**Screen printed tin selenide films used as the counter electrodes in dye sensitized solar cells**

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**Abstract**

In this work, the scalable screen printing process has been adopted to prepare low-cost and earth-abundant tin selenide (SnSe) films to study as the counter electrode in dye-sensitized solar cells (DSSCs). The SnSe powder was synthesized by solid state reaction method and corresponding films were fabricated by screen printing technique. The electrocatalytic activity of SnSe for redox iodide/triiodide (I−/I3−) couple and charge transfer resistance at the CE/electrolyte interface were characterized by cyclic voltammetry and electrochemical impedance spectroscopy. The DSSC with SnSe counter electrode exhibited with power conversion efficiency (PCE) of ~ 5.76 % with open-circuit voltage of 0.63 V and short circuit current density of 12.39 mA/cm2 whereas the DSSC with platinum counter electrode showed PCE of 8.09 % with open-circuit voltage of 0.68 V and short circuit current density of 14.77 mA/cm2. Thus, earth abundant and low cost SnSe films fabricated by screen printing technique could be an alternative to costly platinum counter electrode in DSSC.

**Keywords:** Chalcogenides; SnSe films; counter electrode; Screen printing; DSSC.

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1. **Introduction**

The components of the DSSC contribute towards the cost and efficiency. Among them, transparent conductive oxide substrate accounts for the weight, volume and cost of the DSSC and platinum (Pt) for its high cost.[[1]](#endnote-1) Most recently, researchers have been focussing on the development of novel materials to replace the expensive Pt counter electrode (CE) in order to improve the performance.[[2]](#endnote-2),[[3]](#endnote-3),[[4]](#endnote-4),[[5]](#endnote-5) The main features of the CEs are a high conductivity and good catalytic activity to perform the redox process of the iodide/triiodide electrolyte. Many alternatives materials such as carbon materials,[[6]](#endnote-6),[[7]](#endnote-7) conductive polymers,[[8]](#endnote-8) and inorganic compounds (sulfides,[[9]](#endnote-9) carbides,[[10]](#endnote-10) selenides,[[11]](#endnote-11) and oxides,[[12]](#endnote-12)) with very good catalytic activity are investigated as CEs in DSSC.

Among the carbon materials such as carbon black,[[13]](#endnote-13) carbon nanotubes,[[14]](#endnote-14) fullerenes,[[15]](#endnote-15) graphene,[[16]](#endnote-16) and in combination with Pt are investigated as alternatives to Pt CE. These carbon materials possess excellent electrical conductivity, non-corrosive, with high stability and good electrocatalytic activity. These materials are highly abundant and could be prepared by low cost methods. In the case of conductive polymers such as polyaniline (PANI),[[17]](#endnote-17) poly (3,4-ethylenedioxythiophene),[[18]](#endnote-18) polypyrole (PPy),[[19]](#endnote-19) have been tested as CEs. Especially, in flexible DSSC, these polymers are employed as CE. Good photoconversion efficiencies are obtained when these polymers such as PANI was used in combination with other CEs materials such as sulfides.[[20]](#endnote-20)

Finally other inorganic materials such as Oxides (V2O5,[[21]](#endnote-21) and WO3,[[22]](#endnote-22)), sulfides (Cu2ZnSnS4,[[23]](#endnote-23) CoS2,[[24]](#endnote-24) CoIn2S4,[[25]](#endnote-25) MoS2,[[26]](#endnote-26) CuInS2,[[27]](#endnote-27)), carbides (Fe3C/C,[[28]](#endnote-28) TiC,[[29]](#endnote-29)) selenides (CoSe,[[30]](#endnote-30) NiSe,[[31]](#endnote-31) MoSe2,[[32]](#endnote-32) SnSe,[[33]](#endnote-33) SnSe2,[[34]](#endnote-34) NiCoSe4,[[35]](#endnote-35)) and tellurides (CoTe,[[36]](#endnote-36) and MoTe2,[[37]](#endnote-37)) have been tested as CE electrodes in DSSC. Some of them exhibited excellent photoconversion efficiency higher than Pt.

Some CEs were prepared by combining either carbon or conductive polymers with inorganic compounds and also in combination with Pt are used as CEs in the DSSC. However, these materials exhibit good photoconversion efficiencies but their performance is not as good as Pt. The semiconductor chalcogenides have been investigated extensively in the past two decades owing to their potential application in photovoltaics,[[38]](#endnote-38) batteries,[[39]](#endnote-39) light emitting devices,[[40]](#endnote-40) optoelectronic,[[41]](#endnote-41) thermoelectric devices,[[42]](#endnote-42) and etc. Most recently, tin based chalcogenides have been investigated as a promising material in electronic, optoelectronic, optical and energy applications.[[43]](#endnote-43),[[44]](#endnote-44)

Among them, tin chalcogenides (Sn-X), tin sulfide (SnS) and tin selenide (SnSe) are non-toxic, earth abundant and exists as layered materials.[[45]](#endnote-45),[[46]](#endnote-46),[[47]](#endnote-47) These tin chalcogenides exists in three crystalline phases whereas SnX exists in orthorhombic and SnX2 exists in both hexagonal and monoclinic structures.[[48]](#endnote-48) SnX2 is widely recognised due to its excellent electronic and optoelectronic properties and widely investigated. Even though, SnX has been a promising material for optoelectronics and photovoltaics but has not been investigated until SnSe has exhibited excellent thermoelectric behaviour (ZT = 2.6).[[49]](#endnote-49),[[50]](#endnote-50) Later many reports were published by employing different methods for the SnSe synthesis to obtain phase pure, doping with metals, tuning the morphology and different synthesis procedures.

The unit cell of SnSe is distorted NaCl and exhibits anharmonic and anisotropic bonding due to high Grüneisen parameters and also leads to ultralow thermal conductivity which was originated due to distortion in the structure. SnSe is a narrow bandgap material and banked on the excellent optoelectronic and electronic properties, it can be a potential material for photovoltaics.[[51]](#endnote-51) Thus, SnSe can be considered as an alternative to Pt due to its catalytic behaviour and low cost. On the industrial scale, the replacement of Pt with SnSe reduces the manufacturing cost dramatically.

Thus, SnSe can be considered as an alternative to Pt due to its excellent catalytic behaviour and low cost. On the industrial scale, the replacement of Pt with SnSe reduces the manufacturing cost dramatically. Among them, earth abundant SnSe can be considered as an alternative to Pt due to its excellent catalytic behaviour and low cost. On the industrial scale, the replacement of Pt with SnSe reduces the manufacturing cost dramatically. Only few reports are available in the literature on the use of SnSe as CE in DSSC where the SnSe film is prepared by drop casting yield power conversion efficiency (PCE) of 5.52 %.34 In another report, the SnSe CE based DSSC achieved a PCE of 9.34 % where the CE is prepared by drop casting and exhibited higher efficiency than Pt and 8.9 % where the CE was prepared by spin coating.33 When SnSe composites are employed as CE, with PCE of 7.71 % is achieved.[[52]](#endnote-52) The current state of art of DSSC was 14.3 %.[[53]](#endnote-53)

In this research work, the screen printing of SnSe films on FTO glass has been studied for the first time. The role of SnSe films as a counter electrode in DSSC is investigated using an N719 sensitizer and an iodide/triiodide redox electrolyte. The effect of thickness of the CE has been investigated in this work. The DSSC fabricated with SnSe CE exhibited with the PCE of 5.8 %.

1. **Experimental**

**2.1. Synthesis of SnSe**

Tin selenide (SnSe) was synthesized using solid state reaction by grinding tin powder and selenium in 1:1 molar ratio. After grinding, the mixture was compressed by cold press into a pellet. The pellet was kept in a quartz tube subjected to vacuum and sealed. The quartz tube was annealed at 900 °C for 24 h. As prepared SnSe powder was subjected to ball milling (Fritsch, Germany) for 10 h with 230 rpm to form SnSe nano powder. This SnSe nano powder was used to prepare paste.

**2.2. Preparation of SnSe films**

Initially 20 mg of SnSe nano powder, 5 mg of ethyl cellulose and 0.5 mL of α-terpineol was ground together till a homogenous paste was formed.[[54]](#endnote-54) Using this paste, SnSe films were prepared by manual screen printing on FTO glass substrates. The screen printed films were exposed to acetone vapours for 30 sec followed by drying at 120 °C for 2 min. Screen printing process was repeated multiple times to obtain SnSe films with varying thickness and each film was labelled by the number of layers. (SnSe-1L, SnSe-3L, SnSe-5L, SnSe-7L, SnSe-9L, SnSe-11L, SnSe-13L and SnSe-15L). These films were annealed at 500 °C in N2 atmosphere to overcome the binders.

**2.3. Fabrication of DSSC**

At first, the FTO glass substrates were ultrasonically cleaned with soap, acetone and iso-propanol. Then the FTO glass substrates were immersed in 40 mM TiCl4 for 30 min at 80 °C for the deposition of a compact layer of TiO2. This procedure was repeated twice to ensure the complete formation of the TiO2 compact layer. After formation of TiO2 compact layer, the FTO glass substrates were subjected to manual screening printing using commercial TiO2 paste. In this step, thickness of the film with 8 µm was screen printed using TiO2 transparent paste (Dyesol) and 4 µm with light scattering TiO2 paste (Dye-sol).

After screen printing, the films were subjected to annealing at a cycle of temperatures 325 °C for 5 min, 375 °C for 5 min, 450 °C for 15 min, 500 °C for 15 min. After cooling, the TiO2 films were again treated with 40 mM TiCl4 for 30 min at 80 °C to prepare a compact layer of TiO2. Then the films were subjected to heat treatment at 450 °C for 30 min. After cooling, the samples were soaked in 0.3 mM N719 dye (DyeSol) for 24 hours.

The electrodes were coupled with Surlyn as spacer between the TiO2 electrode and SnSe counter electrode. The redox iodide/triiodide (I−/I3−) electrolyte was filled through the hole drilled in the counter electrode (SnSe). After filling, the hole was closed with a cover glass using a Surlyn. The active area of the DSSC is 0.25 cm2.

**2.4. Characterisation techniques**

Phase purity of the SnSe was tested with X-ray diffraction (Bruker D8 Advance diffractometer) using Cu-Kα radiation. The morphology of the SnSe films were investigated with a scanning electron microscope (FEI Quanta 3D FEG). The catalytic activity of the SnSe film was studied using a Metrohm cyclic voltammetry instrument. The J-V measurements were recorded under AM 1.5G one sun illumination using a solar simulator (Newport). The electrochemical impedance spectroscopy (EIS) was carried out using Metrohm Autolab in the frequency range of 0.1 Hz to 1 MHz with amplitude of 50 mV under dark conditions.

**3. Results and discussion**

**3.1. Structural and morphological characterisation of SnSe**

**3.1.1. X-ray diffraction spectrum**

The X-ray diffraction technique was used to study the phase purity and crystallinity of the synthesized material. The X-ray diffraction pattern of the SnSe is shown in Fig. 1. The X-ray pattern matches with standard JCPDS-ICCD card no. 32-1382 and SnSe has orthorhombic SnSe space group Pnma. The crystalline size was calculated using Debye-Scherrer equation and found to be 12.8 nm. No additional peaks are observed which indicates the formation of SnSe with very few impurities below the limit of detection.



Fig. 1: The XRD pattern of SnSe.

**3.1.2. Morphological studies of SnSe films by FE-SEM**

The SnSe films were investigated with FESEM and shown in Fig. 2. The SEM micrographs reveal that SnSe nanoparticles were distributed uniformly over the film. From the cross-sectional images, it was found that the thickness of SnSe-1L was 1.56 µm whereas the thickness of SnSe-7L is 7 µm and the thickness of the SnSe-15L was found to be 8 µm, showing nonlinear deposition. This may be attributed to the loss of roughness of the surface on consecutive deposition of layers. After each deposition, the pores on the surface were filled with new nanoparticles till the surface becomes smooth. Surface smoothing reached saturation at 7 layers permitting only negligible deposition thereafter depositions.



Fig. 2. Top and cross-sectional SEM images of the with (a) & (b) SnSe-1L, (c) & (d) SnSe-7L and (e) & (f) SnSe-15L, respectively.

**3.1.3. Cyclic voltammetry**

The catalytic activity of the counter electrodes were investigated by cyclic voltammetry. The cyclic voltagrams of the platinum and tin selenide counter electrodes are shown in Fig. 3. To probe the catalytic activity of SnSe, the films were prepared by screen printing on a FTO glass substrate. The concentration of the electrolyte is 10 times smaller than the actual concentration of the electrolyte used in the DSSC device.



Fig. 3. Cyclic voltagrams recorded in I-/I3- electrolyte in acetonitrile.

Fig. 3 shows the cathodic current densities of the Pt-CE and SnSe-CE. The catalytic activity of the CE could be calculated from the peak current density and peak to peak separation (Epp). The Epp of Pt was 0.43 V and Epp of SnSe-7L was -0.68 V. The cathodic peak current density of SnSe-7L was -0.25 mA/cm2 and, the cathodic peak current of Pt was -1.6 mA/cm2, whereas, the cathodic peak potential of SnSe-7L was -0.57 V and cathodic peak potential of Pt was -0.12 V. The anodic peak current density of SnSe-7L was -0.04 mA/cm2 and anodic peak current density of Pt was 2.0 mA/cm2 whereas, the anodic peak potential of SnSe-7L was -0.15 V and the Pt was 0.3 V. The cathodic peak current density was shifted towards negative values indicates the larger resistance of the SnSe-7L, when compared with Pt.

However, Pt shows much higher activity than SnSe because Pt exhibits much higher oxidation and reduction current densities than SnSe. This suggests that the Pt-CE has faster redox activity of I-/I3- when compared with SnSe-CE.[[55]](#endnote-55) In order to study the electrochemical activities of these CEs, EIS measurements have been carried out.

**3.2. Photovoltaic properties of SnSe films as CE in DSSC**

The current density - voltage characteristics of the DSSC are presented in Fig. 4 and photovoltaic parameters are summarized in Table 1. The dark J-V characteristic of SnSe-CE devices and Pt-CE device are shown in Fig. 4. The J-V characteristics of the solar cell under illumination are superposition of its dark J-V characteristics theoretically. From the dark J-V characteristics, the cell parameters such as the shunt resistance, series resistance can be calculated. Illumination is the only difference between the dark and light characteristics and under illumination, the cell experiences oxidation of dye, exciton generation and recombination dynamics. Upon illumination, it was observed non-negligible recombination with oxidised dye molecules and change in the electrolyte concentrations due to current flow takes place.[[56]](#endnote-56) This results that light J-V characteristics cannot be superposition of dark J-V characteristics.[[57]](#endnote-57) From the graph, it is observed that J-V characteristics are nonlinear. This can be attributed due to the bulk resistance, series resistance and interface property of the devices which is one of the important parameter decides the photovoltaic parameters of the solar cells. The ideality factor is affected due to the presence of series resistance and interfacial layer.[[58]](#endnote-58) The photoconversion efficiencies of the SnSe-CEs increased up to the DSSCs assembled with SnSe-1L to SnSe-7L. With the further increase in the thickness of the SnSe films from SnSe-9L to SnSe-15L, the photoconversion efficiencies decreases. The DSSC made with SnSe-7L turned out to be the best cell. The DSSC fabricated with SnSe-7L CE reached an efficiency of 5.76 % which is less than 28.8 % of platinum CE based DSSC (η = 8.09 %). The Pt based DSSC exhibited with open circuit voltage (Voc) = 0.68 V and short circuit current density (Jsc) = 14.77 mA/cm2 with fill factor (FF) = 80.6 %. The Voc of the SnSe based DSSC is about 0.6 ± 0.03V. The Jsc of DSSC with SnSe-1L is 14.67 mA/cm2 and later decreased ~ 12.71 mA/cm2 with SnSe-3L to 12.39 mA/cm2 with SnSe-7L but Jsc of the DSSC with devices SnSe-9L to SnSe-15L shows lesser than 10.0 mA/cm2. The FF of the DSSC made with SnSe-1L is 24.2 % and as the thickness of the SnSe films increases, the FF increased to 74.7 till SnSe-9L. The cells made with SnSe-7L onwards, the FF exhibited more than 70 %. From the table, it is evident that the thickness of the CE plays an important role in the DSSC photoconversion parameters.

As the thickness of the SnSe film increases, the catalytic activity is increasing but the conductivity is also decreasing. As a result, the Jsc decreases with cells made with SnSe-9L onwards. The FF of the cells were increased from 24 % to 75 % from SnSe-1L to SnSe-9L CE. In addition, the FF remained almost constant when further increasing the thickness of the film. Consecutive deposition of the layers has led to the surface smoothing and as a result after SnSe-7L, negligible increase in thickness was observed. This trend was also reflected in the photovoltaic parameters of the respective SnSe CEs.

Table. 1 Photovoltaic parameters DSSC made with SnSe CE.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **S.No** | **Voc (V)** | **Jsc (mA/cm2)** | **FF(%)** | **η(%)** |
| **SnSe-1L** | **0.59** | **14.67** | **24.2** | **2.09** |
| **SnSe-3L** | **0.57** | **12.71** | **56.6** | **4.10** |
| **SnSe-5L** | **0.64** | **12.29** | **59.2** | **4.65** |
| **SnSe-7L** | **0.63** | **12.39** | **73.8** | **5.76** |
| **SnSe-9L** | **0.61** | **9.66** | **74.7** | **4.4** |
| **SnSe-11L** | **0.56** | **7.05** | **70.5** | **2.78** |
| **SnSe-13L** | **0.57** | **7.0** | **72.8** | **2.90** |
| **SnSe-15L** | **0.58** | **8.63** | **73.5** | **3.67** |
| **Pt** | **0.68** | **14.77** | **80.6** | **8.09** |



Fig. 4. J-V characteristics of SnSe CE and Pt CE measure under one sun AM 1.5G (100 mW/cm2) and dark conditions.

**3.4. Impedance spectra of DSSC with different SnSe films**

To understand the electrocatalytic behaviour of SnSe films, an electrochemical impedance analysis was carried out. There are three types of the interfaces counter electrode/electrolyte interfaces; TCO/TiO2/dye/electrolyte interfaces and the diffusion phenomenon in the electrolyte are present in the DSSC. FTO/SnSe interface helps in transport of electron coming from the photoanode.23 The Nyquist and Bode plots of the SnSe CE and Pt CE DSSC are shown in Fig. 5 and Fig. 6, respectively. The Nyquist plots contained two semi-circles for the devices made with SnSe and Pt CEs. The semi-circle in the region of high frequency is due to the charge transfer Rct between the counter electrode and the electrolyte. From the graph, it is evident that the Rct of the SnSe CE DSSC is higher than the Pt CE due to its low catalytic behaviour of the SnSe CE which is shown in Fig. 5. We can observe the third semi-circle in the Nyquist plot at the end of the each curve. From the graph, it is observed that the diffusion phenomenon of the electrolyte is low in these cells.



Fig. 5. Nyquist plots of the DSSC made with SnSe CE and Pt CE measured in dark with applied voltage of -0.7 V.

In the Nyquist plot (Fig.5.), the radius of the semi-circles of SnSe-1L and SnSe-3L was much higher due to the low catalytic activity and high Rct. This might be one of reason of low efficiencies of the DSSC made with SnSe-1L and SnSe-3L. However, in the case of SnSe-9L–SnSe-15L, the Rct is comparable with SnSe-7L and Pt but due to the thickness of the SnSe film, the conductivity decreases, and resulted in less photocurrent generation.



Fig. 6. Bode plots of the DSSC made with SnSe and Pt counter electrode.

1. **Conclusions**

In this study, screen printing approach was adopted for the preparation of SnSe films on FTO substrates. SnSe films of varying thickness (SnSe-1L to SnSe-15L) were investigated as counter electrodes in the DSSC. The optimum photovoltaic parameters were obtained for SnSe-7LCE (η = 5.76 % with Voc = 0.63 V, Jsc = 12.39 mA/cm2 with FF 73.8 %). Consecutive deposition of the layers has led to the surface smoothing and as a result after SnSe-7L, negligible increase in thickness was observed. This trend was also reflected in the photovoltaic parameters of the respective SnSe CEs. Although the maximum efficiency of 5.76 % was obtained by this method, it still falls short of the efficiency of Pt electrode by 28.8 %. The cyclic voltammetry reveals that the electrocatalytic activity of the SnSe films were much lower than Pt which accounts for the lower charge transfer Rct between the CE and the electrolyte.. This study reveals that earth abundant and low cost SnSe could become a promising alternative to platinum counter electrodes. However, methods for the selenium enrichment such as treatment of SnSe films in the selenium environment can be explored in future research to enhance the performance of SnSe-CE and hence to bridge the gap between Pt and SnSe counter electrodes.

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**Declaration of interests:**

The authors declare no competing interests.

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