

Improved efficiency of CdS quantum dot sensitized solar cell with an organic redox couple and a polymer counter electrode



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ARTICLE INFO

Article history:

Received 6 March 2014

Received in revised form 11 June 2014

Accepted 12 June 2014

Available online 20 June 2014

Keywords:

Quantum dot

Sensitized solar cell

Organic electrolyte

Polymer

CdS

ABSTRACT

Quantum dot sensitized solar cells (QDSSCs) based on an organic thiolate/disulfide redox couple ($C_7H_5N_4S^-/C_{14}H_{10}N_8S_2$ or $C_2H_3N_4S^-/C_4H_6N_8S_2$) and a polymer counter electrode [poly (3, 4-ethylenedioxythiophene), PEDOT] were fabricated and their photovoltaic performance were investigated. In CdS QDSSC, the organic $C_7H_5N_4S^-/C_{14}H_{10}N_8S_2$ electrolyte shows better performance than the polysulfide electrolyte, and the PEDOT counter electrode exhibits higher efficiency than that of the Pt counter electrode and the CoS counter electrode. An efficiency of 1.53% was achieved in this QDSSC. The influences of the morphology and the deposition charge of the PEDOT counter electrodes on the cell performance were also studied. Furthermore, it was found that the $C_7H_5N_4S^-/C_{14}H_{10}N_8S_2$ redox couple outperformed the $C_2H_3N_4S^-/C_4H_6N_8S_2$ redox couple due to reduced electron recombination.

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1. Introduction

Semiconductor nanocrystals, also referred to as quantum dots (QDs), have attracted much attention as their several distinct advantages in solar cells [1,2]. Due to the unique multi-electron generation effect, quantum dot sensitized solar cell (QDSSC) which originated from dye sensitized solar cell (DSSC) has a maximum theoretically efficiency as high as 44% which clear overtakes the efficiency of other kinds of solar cells [3]. The efficiency of QDSSC has been rapidly improved to 6% in recent year [4]. However, it's still lower than that of the DSSC and more effort should be made to improve it.

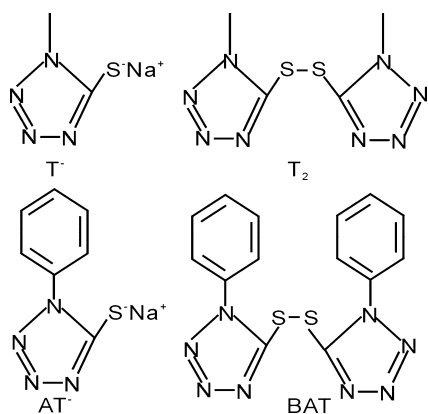
The lack of ideal electrolyte and counter electrode (CE) is the main factor that limits the efficiency of QDSSC [5,6]. Nowadays, the most well-known electrolyte and counter electrode are the polysulfide electrolyte (S_x^{2-}/S^{2-}) and the Pt CE, respectively [7]. Unfortunately, this inorganic polysulfide electrolyte usually leads to a low fill factor (FF) and open circuit photovoltage (V_{oc}) and thus to a low cell efficiency [8]. Therefore, various other electrolytes including inorganic electrolytes such as cobalt complex [9], $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox couple [10] and modified polysulfide electrolyte [11] were investigated by scientists.

However, there are few reports of organic electrolytes used in QDSSCs. Ning et al. employed a pure organic redox couple McMT⁻/BMT in CdS QDSSCs and found that it reinforced the photovoltage and conversion efficiency [12]. The $C_2H_3N_4S^-/C_4H_6N_8S_2$ (T^-/T_2) redox couple was regarded as a excellent thiolate/disulfide mediator in DSSCs due to its slow charge recombination and high sensitizer regeneration efficiency characteristics [13]. Our group developed an organic $C_7H_5N_4S^-/C_{14}H_{10}N_8S_2$ (AT^-/BAT) redox couple for DSSCs and found it could obviously enhance the photovoltage and thus enhance the efficiency of the cell [14].

In addition to the design of electrolytes, the choice of counter electrode material is also critical in determining the cell efficiency. As the poor electrocatalytic activity of the Pt CE in QDSSCs [15], Pt-free materials such as carbon [16,17], metal sulfide [18,19] and conducting polymer [20] were used as counter electrode materials, among which the polymer PEDOT was reported as a promising candidate due to its extremely low cost-availability and excellent electrocatalytic activity [20]. PEDOT was also used as counter electrode in DSSCs and had good performance [21,22].

In an effort to overcome the shortages of the polysulfide electrolyte and the Pt CE, in this paper, the analogous organic redox couples AT^-/BAT and T^-/T_2 (Scheme 1) were first used in CdS QDSSCs, at the same time, a polymer PEDOT counter electrode was also used. The combination of the organic AT^-/BAT redox couple and the PEDOT CE is very successful in improving the efficiency of the QDSSC.

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Scheme 1. Structures of the organic redox couples T^-/T_2 and AT^-/BAT .

2. Experimental details

2.1. Materials

All the chemicals were of analytic grade and used without further purification. F-doped tin oxide glass FTO (15 Ω /square) was obtained from Pilkington UK. The nanoporous TiO_2 film and the TiO_2 scattering layer were prepared using PST-18NR (JGC Catalysts and Chemicals Ltd., Japan) and PST-400C (JGC Catalysts and Chemicals Ltd., Japan), respectively.

2.2. Fabrication of CdS QDSSCs

The 10- μ m-thick nanoporous TiO_2 film was prepared by doctor-blading NR18 paste on FTO glass and then annealed at 500 $^{\circ}$ C for 30 min. Then, a 4- μ m-thick scattering layer of 400-nm TiO_2 particles (PST-400C) were doctor-blade on the film and sintered at 500 $^{\circ}$ C for 30 min. Successive ionic layer adsorption and reaction (SILAR) method was employed to assemble CdS QDs on the TiO_2 film [23]. The final TiO_2 film was dipped into a 0.5 M $Cd(NO_3)_2$ ethanol solution for 5 min, rinsed with ethanol, and then dipped into a 0.5 M Na_2S methanol solution for 5 min, rinsed with methanol. Repeat this procedure for 5 times to get CdS QDs sensitized electrode. The PEDOT film was electropolymerized using a three-electrode system [14], a FTO glass as the working electrode, a platinum foil as the counter electrode, and Ag/AgCl as the reference electrode. The solution for electropolymerization consists of 0.01 M ethylenedioxythiophene and 0.1 M lithium bis(trifluoromethanesulfonyl)imide in acetonitrile. The PEDOT_{HDC} CE and PEDOT_{LDC} CE were prepared by applying a constant potential until a charge capacities of 100 $mC\ cm^{-2}$ and 2 $mC\ cm^{-2}$ was reached, respectively. The Pt CE was prepared by thermal decomposition of hexachloroplatinic acid onto FTO glass. The CoS CE was prepared according to ref [18]. A aqueous solution (pH 11.0, 75 mL) containing 0.017 M $Co(NO_3)_2$, 0.045 M thioacetamide, 0.040 M 3-mercaptopropionic acid was heated at 100 $^{\circ}$ C for 30 min. The color instantly changed to black, indicated the formation of CoS nanoparticles. The resulting CoS nanoparticles were precipitated with ethanol and isolated through centrifugation. Then, the precipitate was dispersed in ethanol (4 mL) to get a CoS paste. Evenly apply a drop of CoS paste (about 0.1 mL) on the FTO glass, dried in an oven at 100 $^{\circ}$ C for 10 min to obtain a CoS CE.

The synthetic routes of the organic AT^-/BAT and T^-/T_2 redox couples have been described elsewhere [13,14]. The synthesis of thiolate forms (AT^- or T^-) started from commercially available isothiocyanate (phenyl isothiocyanate or methyl isothiocyanate) which was transformed into the corresponding 1-phenyltetrazol-5-thiol (AT) or 1-methyltetrazol-5-thiol (T) by cycloaddition

Table 1

The photovoltaic parameters of CdS QDSSCs with different electrolytes and counter electrodes.

samples	$J_{sc}(mA/cm^2)$	$V_{oc}(V)$	FF	$\eta(\%)$
polysulfide-Pt	3.50	0.32	0.47	0.52
AT^-/BAT -Pt	2.61	0.48	0.55	0.70
polysulfide CoS	6.03	0.35	0.52	1.10
AT^-/BAT - CoS	4.84	0.50	0.59	1.42
polysulfide -PEDOT	4.35	0.42	0.66	1.20
AT^-/BAT -PEDOT	3.88	0.55	0.72	1.53

reaction with sodium azide. A solution of 0.05 M isothiocyanate and 0.075 M sodium azide was refluxed for 6 hours. The mixture was cooled and filtered. Then the filtrate was extracted twice with ether. The aqueous layer was acidified to pH 2.5 with concentrated hydrochloric acid to precipitate the corresponding mercaptan compound. This precipitation was filtered, washed with water, and then dried under vacuum at 40 $^{\circ}$ C for 12 h to get purified mercaptan compound. After that, the mercaptan was deprotonated by stirring with an excess of sodium bicarbonate in ethanol for 2 h at room temperature, and then filtered. The pure sodium thiolate (AT^-Na^+ or T^-Na^+) was obtained after evaporation of the solvent in the filtrate and recrystallization. The oxidized species (BAT or T_2) was prepared by oxidation of AT or T with hydrogen peroxide. 1 mL of 30% hydrogen peroxide was added dropwise to 0.01 mole of the corresponding mercaptan compound in 50 mL of ethanol. The mixture was stirred at 30 $^{\circ}$ C for 12 h. The reaction mixture was cooled to 0 $^{\circ}$ C. The purified oxidized species was obtained after filtration and recrystallization.

The AT^-/BAT and T^-/T_2 electrolytes both contained 0.4 M of the reduced species and 0.1 M of the oxidized species together with 0.4 M 18-crown-6 (18-C-6), 0.05 M $LiClO_4$ in acetonitrile. For comparison, the inorganic polysulfide electrolyte with Na_2S (0.5 M), S (0.125 M), and KCl (0.2 M) in a water/methanol (3/7, v/v) solution was prepared. The QDSSCs were fabricated by sealing the photoanodes and CEs together in a sandwich configuration with a 25- μ m-thick hot-melt polymer (Surlyn, Solaronix).

2.3. Characterization

The scanning electron microscopic (SEM) images were performed using a Sirion 200 field emission scanning electron microscope. The photocurrent density-voltage (I-V) characteristics were measured using a Keithley 2400 source/meter and a Newport solar simulator (model 91192-1000) under the illumination of AM1.5 and an intensity 100 mW/cm^2 which was calibrated with a standard Si solar cell. A mask with a window of 0.13 cm^2 was used to define the active area of the cell. The incident photon conversion efficiency (IPCE) was measured using a 150 W xenon lamp (Oriel) fitted with a monochromator (Cornerstone 74004) and recorded using a Newport 2931-C power meter. Electrochemical impedance spectroscopy of the QDSSCs was carried on ZAHNER ENNIUM Electrochemical Workstations in the frequency range 0.1 to 10⁵ Hz with AC amplitude of 10 mV in the dark. EIS analysis was fitted using Z-view software.

3. Results and discussion

To compare the performance of the electrolytes and counter electrodes, the QDSSCs with different electrolytes and counter electrodes were fabricated and their I-V characteristics were measured. Fig. 1. shows the I-V characteristics of CdS QDSSCs with different combinations of electrolytes and counter electrodes. The open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (FF) and conversion efficiency (η) of the QDSSCs are listed in Table 1. It can be seen that, the polysulfide-Pt based QDSSC shows a low efficiency

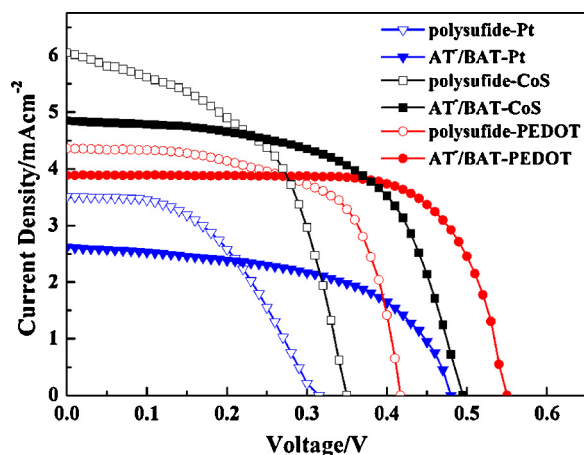


Fig. 1. I-V characteristics of CdS QDSSCs with different electrolytes and counter electrodes.

of 0.52% with very low V_{oc} and FF due to the strong interaction between Pt and sulfide ions which influences the conductivity and catalytic activity of Pt electrode remarkably and leads to poor efficiency of the cell [24]. The polysulfide-CoS based QDSSC shows higher η (1.10%) than that of Pt (0.52%) with all of the photovoltaic parameters increased especially the J_{sc} , indicating CoS has excellent electrocatalytic activity as reported [18,19]. Compared to the polysulfide-Pt based QDSSC, the η of the polysulfide-PEDOT based QDSSC increases from 0.52% to 1.20% with J_{sc} increases from 3.50 to 4.35 mA cm^{-2} , V_{oc} increases from 0.32 to 0.42 V, and FF increases from 0.47 to 0.66, indicating the PEDOT CE has much better electrocatalytic activity than that of the Pt CE. This η (1.20%) is slightly better than that of the polysulfide-CoS based QDSSC (1.10%), although the CoS CE has excellent electrocatalytic activity and exhibits much higher J_{sc} , the PEDOT CE has less charge transfer resistance (R_{ct}) than that of the CoS CE in the polysulfide electrolyte [19,20], and the reduced R_{ct} will lead to a higher FF which usually renders higher V_{oc} , and thereby result in a greater η [25]. In comparison to the polysulfide electrolyte based QDSSCs, the organic AT⁻/BAT electrolyte based QDSSCs shows higher V_{oc} and FF which lead to enhanced efficiency, from 0.52% to 0.7% (Pt CE), 1.10% to 1.42% (CoS CE) and 1.20% to 1.53% (PEDOT CE), this result verified the fact that the organic electrolyte could reinforce the photovoltage, the fill factor and the conversion efficiency of the device because the electron recombination was effectively suppressed with an organic electrolyte [12]. The polysulfide electrolyte based QDSSCs have higher J_{sc} than that of the organic AT⁻/BAT electrolyte based QDSSCs, which can be attributed to the good hole scavenging property of methanol, because the J_{sc} becomes much lower without the addition of methanol in polysulfide electrolyte [7]. The AT⁻/BAT-PEDOT based QDSSC shows the best η of 1.53% with 3.88 mA cm^{-2} of J_{sc} , 0.55 V of V_{oc} , and 0.72 of FF. This η is obvious higher than that of the AT⁻/BAT-Pt based QDSSC (0.7%), slightly higher than that of the AT⁻/BAT-CoS based QDSSC (1.42%), demonstrating the PEDOT CE is also superior to Pt and CoS CEs in the organic electrolyte. The η of 1.53% is more than double that of an organic electrolyte based QDSSC reported previously [12], implying the combination of the organic AT⁻/BAT redox couple and the PEDOT CE is very successful in improving the efficiency of the QDSSC.

The morphology and deposition charge of a PEDOT CE affect its electrochemical activity, in order to optimize the electrochemical activity, the PEDOT electrodes deposited at low deposition charge (PEDOT_{LDC}) and high deposition charge (PEDOT_{HDC}) were prepared and their microstructure and morphology were characterized by SEM. As shown in Fig. 2(a), the PEDOT_{LDC} film has a dense structure with fewer pores, which implies that electrochemical surface

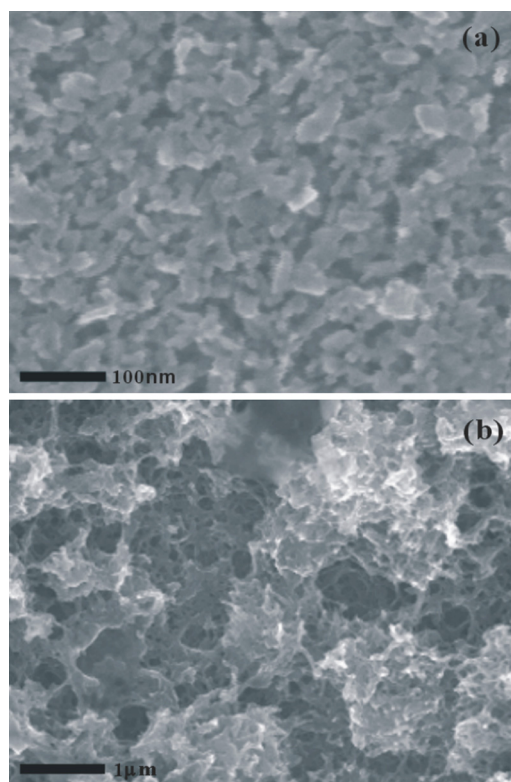


Fig. 2. The SEM images of PEDOT films prepared at low deposition charge (a) and high deposition charge (b).

area and electrolyte penetration are unfavorable for this kind of structure. Fig. 2(b) shows the porous structure of the PEDOT_{HDC} film with net-like fibers of various dimensions. The I-V characteristics of the two kinds of PEDOT CEs based CdS QDSSCs are shown in Fig. 3. The PEDOT_{HDC} and PEDOT_{LDC} based QDSSCs show η of 1.53% and 1.30%, respectively. The porous structure of PEDOT_{HDC} facilitates the electrolyte penetration and increases the electrocatalytic area, which in turn favors higher J_{sc} (3.88 mA cm^{-2}) in QDSSC than that of PEDOT_{LDC} (3.30 mA cm^{-2}). In the meantime, as the deposition charge capacity increases from 2 mC cm^{-2} to 100 mC cm^{-2} , the charge transfer resistances (R_{ct}) value of the PEDOT_{HDC} CE decreases because the R_{ct} value of the PEDOT film decreases with the increase of deposition charge capacity [20]. The lower R_{ct} of the PEDOT_{HDC} CE renders better electrochemical activity for the reduction of electrolyte, which leads to higher FF and J_{sc} and

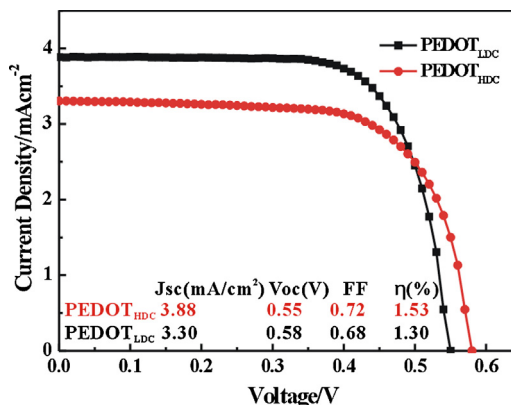


Fig. 3. I-V characteristics of CdS QDSSCs with PEDOT CE deposited at low and high deposition charge.

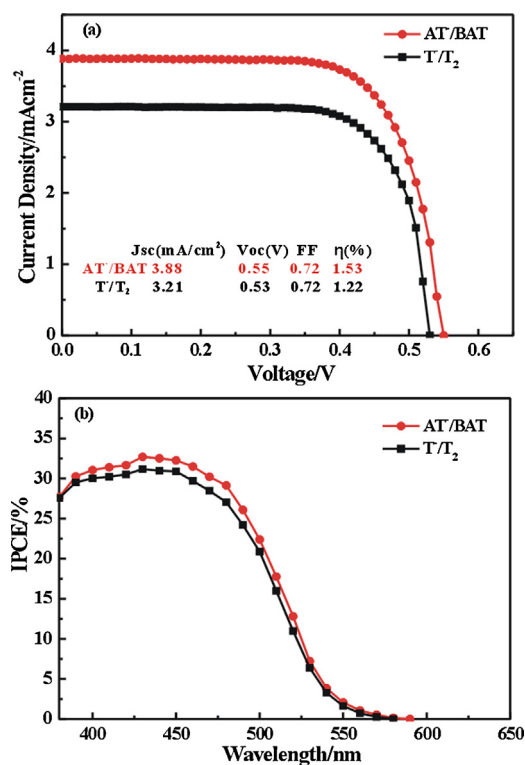


Fig. 4. I–V characteristics (a) and IPCE curves (b) of QDSSCs with organic T[•]/T₂ and AT[•]/BAT electrolytes.

thus enhances the overall efficiency of CdS QDSSC. Therefore, this PEDOT_{HDC} CE was used throughout the experiment process.

Since the organic AT[•]/BAT and T[•]/T₂ redox couples had similar chemical structures and optical absorption properties, and they both exhibited good performance in dye sensitized solar cells, they were used in CdS QDSSCs and their performance were compared. As shown in Fig. 4(a), the AT[•]/BAT redox couple based QDSSC exhibits an efficiency of 1.53% with 3.88 mA cm⁻² of J_{sc}, 0.55 V of V_{oc}, and 0.72 of FF, which is higher than that of the T[•]/T₂ redox couple based QDSSC (1.22% with 3.21 mA cm⁻² of J_{sc}, 0.53 V of V_{oc}, and 0.72 of FF). The AT[•]/BAT redox couple has more positive experimental redox potential(E_{1/2}) than that of the T[•]/T₂ redox couple [14], which can help to increase the V_{oc} as the maximum V_{oc} value is determined by the difference between the quasi Fermi level of TiO₂ (E_{F,n}) and E_{1/2} of the electrolyte (V_{oc} = |E_{F,n} - E_{1/2}|) [26]. But in the meantime, the driving force for charge recombination at the TiO₂/electrolyte interface will become higher with more positive E_{1/2}, and correspondingly leading to faster charge recombination, thus decreasing the photocurrent and photovoltage [27]. However, it is obvious that the AT[•]/BAT redox couple has larger steric bulk than that of the T[•]/T₂ redox couple as the phenyl group replaces the methyl one, the increasing steric bulk of a redox couple can hinder the recombination and accordingly enhance both photovoltage and IPCE performance [28]. As a result, the η of a DSSC enhanced slightly with the V_{oc} increased by 40 mV and the J_{sc} increased by 0.5 mA cm⁻² using the AT[•]/BAT redox couple [14]. In our case, an increase of 20 mV of V_{oc} and an increase of 0.7 mA cm⁻² of J_{sc} can be observed, suggesting the effect of the AT[•]/BAT redox couple in the QDSSC is similar to that in the DSSC, and the AT[•]/BAT redox couple also can improve the performance of the QDSSC. The incident photon-to-electron conversion efficiency (IPCE) spectra of QDSSCs with AT[•]/BAT and T[•]/T₂ redox couples are shown in Fig. 4(b), which shows typical spectral response of CdS sensitized electrode. A maximum IPCE value of 33% at 430 nm is showed with AT[•]/BAT redox couple based QDSSC, which is a litter higher than that of the T[•]/T₂

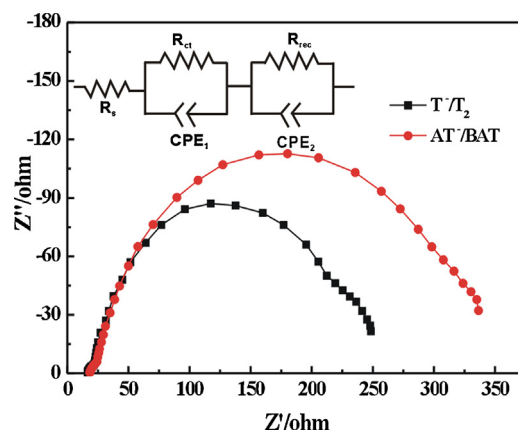


Fig. 5. Nyquist diagrams of the QDSSCs in organic T[•]/T₂ and AT[•]/BAT electrolytes. The inset is the equivalent circuit. Conditions: in the dark and the applied bias of their corresponding V_{oc}. R_s: series resistance; R_{ct}: charge transfer resistance of one electrode; R_{rec}: charge recombination resistance of one electrode; CPE: constant phase element of one electrode.

redox couple based QDSSC (31%). The IPCE can be expressed by the following formula: IPCE = LHE(λ)φ_{inj}η_c, where LHE(λ) is the light harvesting efficiency, φ_{inj} is the quantum yield of charge injection, and η_c is the efficiency of collecting the injected charge at the back contact. The LHE(λ) and φ_{inj} will keep almost the same with the AT[•]/BAT and T[•]/T₂ redox couples. However, the recombination rate of injected electrons with the oxidized electrolyte is an important factor affecting the η_c. Therefore, the higher IPCE indicates that the charge recombination is suppressed effectively with the AT[•]/BAT redox couple. This result is consistent with the photocurrent-voltage characteristics measurement.

Electrochemical impedance spectra (EIS) has been amply used in DSSCs and QDSSCs to determine electronic processes and recombination dynamics [29,30]. To better understand the different performance of the organic AT[•]/BAT and T[•]/T₂ redox couples, the EIS of these two redox couples based QDSSCs were measured in the dark under their open-circuit voltages. The typical Nyquist plots of the devices based on organic AT[•]/BAT and T[•]/T₂ electrolytes are shown in Fig. 5 and the corresponding equivalent shown in the inset [31,32]. Two semicircles are observed in the plots, the semicircle in the high frequency region is assigned to impedance related with the charge transfer processes occurring at the interfaces of the electrolyte/counter electrode, and the semicircle in the low-frequency region is associated with the charge recombination resistance (R_{rec}) between TiO₂ and the electrolyte and the chemical capacitance (CPE₂) of the nanostructured TiO₂ [33,34]. The fitted R_{rec} value of the cell based on AT[•]/BAT redox couple is about 290 Ω, higher than that of the cell based on T[•]/T₂ redox couple (200 Ω), revealing that the charge recombination is efficiently suppressed in the QDSSC based on AT[•]/BAT redox couple, also explains the higher J_{sc} and IPCE values measured for the cell with AT[•]/BAT redox couple.

4. Conclusions

Organic AT[•]/BAT and T[•]/T₂ redox couples were first employed in CdS QDSSCs, and a polymer PEDOT counter electrode was used together. The I–V characteristics demonstrated the organic AT[•]/BAT redox couple and the PEDOT CE are better than the inorganic polysulfide electrolyte and the Pt and CoS CEs in QDSSCs, respectively. A much improved conversion efficiency of 1.53% was obtained combining the AT[•]/BAT electrolyte and the PEDOT CE. We noted that the PEDOT film deposited at high deposition charge had porous structure and exhibited better electrochemical activity than that of deposited at low deposition charge. Furthermore, it was found that

the QDSSC based on AT^-/BAT redox couple outperformed the QDSSC based on T^-/T_2 redox couple due to suppressed charge recombination. This paper provides a way for the efficiency improvement of QDSSCs.

Acknowledgement

This work was supported by National Nature Science Foundation of China (21301055), the Natural Science Foundation of Hubei Province (2013CFB037) and the Project of Educational Commission of Hubei Province (Q20132806).

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