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Morphological and structural study on low cost SnO₂ counter electrode and its applications in quantum dot sensitized solar cells with polysulfide electrolyte

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ABSTRACT

Fabrication of efficient CdS quantum dot sensitized solar cell with a novel stable counter electrode based on a thin film of SnO_2 is revealed. The film was characterized by using Scanning Electron Microscopy (SEM), High-Resolution Tunneling Microscopy, X-ray diffraction (XRD) and UV–Visible spectroscopic techniques. Photovoltaic performances and Electrochemical Impedance Spectroscopic techniques (EIS) were performed on FTO/TiO₂/ CdS/polysulfide/SnO₂/FTO device under the light illumination of 100 mW cm⁻² and comparison was done with the conventional Pt counter electrode. Impressive 43 % efficiency enhancement in these solar cells was achieved compared with the Pt based devices. Porous thick nanostructure of SnO_2 with crystal defects such as oxygen vacancies and Sn vacancies arising from lattice structures as confirmed by SEM, Raman and, XRD spectroscopy could be some of the reasons for this enhancement. Excellent photo enhanced electrocatalytic activity against the polysulfide electrolyte is confirmed by EIS and Cyclic Voltammetry studies.

1. Introduction

Among the third generation of photovoltaics, quantum dot sensitized solar cells (QDSSCs) have been attracting much attention owing to their unique properties existing in the quantum dots, such as tunable band gaps, multiple exciton generation, and large extinction coefficient [1,2]. According to recent literature, significant performance enhancements have been achieved in these solar cells with an increased interest in reaching the maximum theoretical efficiency of ~ 66 %, which is much greater than conventional solar cells [2]. Even though numerous research investigations have been carried out on these QDSSCs, still their power conversion efficiencies and stability are much lower than commercially available conventional Si solar cells.

The main components of QDSSCs are quantum dot sensitized photoanode, counter electrode (CE), and the electrolyte sandwiched inbetween them. Light capturing quantum dot decorated, wide bandgap

mesoporous semiconductors like TiO2, SnO2, ZnO, etc. are the most popular photoanodes employed in these devices [3]. Here the quantum dots are responsible for generating electron-hole pairs from the harvested light, while wide bandgap semiconductors provide electron transport pathways in aid of the current generation and reducing electron-hole recombination. Polysulfide redox mediator (S_n^{2-}/S_2^{-}) is preferred as the electrolyte for the quantum dot regeneration process and hole transportation from the counter electrode. In this context, reduction and oxidation take place at the counter electrode and therefore CE plays a key role in the conversion of S_x^{2-} ions to S_2^{-} ions and vice versa, within the electrolyte which eventually affects the overall performance of the device. Generally, CEs of these QDSSCs consist of a thin film of platinum (Pt) deposited on a conducting substrate as the catalytic materials due to its high electro-catalytic activity [2,3]. Even though it has been widely used as a CE for QDSSCs, several factors have been proved to be disadvantageous for its continuous use. It was reported that

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Fig. 1. Schematic diagram of the fabricated TiO₂/CdS/polysulfide electrolyte/ SnO₂ QDSSC.

Pt shows a reduction in catalytic activity when contacted with polysulfide electrolyte, due to surface adsorbed sulfur and polysulfide which reduce catalyst active surface area and increase charge transfer resistance at the electrolyte/CE interface [4,5]. On the other hand, fabrication processes of these rarely available and expensive noble metal, Pt counter electrodes involved expensive sputtering and electrochemical depositing techniques which would limit the large-scale commercial applications of these devices [3,5]. In order to replace these Pt-based counter electrodes with cheaper materials with good electronic conductivity and efficient electro-catalytic effects for polysulfide reduction, various potential alternative materials such as those prepared with carbon [6], Au [7], structured carbon material [8], CoS [9] and CuS [10], Cu₂S [11], were used as the catalyst materials of the counter. Moreover, conducting polymer materials, such as polythiophene (h = 0.09 %), polypyrrole (h = 0.41 %) and poly(3,4-ethylene dioxythiophene) (h = 1.35 %) have been also suggested [1]. In this context, recently Sajjad et al. have compared the device performances of CdS based QDSSCs fabricated with carbon counter electrodes having either polysulfide electrolyte or iodide electrolyte in these solar cells and achieved higher efficiency in carbon-based CE devices with an overall efficiency of 0.38 compared with 0.10 for iodide based cells [12]. Therefore, finding a low-cost suitable counter electrode for these sulphide-based electrolytes in QDSSCs is one of the major challenges in this area of research. With the aim of addressing these problems, in this study we report comparative photovoltaic studies by using various experimental techniques, on low cost easily fabricable SnO₂ counter electrode based CdS QDSSCs with its counterpart comprising Pt-based devices.

Tin (IV) oxide (SnO₂) could become a promising candidate due to its high chemical stability, high electron mobility, low cost, and environmentally friendly nature. SnO₂ is a wide bandgap semiconductor widely utilized in batteries, sensors, supercapacitors, and the glass coating industry [13-16]. However, SnO₂ CEs are less explored due to their low electrocatalytic activity reported and need improvements with further modifications. Contradictorily, the notable photocatalytic activity of SnO₂, revealed in literature, opens pathways for exploring it as a photoactivated CE material [17–19]. In recent studies, SnO₂ has been widely used as the CE composite material for dye-sensitized solar cells. It was reported that SnO₂ nanoparticles act as a binder in the composite and increase the effective surface area due to the porous nature of the CE [20]. Moreover, it was also reported that $Pt-SnO_2$ nanocomposite CE records improved the photo-conversion efficiency in dye-sensitized solar cells when compared with the conventional Pt CE [13]. Studies related to Pt-decorated SnO₂ nanotubes and hierarchical SnO₂@SnS₂ CEs showed the utilization of the fast electron transport property of SnO₂ in developing CEs [14,15]. A nonstoichiometric SnO_{2-δ} nanocrystal-based CE reports a remarkable performance of dye-sensitized solar cells [16]

and preparation of SnO₂ CE under an N₂ atmosphere imparts electronic structure changes leading to different catalytic activities [21]. However, to our knowledge, no studies have been reported on the feasibility of using thin films of SnO₂ counter electrodes in QDSSCs so far. Therefore, in order to explore the possibilities of employing SnO₂ thin films as the counter electrodes in QDSSCs, in this study, CEs were fabricated by depositing SnO₂ films on fluorine-doped tin oxide (FTO) glass substrates using a simple spray pyrolysis technique and thermal annealing. Performances of CdS sensitized TiO₂ photoanodes were compared by fabricating solar cells with both, Pt CEs prepared by sputtering a thin film of Pt on FTO glass (commercial) and SnO₂ CEs prepared by spray coating a film SnO₂ on FTO glass substrates.

2. Materials and methods

2.1. Materials used

Fluorine doped tin oxide (FTO) coated glass (7 Ω cm⁻², Solaronix), tin (IV) oxide (15 % in H₂O colloidal dispersion, Alfa Aesar), titanium dioxide P90 powder (Evonik), titanium dioxide powder P25 (Degussa), Triton X-100 (Sigma Aldrich), glacial acetic acid (99 %, Fisher), sulfur (99 %, Daejng), sodium sulfide hydrate (>60 %, Sigma Aldrich), cadmium (II) chloride (99.99 %, Sigma Aldrich), potassium chloride (99 %, Aldrich) polyethylene glycol (99.8 %, Sigma Aldrich), ethanol (95 %, Sigma Aldrich), and methanol (99.8 %, Sigma Aldrich), were used as received without any purification.

2.2. Fabrication of SnO₂ counter electrodes

SnO₂ CEs were fabricated by using the spray pyrolysis technique. A spray solution was prepared by mixing appropriate amounts of a colloidal dispersion of SnO₂ nanoparticles (average particle size – 15 nm) in H₂O, glacial acetic acid (0.3 ml in the best composition), Triton X-100 (0.3 ml), and ethanol (80 ml in the best composition) and sonicated for 2 h. This solution was sprayed over FTO glass substrates kept at 200 °C. SnO₂ spray-coated FTO glass substrates were then sintered at different temperatures for different time periods in a muffle furnace. The area of the CE was kept constant at 0.2 cm².

2.3. Fabrication of photo anodes

TiO₂ based photoanodes were fabricated by using two types of TiO₂. At first, a thin layer of TiO₂ P90 (~100 nm) was spin-coated by using a mixed paste of TiO₂ P90 (0.25 g) and diluted 0.1 M HNO₃ (1 ml on well cleaned FTO glass substrates, and films were then sintered at 450 °C for 45 min. The second layer of TiO₂ P25 was deposited by the doctor blade method on the above P90 layer by using a paste prepared by mixing 0.25 g of P25 with diluted HNO₃ (1 ml), 1 drop of Triton-X 100 (~50 μ l), and polyethylene glycol (~50 μ l) and followed by sintering at 450 °C for 45 min. CdS incorporation on the TiO₂ surface was carried out by successive ionic layer adsorption and reaction techniques (SILAR). Aqueous solutions of 0.1 M CdCl₂ and 0.1 M Na₂S were used as precursor solutions for the deposition of CdS quantum dots and photoanodes were finally dried at 100 °C.

2.4. QDSSC device fabrication

Counter electrodes and photoanodes were clipped together by metal clips, sandwiching with the liquid polysulfide electrolyte layer inbetween, to obtain the final structure of the solar cell as shown in Fig. 1. Electrolyte contains sulfur (2 M), Na₂S (0.5 M), and KCl (0.2 M) dissolved in a mixture of deionized water and methanol in the ratio of 3:7 (v/v).



Fig. 2. (a) Photograph of a fabricated SnO₂ counter electrode on FTO substrate together with SEM images of (b) top view and (c) cross sectional view.

2.5. Material characterization

Morphological studies of CEs fabricated with SnO₂ were examined by Scanning Electron Microscopic (SEM) images (ZEISS EVO) and also with High-Resolution Transmission Electron Microscopic (HRTEM) images (AJEOL 2100 TEM). Raman spectra of CEs sintered at different temperatures were examined by using a Renishaw basis Raman microscope operated with 514 nm lasers. X-ray diffraction (XRD) data of SnO₂ CE material were recorded using Bruker D8 advanced eco X-ray diffraction system with Cu K α radiation ($\lambda = 1.54060$ Å). Surface chemical states of the CE material were examined by Thermo Scientific TM ESCALAB Xi +X-ray photoelectron spectrometer (XPS). Optical absorption spectra of different materials were recorded by Shimadzu 2450 UV-vis spectrophotometer. Cyclic voltammetry (CV) experiments were performed with for symmetric cells using a Metrohm Autolab (PGSTAT128 N) potentiostat/galvanostat at a scan rate of 30 mV s⁻¹. For the CV measurements, an electrolyte bath was prepared by stirring 0.1 M S, 0.1 M Na₂S, and 0.1 M KCl in deionized water.

2.6. Device characterization

Current density-voltage (J-V) characterizations of fabricated QDSSCs were carried out under simulated sunlight of 100 mW cm⁻² with AM 1.5 filter by coupling with Oriel Newport LCS-100 solar illumination system with a Metrohm Autolab potentiostat/galvanostat. Electrochemical impedance spectroscopy (EIS) measurements of QDSSCs and symmetrical cells were also performed using the previous setup with an addition of an FRA 32 M Frequency Response Analyzer (FRA) covering the frequency range between 1 MHz and 0.01 Hz.

3. Results and discussion

Basic operation of the photovoltaic device fabricated in this study is explained schematically as shown in Fig. 1. In the photoanode, CdS quantum dots (bandgap \sim 2.4 eV, VB \sim - 6.2 eV) generate electron-hole pairs upon light irradiation and TiO₂, a wide bandgap semiconductor (bandgap ~ 3.2 eV), provides electron pathways for the generated electrons to move to the external circuit. At the photoanode/ electrolyte interface S_2^- ions in polysulfide electrolyte (redox potential ~ - 5.0 eV) oxidize to S_n^{2-} and facilitate regeneration of CdS quantum dots by transferring electrons [22]. Apart from the electron-hole pair generation processes, recombination also occurs due to excited electrons falling back or participating in the redox reactions of electrolytes. Photogenerated electrons flow through the outer circuit until they reach the counter electrode and at last, where participate in electrolyte regeneration. Thus, at the electrolyte/CE interface, S_n^{2-} ions in polysulfide electrolyte reduce back to S2. Apart from that, the photocatalytic activity of SnO₂ (bandgap \sim 3.6 eV, CB \sim - 4.5 eV) under the sunlight which penetrates through the mesoporous photoanode might also facilitate this process, eventually resulting a device working with higher efficiency.

3.1. Morphological and structural characteristics of SnO_2 counter electrode

While Fig. 2(a) shows a photograph of the SnO_2 CE fabricated with optimum conditions on the FTO substrate, Fig. 2(b) and (c) show the SEM images of the top view and the cross-sectional view of the counter electrode respectively. It was noted that adherence of SnO_2 film fabricated by the spray pyrolysis method on the FTO substrate was successful and it was not possible to remove it from the substrate easily. As can be



Fig. 3. HRTEM image of SnO₂ CE material sintered at 450 °C.

seen from Fig. 2(b) surface of the SnO₂ CE is comprised of aggregated SnO₂ nanoparticles resulting in a rich porous morphology. It provides for effective electrolyte diffusion and increased surface area, facilitating improved contacts between catalytic sites of SnO₂ nanoparticles and the electrolyte. The average thickness of the SnO₂ nanoparticle layer is \sim 13.48 μ m as shown in Fig. 2(c).

Further characterization of the CE material was carried out with HRTEM images as shown in Fig. 3. According to the graphical data visualized with ImageJ software, diameters of mostly spherical SnO_2 particles observed belonged to the 7-15 nm range. The interplanar (*d*) spacing value determined from the most intense lattice fringes was 0.33 nm, which belongs to the (110) lattice plane of tetragonal rutile SnO_2 crystals.

3.2. Raman, XRD and XPS analysis of SnO₂ counter electrode

Raman spectroscopy is a vibrational spectroscopy technique used for analysing structural characteristics of materials utilizing the inelastic scattering of photons striking molecules [23]. It can be used to inspect nanocrystal structures, surface defects, and nanoparticle sizes. A series of Raman spectra was obtained for the prepared CEs sintered at different temperatures, in the range of 100–600 °C, with a fixed time interval of 45 min, and the corresponding data were plotted with Origin software as displayed in Fig. 4(a). Raman shifts from 100 to 800 cm⁻¹ were taken into consideration when seeking out the structural changes that occurred in SnO₂ crystals with the sintering temperature. Bands appearing in 3000 cm⁻¹ regions, with low temperatures and disappearing at high temperatures, were due to scattering from residual acetic acid and Triton-x 100, which proceeds to degrade at higher temperatures [24,25]. Raman shifts observed in the range of 100–800 cm⁻¹ have mainly resulted from vibrations of tin and oxygen atoms in SnO₂ nanocrystals. SnO₂ has a tetragonal rutile crystalline structure (cassiterite) with a unit cell comprising six atoms, two tin (Sn) atoms, and four oxygen atoms. Each tin (Sn) atom is surrounded by six oxygen atoms resembling an octahedron and each oxygen atom is surrounded by three tin atoms resembling an equilateral triangle. SnO₂ rutile structure be-

longs to the space group $P4_2/mnm$ (136) and point group D $\frac{14}{4h}$, of

which normal lattice vibrations at the centre of the first Brillouin zone are represented by the following equation [26–28].

$$\Gamma = A_{1g} + A_{2g} + A_{2u} + B_{1g} + B_{2g} + 2B_{1u} + E_g + 3E_u$$

Among these vibrational modes, only four are Raman active, A_{1g} , E_g , B_{1g} , and B_{2g} , where oxygen atoms vibrate while Sn atoms are at rest. Non-degenerated A_{1g} , B_{1g} , and B_{2g} modes vibrate in a perpendicular plane to the vertically oriented c axis while doubly generated E_g vibrates along the direction of the c axis. Classically Raman inactive modes, A_{2u} and E_u modes are Infrared (IR) active while A_{2g} and B_{1u} modes are inactive [26,29].

In order to understand the surface properties and the lattice distortions of SnO₂ nanocrystals (sintered at 450 °C for 45 min), Raman spectroscopic analyses were carried out in the frequency range of 100–800 cm⁻¹, and data were fitted with Lorentzian function as shown in Fig. 4(b). The Raman vibrational bands observed at 103 cm⁻¹, 482 cm⁻¹, 631 cm⁻¹, and 776 cm⁻¹ were attributed to B_{1g}, E_g, A_{1g}, and B_{2g} classical vibrational modes of bulk SnO₂ tetragonal rutile crystalline



Fig. 4. Raman spectra of (a) SnO₂ CEs sintered at temperatures from 100 - 600 °C and (b) SnO₂ CE sintered at 450 °C.



Fig. 5. XRD spectrum of SnO₂ CE material.



Fig. 6. XPS spectra of SnO₂ CE material (a) full spectrum (b) Sn 3d spectrum, and (c) O 1 s spectrum.

structure (cassiterite), respectively [26,30]. Apart from these, additional bands were observed at 236 cm⁻¹, 323 cm⁻¹, 432 cm⁻¹, 523 cm⁻¹, 550 cm⁻¹, 576 cm⁻¹, and 695 cm⁻¹, which might have resulted from the

activation of Raman modes due to surface mode dominance with size reduction to the nanoscale, defects like oxygen vacancies, and lattice distortions. The prominent vibrational band observed at 576 cm^{-1} could



Fig. 7. UV–Visible absorption spectra of semiconductors ((a) SnO_2 , (b) TiO_2 , and (c) TiO_2/CdS) in QDSSCs and band gap calculation of SnO_2 (inset plot).

 Table 1

 Photovoltaic parameters of QDSSCs assembled with SnO2 counter electrodes prepared by using different amounts of the spray solution.

Cell	Solution (ml)	$V_{\rm OC}~({\rm mV})$	$J_{\rm SC}$ (mA cm ⁻²)	FF (%)	Efficiency (η%)
T_1	20	$\begin{array}{c} 396.7 \pm \\ 3.2 \end{array}$	6.79 ± 0.27	$\begin{array}{c} 34.93 \pm \\ 0.42 \end{array}$	$\textbf{0.94} \pm \textbf{0.07}$
T_2	40	$\begin{array}{c} 418.1 \pm \\ 1.7 \end{array}$	$\textbf{6.79} \pm \textbf{0.10}$	$\begin{array}{c} 39.21 \ \pm \\ 0.33 \end{array}$	1.11 ± 0.04
T_3	60	$\begin{array}{c} 420.1 \pm \\ 1.9 \end{array}$	$\textbf{7.41} \pm \textbf{0.12}$	$\begin{array}{c} 45.93 \pm \\ 0.26 \end{array}$	$\textbf{1.43} \pm \textbf{0.02}$
T ₄	80	428.3 <u>+</u> 2.4	7.97 ± 0.22	47.20 ± 0.41	1.61 ± 0.03
T ₅	100	$\begin{array}{c} 431.2 \pm \\ 0.8 \end{array}$	$\textbf{7.93} \pm \textbf{0.14}$	$\begin{array}{c} 46.80 \pm \\ 0.28 \end{array}$	1.60 ± 0.02

Table 2

Photovoltaic parameters of QDSSCs assembled with SnO_2 counter electrodes which were sintered at different temperatures for 45 min.

Cell	Sintering temperature (°C)	V _{OC} (mV)	J _{SC} (mA cm ⁻²)	FF (%)	Efficiency (η %)
S_1	400	$\begin{array}{c} 430.4 \pm \\ 1.3 \end{array}$	7.76 ± 0.07	$\begin{array}{c} 47.92 \pm \\ 0.25 \end{array}$	1.60 ± 0.02
S_2	450	428.3 ± 2.4	7.97 ± 0.22	47.20 ± 0.41	1.61 ± 0.03
S_3	500	$\begin{array}{c} 428.1 \pm \\ 2.5 \end{array}$	$\begin{array}{c}\textbf{8.25} \pm \\ \textbf{0.15} \end{array}$	$\begin{array}{c} \textbf{45.35} \pm \\ \textbf{0.56} \end{array}$	1.60 ± 0.04
S ₄	550	$\begin{array}{c} 422.5 \pm \\ 3.1 \end{array}$	$\begin{array}{c}\textbf{8.13} \pm \\ \textbf{0.27}\end{array}$	$\begin{array}{c} \textbf{46.69} \pm \\ \textbf{0.70} \end{array}$	1.60 ± 0.02
S ₅	600	$\begin{array}{c} 415.6 \ \pm \\ 1.2 \end{array}$	$\begin{array}{c} \textbf{7.69} \pm \\ \textbf{0.05} \end{array}$	$\begin{array}{c} 49.16 \pm \\ 0.30 \end{array}$	1.57 ± 0.06

be assigned to A_{2g} mode, activated as a result of oxygen vacancies and surface defects [26,30]. In this context, Jian et al. have observed that these oxygen vacancies can greatly improve the catalytic activity of SnO₂ for triiodide reduction in dye-sensitized solar cells [16]. Therefore, this might be helping even these QDSSCs to give better performances. The weak vibrational band at 695 cm⁻¹ could be assigned to IR active longitudinal optical phonons (LO) of A_{2u} modes, Raman activated due to disorders [29,31]. As displayed in Fig. 4(a), intensities of different Raman vibrational bands related to SnO₂ vary with increasing temperature due to grain size transformations, changes in lattice distortions,

Table 3

Photovoltaic parameters of QDSSCs assembled with SnO_2 counter electrodes sintered at 450 °C for different time periods.

Cell	Time (min)	$V_{\rm OC}~({\rm mV})$	J _{SC} (mA cm ⁻²)	FF (%)	Efficiency (η %)
C_1	15	$\begin{array}{c} 403.4 \pm \\ 3.1 \end{array}$	$\textbf{6.45} \pm \textbf{0.27}$	$\begin{array}{c} \textbf{45.86} \pm \\ \textbf{0.33} \end{array}$	1.19 ± 0.02
<i>C</i> ₂	30	$\begin{array}{c} 428.2 \pm \\ 1.9 \end{array}$	$\textbf{7.59} \pm \textbf{0.16}$	$\begin{array}{c} 45.30 \pm \\ 0.54 \end{array}$	$\textbf{1.47} \pm \textbf{0.04}$
C ₃	45	$\begin{array}{c} 428.3 \pm \\ 2.4 \end{array}$	$\textbf{7.97} \pm \textbf{0.22}$	$\begin{array}{c} 47.20 \pm \\ 0.41 \end{array}$	1.61 ± 0.03
C ₄	60	$\begin{array}{c} 436.6 \pm \\ 1.4 \end{array}$	$\textbf{7.59} \pm \textbf{0.19}$	$\begin{array}{c} 47.32 \pm \\ 0.26 \end{array}$	1.57 ± 0.03



Fig. 8. Current Density-Voltage (*J-V*) characteristics of QDSSCs with (1) Pt CE and (2) SnO₂ CE.

Table 4

Photovoltaic parameters of QDSSCs assembled with Pt and SnO_2 counter electrode with optimized conditions.

Cell	Counter electrode	$V_{\rm OC}~({\rm mV})$	J _{SC} (mA cm ⁻²)	FF (%)	Efficiency (η%)
Q_1	Pt	436.7 ± 1.5	$\begin{array}{c} \textbf{6.92} \pm \\ \textbf{0.11} \end{array}$	$\begin{array}{c} 37.35 \pm \\ 0.28 \end{array}$	1.13 ± 0.02
Q ₂	SnO ₂	428.3 ± 2.4	7.97 ± 0.22	47.20 ± 0.41	1.61 ± 0.03

and defects. Increasing intensity of A_{1g} vibrational band compared to vibrational band at 576 cm⁻¹ was observed with increasing temperature as a result of minimized vacant lattice sites and lattice disorders [30].

Fig. 5 shows the XRD data of SnO₂ film sintered at 450 °C for 45 min (in ambient air atmosphere), analyzed with Match 3 software. Similar to the Raman spectral analysis, XRD peaks detected could be indexed to the tetragonal rutile structure (cassiterite) of SnO₂ (Entry no. 96–500-0225). XRD peaks observed at 26.59°, 33.89°, 37.96°, 38.99°, 51.79°, 54.77°, 57.86°, 61.89°, 64.79°, 85.98°, 71.31°, and 78.73° angular positions corresponds to (110), (101), (200), (111), (211), (220), (002), (130), (112), (301), (202), and (321) planes of tetragonal SnO₂, respectively [32]. Inter-planar distances (*d*) of (110) and (101) lattice planes obtained according to the prominent XRD peaks observed at 26.59° and 33.89° angular positions, were 0.33 nm (confirmed by HRTEM image, Fig. 3) and 0.26 nm, agreed with the Bragg equation mentioned below,

 $n\lambda = 2dsin\theta$



Fig. 9. EIS Nyquist plots of (a) QDSSCs with Pt CE and SnO₂ CE, under light conditions and (b) symmetric cells with Pt CE (under light conditions) and SnO₂ CE (under light conditions and dark conditions).

Table 5

EIS parameters of QDSSCs assembled with Pt and SnO_2 under illuminated conditions.

Counter Electrode	$R_{\rm s}\left(\Omega ight)$	$R_{1\mathrm{CT}}\left(\Omega\right)$	$R_{\rm 2CT}\left(\Omega ight)$
Pt	19.3	74.6	114
SnO ₂	18.4	8.48	118

Table 6

EIS parameters of symmetric cells assembled with Pt and SnO_2 under illuminated and dark conditions.

Counter Electrode	$R_{\rm s}\left(\Omega ight)$	$R_{1\mathrm{CT}}\left(\Omega\right)$	$R_{\rm 2CT}\left(\Omega\right)$
Pt (light)	1.57	52.4	23.2
SnO ₂ (light)	18.0	8.42	12.1
SnO ₂ (dark)	19.3	23.8	18.2

where λ is the wavelength of X-ray (CuK α 1 – 0.154060 nm), d is the inter-planar distance of lattice planes of the crystal, n is the order of diffraction, and θ is the incident angle [33]. The average crystallite size of the SnO₂ crystals present in the CE was estimated to be 6.53 nm from the XRD peaks corresponding to (110), (101), (211) lattice planes using the following Scherrer equation,

$$D = \frac{k\lambda}{\beta.cos\theta}$$

where, D is the average crystallite size, λ is the wavelength of X-ray (CuKa1 – 0.154060 nm), k is the shape factor (0.94), β is the full width half maximum (FWHM) of the diffraction peak, and θ is the Bragg angle [33–35]. Lattice parameters of the SnO₂ crystals (tetragonal rutile, $a=b\neq c$) were calculated according to the following equation,

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Where, *d* is the inter-planar distance of lattice planes, *h*, *k*, *l* are Miller indices, and a, c are lattice constants. Results obtained based on (110), (101), (211) crystal planes, a = 0.473 nm, and c = 0.318 nm were well matched with standard values for tetragonal rutile SnO₂ [32,35,36]. Peak broadening observed with diffraction data could be attributed to the reduced size of SnO₂ crystallites, lattice strain and asymmetric peak broadening, and slight shifts in angular positions could be due to crystal defects present [37].

In order to understand the surface chemistry related to the composition and chemical states of the fabricated SnO_2 CE material, X-ray photoelectron spectroscopy (XPS) characterization was also carried out. Fig. 6(a) displays the full XPS spectrum obtained for SnO_2 material. Intense peaks were observed for Sn and O elements. The origin of peaks



Fig. 10. Cyclic voltammograms of (a) Pt and (b) SnO_2 symmetrical cells, with a scan rate of 30 mV s⁻¹.

related to K and C elements can be attributed to KOH, used as a stabilizer in commercial SnO₂ colloidal dispersion solution and residual organic materials as observed by Ghahremani et al. [38]. Tin oxide has + 4 (SnO_2) as the prominent oxidation state and + 2 (SnO) as a minor oxidation state. Crystal defects such as oxygen vacancies and Sn vacancies arise from lattice structures arranged with these states [39]. Surface oxygen vacancies results in reduction of work function in SnO₂ (4.74 eV) which contributes to conductivity changes in the material as reported by Geiger et al [40,41]. Fig. 6(b) shows the observed and fitted graphical data for Sn 3d spectrum. The spin-orbit doublet of Sn⁴⁺ was assigned to peaks centred on 486.4 eV (Sn $3d_{5/2}$) and 494.8 eV (Sn $3d_{3/2}$) 2), with a characteristic split orbit splitting energy of 8.4 eV. The asymmetric nature of the observed peaks could be due to the spin-orbit doublet of Sn^{2+} , overlapping with Sn^{4+} [16,42–44]. Fig. 6(c) shows the main deconvoluted peaks of the O 1 s XPS spectrum. The peak centred on 530.3 eV, the lowest binding energy, was assigned to SnO₂ lattice oxygen (O²⁻), making Sn-O-Sn bonds. The peak observed around 532.2 eV was assigned to defective oxygen due to oxygen-deficient regions and a minor peak observed around 534.4 eV was assigned to the oxygen ions chemisorbed on the SnO₂surface [45–48].

3.3. UV–Visible reflectance spectroscopic analysis

UV–Visible reflectance spectra of different materials, employed in the fabrication of QDSSCs, were recorded using the diffuse reflectance method. Reflectance data were converted to absorbance using the following Kubelka- Munk function,

$$F(R_{\infty}) = \frac{\left(1 - R_{\infty}\right)^2}{2R_{\infty}} = \frac{K}{S}$$

where, $F(R_{\infty})$ is the Kubelka- Munk function which corresponds to the absorbance, R_{∞} is the absolute reflectance, K is the absorption coefficient, and S is the scattering coefficient [49,50]. CdS, the light captivating photovoltaic material utilized in the prepared QDSSCs, shows favourable absorption in the 400-550 nm range, while, both TiO2 and SnO2 show strong absorption in the UV region, according to the normalized absorbance plotted against corresponding wavelengths as shown in Fig. 7. This data shows the absorption of SnO₂ was shifted to a lower UV region indicating a higher bandgap than TiO2. Therefore, when the device is exposed to sunlight, most of the photons in the UV range can be absorbed by the TiO₂ film as well as the SnO₂ film at the counter electrode due to the possible penetration through the mesoporous photoanode. These photons will enhance the electronic conductivity of the SnO₂ semiconductor eventually enhancing the counter electrode action in the device. The Tauc equation mentioned below was adopted in order to determine the optical bandgap of the prepared SnO₂ CEs.

$$[F(R_{\infty})h\nu]^{2} = \mathcal{A}(h\nu - Eg)$$

where, $F(R_{\infty})$ is the Kubelka- Munk function, R_{∞} is the absolute reflectance, *h* is the Planck's constant, $h\nu$ is the photon energy, A is the proportional constant, and *E*g is the optical band gap [50,51]. Graphical representation of experimental data according to Tauc relation is displayed in the inset plot in Fig. 7. Extrapolation of the slope yielded an optical band gap value of 3.51 eV for SnO₂, whereas the theoretical value of tetragonal rutile SnO₂ was reported as 3.60 eV [48].

3.4. Photovoltaic performance of QDSSCs

In order to find the optimum amount of SnO_2 (thickness) in the CEs for the best performances of the QDSSCs, solar cells were fabricated and tested with different CEs using different amounts of SnO_2 in the spray solution, as shown in Table 1. The current density–voltage (*J-V*) characteristics of these QDSSCs were studied under light irradiation of 100 mW cm⁻². From the preliminary investigations on testing a large

number of devices, especially considering the surface smoothness and the adherence of the SnO_2 film to the substrate, it was decided to sinter these CEs at 450 °C for 45 min. However, in order to decide the best conditions, detailed studies on the effect of sintering temperature and the time were investigated and will be discussed later.

According to the observed data, when the amount of spraying SnO₂ colloidal solution was increased from 20 ml to 100 ml by 20 ml of increments, open-circuit voltages (V_{OC}) of the assembled solar cells were increased gradually and short circuit current density (JSC) was increased up to 7.97 mA cm⁻² with 80 ml of SnO₂ solution and resulting in an optimized power conversion efficiency of 1.61 % in these QDSSCs. It was also observed that when the amount of solution used to spray was higher than 80 ml, the adherence to the substrates was also poor. By considering these facts it was decided to select this amount (80 ml) to get smooth uniform well adhered SnO₂ film on the FTO substrate and kept constant throughout the fabrication of CEs for other characterization [52]. The thickness of the fabricated CE which was estimated by using cross-sectional SEM photographs (Fig. 2(c)) is found to be $\sim 13.48 \ \mu m$ thick as mentioned earlier. In order to see the effect of the sintering temperature of CE on the properties of solar cells in detail, SnO₂/FTO CEs were thermally treated under different temperatures. Table 2 presents the J-V characteristics of a series of QDSSCs (S₁, S₂, S₃, S₄ and S₅) fabricated with SnO₂ CEs sintered at different temperatures, 400, 450, 500, 550, and 600 $^{\circ}$ C, for 45 min. As can be seen from the table, V_{OC} of QDSSCs was gradually decreased with the increasing sintering temperature of SnO2 CEs. The highest short circuit current density of 8.25 mA cm⁻² was observed with S₃ QDSSC assembled with a CE sintered at 500 °C. However, due to the variations in the fill factor and the open-circuit voltage, the best overall power conversion efficiency was observed with S_2 QDSSC, assembled with a CE sintered at 450 °C.

In order to see the effect of the sintering time of the CE material on the photovoltaic parameters of the QDSSCs in detail, the sintering temperature was kept constantat 450 °C and CEs were sintered under different time periods like 15, 30, 45, and 60 min and devices were labeled as C₁, C₂, C₃, and C₄ respectively. Observed *J*-*V* characteristics of the above solar cells under the same light irradiation of 100 mW cm⁻² are tabulated in Table 3. QDSSC denoted with C₃, assembled with SnO₂ CE fabricated by sintering for 45 min yielded the highest *J*_{SC} and the power conversion efficiency. By considering these results it was decided 45 min was the best sintering time for these CEs.

Performances of QDSSCs fabricated with best SnO₂ counter electrode and Pt counter electrode were also compared. *J-V* characteristics curves of these two devices are shown in Fig. 8 and the extracted photovoltaic parameters are shown in Table 4.

As it is evident from the table QDSSC fabricated with SnO₂ counter electrode showed an impressive enhancement of 43 % in efficiency compared to the QDSSC made with Pt CE. The device with optimized, SnO₂ CE possesses an enhanced photovoltaic performance mainly due to its unique combined effect of efficient binding and adherence to the FTO substrate and optimized nano-porous network made of SnO2 nanoparticles on the substrate as observed from the SEM images. Compared with QDSSCs fabricated with Pt CE, the higher gain achieved by the solar cell fabricated with SnO₂ is mainly due to the increase in both the $J_{\rm SC}$ and the fill factor at the expense of V_{OC} . High fill factor values correspond with low charge transfer resistance at the counter electrode due to efficient hole recovery, causing back electron transfer in the photoanode to be minimized and photocurrent generation to be promoted [53,54]. Furthermore, the enhancement in the J_{SC} could be attributed to the increased effective active surface area of the SnO₂ CE compared to the Pt, and its thickness and porosity as observed by the SEM analysis. An increase in the effective surface area will provide many more reaction sites at the electrolyte/CE interface facilitating the speedy redox reaction while enhancing the electrocatalytic activity of the CE, eventually resulting in an increase in the J_{SC} . Similar observations have been reported by Bondarenko et al. [55] and as well as our group [20] in different systems with SnO₂.

3.5. Electrochemical impedance spectroscopic (EIS) analysis of QDSSCs and CE symmetric cells

In order to understand the kinetics of interfacial charge transfer processes, electrochemical impedance spectroscopic (EIS) measurements have been carried out on QDSSCs based on Pt and SnO₂ CEs under dark and illuminated conditions with 100 mW cm⁻² intensity. Based on these measurements charge transfer resistances of different interfaces in the solar cells can be calculated from the resulting Nyquist plots. Fig. 9 shows the corresponding EIS Nyquist plots of (a) QDSSCs with Pt CE and SnO₂ CE, under light conditions and (b) symmetric cells (CE/polysulfide/CE) with Pt CE (under light conditions) and SnO₂ CE (under light conditions and dark conditions). Acquired impedance data were fitted using equivalent electrical circuit models, with the aid of NOVA software, and EIS parameters were estimated accordingly. Two overlapped semi-circles were observed in the Nyquist plots under light conditions (Fig. 9(a)) with both CEs. The smaller semicircle appearing in the highfrequency region represents redox impedance at the polysulfide electrolyte/CE interface. The second semicircle emerging in the midfrequency region represents impedance at the TiO₂/CdS photoanode/ polysulfide electrolyte interface. Elements in the equivalent circuit symbolize the series resistance (R_s), charge transfer resistance (R_{1CT}), and chemical capacitance (CPE1) at the electrolyte/CE interface, and, charge transfer resistance (R_{2CT}) and chemical capacitance (CPE₂) at the photoanode/electrolyte interface [20,56].

Table 5 shows the estimated parameters by using Fig. 9(a). The estimated series resistance (R_S) of the cell with SnO₂ CE, operating under light conditions, shows slightly lower value corresponding to increased photocurrent flowing in the circuit and a better filling factor of the QDSSC which is consistent with our *FF* values depicted in Table 4 for the QDSSCs with SnO₂ based CE. Similar behaviors were also reported by Chenet al. [57] and Dissanayake et al. [20] in dye-sensitized solar cells with different counter electrodes.

When the electrolyte/CE interface is considered charge transfer resistance R_{1CT} is an important parameter associated with charge transfer across the electrolyte/CE interface and related to the reduction rate of S_n^{2-} . Significant reduction of the most important parameter in this regard, R_{1CT} at the electrolyte/ SnO₂ CE is 8.48 Ω compared to that of the Pt counter electrode, 74.6 Ω . This suggests an improved catalytic activity at the SnO₂ CE surface for the effective reduction of S_n^{2-} to S^{2-} . As it was observed by Jiaoet al. [58] in Nitrogen-doped mesoporous carbons as CEs in QDSSCs, the lower R_{1CT} indicates the effective reduction of S_n^{2-} to S_2^{-} , which favors the improvement of photovoltaic performance, especially the improved J_{SC} value at the expense of V_{OC} as it was observed in our system too (Table 4) [58]. Normally, a decreasing trend in R_{1CT} value is associated with an increasing trend in J_{SC} for most of the dye-sensitized solar cells too [59]. On the other hand, low catalytic activity of Pt towards the reduction of oxidized polysulfide ions, due to the poisoning effect of S attached on the surface, was reported in the literature, and the photocatalytic nature of SnO₂, and increased active surface area of the porous CE work as favorable conditions for the improved catalytic activity of SnO₂ CE [4].

For further understanding of photo-responsive properties of the SnO₂ CEs, EIS studies were conducted for symmetric cells prepared by clipping together two SnO₂ CEs with an area of 1 cm⁻² and injecting polysulfide electrolyte in-between. Results were compared with Pt CEs in a similar setup. Impedance data collected under illuminated (100 mW cm⁻²) and dark conditions (Fig. 9(b)). Electrical elements in the circuit symbolizes series resistance (*R*s), charge transfer resistance (*R*_{1CT}) and chemical capacitance (CPE₁) at the polysulfide electrolyte/SnO₂ CE interface, and, charge transfer resistance (*R*_{2CT}) and charging double layer capacitance (CPE₂) at the solid contact interface between SnO₂ and FTO [10,60]. Based on the calculated EIS parameters stated in Table 6, Pt has a low *Rs* value compared to SnO₂, which can be attributed to better electrical conductivity of Pt metal. Similar to the findings in QDSSC device, charge transfer resistance (*R*_{1CT}) at the polysulfide

electrolyte/CE is significantly higher for Pt CE due to its poorer catalytic activity towards polysulfide. Slight increase can be observed in the *Rs* and R_{2CT} resistance of SnO₂ symmetric cell operated in the dark environment compared to the illuminated environment. Notable reduction of charge transfer resistance (R_{1CT}) at the polysulfide electrolyte/SnO₂ CE interface from 23.8 Ω to 8.42 Ω , under illumination, can be attributed to favorable reduction of S_n² to S²⁻, under the influence of photo enhanced catalytic nature of SnO₂ [60,61].

3.6. Cyclic voltammetry analysis

For further studies on the electrocatalytic properties and the reaction kinetics of both Pt and SnO2 CEs in polysulfide electrolytes, cyclic voltammetry (CV) studies were performed for CE symmetric dummy cells (CE/polysulfide/CE). Fig. 10(a) and (b) shows cyclic voltammograms of symmetric cells fabricated with identical Pt and SnO₂ CEs, respectively. CEs were tested at a scan rate of 30 mV s^{-1} . Positive anodic current of the CV curves is attributed to oxidation processes in the electrolyte, and the negative cathodic current is attributed to the reduction of S_n^{2-} ions in polysulfide electrolyte to S^{2-} ions at the CE surface [10,62]. In order to observe the chemical stability of the SnO₂ CE, both CEs were subjected to a scan of ten continuous cycles and the results evident reflect good stability in SnO₂ CE (Fig. 10(b)) compared to the Pt CE Fig. 10(a), in duplicating current density peaks in continuous scans [63,64]. Reduction of catalytic activity of Pt CE in continuous scan is mainly attributed to the sulphur poisoning on the CE surface [65]. The current density of the primary reduction peak of the SnO_2 curve (Fig. 10(b)) is greater than that of the Pt CE (Fig. 10(a)), indicating more efficient catalytic activity of SnO₂ in the reduction of S_n^{2-} [10,66]. Furthermore, smaller peak to peak separation (E_{PP}) observed in the CV curves of SnO₂ symmetrical cell also confirms efficient catalytic activity of SnO2 towards polysulfide electrolyte and fast reduction of oxidized species in the electrolyte [67,68]. This promising catalytic activity of SnO₂ CE can be attributed to the favourable diffusion of electrolyte, and increased number of catalytic sites in the porous and thick (~13.5 µm) texture of the CE [10,66,69].

4. Conclusion

Simple and low-cost alternative counter electrode for Pt in sulfide electrolytes-based quantum dot sensitized solar cells was fabricated successfully and its performances were tested, with CdS QDSSCs, as a comparison of Pt counter electrode. The spray-coated nanoporous thick structure of SnO₂ provides reactive sites for the efficient electrocatalytic reduction of S_n^{2-} to S_2^{-} ions at the CE promoting fast hole recovery for CdS quantum dot regeneration and increased current density as reflected from the higher J_{SC} in the QDSSCs fabricated with it. The power conversion efficiency of QDSSCs significantly improved from 1.13 % to 1.61 %, with an overall increase of 43 %, when substituting conventional Pt with fabricated SnO₂ CE. The optimized SnO₂ counter electrode with $\sim 13.48 \,\mu\text{m}$ shows a low $R_{1\text{CT}}$ value at CE/electrolyte interface, and according to the CV plots and EIS plots for symmetrical CEs, the SnO₂ counter electrode exhibits enhanced electro-catalytic activity towards the reduction of polysulfide ions at the electrolyte/CE interface. The optimized SnO2 CE can be considered as a low-cost, Pt-free counter electrode in QDSSCs based on polysulfide electrolytes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical limitations but could be provided on request

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