (the same component as the other electrode, ie, PbSe or Pt) was covered on the first electrode and a binder clip was used to clamp the two electrodes to construct the symmetric dummy cells. The active area of the symmetric dummy cells was 0.28 cm^2 .** The potentiostatic current-voltage polarization measurements were carried out in a three-electrode system with PbSe electrode or Pt electrode as working electrode, a Pt foil as counter electrode and an Ag/AgCl electrode as reference electrode. The electrolyte was same as that used for QDSSCs in all electrochemical measurements.

3. Results and Discussion

The deposited samples on FTO substrate by pulsed electrodeposition technique are indexed to cubic structured PbSe according to XRD patterns (Fig. 2a). The peaks of cubic phase PbSe (JCPDS No. 06-0354) can be well distinguished from those of SnO_2 peaks

(JCPDS No. 46-1088) in the substrate. EDS is employed to further determine the chemical composition of the PbSe film (Fig. 2b), which reveals an atomic ratio of 0.65:1 for Pb:Se. Sn signal is originated from the FTO substrate. XRD and EDS results confirm that Se-rich cubic PbSe crystal film could be effectively deposited on FTO glass substrate by pulse voltage electrodeposition method. The amorphous form of selenium detected in the sample by EDS is typical for Se electrodeposited at ambient conditions, since elemental selenium is reported as intermediate for the formation of lead selenide [27]. Elemental selenium is firstly reduced from the solution:

The elemental selenium produced on the surface of the electrode is further electrochemically reduced to selenide:

Then, selenide is combined with Pb^{2+} to produce the final product of PbSe:

As a result, the unreduced selenium is left behind as a by-product of the present electrochemical deposition process.

The extra selenium content is also reported in the similar processes using electrochemical depositions. For example: “The element ratio Pb:Se is 0.43:1 and 0.08:1 for these two types of structures, respectively. XRD data point to only cubic PbSe phase. The excess of Se (in addition to PbSe) detected in the film by EDX does not appear on XRD patterns and represents an amorphous form which is typical for Se electrodeposited at ambient conditions.” [28] and “The Pb content in the deposited Se(Pb) films varies in the ranged from 1 to 30 at.% and increases with Pb^{2+} concentration in solution or when the electrode potential is shifted to more negative values.” [29]. More importantly, the extra selenium is reported to cause *p*-type semiconductor behavior of deposited selenides, while an excess of Pb leads to *n*-type semiconductors [30,31]. The Se-rich *p*-type semiconductor of PbSe thin film is later evidenced in the electrochemical analysis.

The deposited PbSe forms a compact layer on the FTO glass substrate. The smooth surface of PbSe makes the film highly reflective, which behaves like a mirror reflecting the visible light. The logo of SNNU can be well observed in the PbSe “mirror” (Fig. 3a). The reflectance spectra indicate that the PbSe CE has more than 60% reflectivity in the visible light region (400 to 800 nm), which is 6 times higher than that of Pt CE (~10%) (Fig. 3b). The reflection nature of the present PbSe film adds an extra function when it is used as CEs. It reflects the incident light back to the cells and results in higher current in the QDSSC applications [32]. What is more important, PbSe has an absorption in the near infrared region due to the characteristic of its narrow band gap. In the present experiment, the PbSe film has a

strong absorption extending from 1000 to 1600nm (Fig. 3b). The NIR absorption provides additional source for the photon generated electrons.

The surface morphology and size of the PbSe were further characterized by SEM and TEM. It can be observed from SEM images under different magnification that films of compact PbSe particles are pulsed electrodeposited on to the FTO substrate (Fig. 4a, b). The cross-sectional SEM image (Fig. 4c) indicates that the compact PbSe film is firmly anchored to the FTO glass substrate with a thickness of about 200 nm. The size of the PbSe film was evaluated using TEM by scratching off the PbSe film from FTO glass substrate. It can be observed that the PbSe film is composed of nanoparticles with the grain size about 20 nm (Fig. 4d).

In order to assess the electrocatalytic activity of the PbSe CE in the polysulfide electrolyte, electrochemical impedance spectroscopy (EIS) was carried out using symmetric dummy cells assembled with two identical PbSe CEs and filled with the polysulfide electrolyte (1 M S, 1 M Na₂S, and 0.1 M NaOH aqueous solution). For comparison, Pt CE was also measured under the same conditions. **The application of a “symmetric dummy cell” instead of a real QDSSC during the tests is based on the following facts. In the symmetric cell, various interfacial and internal impedances of common QDSSCs are removed, including the impedance at the photoanode/sensitizer interface, internal resistance of the photoanode, and diffusion impedance of the electrolyte into the photoanode. The only two impedances thus left in the symmetric cell are the charge-transfer impedance at the electrolyte/counter electrode interface and the Nernst diffusion impedance of the redox couple in the electrolyte [33]. As a result, the analyses of the equivalent circuit are greatly simplified using the symmetric cells.** Fig. 5 shows Nyquist plots of the PbSe and Pt CEs, respectively. The corresponding equivalent circuit model is shown in the inset of Fig. 5. The Nyquist plots were fitted by using Z-view software and electrochemical parameters are summarized in Table 1. The high frequency intercepts on the real axis corresponds to the ohmic series resistance (R_s). The semicircle at high-frequency region is correlated to charge-transfer resistance (R_{ct}) and the corresponding chemical capacitance (CPE) at the CE/electrolyte interface, while the semicircle at low-frequency region refers to the Warburg diffusion impedance (Z_w) of the polysulfide electrolyte. The results show that R_s , R_{ct} and Z_w values of PbSe CE are 18.1, 1.86 and 57.58 Ω , respectively, which are remarkably lower than those of the Pt CE (R_s : 24.1 Ω , R_{ct} : 4711 Ω , Z_w : 2017 Ω), indicating that the PbSe CE has superior electrical conductivity, electrocatalytic activity and diffusion velocity of the S^{2-}/S_n^{2-} redox couple in the polysulfide electrolyte [7,12,34-36]. Moreover, the PbSe CE has a higher CPE (124.76 μ F) than that of the Pt CE (6.13 μ F). The higher CPE value indicates higher surface area which is reported to generate more active sites for catalyzed S^{2-}/S_n^{2-} reaction in the polysulfide electrolyte, leading

to better catalytic activity [36].

In order to elucidate more clearly the electrocatalytic activity of the PbSe CE, Tafel-polarization measurements were carried out. The exchange current (J_0) directly related to the electrocatalytic activity of the CE, which can be easily obtained from the extrapolated intercepts of the anodic and cathodic branches of the Tafel polarization curves. Fig. 6a shows that the PbSe has a larger J_0 than that of Pt, implying a higher electrocatalytic activity of the PbSe CE. This result is in good agreement with the EIS values in terms of Eq. (1),

$$J_0 = RT / nFR_{ct} \quad (1)$$

where R is the gas constant, T is the absolute temperature, n is the number of electrons involved in the polysulfide reduction, F is the Faraday constant, and R_{ct} is the charge-transfer resistance [12,36]. Furthermore, The PbSe CE shows a higher limiting diffusion current density (J_{lim}) which can be derived at high potential from the Tafel polarization curves. The J_{lim} related to the diffusion of the S^{2-}/S_n^{2-} redox couple in the polysulfide electrolyte. Based on Eq. (2), a higher J_{lim} means a larger diffusion coefficient (D) and faster diffusion velocity of the S^{2-}/S_n^{2-} redox couple in the polysulfide electrolyte.

$$D = lJ_{lim} / 2nFC \quad (2)$$

Where D is the diffusion coefficient of the S_n^{2-} , l is the spacer thickness, n is the number of electrons involved in the reduction of S_n^{2-} at the electrode, F is the Faraday constant, and C is the S_n^{2-} concentration [12].

Tafel polarization measurements were also carried out to evaluate the stability of the PbSe CE in the polysulfide electrolyte [37]. Fig. 6b and c show the Tafel polarization curves of the freshly prepared and aged CEs. It can be seen that no observable variation can be detected in the Tafel curves of the PbSe CE in 90 min (Fig. 6b), while the Tafel curves of the Pt CE suffer from a constantly changing during the period of time. In particular, the equilibrium potential of the Pt CE deviates from the location of zero potential and moves to a more negative potential as time go on (Fig. 6c), which is another evidence for the excess adsorption of S on to the Pt surface generating catalytic poisoning [38]. The results of CV, EIS and Tafel polarization measurements show that PbSe CE possesses a superior electrocatalytic activity and stability in the polysulfide electrolyte.

The p -type conductivity of PbSe CE was proved by the potentiostatic current-voltage polarization measurements in the dark and under irradiation (Fig. 7). Compared to Pt CE, the PbSe CE always exhibited a negative voltage shift at the zero-current position not only in the dark but also under irradiation. The negative voltage shift indicated the p -type conductivity of the PbSe CE because achieving electrode-electrolyte equilibrium (i.e., the zero-current situation) requires a negative voltage bias [3].

The enhanced infrared light utilization, p -type conductivity and better electrocatalytic

activity are reflected in the performance enhancement when PbSe films are used as CE in QDSSCs. CdS/CdSe sensitized TiO₂ photoanode QDSSCs were assembled using PbSe film as CE with a schematic diagram illustrated in Fig. 8a. For comparison, Pt CE QDSSC was also assembled. The J - V curves using different CE are shown in Fig. 8b. The cell parameters such as short circuit current (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), and power conversion efficiency (η) for the cells with PbSe and Pt CE are listed in Table 2. It is clearly seen that the PbSe CE based QDSSCs shows a much higher η than that of Pt CE because of the significant enhancement in all cell parameters of J_{sc} , V_{oc} and FF . This mainly because that the superior electrocatalytic activity of the PbSe CE, which has been proved by EIS and Tafel polarization measurements. In addition, it is worth noting that the PbSe is a typical p -type semiconductor with a narrow band gap. The specific optical-electronic characteristics of PbSe could effectively improve the performance of solar cell by enhancing the efficiency of light utilization and forming tandem junction between the CE and the anode, which would increase V_{oc} and FF [18]. The extended range of light absorption and enhanced efficiency of visible light utilization promoted the photocurrent, which was verified by IPCE (Fig. 8c). The narrow band gap characteristics of PbSe resulted in the absorption of residual long-wavelength solar irradiation by the PbSe CE. This irradiation could excite the PbSe and facilitate the injection of electrons from the conduction band into the electrolyte, leading to a higher J_{sc} and FF [3]. In addition, the obtained PbSe CE reflects the visible light into the cell, which enhances the efficiency of visible light utilization.

4. Conclusion

A p -type narrow band gap PbSe thin film was successfully prepared by a facile one-step pulse voltage electrodeposition method on FTO substrate. The obtained PbSe thin film possesses superior electrocatalytic activity and stability in the polysulfide electrolyte. The superior electrocatalytic activity of PbSe thin film accelerates the catalytic reaction at the interface of the CE/polysulfide electrolyte ($S_n^{2-} + e^- \rightarrow nS^2$). The narrow band gap characteristics and p -type conductivity of PbSe CE enhance the efficiency of light utilization and form tandem junction between the CE and the anode. Using the PbSe thin films as CE in CdS/CdSe QDSSCs, an improved power conversion efficiency of 4.67% has been obtained. The superior electrocatalytic activity and specific optical-electronic characteristics make PbSe become a promising counter electrode material for QDSSCs.

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Figure Captions:

Fig. 1. Experimental system and pulse voltage electrodeposition process of depositing PbSe onto FTO glass.

Fig. 2. (a) Powder XRD patterns of the deposited PbSe and FTO substrate; (b) EDS spectrum of PbSe deposited on FTO substrate.

Fig. 3. (a) Digital photographs of the PbSe and Pt CE; (b) reflection spectra of the PbSe and Pt CE.

Fig. 4. Surface (a), (b) and cross-sectional (c) SEM images of the PbSe CE; (d) TEM images of the PbSe CE.

Fig. 5. Nyquist plots of the symmetric thin layer cells with PbSe and Pt CE. Insets are the equivalent circuit model and the full Nyquist plot of Pt CE symmetric dummy cell.

Fig. 6. (a) Tafel polarization curves of PbSe and Pt CE at the start of the tests; Tafel polarization curves of (b) PbSe and (c) Pt CE over time.

Fig. 7. Potentiostatic current-voltage polarization curves of the PbSe and Pt CE in the dark and under irradiation.

Fig. 8. (a) The schematic diagram of the QDSSCs based on PbSe CEs; (b) J - V curves of QDSSCs with PbSe and Pt CE under one sun illumination (AM 1.5 G, 100 mW cm^{-2}); (c) IPCE spectra of QDSSCs with PbSe and Pt CE.

FIGURES

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Table Captions:

Table 1. EIS parameters of symmetrical cells with PbSe and Pt CE.

Table 2 Photovoltaics Parameters for Pt and PbSe CE.

TABLES

CE	$R_s (\Omega)$	$R_{ct} (\Omega)$	$Z_w (\Omega)$	$C_{PE} (\mu F)$
Pt	24.1	4711	2017	6.13
PbSe	18.1	1.86	57.58	124.76

Table 1.

CE	$J_{sc} (mA/cm^2)$	$V_{oc} (V)$	$FF (\%)$	$\eta (\%)$
Pt	14.33	0.52	32	2.39
PbSe	16.91	0.57	48	4.67

Table 2.