

Contents lists available at ScienceDirect

Materials Science & Engineering B



journal homepage: www.elsevier.com/locate/mseb

A low-cost, vein graphite/tin oxide nanoparticles based composite counter electrode for efficient dye-sensitized solar cells

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ARTICLE INFO

Keywords: Dye-sensitized solar cells Counter electrodes Vein graphite/SnO₂

ABSTRACT

Performance of dye sensitized solar cells made with a novel, low cost graphite/SnO₂ composite counter electrode is demonstrated. The best performance is exhibited by the composite made with 3.0 ml colloidal SnO₂ solution and 0.05 g of graphite powder, sintered at 450 °C. The solar cell efficiency was increased from 6.02% for pure vein graphite to 7.95% for optimized composite graphite/SnO₂ electrode, which is 86% of the efficiency of 9.25% obtained for Pt electrode. This impressive 32% increase in efficiency can be associated with highly porous nanostructure of the graphite/SnO₂ composite providing more reaction sites for triiodide ion reduction as confirmed by Scanning Electron Microscopy, X-ray diffraction and Raman Spectroscopy. Excellent electrocatalytic activity exhibited by the new counter electrode is confirmed by Electrochemical Impedance Spectroscopy and Cyclic Voltammetry, further supported by Tafel plot analysis. This result provides a cost-effective method to fabricate efficient counter electrodes for dye sensitized solar cells.

1. Introduction

Since the first report by Grätzel et al. in 1991 [1], dye-sensitized solar cells (DSSCs) have been a focus of extensive research activities as a major platform of photovoltaics to produce high efficiency solar cells. In the past two decades a considerable research effort has been focussed on developing novel sensitizers, electrolytes and photoanodes to improve the energy conversion efficiency and long-term stability of these solar cells. A typical DSSC consists of three major components: a dye adsorbed semiconductor photoanode, a redox electrolyte and a counter electrode (CE). Generally, in a DSSC, the electrolyte is kept between the photoanode and the CE. The oxidation of dye molecules by photons takes place at the photoanode, and the reduction of redox couple takes place at the counter electrode helping dye regeneration mediated by iodide/ triiodide (I^-/I_3^-) redox couple. Therefore, the counter electrode is a key component in a DSSC, playing the role of conversion of I₃ ions into I⁻ions within the electrolyte and completing the operation of the solar cell [2].

The CE of a DSSC generally consists of a thin film of platinum (Pt) as the catalytic material due to its high conductivity and excellent electrocatalytic activity. Most of the Pt based CEs are prepared by sputtering or electrochemical deposition of platinum and both these methods are expensive and highly energy consuming. Pt is a rarely available and expensive noble metal which would limit the large-scale commercial applications of DSSCs [3,4].In order to replace Pt based counter electrodes with cheaper materials of good electronic conductivity and efficient electro-catalytic effects for tri-iodide reduction, various potential alternative materials have been investigated. Some of them are conducting polymers such aspolyaniline,polypyrrole etc. [5,6], metal sulphides such as nickel sulphide [7,8] and cobalt sulphide etc [9–11] and carbon-based materials such as graphene, reduced graphene oxide etc [12,13]. Among them, low cost carbon-based materials attract much attention as substitutes for Pt.

Carbonaceous materials with various allotropes and structures, such as graphite [14,15], activated carbon [16], hard carbon [17], carbon black [18], grapheme [12,19], fullerene [20] and carbon nanotubes

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https://doi.org/10.1016/j.mseb.2021.115440

Received 6 January 2021; Received in revised form 13 July 2021; Accepted 30 August 2021 0921-5107/© 2021 Elsevier B.V. All rights reserved.

[21], carbon nanofibers [22] have been used as the catalyst in DSSC CEs. Among all these materials, natural graphite is the most abundant and cheaper material with favourable electrical, thermal and catalytic properties. However, pure natural graphite-based CEs exhibit poor energy conversion efficiency in DSSCs. In most cases this is due to the poor adhesion of the graphite material on the conducting glass substrate and influence of basal planner morphology. In general, graphite has basal planes and edge planes. Basal planes exhibit poor electron transport and edge planes exhibit efficient electron transport [23,15]. Therefore, graphite with large size particles shows poor catalytic activity as CE material. Veerappan et al. have compared the performance of DSSCs with the CE prepared using larger size graphite and sub micrometre size graphite and reported that the sub micrometre sized graphite has a higher catalytic effect because of the availability of more edge planes in the sub micrometre graphite [15].

Natural graphite is available in three forms, namely, amorphous graphite, flake graphite and crystalline vein graphite, and they each have unique properties that make them well-suited for certain applications. Crystalline vein graphite is a naturally occurring form of graphite extending through rock like veins and is also known as Sri Lankan graphite, Sri Lankan natural vein graphite has become more attractive and commercially demanding in the world due toits high purity (higher than 95% of pure carbon), high crystallinity and mode of occurrence [24]. In this study a composite of Sri Lankan natural vein graphite and SnO2 has been used to make DSSC counter electrodes. In this work, asimple purification method based on floatation in water as reported by Jayaweera et al. [25] was used to separate fine particles of vein graphite from larger particles. Subsequently, in order to improve the adhesion of vein graphite on conducting glass substrate and to increase the effective surface area of the CE surface by creating a porous structure, SnO₂ nanoparticles were appropriately mixed to vein graphite. This graphite/ SnO2 composite was successfully employed as the DSSC counter electrode with superior catalytic activity to reduce iodide ions. The SnO₂ appears to be functioning as a conducting binder and an effective surface enhancer. This is the first report of the novel graphite/SnO2composite counter electrode which exhibits performance of 86% of the efficiency obtained for Pt electrode in identical DSSCs under similar conditions.

2. Materials and methods

2.1. Materials

To prepare the counter electrode, tin (IV) oxide (SnO₂), 15% in colloidal dispersion and glacial acetic acid purchased from Alfa Aesar and ethanol purchased from VWR chemicals were used. To prepare the photoanode, FTO conducting glass substrates (8 Ω /sq, Solaronix), Ruthenium N719 dye (RuL₂(NCS)₂:2TBA, Solaronix), titanium dioxide P-90 powder (Evonik), titanium dioxide P-25 powder (Degussa), polyethylene glycol (PEG 2000, Merck), triton X-100 (Merck), hydrochloric acid (37%, Merck) was used as received without further purification. To prepare the redox electrolyte, iodine chips (I₂), acetonitrile (anhydrous), valeronitrile, guanidiniumthiocyanate and 4-*tert*-butylpyridine (TBP) (Sigma-Aldrich) were used. Ionic liquid PMII (1-propyl-3-methylimidazolium iodide) was purchased from Solaronix.

2.2. Photoanode preparation

Two layers of TiO₂ were made on the FTO conducting glass substrate in order to prepare the photo anode according to the reported procedure [26]. To prepare the first layer, 0.25 g of P90 TiO₂ powder was mixed with 1 ml of 0.1 M HNO₃and grounded in an agate mortar for 20 min. This mixture was then coated for 60 s on a cleaned FTO substrate using a spin coater working at 3000 rpm. This spin coated glass was sintered at 450 °C for 45 min and allowed to cool down to room temperature. Subsequently, the second layer of TiO₂ was coated on the first sintered layer using a paste prepared as described here. 0.25 g of P25 TiO₂ powderin1.0 ml of 0.1 M HNO₃ was ground well along with 0.02 g of Triton X-100 and 0.05g of PEG 2000 to act as the binder. The resulting creamy paste was then doctor bladed on the first TiO₂ layer to make a cell area of 0.16 cm². After applying the second TiO₂layer, theFTO glass plates were sintered at 450 °C for 45 min. TiCl₄ treatment was carried out for prepared double layered photoanode by dipping in a 0.04 M TiCl₄ solution at 70 °C for 20 min and sintered again at 450 °C for 45 min. These TiO₂ photoanodes were allowed to cool down to room temperature to obtain the final TiO₂porous photoanode. The photoanode was finally dipped in an ethanolic solution of Ru N719 dye for 15 h.

2.3. Preparation of the graphite based counter electrode

To prepare the counter electrode Sri Lankan natural vein graphite was used as the starting material [21]. Graphite was ball-milled and the powder was sieved to obtain graphite particles with size less than $63 \,\mu m$. This powder was then added to de-ionized water and continuously stirred for about 1 h. The graphite layer formed at the surface of the water was collected on a glass slide and vacuum dried for about 12 h. Carbon percentage of this floated graphite powder was determined according to the method of ASTM-561 and weighing the residues. The total carbon percentage of floated graphite powder sample was 99.94%, which confirms the high purity of graphite used in DSSC CEs in the present work. Thecounter electrodes were prepared by using 0.05 g of this dried graphite powder mixed with 2.5 ml of acetic acid and 0.02 g of Triton X-100 and grinding the mixture in an agate mortar for 10 min and finally mixed with 100 ml of ethanol and sonicated for 1 h. This mixture was subsequently sprayed on FTO glass substrate while heating the FTO glass substrate at 100 °C. Finally they were sintered at different temperatures in a muffle furnace to find the optimum sintering temperature/time to obtain well adhered and visually uniform graphite films. This optimized sintering temperature/time was found to be 450 °C and 45 min respectively.

Graphite/SnO₂ composite CE was prepared by using the same spray method and same optimized sintering temperature and time as for the graphite CE. For this, initially a dilute SnO₂ colloidal solution was prepared by mixing a 1.0 ml of SnO₂ colloid with 10 ml of ethanol. Then, different volumes from 1.0 ml to 5.0 mlof this prepared diluted SnO₂ colloidal solution was mixed with 0.05 g of dried graphite powder, 2.5 ml of acetic acid, 0.02 g of Triton X-100 and ground for 10 min in an agate mortar. The resulting paste was finally mixed with 100 ml of ethanol and sonicated for 1 h to make graphite CE as explained above. These spraying mixtures with different amounts of SnO₂ colloidal were sprayed on heated (100 °C) FTO glass substrates separately to obtain the counter electrodes with best and visually uniform graphite/SnO₂ composite layer on FTO glass. Finally, this graphite/SnO₂ composite CEs were sintered at 450 °C for 45 min (optimized temperature/time for graphite CE) in a muffle furnace.

2.4. Liquid electrolyte preparation

To test the performance of DSSCs with Graphite/SnO₂ composite counter electrodes, a liquid electrolyte was prepared by mixing 0.6 M 1-propyl-3-methylimidazolium iodide (PMII) ionic liquid, 0.03 M iodine (I₂), 0.1 M guanidiniumthiocyanate, 0.5 M 4-*tert*-butylpyridine (TBP) dissolved in acetonitrile: valeronitrile solution mixture in the volume ratio 85:15.

2.5. Fabrication of DSSCs and their characterization

Dye sensitized solar cells (DSSCs) were fabricated by placing the liquid electrolyte between the graphite/SnO₂ composite counter electrode and the TiO₂photoanode. The active surface area of the device is 0.16 cm^2 . The current density–voltage (*J-V*) characteristics of the solar cells were measured using a computer-controlled, calibrated solar

simulator(Oriel Newport LCS-100) connected to a Potentiostat/Galvanostat (MetrohmAutolab PGSTAT 128 N) under AM 1.5 illumination (100 mW cm⁻²). A Xenon 100 W lamp with an AM 1.5 filter (400 nm-1100 nm) Class A with spectral Match of 0.75–1.25 was used to obtain the simulated sunlight with above intensity. In order to compare the performance of DSSCs with graphite based and Pt based counter electrodes, DSSCs with the identical TiO₂photoanode and identical electrolyte were also fabricated using Pt CEs. Impedance measurements of DSSCs were taken using a Potentiostat/Galvanostat (Metrohm Autolab PGSTAT 128 N) with Frequency Response Analyzer (Metrohm Autolab FRA 32) covering the frequency range from 0.01 Hz to1.0 MHz. These solar cell measurements were also performed under 100 mW cm⁻² illumination.

2.6. Material characterization

The surface morphology and microstructure of newly prepared graphite/SnO2 composite counter electrodes were studied using fieldemission scanning electron microscopy (FE-SEM, Hitachi SU6600). Elemental mapping of prepared graphite/SnO2 composite CE was carried out by energy dispersive, X-ray spectroscopy (EDS). AJEOL 2100 TEM was used to take TEM images of the graphite/SnO₂ composite. The crystalline structure of proposed graphite/SnO₂ composite was investigated with powder X-ray diffraction (PXRD) using Bruker D8 advanced eco X-ray diffraction system with Cu K α radiation ($\lambda = 1.54060$ Å). XRD data were takenat0.2° step intervals in the 2-theta range of 5° to 80°. The Raman spectra of the graphite and graphite/SnO₂ composite counter electrodes were obtained using a Renishaw basis instrument with 514 lasers. Nitrogen adsorption/desorption isotherms were obtained by a Quantachrome AutoFlow BET + Brunauer-Emmett-Teller (BET) apparatus. The outgas temperature and time used for BET measurement was at 300 °C for 4 h. The chemical composition of the graphite/SnO2 composite material and the valence states of the SnO2 nanoparticles were measured by Thermo Scientific TM ESCALAB Xi + X-ray photoelectron spectrometer (XPS). In order to study the electrocatalytic properties of the synthesized graphite/SnO2 composites, cyclic voltammetry (CV) experiments were done at a scan rate of 50 mV $\rm s^{-1}$ by using a three-electrode set up having a Pt wire counter electrode, Ag/AgCl reference electrode and Pt or graphite/SnO2 based composite working electrode. A solution of acetonitrile prepared with 10 mM LiI, 0.1 M LiClO₄, and 1 mM I₂was used as supporting electrolyte. The Tafel polarization and electrochemical impedance spectroscopy (EIS) measurements of counter electrodes were carried out for symmetrical dummy cells composed of the same CE materials (Pt, pristine graphite and graphite/SnO₂ composite) on both electrodes with active cell area of 1.0 cm². The liquid electrolyte that used to fabricate DSSCs was sandwiched in between the identical counter electrodes for taking Tafel polarization and EIS measurements.

3. Results and discussion

3.1. Morphological and structural characteristics

FE-SEM analysis was conducted in order to obtain the surface morphology and porosity of the pristine graphite, pristine SnO₂ and novel graphite/SnO₂composite and images obtained are shown in Fig. 1. Fig. 1(a) exhibits the surface morphology of the pristine graphite surface with lack of porous morphology for effective electrolyte diffusion. This is a disadvantage for an efficient iodide/triiodide redox reaction at the CE. Fig. 1(b) shows a typical image of pure SnO₂ nanoparticles. It can be seen that the SnO₂nanoparticles are of nano sizeand distribute uniformly. However, the micrograph in Fig. 1(c)–(g) shows a pores rich network of graphite/SnO₂ composite CE surface with different magnification. This confirms the SnO₂ nanoparticles were successfully loaded at the vein graphite surface. It is also clear that graphite/SnO₂ composite film has a highly porous nanostructure with better adhesion onto FTO glass substrate as well as good contact among graphite and SnO_2 nanoparticles. Therefore, this composite counter electrode is expected to show better electro-catalytic activity compared to pristine graphite-based CE as well as pristine SnO_2 based CE, which was confirmed later by CV measurements. Fig. 1(h) shows the cross-section image of graphite/ SnO_2 composite counter electrode with thickness of about 4.28 µm which was subsequently used for DSSC fabrication.

The morphology and the crystal structure of the graphite and graphite/SnO₂ composite CEs were studied using high resolution transmission electron microscopy (HR-TEM), and the results are depicted in Fig. 2(a)–(c). Fig. 2(b) and (c) shows the graphite/SnO2 composite CE with different magnifications to confirm the SnO₂ nanoparticle successfully loaded in to the graphite surface. The graphite sample shows d-spacing of 0.17 nm and 0.34 nm corresponding to (002) and (004) crystal planes. Fig. 2(b) and (c) shows the SnO₂ nanoparticle interconnected graphite in different magnifications with a network structure confirmed by SEM images. The SnO₂ particle sizes are approximately in the 6–8 nm range and the d-spacing of SnO₂structure is 0.33 nm corresponding to the (110) planes. Similar TEM results have been reported by several groups [27–29].

The surface components of the prepared graphite/SnO₂ composite CE were further confirmed by EDS and SEM mappings and the detailed results are shown in Fig. 3. EDS results show that elements C, Sn and O are present in the graphite/SnO₂ composite (Fig. 3(c)–(e)). The Sn species can be seen homogeneously distribute inside the graphite backbone, indicating the successful and uniform intermixing of graphite and SnO₂ particles.

According to the chemical components analysis, the amounts of C, Sn and O in CE in wt% are 60.6 wt%, 30.7% and 8.7%, respectively (elemental analysis, Fig. 3(a)). From EDS spectrum taken randomly at another position the C, Sn and O wt% are found to be, 54.6 wt%, 26.9 wt % and 18.5%. This confirms the presence of graphite and SnO₂ in the counter electrode samples and implies that the basal plane of graphite activated due to the incorporation of SnO₂ particles can contribute to the improved electrochemical performance of the graphite/SnO₂ composite counter electrode

3.2. XRD, Raman and XPS analysis

The XRD diffraction patterns of SnO₂, graphite and graphite/SnO₂ composite are shown in Fig. 4(A). The XRD pattern of the pristine SnO_2 is illustrated in Fig. 4(A) (a). The diffraction peaks of crystalline SnO₂ nanoparticles are clearly distinguishable. The peaks at $2\theta = 26.6^{\circ}$, 33.8° , 37.8°, 51.7°, 54.4°, 58.1°, 61.7°, 65.5° and 71.3° correspond to (110), (101), (200), (211), (220), (002), (310), (301) and (202) planes of SnO₂ respectively. All these strong diffraction peaks are consistent with a tetragonal crystalline SnO₂ phase (JCPDS card no: 41-1445) [30]. Fig. 4(A) (b) shows the XRD spectrum of pristine graphite sample. The peaks at $2\theta = 26.5^{\circ}$, 44.5° , 54.6° and 59.8° indicate (002), (101), (004) and (103) crystal planes of graphite (JCPDS card no: 75-1621), respectively [27]. The XRD pattern of the graphite/SnO₂ composite is shown in Fig. 4(A) (c). Here, the presence of narrow and sharp diffraction peak which is centered at 26.5° corresponds to the oriented crystal plane (002) of hexagonal graphite. In addition, less intense peaks at 44.5°, 54.6° and 59.8° suggests the presence of graphite in the material. Small peaks at 33.8° , 37.8° , 51.7° , 61.7° and 65.5° suggest the presence of SnO₂ in the composite sample. Therefore, from these XRD patterns, it can be confirmed that the graphite/SnO2 composite material consists of a graphite network with SnO₂ nanoparticles attached to its surface, as further confirmed by the SEM data.

The Raman spectra of pristine graphite and graphite/SnO₂ composite samples are presented in Fig. 4(B) in order to show the structural changes due to addition of SnO₂ nanoparticles. Raman spectra of both samples shown in Fig. 4(B) indicate a strong G-band at 1582 cm⁻¹, which arises from the in-plane C—C bond stretching in graphitic materials and it is related to the vibration mode of the sp² graphitic structure



Fig. 1. FE-SEM images of (a) surface of pristine graphite CE, (b) surface of pristine SnO₂ CE, (c), (d), (e) and (f) surface of graphite/SnO₂ composite CE with different magnifications, (d) cross section of graphite/SnO₂ CE. Fig. 1(a) and (g) have the same magnification.



Fig. 2. High resolution TEM images of (a) graphite CE and (b) and (c) graphite/ SnO_2 composite CE with different magnifications. Fig. 1(a) and (b) have the same magnification.



Fig. 3. EDS mapping by EDS spectroscopy, (a) elemental analysis graph with details, (b) selected area for EDS mapping, (c) carbon, (d) tin and (e) oxygen.

[14,27,31]. These Raman peaks corresponding to G bands are sharper in both samples, indicating their high crystallinity. The D-band at 1363 cm⁻¹ corresponds to the degree of disorder in graphite and after introducing SnO_2 nanoparticles to the graphite, the D-band is slightly shifted to 1361 cm⁻¹. The presence of disorder and/or defects induce the D-band in the Raman spectrum. The shifting of the D bands to a lower



Fig. 4. (A) XRD patterns of, (a) pristine SnO₂, (b) pristine graphite and (c) graphite/SnO₂ composite, (B) Raman spectra of, (a) graphite and (b) graphite/SnO₂ composite, (C) XPS general spectra of graphite/SnO₂ composite, and (D) Sn 3d XPS spectra of graphite/SnO₂ composite.

wavenumber indicates that the incorporation of SnO₂ has created more defects in the graphite structure. Similar observations have been reported by Selvakumar et al in the SnO₂-CeO₂/rGO system [32].The 2D-band is assigned to the second order of the D-band. This 2D-band of both samples exhibits two peaks typically related to graphite, at 2725 cm⁻¹. The ratio of the intensities of the D- band and the G-band (I_D/I_G) is generally used to characterize the defect content. The higher the value of I_D/I_G is, the more defects in the material and better the electro-catalytic ability of graphite for I⁻/I₃⁻ [14,25,27]. As shown in Fig. 4(B), the I_D/I_G of the graphite/SnO₂ composite is higher (0.05) than that of pristine graphite (0.03), indicating the higher degree of disorder/defects in graphite/SnO₂ composite. These results suggest that the graphite/SnO₂ composite is better than pristine graphite for application as the CE material in DSSCs, due to better electro-catalytic ability than pristine graphite.

The surface chemistry details of the graphite/SnO₂ composite material obtained from the X-ray photoelectron spectroscopy (XPS) measurement are shown in Fig. 1. Fig. 1(a) shows the full range of XPS survey spectra taken for graphite/SnO₂ composite, which confirms the presence of carbon, oxygen and tin. The peak of C 1 s is obtained mainly due to graphite. The peaks of Sn 3d, 3p, 4d, 4p and 4 s are observed in the full spectrum. The high resolution Sn 3d spectra is shown in Fig. 1 (b). According to Fig. 1(b), spin–orbit doublet peaks of SnO₂ are observed at 487.7 eV and 496.1 eV and are represented as Sn 3d5/2 and Sn 3d3/2, respectively. These peaks are fitted with Sn²⁺ and Sn⁴⁺ and it is clearly shows that the major contribution is from Sn⁴⁺ confirming the presence of SnO₂ nanoparticles on the surface of graphite layers ((Sn⁴⁺ corresponds to purple and blue peaks). Similar results have been reported by Weerasinghe et al. and Liu et al. to confirm the precense of SnO₂ in their materials [30,33].

Fig. 5 shows a schematic diagram of the dye sensitized solar cell of configuration FTO/P90 TiO₂ layer/Dye adsorbed P25 TiO₂ layer/Electrolyte film/Graphite/SnO₂ composite counter electrode/FTO.

3.3. Photovoltaic performance of DSSCs with different counter electrodes

To investigate the effect of sintering conditions on the performance of the graphite CEs, a series of graphite CEs were prepared with different sintering temperatures ranging from 250 $^{\circ}$ C to 550 $^{\circ}$ C. The sintering time was kept as 45 min. Experiments confirmed that the DSSCs prepared with sintered CEs exhibita better photovoltaic performance



Fig. 5. Schematic diagram of the dye sensitized solar cell, FTO/P90 TiO₂ layer/ Dye adsorbed P25 TiO₂ layer/Electrolyte film/Graphite/SnO₂ composite counter electrode/FTO.

compared to the DSSCs made with un-sintered CEs very likely due to the enhanced porous morphology in the sintered composite material. Photovoltaic performance of DSSCs prepared with CEs sintered at different temperatures is shown in Table 1. For each counter electrode, three sets of solar cells were measured and the standard deviation was calculated using three set of data for each photovoltaic parameter listed in Table 1. It can be observed that the open circuit voltage (V_{oc}), the short circuit current density (J_{sc}), the fill factor (*FF*) and the efficiency have increased with increasing sintering temperature up to 450 °C. As depicted in the table, further increase in sintering temperature has decreased the solar cell performance.

DSSCs with CEs sintered at 450 °C for 45 min have exhibited the highest efficiency of 5.01%. Fig. 6(a) shows the J_{sc} vs V_{oc} curves and Fig. 6(b) shows the dependence of the efficiency on sintering temperature. DSSCs fabricated with the Graphite CEs prepared either with sintering at temperatures below 450 °C or above 450 °C showed poor performance possibly due to the presence of more un-decomposed binder at lower temperatures and residual burnt particles at higher temperatures left over in the CEs. Jayaweera et al. have reported somewhat similar results on graphite-based CEs and according to their observations the DSSCs made with these CEs sintered at 350 °C exhibited the best performances [25]. This optimum sintering temperature may vary with the type of binder used and the nature and the particle size of the starting graphite powder.

Fig. 6(c) shows the variation of J_{sc} vs V_{oc} characteristics with the amount of SnO₂ colloidal solution used to make the graphite/SnO₂ composite samples which were sintered at 450 °C for 45 min. Fig. 6(d) shows the variation of efficiency vs the amount of the SnO₂ colloid

Table 1 Parameters of DSSCs with graphite CEs sintered at different temperatures for 45 min.

Counter electrode	Sintering temperature (°C)	$J_{\rm sc}/{ m mA}$ ${ m cm}^{-2}$	V _{oc} /mV	FF%	Efficiency %
Graphite	Not sintered	$\begin{array}{c} 11.26 \pm \\ 0.04 \end{array}$	$\begin{array}{c} 551.2 \\ \pm \ 0.6 \end{array}$	$\begin{array}{c} \textbf{35.19} \pm \\ \textbf{0.20} \end{array}$	$\begin{array}{c}\textbf{2.18} \pm \\ \textbf{0.08} \end{array}$
Graphite- 250	250	$14.25~\pm$ 0.06	$\begin{array}{c} 582.4 \\ \pm \ 0.8 \end{array}$	$\begin{array}{c} \textbf{42.87} \pm \\ \textbf{0.12} \end{array}$	3.56 ± 0.07
Graphite- 350	350	15.16 ± 0.03	623.7 + 0.6	44.27 ± 0.17	4.40 ±
Graphite- 450	450	15.66 ± 0.08		45.55 ± 0.15	5.01 ± 0.06
Graphite- 550	550	$\begin{array}{c} 12.70 \ \pm \\ 0.05 \end{array}$	666.2 ± 0.7	$\begin{array}{c} 46.03 \pm \\ 0.14 \end{array}$	$\begin{array}{c} 3.96 \pm \\ 0.10 \end{array}$



Fig. 6. (a) Current Density-Voltage characteristics graphs of DSSCs with pristine graphite CEs sintered at different temperatures, (b) Efficiency variation of DSSCs with the sintering temperature of graphite CEs (c) Variation of current density–voltage characteristics of DSSCs made with graphite/SnO₂ CEs with different SnO₂ amounts, all sintered at 450 °C and (d) Efficiency variation of DSSCs with added SnO₂ amount in the graphite/SnO₂ composite CEs all sintered at 450 °C.

added to the graphite/SnO₂ composite mixture. Table 2 summarizes the corresponding photovoltaic parameters of DSSCs with graphite/SnO₂ composite CEs.

It can be seen from Fig. 6(c) and Table 2 that power conversion efficiency of DSSC has increased with increasing amounts of SnO2 in the CE. Fig. 5(d) shows the efficiency variation with added amount of SnO₂ and the highest is obtained when the CE is prepared with 3.0 ml SnO₂ colloid which is equivalent to \sim 30% SnO2 as confirmed by EDS mapping results. DSSC made with this graphite/SnO2 composite CE (D) has the highest power conversion efficiency of 6.71% along with highest J_{sc} , $V_{\rm oc}$ and Fill factor values. Also, it was observed that this optimized CE with SnO₂ showed good mechanical stability and superior adhesion properties compared to the CEs fabricated with pristine graphite. SnO₂ in the graphite/SnO₂ composite electrode (D) very likely acts as a binder as well as a network to adhere graphite layers into one another as well as graphite layers on to FTO substrate, which could also increase the fill factor. However, by adding more SnO₂ above the optimum amount has decreases the DSSC performance which may possibly be due to the decrease of the catalytic effect of the CE caused by the insufficient amounts of graphite present. Similar results were reported by Sun et al. for carbon/SnO₂/TiO₂nanocomposite CEs [28]. According to these

Table 2

Photovoltaic parameters of DSSC with six graphite/SnO_2 composite CEs with added amounts of SnO_2and sintered at 450 $^\circ C$ for 45 min.

Counter electrode composition (Label)	$J_{\rm sc}/{ m mA}$ cm $^{-2}$	V _{oc} /mV	FF%	Efficiency %
Graphite (A)	$\begin{array}{c} 15.66 \pm \\ 0.08 \end{array}$	670.1 ± 0.4	$\begin{array}{c} 45.55 \pm \\ 0.15 \end{array}$	5.01 ± 0.06
Graphite-1 ml SnO ₂ (B)	15.41 ± 0.06	685.8 ± 0.5	49.94 ± 0.12	5.28 ± 0.09
Graphite-2 ml SnO ₂ (C)	16.76 ±	687.7 ±	51.45 ±	5.93 ±
Graphite-3 ml SnO ₂ (D)	18.47 ±	693.8 ±	52.30 ±	6.71 ±
Graphite-4 ml SnO ₂ (E)	0.05 17.38 ±	$673.3 \pm$	0.13 49.90 ±	0.07 5.84 ±
Graphite-5 ml SnO ₂ (F)	$\begin{array}{c} 0.07 \\ 14.08 \pm \\ 0.08 \end{array}$	$0.8 \\ 666.7 \pm 0.5$	$0.15 \\ 51.17 \pm 0.11$	$\begin{array}{c} 0.10 \\ 4.91 \pm \\ 0.09 \end{array}$

authors the reason of the difference in DSSCs performance with different SnO_2 amounts could be due to the difference in the effective surface areas of the different composite electrodes. In their work also, the two parameters J_{sc} and V_{oc} increased first with increasing amounts of SnO_2 and then started to decrease after reaching the optimum point very much similar to the present work. We have carried out the BET measurements for pristine graphite powder and graphite/SnO₂ optimum composition to compare the effective surface area. According to our BET results it was observed that the effective surface area of pristine graphite was improved by adding SnO_2 nanoparticles from 42.21 m²/g to 71.16 m²/g for the optimized counter electrode D.

We have compared the performance of DSSCs made with the graphite/SnO₂ (corresponding to 3 ml SnO₂ added system) composite CE with those made with Pt CE as well as with pristine graphite CEs. This optimized CE, labeled as D made by adding 3 ml SnO₂ to graphite and sintering at 450 °C for 45 min was used for all subsequent studies made under present work. Fig. 7(a) shows their current density-voltage characteristics corresponding to these three types of CEs. After testing a large number of devices, corresponding photovoltaic parameters were selected by observing the reproducibility of those values and average values were tabulated in Table 3. As expected Pt CE gives the best DSSC efficiency of 8.12% due to its excellent electro catalytic and conducting properties. The DSSC with graphite CE showed 5.01% efficiency whilethe best DSSC with graphite/SnO2 composite CE showed the highest efficiency of 6.71%. This is an impressive enhancement of 33.9% in efficiency compared to the DSSC made with pristine graphite CE. Compared with pristine SnO₂ and pristine graphite-based CEs, the optimized, graphite/SnO2composite CE (D) 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 graphite layered surfaces. Compared with DSSCs made with Pt CE, the highestgain exhibited by the DSSC with graphite/SnO2composite CE is due to the increase in $J_{\rm sc}$ at the expenses of both $V_{\rm oc}$ and the fill factor. This enhancement in the J_{SC} could be attributed to the increased effective active surface area of the graphite/SnO2composite electrode (D) compared to the Pt, and its thickness and the porosity as observed by the SEM and FE-TEM analysis. 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 increase in the Jsc. Similar observations have been reported by Bondarenko et al confirming the enhancement of electrocatalytic activity combined with high electrical conductivity and high chemical stability with SnO2/rGO composite films [52].

Further, this is also associated with the higher series and charge transfer resistances of the composite CE as described in next section under the analysis of the Electrochemical Impedance Spectra (EIS) shown in Fig. 7b.



Fig. 7. (a) Current density vs photovoltage characteristics of DSSCs with Pt CE, graphite CE and graphite/SnO₂ composite CE, (b) EIS spectra of the DSSCs made with three different counter electrodes, platinum, graphite and graphite/SnO₂ composite as listed in Table 4.

Table 3

Photovoltaic parameters of DSSCs made with Pt, graphite, SnO_2 and graphite/ SnO_2 composite CEs with normal photoanode.

Counter electrode used in DSSC (normal photoanode)	$J_{\rm sc}/{ m mA}$ cm $^{-2}$	V _{oc} /mV	FF%	Efficiency %
Pt	$\begin{array}{c} 16.43 \pm \\ 0.03 \end{array}$	$\begin{array}{c} 803.4 \pm \\ 0.4 \end{array}$	$\begin{array}{c} \textbf{70.24} \pm \\ \textbf{0.11} \end{array}$	$\begin{array}{c} \textbf{8.12} \pm \\ \textbf{0.05} \end{array}$
Graphite	$\begin{array}{c} 15.66 \pm \\ 0.08 \end{array}$	$\begin{array}{c} 670.1 \pm \\ 0.4 \end{array}$	$\begin{array}{c} 45.55 \pm \\ 0.15 \end{array}$	$\begin{array}{c} 5.01 \pm \\ 0.06 \end{array}$
Graphite/SnO ₂ (D)	$\begin{array}{c} 18.47 \pm \\ 0.05 \end{array}$	$\begin{array}{c} 693.8 \pm \\ 0.4 \end{array}$	$\begin{array}{c} 52.30 \ \pm \\ 0.13 \end{array}$	$\begin{array}{c} \textbf{6.71} \pm \\ \textbf{0.07} \end{array}$

3.4. Analysis of electrochemical impedance spectroscopy (EIS) results of DSSCs

Electrochemical impedance spectroscopy (EIS) offers an important method to study the kinetics of interfacial charge transfer processes in DSSCs. The charge transfer resistances can be calculated from the corresponding Nyquist plots. In an ideal EIS spectrum, three semicircles could be seen, the first one in the high-frequency region is generally attributed to the electrochemical reaction resistance at the counter electrode/electrolyte interface ($R1_{CT}$). The middle one in the midfrequency region ($R2_{CT}$) is attributed to the charge transfer resistance at the TiO₂ photoanode/electrolyte interface while the last one in the low frequency region is associated with the ionic diffusion taking place within the electrolyte ($R3_{CT}$). However, in the present work only the first two semicircles appear and the third one is missing due to the frequency limitation of the instrument [26,34]. The equivalent circuit model was used to extract impedance parameters and the fitted lines are shown in Fig. 7(b) and the resistance values are depicted in Table 4.

The main function of a CE in a DSSC is to act as a catalyst to reduce the oxidized redox couple at the surface of the CE by accepting electrons from the external circuit and to subsequently enable the reduction of the oxidized dye at the photoanode by collecting electrons from ions transported through the redox electrolyte. Generally, the power conversion efficiency and the fill factor of DSSCs made with Pt-based CEs exhibit better performance compared to those made from graphite or carbon-based counter electrode, due to the high conductivity and high electro-catalytic nature of Pt. However, the short-circuit current densities of DSSCs made with graphite-based counter-electrodes are generally higher than those made with Pt counter electrodes, because of the reasonably high catalytic activity coupled with high effective specific surface area of the nanoporous graphite-based CEs that facilitates the redox reactions of a larger number of ionic species/sec.

In the present case, the DSSCs fabricated with the optimized graphite/SnO₂ composite CE exhibits the highest J_{SC} value of 18.47 mA cm⁻² which is even higher than the value 16.43 mA cm⁻² obtained for the Pt CE based DSSCs. These results are generally consistent with results reported by other groups for DSSCs made with graphite-based counter electrodes [15,25,34]. This is evidently due to the larger effective specific surface area of the graphite/SnO₂ electrode due to its nanoporous and layered structure as seen from SEM and FE-TEM images, compared to planar Pt CE. The nanoporous 3D structure allows more redox ionic species per unit area to be in contact with the total CE surface area and undergo catalytic redox reactions I_3^- to $3I^-$ by gaining an

Table 4

 $R_{s},\,R1_{CT}$ and $R2_{CT}$ data extracted from EIS spectra of Fig. 7(b) using the equivalent circuit model for DSSCs fabricated with different types of counter electrodes and normal TiO₂ phtoanode used in this work.

Counter electrode used in DSSC (normal photoanode)	$R_{\rm s}\left(\Omega ight)$	R1 _{CT} (Ω)	$R2_{\rm CT}(\Omega)$
Pt	10.90	3.78	25.13
Graphite	31.80	7.11	50.05
Graphite/SnO ₂	25.30	6.55	43.75

electron from the external circuit. In the case of rGO/SnO_2 based CE's, Sun et al have reported a higher J_{SC} value in their DSSCs compared to the J_{SC} value obtained for an identical DSSC made with a Pt CE [28]. Similar results have been reported by several other research groups [18,25,35,36,37].

The CE plays a major role in determining the open circuit voltage (V_{OC}) of the DSSC. The maximum theoretical photovoltage of a DSSC depends on the energy difference between the Fermi level of the semiconductor photoanode and the redox potential of the mediator and can be realized only when the current is zero. However, when a load is present, the output photovoltage becomes less than V_{OC} . This difference in voltage arises from the total overpotential of the counter electrode and originates from the mass-transfer overpotential due to the passage of current through the electrolyte and through the kinetic over potential or charge-transfer over potential at the electrolyte/CE interface. The first one mainly depends on the ionic conductivity of the redox electrolyte and the migration of redox mediator ionic species from CE to TiO₂ photoanode, whereas the magnitude of the latter depends on the catalytic properties of the CE surface related to mediator reduction. Therefore, an efficient CE should have good electronic conductivity along with reasonably high electro-catalytic activity for the reduction reaction of the redox mediator. Thus, for minimizing the charge transfer over potential, the CE materials should either be metals like Pt or be catalytic materials coated on a conducting substrates such as FTO to facilitate the redox reaction. In the present case, the conducting and catalytic properties of graphite have been combined with conducting and adhesion properties of SnO₂ to achieve this purpose.

A lower R_s corresponds to a higher conductivity of the catalytic counter electrode and a better filling factor of the DSSC which is consistent with our FF values depicted in the table 3 for the Pt CE [38]. The charge transfer resistance $R1_{CT}$ is an important parameter associated with charge transfer across the electrolyte/CE interface. As expected, the lowest $R1_{CT}$ value of 3.78 Ω shown in Table 4 corresponds to the Pt/electrolyte interface. The (graphite/SnO₂)/electrolyte interface shows slightly higher $R1_{CT}$ value of 6.55 Ω compared to the Pt/electrolyte interface. This is very likely caused by the higher resistivity of the nanoporous graphite/SnO₂ composite compared to Pt. The $R1_{CT}$ value of graphite CE based DSSC is 7.11 Ω . It is evident that a lower value of $R1_{CT}$ gives better DSSC performance. Normally, a decreasing trend in $R1_{CT}$ value is associated with an increasing trend in J_{SC} for most of the DSSC systems studied [37].

The graphite/SnO₂ based DSSC shows a lower V_{oc} value of 693.8 mV compared to the value of 803.4 mV obtained for DSSC with Pt CE. Chen et al. [38] have reported that DSSC made with nitrogen-doped graphene (NGr) and poly(3,4-ethylenedioxythiophene) (PEDOT) based composite counter electrode showing higher J_{sc} and lower V_{oc} values compared to a similar DSSC based on Pt CE. In a DSSC with activated carbon-based CE, the reduction of $V_{\rm oc}$ has been attributed to the increase in electrical resistance of the CE [39]. The series resistance R_S is attributed to the total electrical resistance of the FTO layer, the TiO₂ layer, the redox electrolyte and the graphite/SnO₂ layer. The increased resistance $R1_{CT}$ of the graphite/SnO2 CE/electrolyte interface therefore contributes to increased overall resistance R_S of the DSSCs. The charge-transfer resistance of the counter electrode $R1_{CT}$ is also dependent on its catalytic activity for reducing the tri-iodide ion. Lower VOC can be due to overvoltage losses caused by the limited catalytic activity required for the reduction of tri-iodide by the graphite/SnO₂ CE compared to the Pt CE. With a smaller $R1_{CT}$ value of 3.78 Ω , Pt CE exhibits the highest activity for I3⁻ to I⁻ reduction compared to the catalytic activity of graphite/ SnO₂ CE which has a higher $R1_{CT}$ value of 6.55 Ω . The higher $R1_{CT}$ value of the graphite/SnO2 CE/electrolyte interface, compared to the Pt/ electrolyte interface makes it difficult for the oxidation of I⁻, as also supported by CV studies, thus contributing to the slowing down of the dye regeneration at the photoanode. This will increase the recombination and hence lower the Fermi level thus contributing to a decrease in V_{OC} with respect to the DSSC with Pt CE.

3.5. Improvement of DSSC performance by $TiCl_4$ treatment on TiO_2 photoanode

The TiCl₄ treatment was carried out on the surface of TiO₂ layer by immersing the photoanode in a 0.04 M TiCl₄ solution in order to further improve the performance of DSSC made with graphite/SnO₂ composite based CE. The TiO₂ based photoanodes were immersed in TiCl₄ solution at 70 °C temperature for 20 min and later sintered at 450 °C for 45 min. This treatment of the TiO₂ layers allows the formation of very small TiO₂ particles of size around 3 nm to be attached to the bigger particles. Due to this, the roughness of the layer with the small TiO₂ particles is changed and the interconnection between the smaller TiO₂ particles with bigger particles creates additional paths for electrons to reach to FTO conducting layer and also to the external load [40,41]. By this mechanism, the TiCl₄ treatment has improved the power conversion efficiency of DSSCs caused by the enhancement in both J_{sc} and V_{oc} as shown in Fig. 8(a) and Table 5.

Fig. 8(b) depicts the Nyquist plots taken for DSSCs with TiCl₄ treatments and Table 6 summarizes all the corresponding EIS parameters obtained by fitting the spectra with the equivalent circuit diagram, as appear in the inset figure. It can be seen clearly in Fig. 8(b) and the Table 6, the EIS parameters were enhanced after the TiCl₄ treatment. This may be mainly due to suppression of recombination electron at the TiO₂/electrolyte interface. However, an improvement of power conversion efficiency indicates that this TiCl₄ chemical treatment played an important role in charge separation and charge collection on the TiO₂ and electrolyte interface of DSSC [42].

An efficiency comparison of several DSSCs fabricated with graphite/ RGO based CEs, reported by other groups in the literature with their preparation methods, sintering temperatures and type of the electrolyte are given in Table 7. Efficiencies of the DSSCs based on Pt CE in respective studies are also shown for comparison. Results of the present work based on Graphite/SnO₂ CE are included in the last row

3.6. Cyclic voltammetry analysis

To study the electrocatalytic properties and reaction kinetics of the CEs, cyclic voltammetry (CV) studies were conducted using a threeelectrode electrochemical cell by changing the working electrode as mentioned previously. Fig. 9(a) shows the cyclic voltamograms obtained for Pt, graphite, SnO₂ and graphite/SnO₂ CEs in the electrolyte with I⁻/I₃⁻, at the 50 mV s⁻¹ scan rate and an applied sweep potential window of -1.0 V to 1.0 V vs Ag/AgCl reference electrode. CV plots of all the electrodes show two anodic current peaks and two cathodic current peaks (Oxidation-1/Reduction-1, Oxidation-2/Reduction-2) as depicted in Fig. 9(a). These oxidations and reductions correspond to Eqs. (1) and (2) respectively [44,45].

$$3I^{-} - 2e^{-} \rightarrow I_{3}^{-}(Ox1), I_{3}^{-} + 2e^{-} \rightarrow 3I^{-}(Red1)$$
 (1)



Fig. 8. (a) Current density vs photovoltage characteristics of DSSCs with $TiCl_4$ treated TiO_2 photoanode and Pt CE, graphite CE and graphite/SnO₂ composite CE, (b) EIS spectra of the DSSCs made with $TiCl_4$ treated TiO_2 photoanode and three different counter electrodes shown in Table 6.

Table 5

Photovoltaic parameters of DSSCs made with $TiCl_4$ treated TiO_2 photoanode and with Pt, graphite, SnO_2 and graphite/ SnO_2 composite CEs.

Counter electrode used in DSSC	$J_{\rm sc}/{ m mA}$ cm ⁻²	$V_{\rm oc}/{\rm mV}$	FF %	Efficiency %
Pt (with TiCl ₄ treated photoanode) Graphite (with TiCl ₄ treated photoanode) Graphite/SnO ₂ (with TiCl ₄ treated photoanode)	$\begin{array}{c} 17.00 \pm \\ 0.04 \\ 16.40 \pm \\ 0.06 \\ 18.50 \pm \\ 0.05 \end{array}$	$\begin{array}{c} 806.2 \pm \\ 0.5 \\ 666.1 \pm \\ 0.6 \\ 730.9 \pm \\ 0.5 \end{array}$	$\begin{array}{c} 68.06 \pm \\ 0.12 \\ 55.10 \pm \\ 0.14 \\ 58.88 \pm \\ 0.11 \end{array}$	$\begin{array}{l} 9.24 \ \pm \\ 0.08 \\ 6.02 \ \pm \\ 0.05 \\ 7.95 \ \pm \\ 0.06 \end{array}$

Table 6

 R_{s} , $R_{1_{CT}}$, and $R_{2_{CT}}$ data extracted from EIS spectra of Fig. 8(b) using the equivalent circuit model for DSSCs fabricated with TiCl₄ treated TiO₂ photoanode and three different types of counter electrodes used in this work.

Counter electrode used in DSSC (with TiCl_4 treated photoanode)	$R_{\rm s}\left(\Omega ight)$	R1 _{CT} (Ω)	$R2_{\rm CT}(\Omega)$
Pt	9.73	2.82	20.46
Graphite	27.47	5.08	60.95
Graphite/SnO ₂	26.10	3.40	40.97

$$2I_{3}^{-} - 2e^{-} \rightarrow 3I_{2}(Ox2), 3I_{2} + 2e^{-} \rightarrow 2I_{3}^{-}(Red2)$$
(2)

The electro-catalytic activity or the kinetic redox ability of the CE is quantitatively described using the two peak current densities (J_{Ox1} , J_{Red}) and the peak to peak voltage difference or peak spacing (ΔE_p) of Oxidation-1 and Reduction-1 process, because they reduce the tri-iodide ions to iodide ions at the CE. The magnitude of the ΔE_p value is associated with the catalytic activity of the CEs to the I^-/I_3^- redox couple and smaller ΔE_p values give superior catalytic activities [38]. Further, improved electro-catalytic activity of the CE is shown by higher values of J_{Ox1} and J_{Red1} . Therefore, kinetic redox ability of the CE materials can be directly correlated with these peak currents. The absolute values of J_{Ox1} and J_{Red1} of all the CEs are tabulated in Table 8. The graphite/SnO₂ CE showed the anodic peak current density (J_{Ox1}) of 1.73 mA cm⁻², which is higher compared to the graphite CE (0.63 mA cm⁻²), illustrating excellent catalytic activity of graphite/SnO₂ composite CE toward tri-iodide reduction compared to the pristine graphite CE.

Furthermore, this graphite/SnO₂ composite CE shows slightly higher J_{Ox1} value than that of the Pt CE electrode (1.08 mA cm⁻²) and it is correlated with the highest J_{sc} of 18.50 mA cm⁻² obtained for the DSSC fabricated with graphite/SnO₂ CE. Similar trend is also observed by Chen et al in different studies [38]. This could be due to the thicker nano-porous structure of graphite/SnO₂ layer with higher effective active surface area than that of the Pt as seen from the SEM and FE-TEM images [25,46]. As depicted in the table 8, J_{Red1} (-0.41 mA cm⁻²) of the graphite/SnO₂ CE is much greater than that of the pure graphite CE. This

Table 7

Comparison of the performance of graphite/RGO based CEs in literature with the present work.

further supports the superior electrocatalytic ability of the composite counter electrode and its efficient reduction ability of I_3^- . However, the Pt CE shows the highest J_{Red1} value (-0.84 mA cm⁻²) than both graphite/SnO₂ composite CE and pristine graphite CE than both graphite/SnO₂ composite CE and pristine graphite CE.

As mentioned previously the magnitude of the ΔE_p value is associated with the electrocatalytic ability of the CE and the lower ΔE_p values are associated with superior electrocatalytic ability. According to the values depicted in Table 8, the Pt CE has the lowest ΔE_p value of 0.45 V while the pristine graphite CE has the highest ΔE_p value of 0.93 V. The Graphite/SnO₂ composite electrode has an intermediate ΔE_p value of 0.78 V. These values further confirm the higher electrocatalytic ability of graphite/SnO₂ composite compared to the pristine graphite CE while Pt is still the best CE out of the three CEs studied in this work. Therefore, in spite of the high resistance of the graphite/SnO₂ CE, by considering its favourable electrocatalytic ability, it can be used as a good low cost CE material in DSSCs [35,46,47].

In order to examine the stability of the graphite/SnO₂ CE, 10 cyclic voltammograms were obtained continuously by applying a scan rate of 50 mV s^{-1} as shown in Fig. 9(b). This voltammetry graph exhibits good reproducibility of the positions of the oxidation and reduction peak currents demonstrating stability of the graphite/SnO₂ composite CE. Fig. 9(c) shows the cyclic voltammetry graphs of graphite/SnO₂ composite CE at various scan rates starting from 20 mV s⁻¹. The anodic peak current densities (J_{Ox1}) gradually shifts in positive direction with increasing the scan rate [48,49]. An arrow mark in Fig. 9(c) indicates this increment of J_{Ox1} with increasing the scan rate. The Fig. 9(d), shows the relationship between the peak current density (J_{OX1}) and the square root of scan rate. As suggested by the linear relationship, the ionic diffusion of redox species within the electrolyte is directly related to the redox reaction rate at the graphite/SnO₂ CE. To find the relationship between increased active sites and diffusion of iodide in the graphite/ SnO₂ composite CE, Randles-Sevcik theory mentioned by Eq. (3) can be used.

$$J_{Red} = Kn^{1.5} A C D_n^{0.5} v^{0.5}$$
(3)

where J_{Red} is the peak current density of reduction-1 (mA cm⁻²), *K* is a constant, *n* (=2) is the number of electrons involved in the charge transport process, *A* is the electrode area (cm²), *C* is the bulk concentration of triiodide ions (mol⁻¹ L⁻¹), *D*_n is the diffusion coefficients of triiodide ions and *v* is the applied scan rate. The calculated values of the diffusion coefficients of triiodide ions at different CEs are listed in Table 8. According to the results in Table 8, the highest value of the diffusion coefficient, $2.44 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, is obtained for the Pt CE. The largest J_{Red1} , smallest ΔE_p , and highest D_n of Pt CE demonstrate the highest electrocatalytic activity which is consistent with the power conversion efficiency of the DSSC. The graphite/SnO₂ composite CE also shows a relatively higher D_n value of $0.94 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ compared to

Graphite/RGO based CE material	Binder	Preparation method	Sintering temperature	η of DSSC made with graphite/RGO CE (%)	η of DSSC made with Pt CE (%)	Redox Electrolyte	Ref & Year
Sub-micrometer sized Graphite	Carboxyl-methyl cellulose	Screen printing method	300 °C/30 min	6.2	6.8	I^{-}/I_{3}^{-}	[15] 2011
Carbon/SnO ₂ /TiO ₂	N/A	Doctor-blade method	450 °C/12 h	6.15	6.48	I^{-}/I_{3}^{-}	[28] 2012
RGO/SnO ₂	N/A	N/A	200 °C/12 h	6.78	7.22	I^-/I_3^-	[43] 2015
Graphite	Morphol	Doctor-blade method	350 °C	6.47	9.60	I^{-}/I_{3}^{-}	[25] 2017
Graphite/fumed silica	Carboxy-methyl cellulose	Tape casting method	280 °C/30 min	6.42	7.32	I^{-}/I_{3}^{-}	[34] 2018
Acytylene carbon black/ Graphite	Ethyl cellulose	Doctor-blade method	450 °C/1 h	5.06	6.43	I^{-}/I_{3}^{-}	[18] 2019
Graphite/SnO ₂	Triton X-100	Spray method	450 °C/45 min	7.95	9.24	I^{-}/I_{3}^{-}	This work



Fig. 9. (a) Cyclic voltammograms taken with Pt, Graphite and Graphite/SnO₂ counter electrodes using a three-electrode arrangement with a 50 mV s⁻¹ scan rate, (b) Cyclic voltammograms of Graphite/SnO₂ counter electrode for 10 cycles at a scan rate of 50 mVs⁻¹, (c) Cyclic voltammograms of Graphite/SnO₂ electrode at different scan rates from 20 to 50 mV s⁻¹ (20, 30, 40 and 50 mVs⁻¹), (d) The linear relationship of peak current densities (J_{ox1}) vs square root of the scan rate for graphite/SnO₂ composite CE.

Table 8

Electrochemical parameters obtained for the three counter electrodes obtained from CV measurements.

Electrode	J _{Ox1} /mA cm ⁻²	J _{Red1} /mA cm ⁻²	$\Delta E_{\rm p}/V$	$D_n(\times 10^{-5})/cm^2$ s ⁻¹
Pt	1.08	-0.84	0.45	2.44
Graphite	0.63	-0.45	0.93	0.70
Graphite/SnO ₂ (D)	1.73	-0.52	0.78	0.94

the lowest D_n value of 0.70×10^{-5} cm² s⁻¹ obtained for the pristine graphite CE. This result also supports the presence of enhanced active sites between graphite and SnO₂ nanoparticles capable of reducing I_3^- and accelerating charge transfer within the graphite/SnO₂ composite CE [46,50].

3.7. Electrochemical analysis of CEs by EIS and Tafel plots

In order to understand the charge transport process at CE/electrolyte interface, EIS experiments were carried out for three different counter electrodes with dummy cells fabricated with two identical CEs. The resulting Nyquist plots are shown in Fig. 10(a) and the appropriate equivalent circuit of the symmetrical cell is present in the inset of the graph. The values of R_s and R_{ct} impedance parameters are listed in

Table 9. The intercept on the real axis is attributed to series resistance (R_s) , which can be mainly attributed to conductive substrate resistance which depends on the degree of adhesion of materials on to FTO conducting substrate [40,51]. The semicircle is attributed to the charge-transfer resistance (R_{ct}) and the corresponding constant phase element (CPE) at the electrode/electrolyte interface.

The R_s and R_{ct} values for graphite/SnO₂ CE are 22.80 Ω and 3.42 Ω , which is much smaller than those of pristine graphite (24.30 Ω , 13.60 Ω respectively). The low R_{ct} suggests that the charge transfer resistance is effectively decreased facilitating the transport of electrons and enhancing the photovoltaic performance of DSSCs.

The Bode plot extracted from EIS measurement provides further information on the reaction rate of I_3^- reduction at the CE/electrolyte interface. Fig. 10(b) depicts the Bode plots for the symmetric cells with three different CEs. Eq. (4) can be used to calculate the electron lifetime (τ).

$$\tau = 1/2\pi f_{max} \tag{4}$$

where f_{max} is the peak frequency of the Bode phase plot [48,51]. τ values for the three different CEs are listed in Table 9. Generally, a smaller τ value represents a rapid reaction for I_3^- reduction. The τ values from different symmetrical cells follow the trend Pt < graphite/SnO₂ composite < graphite CEs, thereby confirming the outstanding electrocatalytic activity of graphite/SnO₂ composite CE.



Fig. 10. (a) Nyquist plots, (b) Bode phase plots and (c) Tafel polarization curves for symmetric cells with Pt, pristine graphite and graphite/SnO₂ composite CEs.

Table 9

Electrochemical parameters of the three electrodes obtained from EIS measurements and Tafel plot measurements.

Counter electrode	$R_{\rm s}\left(\Omega ight)$	$R_{ct}\left(\Omega ight)$	$\tau/\mu s$	$J_0/{ m mA~cm^{-2}}$	$J_{lim}/{ m mA~cm^{-2}}$
Pt Graphite	1.86 24.30	2.10 13.60	10.23 43.02	1.87 0.88	1.94 1.46
Graphite/SnO ₂ (D)	22.80	3.42	11.22	1.20	1.77

Tafel polarization curves were also obtained using three symmetrical dummy cells similar to the cells used for the EIS measurements in order to compare the electrocatalytic properties and the charge transport at different CEs. Fig. 10(c) shows the Tafel curves with logarithmic current density plotted as a function of the applied voltage. Generally, the Tafel curve is divided into three major zones called the limiting diffusion zone, the Tafel zone and the polarization zone. The graph at high potential region is attributed to the limiting diffusion zone which is associated with the transport of I_3^- and I^- ions in the electrolyte. The curve at middle potential region corresponds to the Tafel zone in which the voltage follows a linear relationship with log *J*. The curve in the low potential region or the polarization zone arises from electrochemical reactions.

The exchange current density (J_0) is very closely associated with the catalytic activity of the CE. The ability of the CEs to reduce iodide ions can be evaluated by the J_0 value. A larger J_0 value indicates a better catalytic activity by the CE for the reduction of iodide ions [44]. The limiting diffusion current density (J_{lim}), which corresponds to intersection of the cathodic branch with the Y- axis, can be used to estimate the diffusion performance of the redox couples. Table 9(c) shows the J_0 and J_{lim} values for the three different CEs. As shown in Fig. 10(c) and Table 9, the magnitude of J_0 follows the order, Pt > graphite/SnO₂ > graphite, which matches with the order of R_{ct} because J_0 is associated with the R_{ct} by the Eq. (5),

$$J_0 = RT/nFR_{ct} \tag{5}$$

where *R* is the universal gas constant, *T* is the absolute temperature, *n* is the number of electrons contributing to the charge transfer at the interface and *F* is the Faraday's constant. According to the Eq. (5), J_0 is inversely proportional to R_{ct} and therefore, the results obtained from EIS

and Tafel Plots agree with each other. Also, the order of J_{lim} is Pt > graphite/SnO₂ > graphite, indicating that graphite/SnO₂ composite possess a higher diffusion velocity for the reduction of triiodide in the electrolyte compared to the pristine graphite CE.

The optimized graphite/SnO₂ composite CE prepared in this study has significantly improved the charge transfer ability within CEs, as evident by the higher J_{sc} value obtained for the corresponding DSSC. Based on a comparative analysis of the results obtained for DSSCs fabricated with different CEs, it can be concluded that their performance is consistent with results obtained from CV, EIS and Tafel polarization measurements.

4. Conclusions

We have successfully fabricated SnO₂ nanoparticle incorporated graphite counter electrodes by spray method for applications in dyesensitized solar cells. This simple and low cost preparation method provides the formation of a nanoporous structure with improved interconnections and pathways for improved electrocatalytic effect for triiodide ion reduction at the CE and efficient ionic mobility for iodide/ triiodide ions in the electrolyte medium. The energy conversion efficiency of DSSCs is improved from 6.02% for the pristine graphite- CE to 7.95% for the optimized graphite/SnO2 composite CE exhibiting an overall efficiency enhancement of 32%. This is about 86% of the efficiency of 9.25% obtained for the DSSC with Pt electrode operating under the same conditions. SEM and TEM images showed the morphology of graphite/SnO₂ composite films possessing a 2D nanoporous structure of distributed SnO₂ nanoparticles within the layered graphite structure. The optimized graphite/SnO₂ composite structure shows low R1_{CT} value at CE/electrolyte interface, and according to the CV plots, EIS and Tafel plots for symmetrical CEs, the composite structure exhibits enhanced electrocatalytic activity towards the reduction of tri-iodide ions at the electrolyte/CE interface. The optimized graphite/SnO2 composite structure provides a novel, Pt free, low cost composite material for application in DSSCs.

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.

Acknowledgements

The authors gratefully acknowledge the National Science Foundation of Sri Lanka for research support under grant No. NSF-PSF/ICRP/2017/EA&ICT/04.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical limitations.

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