1. Introduction

Exploring photovoltaic cells with high efficiency and low cost is believed to be a promising way to solve the urgent energy and environment issues.\(^1\)\(^2\) Being a new type of photovoltaic cell, quantum dot sensitized solar cells (QDSCs) are attracting increasing research interest due to a variety of unique advantages of semiconductor QD light harvesting materials such as: high absorption coefficient, tunable light harvesting range, solution processability, high stability toward light, heat, and moisture, as well as high theoretical power conversion efficiency (PCE) due to multi-exciton generation possibilities.\(^3\)\(^-\)\(^9\) In the past several years, the reported highest PCE for QDSCs has been increased from less than 5% to over 12%.\(^10\)\(^-\)\(^19\) The enhancement of PCE for QDSCs has been achieved mainly through two approaches: (i) by exploring new types of counter electrode (CE), mainly Cu\(_2\)S/brass and mesoporous carbon/titanium mesh CEs, to improve the fill factor (FF), and open-circuit voltage (\(V_{oc}\)) of a cell device;\(^16\)\(^,\)\(^11\)\(^,\)\(^20\)\(^-\)\(^22\) (ii) by expanding the solar light harvesting range through the adoption of near infrared adsorption QD sensitizers, mainly Cd–Se–Te, and Cu–In–Se based QDs, and exploring effective QD sensitization methods to ensure high QD loading amount on TiO\(_2\) film electrodes to realize the full capture of solar light and the enhancement of short-circuit current (\(J_{sc}\)) from the aspect of photoanodes.\(^12\)\(^-\)\(^19\)\(^,\)\(^23\)

Compared to the extensively studied photoanodes and CEs, the other vital component redox couple electrolyte is significantly less concerned. In fact, electrolyte plays the crucial role of QD regeneration and charge transfer between photoanode and CE, which is critical in determining the photovoltaic performance of a cell device, especially \(V_{oc}\) and FF values.\(^24\)\(^,\)\(^25\) Up to date, polysulfide/sulfide (\(S_n^{2-}/S^{2-}\)) redox couple electrolyte is the most commonly used one in QDSCs since this electrolyte media can stabilize the commonly adopted QD light-absorbers, and enables effectively scavenging photo-induced holes to neutralize and regenerate oxidized QDs and make circulatory cells practicable. However, due to the undesirable high redox potential of \(S_n^{2-}/S^{2-}\) redox couple, a high overpotential is required for QD regeneration. This results in a relatively low \(V_{oc}\) value in the corresponding cell devices.\(^10\)\(^-\)\(^19\) In order to overcome this shortage, new redox couples, such as \(\Gamma^{-}/I^3-\), \(Co^{3+/2+}\)
complexes, and organic redox couples, have been exploited for QDSCs in recent years. Unfortunately, these redox couples failed in achieving better photovoltaic performance due to the incompatibility of QDs in these redox couple electrolyte media or the existence of severe unwanted charge recombination. Therefore, at current stage it is a wise strategy to modify electrochemical features of the conventional polysulfide electrolyte with introduction of suitable organic or inorganic additives. This strategy can usually bring forward three beneficial effects based on literature results: (i) improving $V_{oc}$ of the cells due to the adsorption of organic polymer on the surface of QD sensitized TiO$_2$ film electrode and the formation of energetic barrier layer to impede the charge recombination processes occurring at photoanode/electrolyte interface; (ii) improving device stability due to the gelation effect by the strong water-absorbing capacity of the polymer additives; (iii) tuning the potential of redox couple, or even shifting the conduction band edge of the TiO$_2$ substrate in the case of some small molecule additives. However, there are few reports about the effect of electrolyte additives on the performance of CE in sensitized solar cells.

Herein, we systematically investigated the effects of polyethylene glycol (PEG) additives with various molecular weights ($M_w$ from 300 to 20 000) in polysulfide electrolyte on the performance of QDSCs and explored the origin of the observed effects. Two representative QDSCs, CdSe, and Zn–Cu–In–Se (ZCISe), were used as the model device to evaluate these effects. It was found that all kinds of PEG additives have a positive effect on $V_{oc}$ and $FF$, negligible effect on $J_{sc}$ value in CdSe QDSCs. In ZCISe QDSCs system, the positive effect on $V_{oc}$ by PEG additives was also realized, while with the increase of $M_w$ of PEG, the positive or neutral effects on FF and $J_{sc}$ turned into negative ones gradually. Relying on the electrochemical impedance measurements, the effects of PEG additives on the performance of photoanodes and CEs, and therefore the influence on photovoltaic parameters of $V_{oc}$, $J_{sc}$, FF, and PEC were explored. Furthermore, a facile and general route for remarkably improving photovoltaic performance of QDSCs was offered with introduction of low $M_w$ PEG additives into the polysulfide electrolyte.

2. Experimental section

QDs synthesis and cell device fabrication

The oleylamine-capped 5.2 nm CdSe QDs, and 4.1 nm ZCISe QDs were synthesized according to literature method. Water-soluble mercaptopropionic acid (MPA) capped QDs were obtained via a ligand exchange process with use of MPA as phase transfer reagent. The TiO$_2$ mesoporous film electrodes were prepared according to standard literature method. The water-soluble QDs were tethered on the TiO$_2$ mesoporous film through the capping ligand induced self-assembly route by dipping the QD solution on the film and staying for a certain period. Thereafter, ZnS, and SiO$_2$ passivation layer were deposited on the QD sensitized TiO$_2$ film electrodes and served as photoanodes. Sandwich structured cell devices were fabricated through assembling the photoanode, and Cu$_2$S/brass electrode CEs, and filling with electrolyte aqueous solutions with composition of 2.0 M S and Na$_2$S, 0.2 M KCl, and different $M_w$ PEG additives (i.e. 20 wt% for both PEG-300, and PEG-1K, 15 wt% for PEG-4K and 8 wt% for PEG-20K). For the reference sample, plain polysulfide/sulfide electrolyte without the existence of any PEG additives. To ensure the reliability of the data, 5 pieces of cells under each condition were fabricated and measured.

Characterization

The performance of QDSCs was tested using a Keithley 2400 source meter under the illumination of simulated AM1.5G solar light (Oriel, model no. 94022A) with intensity of 100 mW cm$^{-2}$ (1 full solar light). The light intensity was calibrated by a NRELS standard Si solar cell. The effective area of the cells was determined by a 0.235 cm$^2$ black mask. The conductivity of the electrolyte solutions was tested by DDSJ-308A conductivity meter at 25 °C. Electrochemical impedance spectroscopy (EIS) measurements were carried out on a Zennium electrochemical workstation (Zahner). The EIS spectra for a full solar cell were obtained under dark conditions at different forward bias ranging from −0.35 to −0.65 V, applying a 20 mV AC sinusoidal signal over the constant applied bias with the frequency ranging from 1 MHz to 0.1 Hz. The EIS spectra and Tafel-polarization curves for symmetric dummy cells consisting of two identical Cu$_2$S/brass electrode were measured by applying a 20 mV AC sinusoidal signal over the constant applied bias with the frequency range of 100 mHz to 100 kHz.

3. Results and discussion

Influence of PEG molecular weight of on the cell performance

According to our previous results, high molecular weight ($M_w$) PEG modifying polysulfide electrolytes can improve the photovoltaic performance of CdSe QDSCs, but fails flat for ZCISe QDSCs. In this work, we systematically studied the influence of PEG additives with different $M_w$ on the photovoltaic performance of the most commonly studied CdSe and ZCISe QDSCs. On the other hand, the selected ZCISe QDSCs exhibit best performance among all kind of QDSCs. Commercially available PEG with $M_w$ of 300, 1000, 4000, and 20 000 (noted as PEG-300, PEG-1K, PEG-4K, and PEG-20K, respectively henceforth) were selected and evaluated in this study. QDSC cell devices were constructed according to literature method by assembling QD sensitized photoanodes and Cu$_2$S/brass CEs. Electrolyte solutions were derived from conventional polysulfide/sulfide aqueous solution electrolyte with addition of optimum weight fractions of different PEG additives. Detailed procedure for the fabrication and measurement of QDSCs can be found in the Experimental section. Under each condition, five cells were fabricated and measured in parallel, and the average values were used in the evaluation of the photovoltaic performance in order to ensure the validity of the reported results.

First, optimum concentrations for all selected PEG additives in polysulfide electrolyte were determined, and the corresponding $J$–$V$ curves are illustrated in Fig. S1 of the ESL.
Experimental results indicate that the optimum concentration range for low $M_w$ PEG-300 and PEG-1K is located in 20–30 wt%. While for high $M_w$ PEG-4K and PEG-20K, their optimum concentrations correspond to their corresponding highest solubility in this electrolyte solution, i.e. 15 wt% and 8 wt%, respectively. Correspondingly, in the following experiments, 25 wt% was chosen for PEG-300 and PEG-1K, while 15 wt% for PEG-4K, and 8 wt% for PEG-20K. After that, cell performances corresponding to polysulfide electrolyte containing different PEG additives under their optimum concentrations were measured together with reference sample without any PEG additives in polysulfide electrolyte. The detailed $J$–$V$ curves and corresponding extracted main photovoltaic parameters ($V_{oc}$, $J_{sc}$, FF, and PCE,) are available in Fig. S2, S3, Tables S1 and S2.

**Table 1** Average photovoltaic performance of CdSe QDSCs with different PEG additives modified electrolyte under AM 1.5G illumination

| PEG additives | $J_{sc}$ (mA cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|---------------|-------------------------|--------------|--------|---------|
| Ref.          | 15.81 ± 0.17            | 0.654 ± 0.005| 66.0 ± 0.8 | 6.81 ± 0.11 |
| PEG-300       | 15.72 ± 0.15            | 0.688 ± 0.007| 69.7 ± 1.1 | 7.54 ± 0.11 |
| PEG-1K        | 15.8 ± 0.20             | 0.691 ± 0.005| 69.6 ± 0.9 | 7.60 ± 0.05 |
| PEG-4K        | 15.84 ± 0.12            | 0.685 ± 0.005| 68.8 ± 0.6 | 7.50 ± 0.04 |
| PEG-20K       | 15.83 ± 0.17            | 0.685 ± 0.006| 68.3 ± 0.4 | 7.38 ± 0.07 |

Fig. 1 illustrates the dependence of main photovoltaic parameters on polysulfide electrolyte containing different PEG additives for both CdSe and ZCISe QDSC systems, and the detailed average photovoltaic parameters are summarized in Tables 1 and 2. From Fig. 1a, d, Tables 1 and 2, we can find that all kinds of PEG additives in polysulfide electrolyte can enhance $V_{oc}$ values for both CdSe and ZCISe cells in comparison with reference samples without any PEG additives (in CdSe cells, $V_{oc}$ improving from 0.65 V to 0.68–0.69 V; in ZCISe cells, $V_{oc}$ improving from 0.59 V to 0.62–0.63 V). In the case of $J_{sc}$ parameter, the effects of PEG additives for CdSe and ZCISe QDSCs are different. All PEG additives have negligible effects on CdSe QDSCs (the $J_{sc}$ value keeping nearly constant in a narrow range of 15.68–15.84 mA cm$^{-2}$). While for ZCISe QDSCs, low $M_w$ PEG (PEG-300, and PEG-1K) additives have insignificant effects on $J_{sc}$, but high molecular weight PEG (PEG-4K and PEG-20K) additives have slightly negative effects on it (decreasing from 26.55 to 26.02, and 25.55 mA cm$^{-2}$, respectively). For the FF value, low $M_w$ PEG additives (PEG-300 and PEG-1K) have positive effect for both CdSe and ZCISe QDSCs (in CdSe, improving from 66.0% to 68.8–69.1%; in ZCISe, improving from 59.0% to 61.1%, and 60.8%); high $M_w$ PEG (PEG-4K and PEG-20K) additives still have positive effects for CdSe cells (improving to 68.3%, and 68.8%, respectively), but negative effects for ZCISe cells (decreasing the FF value to 58.5%, and 55.6%, respectively). Correspondingly, for PCE value, all PEG additives have positive effect without significant difference for CdSe QDSCs in comparison with reference samples (improving from 6.81% to 7.38–7.60%); for ZCISe...
QDSCs, with the increase of \( M_\text{w} \) of PEG additive, the extent of improving PEC value decreases systematically. In detail, low \( M_\text{w} \) PEG-300, and PEG-1K can remarkably improve the PEC of ZCISe QDSCs from 9.26\% to 10.20\%, and 10.14\%, respectively, while PEG-4K can only slightly enhance the PEC value to 9.62\%; inversely, PEG-20K even has negative effect and decrease the value to 9.11\%. In summary, low \( M_\text{w} \) PEG 300 and PEG-1K can serve as a general photovoltaic performance enhancement additive for the representative CdSe and ZCISe QDSCs. High \( M_\text{w} \) PEG, especially PEG-20K, can only improve the performance of CdSe QDSCs, but fails flat in ZCISe cells due to the negative effects on FF and \( J_{sc} \).

### Impedance spectroscopy of full cell devices

In order to unravel the intrinsic mechanism for the influence of different PEG additives in polysulfide/sulfide electrolyte on the photovoltaic performance of CdSe and ZCISe QDSCs, electrochemical impedance spectroscopy (EIS) for a full cell device was employed. This is because EIS is a well-established technique to distinguish the electrochemical features corresponding to different constituents in a cell device.\(^{48\text{-}49} \) EIS measurements were carried out under dark condition with forward bias voltage in a range from \(-0.35 \) to \(-0.65 \) V by applying a 20 mV AC sinusoidal signal in a frequency range of 100 kHz to 0.1 Hz. Nyquist curves for each QDSCs corresponding to different electrolyte systems under different bias are available in Fig. S4–S6.† Main EIS parameters including series resistance \( (R_s) \), chemical capacitance \( (C_m) \) and charge recombination resistance \( (R_{\text{rec}}) \) were deduced from the EIS curves with use of a standard simulation circuit as reported in literature.\(^{48} \) It is noted that chemical capacitance \( (C_m) \) stands for the change of electron density as a function of Fermi level, and the parameter charge recombination resistance \( (R_{\text{rec}}) \) corresponds to the charge recombination resistance at the photoanode/electrolyte interfaces.\(^{48\text{-}49} \) The applied bias \( (V_{\text{app}}) \) dependent chemical capacitance, and charge recombination resistance values were illustrated in Fig. 2.

From Fig. 2a and d, we can find that in both CdSe and ZCISe QDSCs, the extracted \( C_m \) values exhibit a near linear relationship to the forward bias voltage in each electrolyte system, and all these curves are overlapped together. This means that cell devices with different electrolyte systems show ignorable variation in the obtained \( C_m \) values. This indicates that the introduction of PEG additives in the initial polysulfide electrolyte solution does not alter the conduction band edge or the electron density of the states of TiO\(_2\) matrix.\(^{48\text{-}50} \) This result is also in accordance with previous reports,\(^{34\text{-}37\text{,}38} \) wherein other water-soluble polymers such as poly(vinylpyrrolidone) (PVP), sodium carboxymethylcellulose (CMC-Na), and sodium polycrylate (PAAS) were used as additives to modify the polysulfide/sulfide electrolyte in the construction of QDSCs.\(^{34\text{-}37\text{,}38} \) However, from Fig. 2b and e it can be found that with the increase of \( M_\text{w} \) of PEG additives in electrolyte solutions, the obtained \( R_{\text{rec}} \) values exhibit systematically, and the \( R_{\text{rec}} \) values show a near linear relationship to the forward bias in each electrolyte system. For clarity, Nyquist plots of cell devices under forward bias near the \( V_{\text{oc}} \) value (herein of \(-0.65 \) V) are shown in Fig. 2c and f. Accordingly, the extracted EIS parameters based on these plots are listed in Table 3. We can find that accompanying with the increase of \( M_\text{w} \) of PEG additives in the electrolyte, the diameter of the EIS semicircles increases systematically. This indicates that with the presence of PEG additives, the \( R_{\text{rec}} \) value at photoanode/electrolyte interface are improved accordingly, and the effect is strengthened systematically with the increase of \( M_\text{w} \) of PEG additives. As listed in Table 3, we can find that the \( R_{\text{rec}} \) value of the PEG modified electrolyte system is increased systematically in both CdSe and ZCISe QDSC systems (for CdSe, increasing from 78.2 to 160.6 \( \Omega \) \( \text{cm}^2 \); for ZCISe, increasing from 72.4 to 141.8 \( \Omega \) \( \text{cm}^2 \)). These results indicate that the charge recombination from photoanode to oxidation species (herein \( S_\text{n}^{2-} \)) of electrolyte at photoanode/electrolyte interfaces is effectively suppressed by the PEG additives, and the extent is strengthened with the increase of PEG \( M_\text{w} \). Therefore, an increase of \( V_{\text{oc}} \) can be observed in the corresponding cell devices.

The mechanism for the observed retarded charge recombination is due to the adherence of PEG molecules on photoanode surface. This is because the presence of terminal hydroxyl groups and ether bonding oxygen atoms in the PEG molecules, which have strong coordinating capacity to TiO\(_2\) substrate.\(^{51\text{-}53} \) The adsorbed PEG molecules act as a passivation layer and an insulating energetic barrier layer, which prevent the direct contact of electrons on the surface of photoanode and electrolyte in the aspect of stereoscopic space and energetic field, and therefore inhibit the charge recombination processes through the surface defects in photoanode or with oxidation species in electrolyte.\(^{19} \) With the increase of \( M_\text{w} \) of PEG additives, the insulating feature, as shown in Tables 1–4, become intensified. Simultaneously, stereoscopic shielding effect has also been improved with the increase of \( M_\text{w} \). The increased insulating property combined with the improved stereoscopic shielding effect result in better barrier effect in isolating photogenerated electrons on photoanode surface with redox couple in the electrolyte, and therefore inhibiting the charge recombination.

### Table 2

| PEG additives | \( J_{sc} \) (mA cm\(^{-2} \)) | \( V_{oc} \) (V) | FF (%) | PCE (%) |
|---------------|-----------------|---------------|--------|--------|
| Ref.          | 26.55 ± 0.23    | 0.591 ± 0.004 | 58.96 ± 0.7 | 9.26 ± 0.10 |
| PEG-300       | 26.58 ± 0.18    | 0.629 ± 0.003 | 61.06 ± 0.7 | 10.20 ± 0.09 |
| PEG-1K        | 26.56 ± 0.26    | 0.628 ± 0.003 | 60.8 ± 0.6  | 10.15 ± 0.04 |
| PEG-4K        | 26.03 ± 0.12    | 0.630 ± 0.003 | 58.6 ± 0.4  | 9.62 ± 0.03  |
| PEG-20K       | 25.55 ± 0.42    | 0.630 ± 0.004 | 56.6 ± 0.7  | 9.11 ± 0.12  |
process more effective. This can give a reasonable explanation for the enhancement of charge recombination resistance value with the increase of $M_w$ of PEG additives in electrolyte solutions as observed in Fig. 2b, e and Table 3. The reason for the decrease of overall photovoltaic performance of cell devices with the increase of $M_w$ of PEG additives can be ascribed to the decrease of electric conductivity of corresponding electrolyte systems as shown in Table 4. The decrease of conductivity is mainly derived from the lower diffusion coefficient for higher $M_w$ PEG. The conductivity ($\sigma$) of an electrolyte solution is defined by the equation:

$$\sigma = \sum_i |Z_i|F_iD_i$$

where $Z_i$, $c_i$ and $D_i$ are the charge, concentration, diffusion coefficient of the conducting ions, and $F$ is the Faraday constant. Since the role of electrolyte in a cell device is responsible for the charge transport shuttling between photoanode and CE, the conductivity of the electrolyte would have a direct influence on the generation of electricity, and therefore on overall photovoltaic performance of the cell device. The poor ionic conductivity of the electrolyte with high $M_w$ PEG deteriorates the performance of the resultant devices. In the tradeoff between the recombination resistance and conductivity, the electrolyte with low $M_w$ PEG (PEG-300, and PEG-1K) showed the best performance, as shown in Fig. 2d, Tables 1 and 2.

### Table 3

| QDSCs   | PEG additives | $R_s$ (Ω cm$^2$) | $R_{\text{rec}}$ (Ω cm$^2$) | $C_m$ (mF cm$^{-2}$) |
|---------|---------------|------------------|---------------------------|---------------------|
| CdSe    | Ref.          | 7.6              | 78.2                      | 11.0                |
|         | PEG-300       | 7.8              | 117.1                     | 11.2                |
|         | PEG-1K        | 7.9              | 132.6                     | 11.2                |
|         | PEG-4K        | 7.8              | 145.6                     | 11.2                |
|         | PEG-20K       | 7.8              | 160.6                     | 11.3                |
| ZCISe   | Ref.          | 6.8              | 72.4                      | 10.3                |
|         | PEG-300       | 7.1              | 116.2                     | 10.7                |
|         | PEG-1K        | 7.4              | 128.9                     | 10.4                |
|         | PEG-4K        | 7.2              | 135.3                     | 10.7                |
|         | PEG-20K       | 7.4              | 141.8                     | 11.1                |

### Table 4

| PEG additives | $R_s$ Ω cm$^2$ | $R_t$ Ω cm$^2$ | $R_{\text{ct}}$ Ω cm$^2$ | Conductivity mS cm$^{-1}$ |
|---------------|----------------|----------------|--------------------------|--------------------------|
| Ref.          | 0.33           | 0.84           | 4.42                     | 82.5                     |
| PEG-300       | 0.39           | 0.55           | 2.87                     | 59.1                     |
| PEG-1K        | 0.38           | 0.55           | 3.03                     | 58.4                     |
| PEG-4K        | 0.72           | 1.34           | 10.63                    | 45.0                     |
| PEG-20K       | 1.02           | 1.54           | 12.30                    | 39.8                     |

Fig. 2  EIS characterizations of CdSe (up), and ZCISe (bottom) QDSCs with electrolyte containing different PEG additives: (a and d) chemical capacitance $C_m$, (b and e) recombination resistance $R_{\text{rec}}$, dependent on applied voltage $V_{\text{app}}$, and (c and f) Nyquist plots under forward bias of $-0.65$ V.
Impedance spectroscopy of symmetric dummy cells

Since all kinds of PEG additives can suppress the charge recombination dynamics occurring at photoanode/electrolyte interface and bring forward an enhancement of \( V_{oc} \) value in the resulting cell devices, the question of what causes the different effects on FF value for both CdSe and ZCISe QDSCs by PEG additives in electrolyte comes naturally. Generally, the FF in a sensitized solar cell is largely a function of the charge transfer resistance \( \text{R}_{ct} \) at the counter electrode/electrolyte interface and simply the measurement system. The conduction and adsorption interference from photoanode and catalytic properties of the catalyst. 

In order to explore the origin of different FF values in cell devices, EIS measurements were carried out using symmetric dummy cells consisting of two identical Cu\textsubscript{2}S/brass CEs placed face to face in a sandwich configuration and filling with polysulfide electrolyte solutions containing different PEG additives. The configuration of symmetric form can rule out the interference from photoanode and simply the measurement and analysis. The obtained Nyquist curves corresponding to different PEG additive systems are shown in Fig. 3a. As expected, Nyquist plots for each electrolyte system consist of two semicircles, which are related to the internal resistance in different systems. Therefore, in the investigated systems, FF is mainly determined by the \( \text{R}_{ct} \) values.

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With the introduction of low \( M_w \) PEG-300, and PEG-1K in the electrolyte solution, charge transfer resistance \( \text{R}_{ct} \) at CE/electrolyte interface decreased remarkably (from 4.42 to 2.87, and 3.03 \( \Omega \) cm\textsuperscript{2}). In contrast, the introduction of high \( M_w \) PEG-4K, and PEG-20K led to a significant increase of \( \text{R}_{ct} \) value (10.63, and 12.30 \( \Omega \) cm\textsuperscript{2}). Generally, \( \text{R}_{ct} \) can significantly influence the cell performance from two aspects. First, \( \text{R}_{ct} \) is considered to be a major hurdle in attaining a high FF value as stated in the above section. Second, \( \text{R}_{ct} \) is directly related to the reaction barrier of redox couple reduction reaction at the CE/electrolyte interface and hence plays a significant effect on the electrocatalytic properties of the catalyst. High \( \text{R}_{ct} \) value means slow charge transfer rate at the counter electrode. This leads to a high overpotential for the redox couple reduction reaction and creates a bottleneck for the electron flowing from CE to electrolyte, thereby promoting back electron transfer at the photoanode. These effects would result in a low \( J_{sc} \) and FF for the corresponding cell devices.

Origin of the PEG additives effect difference between CdSe and ZCISe QDSCs

The origin of the decrease of the CE/electrolyte charge transfer resistance by the introduction of PEG additives should be related to the contact of electrode substrate and catalytic material, the catalytic activity of CE catalytic materials, and conductivity of electrode and electrolyte. Standard equivalent circuit as reported in literature are used to extract the EIS data from the Nyquist plots, and key parameters including \( \text{R}_{ct} \) and \( \text{R}_{i} \) are listed in Table 4. Owing to the outstanding conductivity of the brass substrate, the \( \text{R}_{i} \) values of all CE systems are small, but with the increase of \( M_w \) of PEG additives, the corresponding \( \text{R}_{ct} \) value increases systematically (from 0.33 to 1.02 \( \Omega \) cm\textsuperscript{2}) in comparison with reference sample without the presence of any PEG additives. The observed increase of \( \text{R}_{ct} \) value should be ascribed to the decrease of electrical conductivity with the introduction of insulating PEG additives, especially with the increase of \( M_w \), as shown in Table 4.

The obtained Nyquist curves corresponding to different electrolyte solutions containing different PEG additives are shown in Fig. 3a. As expected, Nyquist plots for each electrolyte system consist of two semicircles, which are related to the resistance and capacitance \( (\text{R}_{1} \) and \( \text{C}_{1} \)) of the solid–solid contact between Cu\textsubscript{2}S catalytic materials and brass substrate, and charge transfer resistance and capacitance \( (\text{R}_{ct} \) and \( \text{C} \)) at the CE/electrolyte interface, respectively. The high frequency intercept on the real axis corresponds to the series resistance \( (\text{R}_{s}) \). These three parameters are related to the contact of electrode substrate and catalytic material, the catalytic activity of CE catalytic materials, and conductivity of electrode and electrolyte. Standard equivalent circuit as reported in literature are used to extract the EIS data from the Nyquist plots, and key parameters including \( \text{R}_{ct} \) and \( \text{R}_{i} \) are listed in Table 4. Owing to the outstanding conductivity of the brass substrate, the \( \text{R}_{i} \) values of all CE systems are small, but with the increase of \( M_w \) of PEG additives, the corresponding \( \text{R}_{ct} \) value increases systematically (from 0.33 to 1.02 \( \Omega \) cm\textsuperscript{2}) in comparison with reference sample without the presence of any PEG additives. The observed increase of \( \text{R}_{ct} \) value should be ascribed to the decrease of electrical conductivity with the introduction of insulating PEG additives, especially with the increase of \( M_w \), as shown in Table 4.

With the introduction of low \( M_w \) PEG-300, and PEG-1K in the electrolyte solution, charge transfer resistance \( \text{R}_{ct} \) at CE/electrolyte interface decreased remarkably (from 4.42 to 2.87, and 3.03 \( \Omega \) cm\textsuperscript{2}). In contrast, the introduction of high \( M_w \) PEG-4K, and PEG-20K led to a significant increase of \( \text{R}_{ct} \) value (10.63, and 12.30 \( \Omega \) cm\textsuperscript{2}). Generally, \( \text{R}_{ct} \) can significantly influence the cell performance from two aspects. First, \( \text{R}_{ct} \) is considered to be a major hurdle in attaining a high FF value as stated in the above section. Second, \( \text{R}_{ct} \) is directly related to the reaction barrier of redox couple reduction reaction at the CE/electrolyte interface and hence plays a significant effect on the electrocatalytic properties of the catalyst. High \( \text{R}_{ct} \) value means slow charge transfer rate at the counter electrode. This leads to a high overpotential for the redox couple reduction reaction and creates a bottleneck for the electron flowing from CE to electrolyte, thereby promoting back electron transfer at the photoanode. These effects would result in a low \( J_{sc} \) and FF for the corresponding cell devices.

The obtained Nyquist curves corresponding to different electrolyte solutions containing different PEG additives are shown in Fig. 3a. As expected, Nyquist plots for each electrolyte system consist of two semicircles, which are related to the resistance and capacitance \( (\text{R}_{1} \) and \( \text{C}_{1} \)) of the solid–solid contact between Cu\textsubscript{2}S catalytic materials and brass substrate, and charge transfer resistance and capacitance \( (\text{R}_{ct} \) and \( \text{C} \)) at the CE/electrolyte interface, respectively. The high frequency intercept on the real axis corresponds to the series resistance \( (\text{R}_{s}) \). These three parameters are related to the contact of electrode substrate and catalytic material, the catalytic activity of CE catalytic materials, and conductivity of electrode and electrolyte. Standard equivalent circuit as reported in literature are used to extract the EIS data from the Nyquist plots, and key parameters including \( \text{R}_{ct} \) and \( \text{R}_{i} \) are listed in Table 4. Owing to the outstanding conductivity of the brass substrate, the \( \text{R}_{i} \) values of all CE systems are small, but with the increase of \( M_w \) of PEG additives, the corresponding \( \text{R}_{ct} \) value increases systematically (from 0.33 to 1.02 \( \Omega \) cm\textsuperscript{2}) in comparison with reference sample without the presence of any PEG additives. The observed increase of \( \text{R}_{ct} \) value should be ascribed to the decrease of electrical conductivity with the introduction of insulating PEG additives, especially with the increase of \( M_w \), as shown in Table 4.

With the introduction of low \( M_w \) PEG-300, and PEG-1K in the electrolyte solution, charge transfer resistance \( \text{R}_{ct} \) at CE/electrolyte interface decreased remarkably (from 4.42 to 2.87, and 3.03 \( \Omega \) cm\textsuperscript{2}). In contrast, the introduction of high \( M_w \) PEG-4K, and PEG-20K led to a significant increase of \( \text{R}_{ct} \) value (10.63, and 12.30 \( \Omega \) cm\textsuperscript{2}). Generally, \( \text{R}_{ct} \) can significantly influence the cell performance from two aspects. First, \( \text{R}_{ct} \) is considered to be a major hurdle in attaining a high FF value as stated in the above section. Second, \( \text{R}_{ct} \) is directly related to the reaction barrier of redox couple reduction reaction at the CE/electrolyte interface and hence plays a significant effect on the electrocatalytic properties of the catalyst. High \( \text{R}_{ct} \) value means slow charge transfer rate at the counter electrode. This leads to a high overpotential for the redox couple reduction reaction and creates a bottleneck for the electron flowing from CE to electrolyte, thereby promoting back electron transfer at the photoanode. These effects would result in a low \( J_{sc} \) and FF for the corresponding cell devices.
Based on previous literature data, ZCISe cells are different from QDSCs. However, the results for PEG-20K additive on CdSe and 29964 | RSC Adv., 2018, 8, 29958–29966

It is well established that this energy difference between QD and TiO2 serves as the driving force to ensure the effective injection of photo-generated electron from light absorber QD to TiO2 substrate.13–15,58,59 In the construction of high efficiency QDSC, a higher $V_{CB}$ of QDs relative to that of TiO2 electron acceptor is a prerequisite for QD sensitizers. The fact that the higher energy difference is accompanied with a greater electron injection rate ($K_e$) from QD to TiO2 electron acceptor has been well studied in previous reports.13,18,59 Meanwhile, the greater $K_e$ value can bring forward not only greater photocurrent, but also more effective transfer of photogenerated electrons through the photoanode film, and from external circuit to electrolyte via CE. This means that higher $V_{CB}$ in QD light absorber would favor $V_{oc}$ and FF of the resulting QDSCs. Therefore, the relatively high $V_{CB}$ in CdSe QDs would offset the negative effects by high $M_w$ PEG additive in electrolyte, and ensure high $V_{oc}$ and FF values in the resultant QDSCs. In fact, literature results have well demonstrated that with the enhancement of $V_{CB}$ via alloying process, the $V_{oc}$ and FF values in the Zn–Cu–In–S, and Zn–Cu–In–Se based QDSCs are remarkably higher than those of Cu–In–S, and Cu–In–Se QDSCs.14,60

4. Conclusions

In summary, the origin for the effects of different $M_w$ PEG additives in polysulfide electrolyte on the performance of QDSCs has been explored. Furthermore, a facile and general route for remarkably improving photovoltaic performance of QDSCs is achieved with introduction of low $M_w$ PEG additives into the polysulfide electrolyte. The energetic barrier effect due to the insulating feature together with the passivation effect on photoanode surface from PEG additives bring forward the suppression of charge recombination at photoanode/electrolyte interface, accompanied with the improvement of $V_{oc}$ of the resultant cell device. The wetting effect of the PEG surfactant reduces the charge transfer resistance at CE/electrolyte interface, and results in the improvement of FF and $J_{sc}$. The intensified insulating feature with the increase of $M_w$ of PEG favors the $V_{oc}$ value, but has a negative effect on FF and $J_{sc}$ for the resulting cell devices. Due to the relative high conduction band edge of CdSe light absorber, the negative effect on FF by high $M_w$ PEG additive in ZCISe QDSCs is not realized in CdSe QDSCs.

Conflicts of interest

There are no conflicts to declare.
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