



Short communication

Efficient polysulfide electrolyte for CdS quantum dot-sensitized solar cells

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ABSTRACT

A polysulfide electrolyte considering simultaneously the penetration of the electrolyte in a mesoscopic TiO₂ film and the ion dissociation in the solution is developed for application in a CdS-sensitized solar cell (CdS-DSSC). A methanol/water (7:3 by volume) solution was found to be a good solvent for fitting the requirement mentioned above. The optimal composition of the electrolyte, based on the performance of the CdS-DSSCs, was found to contain 0.5 M Na₂S, 2 M S, and 0.2 M KCl. By using a photoelectrode prepared after 4 cycles of chemical bath deposition, FTO/TiO₂/CdS-4, the efficiency of the CdS-DSSC obtained for this polysulfide electrolyte is 1.15% under the illumination of 100% sun (AM1.5, 100 mW cm⁻²). This efficiency is less than that obtained using I⁻/I₃⁻ redox couple (1.84%), mainly caused from the smaller values of fill factor and open circuit potential. However, the CdS sensitizer is stable and, furthermore, a much higher short circuit current and IPCE (80%) are obtained by using the polysulfide electrolyte.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted a lot of academic and commercial interests due to their characteristics of low cost, surrounding friendly, and high energy conversion efficiency. For a DSSC, a nanocrystalline TiO₂ film is used as an electron collecting electrode on which dye is adsorbed to enhance the light harvest of the photoelectrode [1,2]. Energy conversion efficiency as high as 11% was reported using ruthenium complex as a sensitizer [2]. In addition to the organic dyes, semiconductor quantum dots (QDs) which absorb light in the visible region, such as CdS [3–5], CdSe [6–8], InP [9], PbS [10,11], PbSe [12], have also been used as sensitizers of DSSCs. The advantage of a QD sensitizer over conventional dyes is on its quantum confinement effect [13–15] including the impact ionization, Auger recombination, and miniband effect [16,17]. These effects are known to increase the exciton concentration, quantum yield, lifetime of hot electron, and therefore, the performance of a QD-sensitized DSSC.

Despite the advantage known for a QD-sensitizer, the studies on the QD-sensitized DSSCs are fewer in comparison with the works using organic dyes. The energy conversion efficiencies reported for the QD-sensitized DSSCs are still low (less than 1.8%) [4]. The problems one would encounter in fabricating a QD-DSSC include the assembling of the QDs into a mesoporous TiO₂ matrix, and the selection of an efficient electrolyte in which the QDs can run stably without serious degradation. In a previous paper, CdS QDs were

assembled into a TiO₂ film using a chemical bath deposition (CBD) process performed in alcohol solutions [4]. The modified CBD process has proved to be efficient to assemble CdS-QDs into a TiO₂ mesoporous film and the energy conversion efficiency measured for the corresponding DSSC device, under one sun illumination in iodide/triiodide (I⁻/I₃⁻) electrolyte, is 1.84% [4]. Although the I⁻/I₃⁻ redox couple has ideal kinetic properties in regeneration the oxidized dye and in inhibition the recombination of an excited electron to the electrolyte, it is corrosive to most metals and semiconductor materials. For a QD-sensitized DSSC, the decay of the QDs in an I⁻/I₃⁻ redox system causes a rapid decrease of the photocurrent. Therefore, finding an efficient electrolyte with non-corrosive redox couple is important to the development of QD-sensitized DSSCs.

In the literature, various redox couples including Co(II)/Co(III) [13–15], Fe²⁺/Fe³⁺ [16], triethanolamines [17,18], and mixed systems of redox couples [14] have been employed to substitute I⁻/I₃⁻ to enhance the durability of DSSCs. However, these studies are mainly focused on DSSCs using dyes of ruthenium complexes. For the QD-sensitized photoelectrodes using cadmium chalcogenide (S, Se or Te) as sensitizers, redox couple of polysulfide (S²⁻/S_x²⁻) [6,19,20] is a suitable system for stabilizing the QDs.

Polysulfide redox couples were commonly prepared using aqueous solution and employed for photoelectrochemical cells in a three-electrode configuration. For the application in a practical solar cell that has a sandwich structure, only few papers were found [21,22]. Diguna et al. used an aqueous polysulfide solution for a TiO₂ inverse opal electrode with pore sizes of 300–400 nm [21]. For the application on a nanocrystalline TiO₂ electrode, Tachibana et al. utilized a polysulfide electrolyte for a CdS-sensitized solar cell and compared its performance with other redox systems [22].

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Polysulfide was reported to have a superior property in terms of cell performance and stabilization for the CdS [22]. Because an aqueous electrolyte always has a higher surface tension and it is difficult for this electrolyte to penetrate into the mesoporous matrix of a TiO₂ film. Without intimate contact between photoelectrode and electrolyte, the cell performance is poor. To solve this problem, polar solvent such as alcohol can be used to substitute water. However, the dissociation of electrolyte in the alcohol is less than in the water. To consider both the penetration and ion dissociation abilities of the electrolyte, an alcohol/water solution is used as a co-solvent of the polysulfide electrolyte. The optimal ratio of alcohol to water, as well as the compositions of the ingredients contained in the electrolyte, is determined according to the performance of the QD-DSSCs.

2. Experimental

2.1. Preparing of TiO₂ photoelectrodes

F-doped tin oxide (FTO, about 8 Ω sq⁻¹, Solaronix SA) or In-doped tin oxide (ITO, about 13 Ω sq⁻¹, Solaronix SA) is used as transparent conducting oxide substrate (TCO). Mesoscopic TiO₂ films were prepared by spin coating of TiO₂ paste (Degussa P25) on the substrate, followed by sintering at 450 °C for 30 min. The thickness of the TiO₂ film, measured from the cross sectional image of a scanning electron microscope, was about 5.5 μm. CBD is used to assemble CdS-QDs into the TiO₂ photoelectrode as the procedure described in a previous paper [4]. A TiO₂ film was dipped into a 0.5 M Cd(NO₃)₂ ethanol solution for 5 min, rinsed with ethanol, and then dipped for another 5 min into a 0.5 M Na₂S methanol solution and rinsed again with methanol. The two-step dipping procedure is termed as one CBD cycle and the incorporated amount of CdS can be increased by repeating the assembly cycles.

2.2. Measurements

The CdS-sensitized TiO₂ electrode and a Pt-coated counter electrode were sandwiched using 60 μm thick sealing material (SX-1170-60, Solaronix SA). The active area of the cell is 0.16 cm². The photocurrent–voltage (*I*–*V*) characteristics of the QD-DSSCs were measured under an illumination of a solar simulator (Newport, Oriel class A, 91160A) at one sun (AM1.5, 100 mW cm⁻²). An Eco Chemie Autolab potentiostat/galvanostat was used to record the current–voltage (*I*–*V*) relationship. An Oriel 500 W xenon arc lamp and Keithley 2400 electrometer were used during the measurements of IPCE (incident photon to current conversion efficiency).

UV–vis absorption spectra of the photoelectrodes were analyzed with a UV–vis spectrometer constructed by GBC Scientific Equipment, Australia (model GBC Cintra 10e).

3. Results and discussion

The stability of the CdS in electrolyte solutions was investigated first by dipping the CdS-modified TiO₂ photoelectrode in electrolyte solutions for 5 min. The photoelectrodes, before and after the dipping, were analyzed by an UV–vis spectroscopy and the results are shown in Fig. 1. The CdS-modified photoelectrode is found to be stable in the polysulfide electrolyte as indicated by the consistent UV–vis spectra measured before and after dipping in a 0.1 M Na₂S aqueous solution. For the electrolyte of I⁻/I₃⁻ redox couple, the absorbance decreases significantly after dipping in a 3-methoxypropionitrile solution consisting of 0.1 M lithium iodide and 0.05 M iodine, implying the etching effect of I⁻/I₃⁻ redox couple to the CdS.

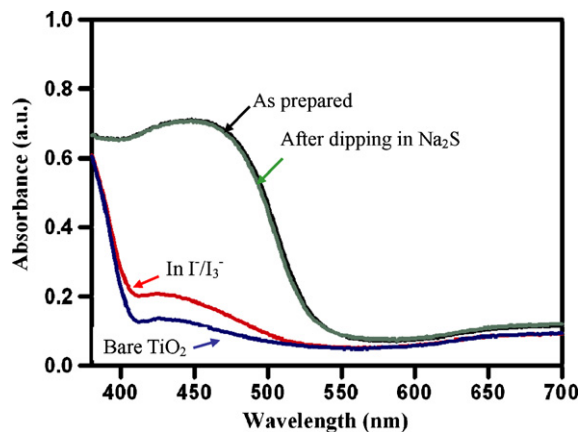


Fig. 1. The UV–vis spectra of as prepared TiO₂/CdS-3 photoelectrode and the electrode after dipping in 0.1 M Na₂S aqueous solution or in I⁻/I₃⁻ electrolyte for 5 min.

3.1. The optimum solvent

In the literature, the applications of polysulfide electrolyte for photoelectrodes of cadmium chalcogenide were performed nearly all in electrochemical cells using aqueous solution [6,7,11,19,20–22]. According to our experiment, an aqueous solution with high surface tension results in a poor penetrating and wetting of the solution in the TiO₂ porous matrix, leading to a poor efficiency of a DSSC. To solve this problem, methanol was used as a co-solvent to reduce the surface tension of the electrolyte. However, the dissociation and solubility of Na₂S in the methanol has to be considered.

In a single-compartment electrochemical cell, a CdS-modified TiO₂ photoelectrode prepared by 3 CBD cycles (ITO/TiO₂/CdS-3) was used to evaluate the dissociation of 0.1 M Na₂S in water and methanol. The reference and counter electrodes are Ag/AgCl and Pt, respectively. Fig. 2 shows the photoactivation current density measured under Xe lamp illumination (100 mW cm⁻²). The lower photocurrent obtained for the methanol, compared with that for the water, indicates a less dissociation of Na₂S in methanol. A low dissociation of Na₂S leads to a lower ion concentration and a slow rate of hole recovery. The lifetime of the excited CdS would be shorter and, therefore, a lower photocurrent is resulted. To consider both effects of surface tension and Na₂S dissociation, methanol–water co-solvent is used to tune an optimum composition. Co-solvents with various volume ratios of methanol to water are used to prepare 0.1 M Na₂S solutions. These solutions were used as electrolytes of CdS-sensitized DSSC using a photoelec-

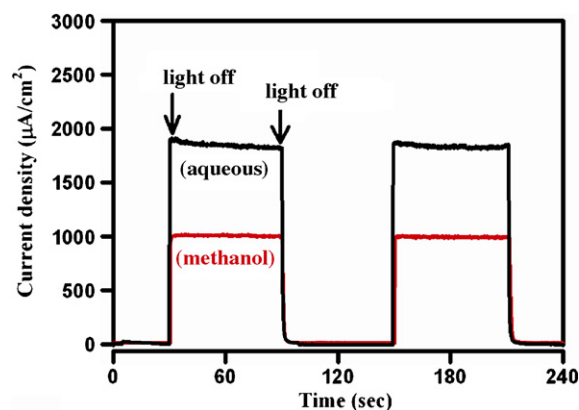


Fig. 2. Photoactivation current measured for ITO/TiO₂/CdS-3 photoelectrode under Xe light illumination (100 mW cm⁻²) in aqueous or methanol solution containing 0.1 M Na₂S.

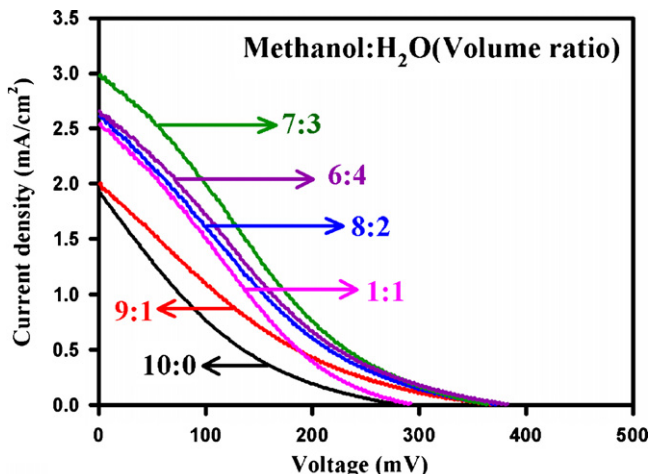


Fig. 3. I - V characteristics of CdS-sensitized DSSCs using 0.1 M Na_2S electrolyte dissolved in methanol/water co-solvents of various volume ratios. The photoelectrode is ITO/ TiO_2 /CBD3 and the measurement is performed under illumination of 100% sun (AM1.5, 100 mW cm^{-2}).

trode of ITO/ TiO_2 /CdS-3. The photocurrent–voltage (I - V) curves for these cells are measured at an illumination of 100% sun (AM 1.5, 100 mW cm^{-2}), and the results are shown in Fig. 3. The open circuit potential (V_{OC}), short circuit current (I_{SC}), fill factor (ff), and the total energy conversion efficiency (η) corresponding to the curves in Fig. 3 are listed in Table 1. The efficiency is as low as 0.08% when pure methanol is used. With increasing ratio of water, the efficiency increases gradually, attains the maximum value (0.21%) at a methanol/water ratio of 7/3 (by volume), and then decreases with further increasing ratio of water. Therefore, the solvent with methanol/water ratio of 7/3 is used for further studies to adjust the concentrations of other ingredients in the electrolyte.

3.2. Modulate the donor concentration and ingredient of the electrolyte

It is noteworthy that the performances of the QD-DSSCs using 0.1 M Na_2S as electrolyte (the results in Table 1) are less than that using I^-/I_3^- redox couple [4]. Although these results is ascribed to the lower ability of polysulfide, compared to the I^-/I_3^- , in regeneration the oxidized CdS, it is possible to enhance the performance of the electrolyte by adjusting the donor concentration or by introduction other ingredients. The modulation begins with increasing of Na_2S concentration. It is anticipated that a higher S^{2-} concentration can give a faster hole recovery, leading to a higher V_{OC} and I_{SC} . This inference is examined by raising the Na_2S concentration up to its solubility limit in the co-solvent (about 0.5 M). The I - V curves measured for these cells are shown in Fig. 4 and the characteristic parameters are list in Table 2. Both V_{OC} and I_{SC} increase due to the

Table 1
Parameters obtain from the I - V curves of CdS-sensitized DSSCs using 0.1 M Na_2S electrolyte dissolved in methanol/water co-solvents of various volume ratios

MeOH:H ₂ O	I_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF	η (%)
10:0	1.94	282.4	0.14	0.08
9:1	2.00	370.0	0.15	0.11
8:2	2.63	375.4	0.17	0.17
7:3	2.97	366.8	0.19	0.21
6:4	2.65	389.3	0.18	0.18
1:1	2.55	300.6	0.20	0.15

(Corresponding to Fig. 2.)

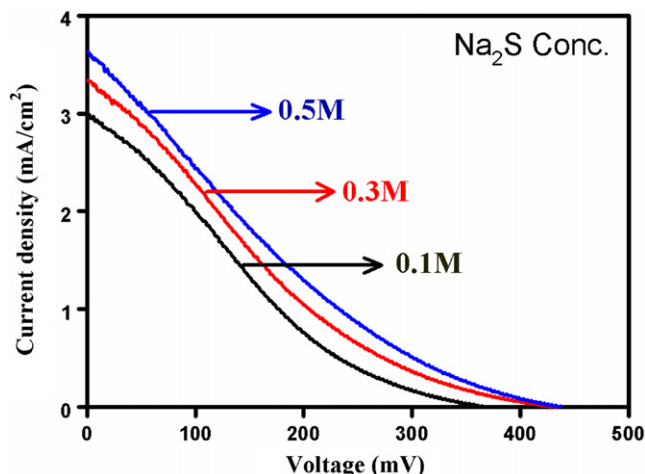


Fig. 4. I - V characteristics of CdS-sensitized DSSCs fabricated using Na_2S electrolyte of various concentrations dissolved in a methanol/water (7:3 by volume) co-solvent. The photoelectrode is ITO/ TiO_2 /CBD3 and the measurement is performed under illumination of 100% sun (AM1.5, 100 mW cm^{-2}).

elevation of Na_2S concentration, without significant change to the fill factor. The best efficiency increases to 0.28% at 0.5 M Na_2S .

By using an electrolyte containing only Na_2S , a fill factor less than 0.2 is obtained for the QD-DSSCs shown above. The small fill factor implies a significant charge recombination at the photoelectrode/electrolyte interface, ascribed to the slow hole-recovery rate of the electrolyte to the oxidized CdS-QDs. In the literature, polysulfide electrolytes, formed by dissolution of sulfide salt and sulfur in a solution, were always used instead of single sulfide salt for photoelectrochemical cells. Although the exact chemical species and chemical mechanisms involved in a polysulfide electrolyte are very complicated and presently not well understood, it was reported that supersulfide (S_2^-) has an intimate relationship to the hole-recovery in a photoelectrochemical system [23]. The presence of sulfur simultaneously with S^{2-} leads to the formation of polysulfide (S_x^{2-} , $x=2-5$), and the supersulfide (S_2^-) is formed through a reaction of tetrasulfide ($\text{S}_4^{2-} \rightarrow 2\text{S}_2^-$). Adsorption of supersulfide on a CdS surface takes important contribution to the hole-recovery and electron-hole separation. Furthermore, the polysulfide (S_x^{2-}) also plays as an electron acceptor to receive electron from Pt counter electrode through the following reaction.



Both effects are anticipated to give a better hole-recovery rate and, therefore, a higher efficiency of the cell.

Various amounts of sulfur are added to the electrolyte containing 0.5 M Na_2S . The maximum concentration of sulfur added to the electrolyte is 2 M, determined by the solubility of sulfur in the electrolyte. The I - V curves and related parameters of the CdS-sensitized DSSCs using these electrolytes are shown in Fig. 5 and Table 3, respectively. The results show that the fill factor and efficiency increase with increasing concentration of sulfur, implying that polysulfide is a superior redox couple than S^{2-} in enhancing the performance of CdS-sensitized DSSCs. With addition of 2 M sul-

Table 2
Effect of Na_2S concentration on the performance of CdS-sensitized DSSCs

Na_2S conc. (M)	I_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF	η (%)
0.1	2.97	366.8	0.19	0.21
0.3	3.33	435.2	0.17	0.24
0.5	3.63	438.4	0.17	0.28

The parameters are obtained from the I - V curves shown in Fig. 4.

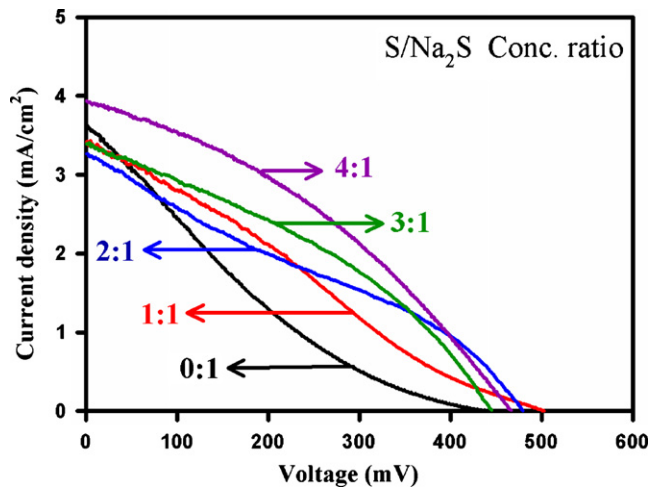


Fig. 5. Effect of sulfur/sulfide concentration ratio on the I - V characteristic of a CdS-sensitized DSSC. Various concentrations of sulfur are added to a methanol/water (7:3 by volume) solution containing 0.5 M Na_2S . The photoelectrode is ITO/TiO₂/CBD-3 and the measurement is performed under illumination of 100% sun (AM1.5 , 100 mW cm^{-2}).

Table 3

Effect of sulfur/sulfide concentration ratio on the I - V characteristic of a CdS-sensitized DSSC

S:S ²⁻	I_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	η (%)
0:1	3.63	438.4	0.17	0.28
1:1	3.38	503.5	0.25	0.43
2:1	3.27	480.0	0.30	0.46
3:1	3.39	445.9	0.35	0.54
4:1	3.94	465.1	0.36	0.65

The electrolytes were prepared using a methanol/water (7:3 by volume) solution containing 0.5 M Na_2S and various concentration of sulfur. The parameters are obtained from the I - V curves shown in Fig. 5.

fur, the efficiency increases from 0.28 (without sulfur addition) to 0.65, mainly attributed to the increase in fill factor.

In the I^-/I_3^- electrolyte system used for dye of ruthenium complex, the presence of other ingredients such as 1-propyl-2,3-dimethylimidazolium iodide (DMPII) and 4-*tert* butylpyridine (TBP) were proved to enhance the performance of the electrolyte. Unfortunately, these ingredients are not suitable for the present study because TBP cannot dissolve well and DMPII is unstable in the methanol/water solution used in the present system. In this work, KCl is used as an additive to enhance the conductivity of the electrolyte. Electrolytes of various KCl concentrations are prepared by introduction KCl to the methanol/water (7/3 by volume) solution containing 0.5 M Na_2S and 2 M S. The effect of KCl concentration on the performance of the CdS-sensitized solar cell is summarized in Table 4. The result shows that introduction of KCl is advantageous to the increase of short circuit current and fill factor, but the V_{oc} decreases as a result. The energy conversion efficiency η increases with increasing of KCl concentration and approaches a maximum

Table 4

Parameters obtain from the I - V curves measurement of the ITO/TiO₂/CBD3 cell constructed by adding various KCl concentration

KCl conc. (M)	I_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	η (%)
0	3.94	465.1	0.36	0.65
0.1	3.90	425.6	0.40	0.68
0.2	4.14	437.0	0.43	0.77
0.3	4.36	418.1	0.42	0.76
0.4	4.47	420.2	0.41	0.77

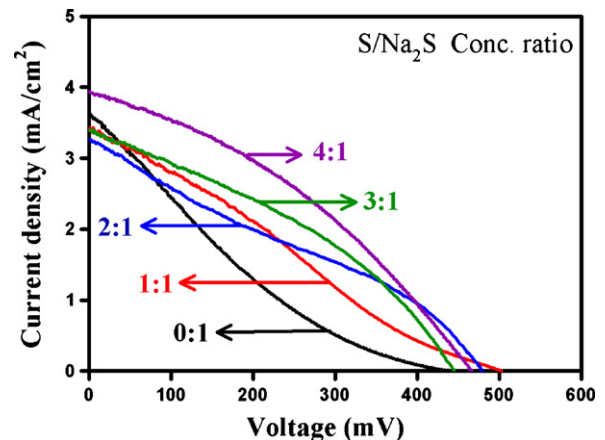


Fig. 6. A comparison between I and V characteristics of CdS-sensitized DSSCs using I^-/I_3^- redox couple or polysulfide as electrolytes. The photoelectrode is FTO/TiO₂/CBD-4 and the measurement is performed under illumination of 100% sun (AM1.5 , 100 mW cm^{-2}).

value (0.77) at about 0.2 M KCl. Further increase of KCl concentration gives little effect to the efficiency because the solubility of KCl in the solution is limited at about 0.2 M. Apparently, the introduction of KCl increases the solution conductivity and therefore, enhances the performance of the cell.

3.3. Comparison between performance of CdS-sensitized DSSCs using electrolytes of polysulfide and I^-/I_3^- redox couple

The optimal composition of the polysulfide electrolyte for a CdS-DSSC is now prepared by using methanol/water (7/3 by volume) solution containing 0.5 M Na_2S , 2 M S, and 0.2 M KCl. In a previous work, I^-/I_3^- redox couple was used in an electrolyte to fabricated QD-sensitized DSSCs using CdS-QDs prepared by CBD process. The best device was obtained for a photoelectrode prepared by 4 CBD cycles and the efficiency was 1.84%. The same photoelectrode (FTO/TiO₂/CdS-4) is used in this work to evaluate the performance of the polysulfide electrolyte. Fig. 6 shows the I - V curves of the devices using the two electrolytes and the related parameters are listed in Table 5. Compared with the device using I^-/I_3^- redox couple, the device using polysulfide has a much higher I_{sc} , but lower values of FF and V_{oc} . As a result, the efficiency obtained for the polysulfide electrolyte (1.15%) is lower than that for an I^-/I_3^- system (1.84%) [4]. A low FF or V_{oc} always implies significant recombination of excited electrons to the oxidized species at the electrode/electrolyte interface. For the polysulfide electrolyte, the lower FF and V_{oc} may be ascribed to the lower hole-recovery rate of polysulfide which leads to a higher probability for charge recombination. On the contrary, the higher I_{sc} for the polysulfide electrolyte is ascribed to the higher stability of CdS in this electrolyte, which also implies that, in the I^-/I_3^- system, some of the CdS-QDs have been degraded by the electrolyte before measurement of the I - V characteristic. This inference is confirmed by the variation of I_{sc} with repeated measurements. For the I^-/I_3^- electrolyte, the device performance decreases steadily with repeated

Table 5

Parameters obtain from the I - V curves measurement of the FTO/TiO₂/CBD4 cell compared between iodide/triiodide and polysulfide electrolyte

Redox couple	I_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	η (%)
$\text{S}^{2-}/\text{S}_x^{2-}$	6.16	466.2	0.40	1.15
I^-/I_3^-	4.30	680.8	0.63	1.84

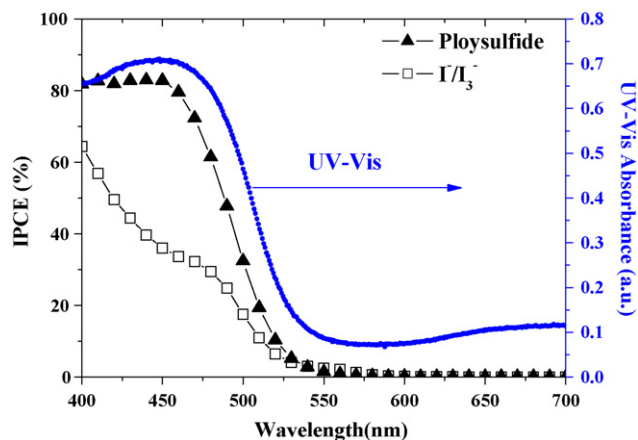


Fig. 7. A comparison between IPCE spectra of CdS-sensitized DSSCs using I^-/I_3^- redox couple or polysulfide as electrolytes. The photoelectrode is FTO/TiO₂/CBD-4 and its UV-vis absorption spectrum is also shown in this figure.

measurements, while no apparent change was observed for the polysulfide system.

The incident photon to current conversion efficiencies (IPCE) measured from the I_{SC} monitored at different excitation wavelengths are shown in Fig. 7 for both devices using different electrolytes. For the polysulfide electrolyte, the IPCE values are higher than those for the I^-/I_3^- redox couple, consistent with its higher I_{SC} shown in Table 5. By using the polysulfide, IPCE values as high as 80% can be obtained for wavelengths lower than 450 nm and, furthermore, the spectrum of the IPCE closely resembles that of the UV-vis absorption spectrum (also shown in Fig. 7). On the contrary, the IPCE spectrum for the device using I^-/I_3^- is deviated from the UV-vis spectrum, attributable to the degradation of CdS by I^-/I_3^- electrolyte during the IPCE measurement. Because the wavelength was scanned from short to long region, a degradation of CdS in the earlier measurement (short wavelength) leads to a lower value of photocurrent measured at the latter stage and, therefore, a smaller IPCE is obtained for the long wavelength. Compared with the result reported by Tachibana et al. [22], the IPCE obtained using methanol/water co-solvent is higher than using aqueous polysulfide electrolyte (about 70%), which demonstrates the superior function of the present system.

Although the efficiency obtained for this CdS-sensitized solar cell is still low compared with that of DSSCs using ruthenium complexes as sensitizers, this study opens a possibility to use a non-aqueous polysulfide electrolyte for QD-sensitized solar cell studies. For the present study, the low efficiency of the CdS-DSSC is caused by the lower fill factor of the electrolyte, as well as the narrow-range absorption of CdS to the sunlight. Using other additive to inhibit the

charge recombination at the TiO₂ photoelectrode–electrolyte interface is a possible method to increase the fill factor of a QD-DSSC. By using a QD-sensitizer that has a narrower band-gap (i.e. CdSe, CdTe), it is anticipated to increase the light adsorption range and elevate the cell efficiency. These issues are being studied in our lab.

4. Conclusion

We have successfully developed an efficient and non-corrosive polysulfide electrolyte for CdS QD-sensitized solar cell application. A methanol/water (7:3 by volume) solution was shown to be a good solvent for the electrolyte in terms of penetration ability of solvent in a mesoporous TiO₂ photoelectrode, and the degree of ion dissociation in the electrolyte. The optimal composition of the electrolyte was found to contain 0.5 M Na₂S, 2 M S, and 0.2 M KCl. By using a photoelectrode of FTO/TiO₂/CdS-4, the efficiency of the CdS-DSSC obtained for this polysulfide electrolyte is 1.15%. Although this efficiency is smaller than that obtained using I^-/I_3^- redox couple (1.84%), the CdS sensitizer is stable in the polysulfide electrolyte and a IPCE value as high as about 80% is obtained by the present system.

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