The Influence of Polysulfide Solvent on the Performance of Cadmium Sulfide Sensitized Zirconium Dioxide-Based Quantum Dots

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Abstract

The effect of two different types of polysulfide solvents (i.e., distilled water and methanol) was investigated for zirconium dioxide (ZrO₂) based quantum dots sensitized solar cells (QDSSCs). This was mainly depending upon how easily the injection of electrons in the conduction band of CdS particles to the ZrO₂ photoanode. Compared to that with methanol solvent-based polysulfide, distilled water-based polysulfide (S²⁻/S₆²⁻) electrolytes have efficient electron transportation characteristics at the interface of ZrO₂/CdS photoanode and carbon counter electrode. Solar cell efficiency using distilled water-based polysulfide for ZrO₂/CdS reaches 1%. The catalytic reaction due to incorporation of polysulfide solvents positively affects the solar cell performance as evident from Nyquist plots. Distilled water-based polysulfide electrolyte has significant impacts on the overall performance of QDSSCs.

Keywords: Zirconium dioxide; Cadmium sulfide; Electron transport; Polysulfide.
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1. Introduction

Last two decades, several metal oxides and chalcogenide semiconductors such as titanium dioxide (TiO₂),[1] zinc oxide,[2] tungsten oxide,[3] zinc sulfide[4] and cadmium sulphide[5] were applied for the solar cells, supercapacitors and quantum dots application perspective. Zirconium dioxide or zirconia (ZrO₂) is one of the newly explored metal oxides used as photoanodes in dye-sensitized solar cells (DSSCs) and quantum dots (QD) SSCs.[6] However, ZrO₂ shows prolonged stability for QD based solar cells compared to the dye-based SCs even at the high temperature of oxidation.[7]

The reported band gaps of ZrO₂ can be stretched between 3.35 to 5.11 eV depending upon the synthesis process and phase of the crystal structure.[8] The reported porous structure and crystallinity nature of ZrO₂ provide surface sites for the reactants to satisfy all requirements for the light-harvesting photoanodes.[9] On account of all these characteristics, ZrO₂ becomes a new class of photoelectrode for photovoltaic applications.[10, 11] Due to wide bandgap nature, ZrO₂ is capable of absorbing only ultraviolet (UV) range of photons; however, these are only a small fraction of the solar spectrum. For harvesting visible light, it is necessary to extend their absorption range in the visible regions. Thus, it needs to combine two semiconductors films, i.e., one for UV light absorber (ZrO₂) and one with the visible light absorber or sensitizers (CdS). Among the sensitizers, CdS is one of the efficient QD sensitizers for the application of QDSSCs because of its suitable bandgap (2.25 to 2.42 eV depending upon the synthesis process and phase of the crystal structure) for harvesting broad visible range of photons from the solar spectrum.[12-14]

Although ZrO₂ is a direct band gap metal oxide having an optical band gap around 5.11 eV, it is transparent for the visible range of photons, possesses high refractive index, good adhesion to the substrates and exhibits high thermal stability.[15-18] After the deposition of CdS QDs over ZrO₂ photoanode, a boundary layer in between energy levels of CdS QDs and conduction band of ZrO₂ is formed.[19] For easy transition or injection of electrons, the conduction band edge of photoanodes must be at the lower level than the conduction band edge of sensitizers or window materials. However, in this case of ZrO₂/CdS, the conduction band edge of ZrO₂ is almost...
at the same level of the conduction band of CdS, resulting in the injection of electrons or smooth transition of electrons from the conduction band of CdS into the conduction band edge of ZrO$_2$.\cite{20} Therefore, there is little probability for electrons to get transition smoothly from the conduction band of CdS into the conduction band edge of ZrO$_2$.

For the ZrO$_2$/CdS based QDSSC, two types of CdS QD or sensitizers were grown by chemical route over ZrO$_2$ films. Apart from these, two different solvents were used for the preparation of polysulfide i.e., distilled water and methanol. In the current study, Nyquist, Bode plots and equivalent circuits were used to analyze the role of polysulfide electrolytes for the performance of solar devices and their electron transport properties and the mechanism of QDSSC. Polysulfide electrolyte\cite{21} is a well-known electrolyte for QDSSC because its redox couple ($S^{2-}/S_{ul}$) can stabilize most QDs.

2. Experiments
Zirconia powder, ethyl cellulose, terpineol, acetyl acetone, cadmium sulphate, thiourea, ammonium hydroxide, aqueous ammonia, sulfur powder, and sodium sulfide were purchased from SRL Chemicals Ltd. India. Methanol and ethanol were purchased from C. H. Fine Chemicals Co. Ltd. and used as received without any further purification.

2.1 Synthesis of CdS nanoparticles
The synthesis technique of colloidal CdS particles, bulk CdS and CdS QDs is mentioned in our previous published article.\cite{22} The three different types of CdS quantum dots are named as type-a, type-b and type-c, which contains 0.05 M cadmium sulfate, 0.05 M thiourea, and 20% ammonium hydroxide at room temperature. Excess aqueous ammonia (NH$_4$OH) was added to the growth solution to attain pH.

2.2 Fabrication of ZrO$_2$ photoanodes
The ZrO$_2$ powder and ethyl cellulose were grinded in mortar pastel by adding Terpineol solution, the assembly was maintained in an ultrasonication bath for 3 hrs. The acetyl acetone was added during the ultrasonication at room temperature. The slurry formed was pasted on the fluorine doped tin oxide (FTO) substrate by the doctor blade technique. The as synthesized type-a, type-b and type-c CdS nanoparticles were deposited on ZrO$_2$ photoelectrode using a chemical bath deposition technique.

2.3 Synthesis of polysulfide electrolyte
A non-aqueous polysulfide redox electrolyte composed of 0.98 g Na$_2$S in 22.5 mL methanol and 0.08 g sulfur powder in 5 mL ethanol solution is a mixed and grinded for 15 min. Finally, polysulfide electrolytes were synthesized in two different types of solvents methanol and distilled water. In the methanol case, 0.98 g of sodium sulfide (Na$_2$S) was crushed using mortar pestle and 22.5 mL of methanol was used to form a solution, 0.08 g of sulfur powder with 5 mL of methanol was added into the resultant solution of Na$_2$S to form methanol based polysulphide electrolyte; whereas in the distilled water case, 0.78 g of Na$_2$S was dissolved in the 25 mL of distilled water, pallets of sodium hydroxide (NaOH) and of sulfur powder, were crushed and added to the Na$_2$S solution to form the distilled water based polysulphide electrolyte.

The X-ray diffraction (XRD) (model: XRD, Rigaku “D/B max-2400”, Cu Ka, $\lambda$ = 1.54 Å) was used to determine the crystalline nature, phase, and crystallite size of ZrO$_2$ films. and field emission scanning electron microscopy (FESEM) (Carl Zeiss, Merlin Compact) techniques were used for the structural and morphological properties of the samples, respectively. Optical absorption spectra is obtained using UV–Vis spectrophotometer (JASCO V-670) in the wavelength range of 200–1000 nm and the Electrochemical Impedance Spectroscopy (EIS) studied by Potentiosstat/Galvanostat (IVIUM Vertex model), whereas J-V characteristics were obtained from the 2420 Kethley Source meter.

![Fig. 1 XRD patterns for (a) CdS sensitized ZrO$_2$ photoanodes and (b) ZrO$_2$ film on FTO substrate.](image)
3. Results and Discussion

3.1 Structural properties

The XRD patterns of CdS, ZrO₂, and ZrO₂ based QDSSC sensitized by CdS are shown in Fig. 1(a). The observed diffraction peaks are corresponding to 24.2(011), 28.4(111), 31.7(220) and 34.4(221) for the monoclinic (m) phase of ZrO₂ confirmed by JCPDS card no. 37-1484. But 24.2, 34.4, 49.9, 54.3 and 55.7˚ show doublet peaks with some other unknown peaks, which are the significant peaks assigned for m-ZrO₂, as shown in Fig. 1(b). The reported phase for this peak is due to Õ₂-deficient ZrO₉₃₅ confirmed by JCPDS card no. 17-0385, space group P6322 having the hexagonal phase not shown in Fig. 1.¹ The characteristic peaks along (111), and (200) planes at 2θ values are at 26.7, 50.3 and 60.1˚ corresponding to CdS with the cubic crystal structure (JCPDS Card No. 27-0997). However, the characteristic peaks at 35.3, 50.1 and 59.8˚ having lattice planes (110), (200) and (211) respectively confirmed the tetragonal phase of ZrO₂ (JCPDS card No. 05-0665). The crystal phase purity shows that monoclinic, tetragonal and cubic phases are 67%, 22%, and 10% respectively whereas the remaining 1% is due to Õ₂-deficient ZrO₉₃₅. The diffraction peaks for the m-ZrO₂ show the highest intensities compare to e-ZrO₂ and t-ZrO₂ which represents m-ZrO₂ and t-ZrO₂ as shown in Fig. 1 (b).

3.2 Optical properties

The deposition of three types of colloidal CdS particles over ZrO₂ photoanode is carried out using a chemical method. The band gap (E₉) for CdS type-a, b and c are 2.38, 2.49 and 2.61 eV respectively, as shown in Fig. 2(a). The E₉ for ZrO₂ photoanode is calculated as 5.11 eV, the corresponding E₉ in the UV optical spectrum is at 240 nm as shown in Fig. 2(b). But after depositing CdS on ZrO₂, the corresponding E₉ for CdS-ZrO₂ film shows red shifts towards longer wavelengths as shown in Fig. 2(a). The thickness (d) of the ZrO₂ film is ~10 μm. Hence despite ZrO₂ is a wide band gap metal oxide, after the deposition of colloidal CdS particles as sensitizers or window materials, the combined ZrO₂ and CdS gives typical metal oxide based like solar devices having better efficiency (PCE), fill factor (FF), current density (Jₐc) and open circuit voltage (Vₜc), which have not been reported yet in the literature.

Fig. 3 shows the SEM images of the obtained films. The images were obtained at a various magnification of x3000, x10, 000 and x30, 000. SEM images for bare ZrO₂ photoanode a₁ to a₃; whereas b₁ to b₃ for ZrO₂/CdS type-a to type-c respectively show the comparable morphology. ZrO₂ film structure is a granular type having macroporous morphology (> 50 nm). After the deposition of CdS, type-b shows macroporous morphology having flakes as shown in (b₂). However, these flake shapes of macroporosity almost disappear in the case of type-c, hence in the J-V measurement of ZrO₂/CdS type-c based QDSSC, very low Jₐc, Vₜc and hence low FF and efficiency are observed. The J-V-measurement for ZrO₂/CdS type-a gives an intermediate response between type-c and type-b, this could be verified from the intermediate porous morphology for ZrO₂/CdS type-a film.

3.3 Fabrication of solar cells

The fabricated and chemical bath deposited CdS photoanodes (CdS/ZrO₂) are used for the fabrication of solar cells, the carbon suites is used as counter electrode, which is fabricated on the FTO substrate.
Fig. 3 SEM images of CdS, ZrO$_2$ and ZrO$_2$/CdS films: (a$_1$-a$_3$) are for bare film of ZrO$_2$. Bulk and nano size CdS particles deposited on ZrO$_2$ films (b$_1$) for ZrO$_2$/CdS type-a (b$_2$) for ZrO$_2$/CdS type-b and (b$_3$) for ZrO$_2$/CdS type-c.

### 3.4 Performance measurement

**Table 1.** Solar cell parameters for ZrO$_2$ based QDSSC where CdS type-a and type-b used for the sensitization (methanol based electrolyte) (30 mW/cm$^2$).

<table>
<thead>
<tr>
<th>ZrO$_2$/CdS QDSSCs</th>
<th>Open circuit voltage ($V_{oc}$) (V)</th>
<th>Current density ($J_{sc}$) (mA/cm$^2$)</th>
<th>Fill factor (FF)</th>
<th>Metastable state, $\tau_e$ (ms)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>For type-a</td>
<td>0.38</td>
<td>0.31</td>
<td>0.15</td>
<td>0.79</td>
<td>0.058</td>
</tr>
<tr>
<td>For type-b</td>
<td>0.55</td>
<td>0.55</td>
<td>0.21</td>
<td>4.37</td>
<td>0.212</td>
</tr>
<tr>
<td>For type-c</td>
<td>0.055</td>
<td>0.03</td>
<td>0.23</td>
<td>0.05</td>
<td>0.006</td>
</tr>
</tbody>
</table>

The methanol-based polysulfide electrolyte shows that the current densities ($J_{sc}$) for ZrO$_2$/CdS type-a, b and c are 0.31, 0.55 and 0.03 mA/cm$^2$, whereas open circuit voltage ($V_{oc}$) are 0.38, 0.55 and 0.06 V respectively. PCE for CdS-type-b coated ZrO$_2$ solar device is 0.21% which is greater among the CdS type-a and c. Only CdS type-b is compatible with mesoporous structure of ZrO$_2$. Excited states of CdS type-a (Bulk) are not at the same level with conduction band of ZrO$_2$. For type-c due to large band gap, only few electrons are diffused. Hence mesoporous ZrO$_2$ is compatible with CdS type-b only. Thus, the PCE for CdS type-a and type-c are 0.06 and 0.006% respectively. Thus ZrO$_2$/CdS type-c solar device shows a negligible PCE. However, the FF for CdS type-c is 0.23 compare to CdS type-a (0.15) and type-c (0.21). Current densities for CdS type-a and b are noticeable, 0.31 and 0.55 mA/cm$^2$ respectively. The solar cell parameters for methanol-based electrolyte are shown in Fig. 4 and are summarized in Table 1. It is observed that the $J_{sc}$, $V_{oc}$, and $\eta$ initially increased and then decreased with decreasing the size of colloidal CdS particles. For distilled water-based polysulfide electrolyte, the $J_{sc}$ is higher for ZrO$_2$/CdS type-b compared to CdS type-a and CdS type-c. It is also found that the FF for type-b (0.34) also shows a better performance than that for CdS type-a (0.30) and CdS type-c (0.24). Since not only the solar cell parameters but the stability for distilled water-based electrolyte are able to retain prolonged electron life time compared to the methanol based electrolyte.

**Table 2.** Solar cell parameters for ZrO$_2$ based QDSSC where CdS type-a and type-b used for the sensitization (dw electrolyte) (30 mW/cm$^2$).

<table>
<thead>
<tr>
<th>ZrO$_2$/CdS QDSSCs</th>
<th>Open circuit voltage ($V_{oc}$) (V)</th>
<th>Current density ($J_{sc}$) (mA/cm$^2$)</th>
<th>Fill factor (FF)</th>
<th>Metastable state, $\tau_e$ (ms)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>For type-a</td>
<td>0.77</td>
<td>0.89</td>
<td>0.30</td>
<td>13</td>
<td>0.68</td>
</tr>
<tr>
<td>For type-b</td>
<td>0.61</td>
<td>1.44</td>
<td>0.34</td>
<td>9.55</td>
<td>1</td>
</tr>
<tr>
<td>For type-c</td>
<td>0.44</td>
<td>1.78</td>
<td>0.24</td>
<td>1.66</td>
<td>0.62</td>
</tr>
</tbody>
</table>

The solar cell parameters for distilled water based polysulfide electrolyte are summarized in Table 2. It is observed that the $J_{sc}$, $V_{oc}$, $\eta$ initially increased and then decreased with decreasing the particle size of CdS from type-a to type-c. The maximum PCE for CdS type-b is 1.0%, which is higher than other two CdS type-a and type-c. The result of PCE and their variation clearly indicates that Polysulphide electrolyte gives a stable performance when used in solar cell devices.
process, some of them lose due to recombination at ZrO₂/CdS and leakage at CE, these losses of electrons created the Resistance (i.e., $R_e$ or $R_i$) due to electron transport process. For ZrO₂/CdS type-b, the $R_i = 618 \, \Omega$ is connected in the series with the charge transfer resistance, $R_{ct} = 9.56 \, k\Omega$ which is in parallel capacitor $C_1 = 0.57 \, \mu F$. $R_i$ is due to the recombination process after the electrons are injected from CdS QDs to ZrO₂ while $C_1$ acts as capacitive elements (constituent of reactance elements such as interface at conduction band and surface states of ZrO₂ photoanodes).[22] Because of the recombination process, all the electrons do not contributed to current densities, some of the electrons recombined with the holes. These recombined electrons are responsible for capacitive elements in the porous structure of ZrO₂ photoanode.[23, 24]

Semicircle in the lower frequency region shows a series combination of $R_i$ with $R_{ct}/C_1$, whereas the first semicircle represents the charge transfer at electrolyte/CE-FTO interface under higher frequency region shown in Fig. 6(a). This charge transfer also suffers from some electron losses at the interface of electrolyte/CE-FTO, which results in another charge transfer resistance, $R_{ct} = R_1 = 650 \, \Omega$ for ZrO₂-CdS type-b. Counter electrodes are the carbon electrodes. Since the capacitive element $C_1$ with $R_i$ is attributed to the recombination process at the interface of ZrO₂/CdS and the electrolytes.

Higher $C_{tr}$ in this case, indicates a higher related resistance to the recombination process. Another capacitance is observed at the interface of electrolyte and counter electrode, $C_2 = 1.63 \, \mu F$ which is less than $C_1$. $C_2$ is due to a reduction at electrolyte/CE-FTO interface. The details for ZrO₂-CdS type-c are summarized in Table 3. Whereas details for distilled water-based polysulfide are summarized in Table 4. Equivalent circuits fitted on Nyquist plots are shown in Fig. 7.

The metastable state for methanol-based electrolyte: ZrO₂/CdS type-b has a longer electron lifetime (0.7 ms) compared to 0.12 and 0.008 ms for ZrO₂/CdS type-a and type-c based QDSSCs respectively. Similar results were obtained for distilled water based electrolytes, but in this case $J_{sc}$, $V_{oc}$, and $\eta$ are better than methanol-based polysulfide as shown in Fig. 5(b) and 6(b). Thus, the transition of electrons in ZrO₂/CdS type-b for both the cases of methanol and distilled water-based electrolytes is in the lower frequency region compared to ZrO₂/CdS type-a and type-c as explained in Scheme 1.

Higher capacitance ($C_{tr}$) in the range of micro Farad is due to electron recombination and regeneration process during the oxidation of polysulfide, holes in CdS QDs were replaced by electron from polysulfide whereas lesser capacitance ($C_2$) is due to reduction at the interface of electrolyte and counter electrode as shown in the Scheme 1.[23] It is not necessary higher is the electron life time, but a better PCE.[24] For both the cases of distilled water and methanol based polysulfide, electron life time in Bode phase plot is higher for ZrO₂/CdS type-a as shown in of Fig. 4(b) and 5(b) but the PCE associated with CdS type-a is lower.

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**Fig. 4** J-V characteristic of CdS sensitized ZrO₂ photoanodes using (a) methanol based (b) DW based polysulfide electrolytes.

### 3.5 Equivalent circuit Analysis

The potentiostat/galvanostat is used to measure the photocurrent and photovoltage responses with respect to time and electrochemical impedance spectra. The solar devices were measured at -1.0 V bias voltages under the dark condition having frequencies from $10^{-1}$ to $10^5$ Hz at 25 °C. EIS measurement involves the investigation of charge transport properties for ZrO₂ based QDSSCs. For CdS type-b/ZrO₂ based QDSSCs, there is a semicircle observed in the Nyquist plot. Equivalent circuit is fitted for this semicircle. Resistance is due to (1) electron transport, $S^2$ loses its electrons to the hole (h$^+$) in valence or lowest unoccupied molecular orbital (LUMO) level of ZrO₂/CdS QDs to become S, this sulfur then takes electrons from sulfide ion ($S^{2-}$) whereas (2) at the counter electrode (CE), a reduction of $S^{2-}$ occurs with the gain of electrons from $S^{2-}$ to the $S^{2-}$. Thus, since redox reactions for regeneration and diffusions occur at the two interfaces, not all the electrons contributed to the redox
Scheme 1. Resistance and capacitance represent various processes within the solar device. Equivalent circuit represents the mechanism of QDSSC.

Enhanced electron lifetime with CdS type-a as a sensitizer over ZrO₂, the photoanode material is probably due to lower concentration of oxygen vacancies in ZrO₂ as compared to TiO₂ and ZnO. ZrO₂ in this case possesses four crystal phases; monoclinic (67%), tetragonal (22%), cubic (10%) and hexagonal (1%). As reported earlier, monoclinic ZrO₂ contained only 3% of oxygen vacancies. Thus in contact with ZrO₂ photoanode with CdS colloidal particles, most of the electrons contributed to the electron transition process and very few got absorbed with the oxygen vacancies.

However, very few electrons in the energy levels of CdS QDs have been injected towards discrete energy levels of ZrO₂ because of the band to band positions. These discrete energy levels are not compatible for electron transitions between ZrO₂ and CdS QDs. Hence, most of the electrons from polysulfide are recombined within CdS QDs before being injected into ZrO₂ photoanode. Unusual higher capacitance (C₁) for both the polysulfide cases represents this effect. Therefore, despite of higher electron lifetime, the highest PCE observed for ZrO₂-CdS type-b is 1% less than that of ZnO and TiO₂-CdS type-b (distilled water based polysulfide).

3.6 Electron transport properties:
Since the diffusion length (D_l) of an electron is the mean distance traveled by charged carriers from the point of generation to the recombination sites. It is observed for CdS type-a, D_l is higher than that of type-b and c. However, for the materials having more defects or surface states, the recombination rates will be higher. It may be seen that for CdS type-b/ZrO₂, the D_l is 1.29 and 3.23 for methanol and distilled water based polysulfide, respectively, inferring to the better performance for the latter, as analyzed in Table 5 and 6. These different values of D_l show that polysulfide prepared in different solvents have different interactions with CdS/ZrO₂ photoanodes, hence D_l is higher for methanol based polysulfide and lower in the case of distilled water based polysulphide for CdS type-a and type-c/ZrO₂ based QDSSCs.
Fig. 6 (a) Nyquist plot and (b) Bode plot for ZrO$_2$/CdS QDSCs using DW based polysulfide.

Table 3. Details about Equivalent circuit parameters (Methanol based polysulfide).

<table>
<thead>
<tr>
<th>QDSSCs</th>
<th>Electron transport at ZrO$_2$/CdS/PS and PS/CE</th>
<th>Charge transfer FTO/ZrO$_2$/CdS</th>
<th>CE/FTO</th>
<th>Capacitance</th>
<th>Effective mean electron life time ($\mu$s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS type-a</td>
<td>$R_\text{ct} = R_2$ (Ω)</td>
<td>$R_\text{ct} = R_4$ (Ω)</td>
<td>$R_\text{ct}' = R_3$ (Ω)</td>
<td>$C_1$ (μF)</td>
<td>$C_2$ (μF)</td>
</tr>
<tr>
<td>CdS type-b</td>
<td>618</td>
<td>9.56 k</td>
<td>-</td>
<td>0.57</td>
<td>-</td>
</tr>
<tr>
<td>CdS type-c</td>
<td>854</td>
<td>1.43 k</td>
<td>650</td>
<td>4.70</td>
<td>1.63</td>
</tr>
</tbody>
</table>

CdS type-c $\tau_{\text{eff}}$ values for DW based polysulfide.

Fig. 7 Equivalent circuits for Nyquist plots: for methanol and DW based polysulfide.
Table 4. Details about Equivalent circuit parameters (DW based polysulfide).

<table>
<thead>
<tr>
<th>QDSSCs</th>
<th>Electron transport at ZrO2/CdS/PS and PS/CE</th>
<th>Charge transfer FTO/ZrO2/ CdS</th>
<th>Capacitance</th>
<th>Effective mean electron life time (τeff) (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R_Ω = R_ε (Ω)</td>
<td>R_Ω = R_ε (Ω)</td>
<td>C_1 (μF)</td>
<td>C_2 (μF)</td>
</tr>
<tr>
<td>CdS type-a</td>
<td>395</td>
<td>710</td>
<td>191</td>
<td>5.88</td>
</tr>
<tr>
<td>CdS type-b</td>
<td>149</td>
<td>1.59 k</td>
<td></td>
<td>2.59</td>
</tr>
<tr>
<td>CdS type-c</td>
<td>2.11 k</td>
<td>2.31 k</td>
<td>2.10 k</td>
<td>0.71</td>
</tr>
</tbody>
</table>

Table 5. Electron transport properties of ZrO2/CdS based QDSSCs (Methanol based polysulfide).

<table>
<thead>
<tr>
<th>QDSSCs</th>
<th>Diffusion length (D_f) (μm)</th>
<th>Effective electron diffusion coefficient (D_f) x 10^{-7} cm²/s</th>
<th>Charge collection efficiency (η_c) %</th>
<th>Effective electron diffusion length (L_f) (μm)</th>
<th>Effective electron diffusion time (τ_{eff}) (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS type-a</td>
<td>3.93</td>
<td>19.6</td>
<td>93</td>
<td>39.3</td>
<td>0.051</td>
</tr>
<tr>
<td>CdS type-b</td>
<td>1.29</td>
<td>0.38</td>
<td>40</td>
<td>12.9</td>
<td>2.61</td>
</tr>
<tr>
<td>CdS type-c</td>
<td>1.36</td>
<td>36.9</td>
<td>45</td>
<td>13.6</td>
<td>0.027</td>
</tr>
</tbody>
</table>

Now the charge collection efficiency (\(η_c\)) in the case of methanol-based polysulfide, for CdS type-a/ZrO2 combination, shows \(η_c \sim 93\%\), however, for CdS type-b and type-c, it is just \(η_c \sim 40\%\) and \(45\%\) respectively. In the working principle of QDSSCs, the concentration gradients occur at the interface of (1) polysulfide/counter electrode and (2) CdS/ZrO2 photoanodes/polysulfide. In the case of methanol based polysulfide, the effective electron diffusion co-efficient \(D_f\) for CdS type-c/ZrO2 is about 36.9 x 10^{-7} cm²/s compared to CdS type-a and type-b/ZrO2 combinations, which are 19.6 and 0.38 x 10^{-7} cm²/s, respectively as analyzed in Table 5. Despite of higher \(D_f\) for CdS type-c/ZrO2 combination, higher solar cell efficiency is shown for the CdS type-b/ZrO2 as shown in Fig. 4.

However, in the case of distilled water based polysulfide, solar cell efficiency for CdS type-c/ZrO2 combination supports the higher \(D_f\) values compared to other combinations of CdS type-a and CdS type-c as analyzed in Table 6. Similar results are true for effective electron diffusion length \(L_f\), 32.3 μm for CdS type-b/ZrO2 compared to other CdS types.

Finally, effective electron diffusion time \(\tau_{eff}\) is higher, 7.23 ms for CdS type-a/ZrO2 combination not for CdS type-b/ZrO2. The reason behind the displayed all these electron transport properties is still being investigated as they are in correct correlation with the efficiency of QDSSCs. Kadam et al. calculated the electronic transport properties for DSSCs.[21] Using these formulae, the calculated electron transport properties within QDSSCs are summarized in Tables 5 and 6. From the equivalent circuits \(R_1 = R_Ω\) and \(R_2 = R_ε\).

Table 6. Electron transport properties of ZrO2/CdS based QDSSCs (DW based polysulfide).

<table>
<thead>
<tr>
<th>QDSSCs</th>
<th>Diffusion length (D_f) (μm)</th>
<th>Effective electron diffusion coefficient (D_f) x 10^{-7} cm²/s</th>
<th>Charge collection efficiency (η_c) %</th>
<th>Effective electron diffusion length (L_f) (μm)</th>
<th>Effective electron diffusion Time (τ_{eff}) (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS type-a</td>
<td>1.34</td>
<td>0.14</td>
<td>44</td>
<td>13.4</td>
<td>7.23</td>
</tr>
<tr>
<td>CdS type-b</td>
<td>3.23</td>
<td>1.09</td>
<td>90</td>
<td>32.3</td>
<td>0.91</td>
</tr>
<tr>
<td>CdS type-c</td>
<td>1.05</td>
<td>0.66</td>
<td>8.6</td>
<td>10.4</td>
<td>1.52</td>
</tr>
</tbody>
</table>
4. Conclusions
Electron transport properties of three different CdS particles sensitized ZrO$_2$ based QDSSCs show that CdS type-b/ZrO$_2$ is a more active combination compared to CdS type-a and c. Optical absorption and surface morphologies of CdS type-b/ZrO$_2$ are favorable for the electron regeneration and electron injections at the interface of polysulfide/CdS/ZrO$_2$. The current density ($J_{sc}$) for CdS type-b coated QDSSCs is 1.44 mA/cm$^2$. The measurements were recorded using 30 mW light source as an input power. Electron transport mechanism shows polysulfide prepared in distilled water based solvent is better electrolyte compared to methanol. Distilled water based polysulfide shows a higher solar cell efficiency (1.0%) for CdS type-b sensitized ZrO$_2$.

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Conflict of Interest
There is no conflict of interest

Supporting Information
Not applicable.

References

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