Contents lists available at ScienceDirect

Solar Energy

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

Low cost, platinum free counter electrode with reduced graphene oxide and polyaniline embedded SnO₂ for efficient dye sensitized solar cells

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ARTICLEINFO

Keywords: Dye sensitized solar cells Reduced grapheme oxide based counter electrode SnO₂ Polyanniline

ABSTRACT

A composite consisting of Reduced Graphene Oxide (RGO), Tin Oxide (SnO₂) nanoparticles and Polyaniline (PANI) conducting polymer was studied as a potential counter electrode material for Dye Sensitized Solar Cells (DSSCs). This RGO/SnO₂/PANI composite CE was fabricated by spray method and used as an alternative to Platinum (Pt) counter electrode (CE). In the fabrication of RGO/SnO₂/PANI composite CEs, several optimizations were carried out to obtain the optimum RGO sintering temperature and the optimum amounts of RGO, SnO₂ and PANI. The photovoltaic performance of the DSSCs based on the newly prepared CEs was studied by using I-V measurements. The efficiency of the DSSC with the CE with optimized RGO/SnO₂/PANI composition having 9.8 μ m thickness was 7.92% under the 100 mW cm⁻² (1.5AM) light illumination. After the TiCl₄ treated TiO₂ photoanode was used, the maximum power conversion efficiency of the DSSC based on the RGO/SnO2/PANI composite CE was increased to 8.68%, which corresponds to an impressive 94% of the efficiency of 9.22% obtained for the control DSSC made with Pt CE and TiCl₄ treated photoanode measured under same light illumination. These composite CEs were characterized by X-ray diffraction, Raman spectra, FTIR spectra, SEM and TEM. Cyclic voltammetry (CV) analysis showed the excellent electro-catalytic activity of the composite CE. With high energy conversion efficiency and improved charge-transfer process of DSSCs in combination with simple preparation and relatively low-cost technique, the RGO/SnO2/PANI composite electrode demonstrates the beneficial use of this novel composite material as CEs in DSSCs.

1. Introduction

Dye-sensitized solar cell (DSSC), first reported by O'Regan and Grätzel in 1991, is an electrochemical device that converts solar energy into electricity (O'Regan and Grätzel, 1991). A typical structure of a DSSC includes three major components: a dye adsorbed TiO_2 photo-anode, a redox electrolyte and a counter electrode (CE). The counter electrode plays a key role in regulating the performance of a DSSC working as a catalyst for the redox couple regeneration and as an electron collector from the external circuit (Kaniyoor and Ramaprabhu, 2012; Wu and Ma, 2012; Yin et al., 2011).

Generally, thin layer of platinum (Pt) deposited on Fluorine-doped tin oxide (FTO) conductive glass is used as the CE due to its excellent electro-catalytic activity for the tri-iodide reduction, high electronic conductivity and good chemical stability. Nevertheless, Pt is an expensive noble metal with limited natural abundance which limits the large scale application of the material (Deng et al., 2010; Jiang et al., 2010).

To fabricate novel CEs with DSSC performance close to that of cells with Pt based electrodes and with low cost, high electronic conductivity and comparable electro-catalytic effects for tri-iodide reduction, various potential alternative materials have been investigated. Carbon based materials such as graphite (Li et al., 2015; Veerappan et al., 2011), graphene oxide(Mahmoud et al., 2019), reduced graphene oxide (Mohan et al., 2019) and graphene (Roy-Mayhew et al., 2010; Zhang et al., 2011) etc., conducting polymers such as polyaniline (Amalina et al., 2019; Li et al., 2008), polypyrrole (Chen et al., 2013), PEDOT-PSS (Yue et al., 2012, 2013), and metal alloys such as nickel cobalt sulfide (Wei et al., 2019b; Wei et al., 2021) are some of the preferred alternative CE materials presently being developed for DSSC applications. Out of

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https://doi.org/10.1016/j.solener.2021.10.022

Received 1 July 2021; Received in revised form 5 October 2021; Accepted 8 October 2021 Available online 15 October 2021 0038-092X/© 2021 International Solar Energy Society. Published by Elsevier Ltd. All rights reserved.







these, the single use of carbonaceous materials or conducting polymers is always associated with some problems such as low adhesion to the conducting substrate, unsatisfactory redox performance of carbon materials and low charge-transfer ability and low electrical conductivity of conducting polymers (Dinari et al., 2016; He et al., 2014; Wei et al., 2019a, 2019b).

In a recent study of graphite/SnO2 composite counter electrodes reported by us, we have demonstrated that SnO₂ nanoparticles can be used 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 (Dissanayake et al., 2021). This graphite/ SnO2 composite was successfully employed as the DSSC counter electrode with superior electro-catalytic activity to reduce iodide ions, and improved photovoltaic performance. The role of the SnO2 was mainly to function as a conducting binder while offering a high specific surface area for iodide ion reduction. Therefore, a possible novel strategy would be to use a composite of Reduced Graphene Oxide (RGO) for catalytic activity, polyaniline (PANI) conducting polymer for electronic conductivity and nanoparticle SnO2 for improved adhesion and porous structure in designing a novel counter electrode with improved DSSC performance. It is interesting to note that few similar composite materials, consisting of graphene or reduced graphene oxide with SnO₂ and PANI have been developed to be used as anode material in Li⁺ ion secondary batteries. The RGO/SnO2/PANI composite structure possessed high specific surface area and mesoporosity that provided paths for Li⁺ ion transport resulting in superior electrochemical performance with high capacity (Dong et al., 2015; Liang et al., 2011; Liu et al., 2016).

In the present study Reduced Graphene Oxide (RGO) synthesized from Sri Lankan graphite was used as the major component to fabricate low-cost CEs for DSSC. First, the amount of RGO used and the sintering temperature were optimized using DSSC characteristics obtained with prepared CEs. Then, to improve the adhesion of RGO material on conducting glass substrate and to enhance the effective surface area by creating a porous structure in the CE SnO2 nanoparticles were incorporated to RGO. The composition of this RGO/SnO2 composite CE was optimized using DSSC characteristics. Similar results were reported by Du et al by preparing SnO₂/RGO composite CE using a solvothermal method and DSSCs fabricated with this CE exhibited a power conversion efficiency of 6.78% (Du et al., 2015). According to another study, SnO₂ decorated graphene oxide based CE was used in DSSCs to obtain an efficiency of 4.57% (Mahmoud et al., 2019). Our group has also studied the performance of DSSCs with CE based on Graphite/SnO₂ composite and results were published very recently (Dissanayake et al., 2021). Polyaniline (PANI) conducting polymer has also been widely used as CEs in DSSCs due to its facile synthesis, relatively high electronic conductivity, reasonable electro-catalytic activity and low price.

In the present study we introduced polyaniline (PANI) conducting polymer as the third component to the optimized RGO/SnO₂ composite and used it as a CE for DSSCs. In this study, we observe that the optimized RGO/SnO₂/PANI composite based CE improves the DSSC performance significantly due to the favourable properties of its components, such as the electro-catalytic activity of RGO, adhesion and porosity of SnO₂ and the electronic conductivity of PANI. As far as we are aware, this is the first report of a DSSC fabricated with the three-component RGO/SnO₂/PANI composite counter electrode exhibiting impressive photovoltaic performance close to that of DSSCs based on a Pt counter electrode working under identical conditions.

2. Experimental

2.1. Materials

To prepare the counter electrodes, RGO was purchased from Ceylon Graphene Pvt. Ltd, Sri Lanka. Tin (IV) oxide (SnO₂), 15% in colloidal dispersion and acetic acid, glacial were purchased from Alfa Aesar and ethanol was purchased from VWR chemicals. To prepare the photoanodes, fluorine doped tin oxide (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 electrolyte, iodine chips (I₂), acetonitrile (anhydrous), valeronitrile, guanidinium thiocyanate and 4*tert*-butylpyridine (TBP) were purchased from Sigma-Aldrich and Ionic liquid PMII (1-propyl-3-methylimidazolium iodide) were purchased from Solaronix.

2.2. Photo-anode preparation

Photo-anode containing two layers of TiO2 on the Fluorine doped tin oxide (FTO) conducting glass substrate was prepared by following the previously reported procedure (Kumari et al., 2017). In summary, to prepare the first compact layer, 0.25 g of P90 TiO₂ powder was ground well with 1 ml of 0.1 M HNO₃ in an agate mortar for about 20 min. Then this paste was coated on the well cleaned FTO glass substrate with a spin coater with 3000 rpm for 60 s. This spin coated glass plate was sintered at 450 °C for 45 min. After cooling down to room temperature, the second layer of TiO₂ was coated on the first layer using P25 TiO₂ powder. For the second layer, 0.25 g of TiO₂ powder and 0.1 M HNO₃ 1.0 ml solution was mixed and ground using mortar and pestle. 0.02 g of Triton X-100 and 0.05 g of PEG 2000 was used as the binder. These chemicals were mixed and ground well until the mixture became a creamy paste. The paste was doctor bladed on the first TiO₂ compact layer on a 0.16 cm^2 cell area. After the application of this second TiO₂ layer, the glass plates (photoanodes) were sintered at 450 °C for 45 min to obtain a porous TiO₂ layer at the top. For some of these double layered photoanodes, the TiCl₄ treatment was carried out by dipping them in a 0.04 M TiCl₄ solution at 70 °C for 30 min and sintering again at 450 °C for 45 min. These TiO₂ photoanodes were allowed to cool down to room temperature and were finally dipped in an ethanolic solution of Ru N719 dye for 15 h for dye sensitization.

2.3. Preparation of RGO/SnO₂/PANI composite counter electrodes

To prepare the counter electrodes, initially 5 mg of RGO powder was mixed with 2.5 ml of acetic acid and 0.02 g of Triton X-100 in an agate mortar for 10 min and finally mixed with 100 ml of ethanol and sonicated for 1 h. Then this mixture was sprayed on a FTO glass substrate while keeping the substrate at 100 °C. Finally, the FTO/RGO plates were sintered at different temperatures in a muffle furnace to obtain the best sintering temperature based on their performance in trial DSSCs. As the best sintering temperature was found to be 250 °C, more CEs were prepared by varying the amount of RGO powder and sintered at the same temperature and used them in trial DSSCs to obtain the best RGO amount and corresponding CE film thickness. For this purpose, the RGO amount was varied from 0.005 g to 0.020 g in 0.005 g steps and the optimized RGO amount was found to be 0.015 g. A colloidal solution of SnO₂ was prepared by mixing a 1.0 ml of SnO₂ colloid with 10 ml of ethanol. Then, different volumes (from 0.5 ml to 1.5 ml) of this diluted SnO₂ colloidal solution were mixed with 0.015 g of RGO powder, 2.5 ml of acetic acid, 0.02 g of Triton X-100 in an agate mortar for 10 min and finally mixed with 100 ml of ethanol and sonicated for 1 h as prepared to make RGO/SnO₂ composite CE as explained above. These spraying mixtures with different amounts of SnO2 colloidal solution were sprayed on heated (100 $^{\circ}$ C) FTO glass substrates to obtain the counter electrodes with visually uniform RGO/SnO₂ composite layers formed on FTO glass. Finally, these RGO/SnO_2 composite CEs were sintered at 250 $^\circ\text{C}$ for 45 min (optimized temperature/time) in a muffle furnace. Based on I-V measurements of trial DSSCs made with different RGO/SnO2 CEs, 1.0 ml of SnO₂ colloidal solution was found to give the best DSSC performance with highest efficiency. To optimize the added PANI amount to the

already optimized RGO/SnO_2 composite CE, different weights of PANI was added to the RGO/SnO_2 mixture by changing the ratio of RGO:PANI from 1:0 to 1:10. Similar optimization procedure explained above was used to prepare the best $RGO/SnO_2/PANI$ composite CEs. Fig. 1 schematically shows the steps used in the fabrication process of above CE.

2.4. Liquid electrolyte preparation

A liquid electrolyte was used to test the performance of DSSCs with RGO, RGO/SnO₂ and RGO/SnO₂/PANI composite counter electrodes as mentioned above. This liquid electrolyte contained 0.6 M 1-propyl-3-methylimidazolium iodide (PMII), 0.03 M iodine (I₂), 0.1 M guanidinium thiocyanate, 0.5 M 4-*tert*-butylpyridine (TBP) dissolved in Acetonitrile/valeronitrile in volume ratio 85:15.

2.5. Characterization of materials and counter electrodes

For structural characterization of prepared RGO/SnO2/PANI composite materials, the Fourier transform infrared (FTIR) spectra were obtained using a Bruker Alpha FTIR spectrometer in the range from 400 to 4000 cm⁻¹. The X-ray diffraction (XRD) patterns were recorded using BrukerD8 advanced eco X-ray diffraction system with Cu K α radiation (λ = 1.54060 Å). XRD data were collected with a step interval of 0.2° in the 2-theta range of 5° to 80° . The Raman spectra of the samples were obtained using a Renishaw basis series with 514 lasers. The surface morphologies were studied using field-emission scanning electron microscopy (FE-SEM, Hitachi SU6600) and transmission electron microscopy (TEM, JEOL 2100). Elemental mapping of prepared RGO/ SnO₂/PANI composite CE was carried out by energy dispersive X-ray spectroscopy (EDS). To investigate the electrocatalytic properties of the synthesized RGO/SnO2/PANI composite material, cyclic voltammetry (CV) experiments were carried out using a three-electrode system with a Pt wire as the counter electrode, Ag/AgCl electrode as reference

electrode and Pt/FTO or RGO/SnO₂/PANI/FTO composite as the working electrode. An acetonitrile solution containing 10 mM LiI, 1 mM I₂ and 0.1 M LiClO₄ was used as supporting electrolyte at a scan rate of 20 mV s⁻¹. The Tafel polarization and electrochemical impedance spectroscopy (EIS) measurements of counter electrodes were carried out using symmetrical dummy cells (with RGO/SnO₂/PANI/FTO on both sides) with the active cell area of 1.0 cm².

2.6. DSSC fabrication and their characterization

Dve sensitized solar cells (DSSCs) were fabricated by sandwiching the prepared liquid electrolyte between the TiO₂ photoanode and the RGO/SnO₂/PANI composite based counter electrode with the active cell area of 0.16 cm². The current density–voltage (*J-V*) characteristics of the cells were measured under the illumination of 100 mW cm^{-2} (AM 1.5) calibrated, solar illumination system (Oriel Newport LCS-100) connected with a Metrohm Autolab potentiostat/galvanostat (Metrohm Autolab PGSTAT 128 N). A 100 W ozone free Xenon lamp was used with AM 1.5 filter to obtain the simulated sunlight with above intensity. There were several optimization steps performed using trial DSSCs to obtain the best CE. First, in order to investigate the effect of sintering temperature of the RGO based CEs on the performance of DSSCs a series of RGO CEs were prepared with different sintering temperature at 150 °C, 250 °C and 350 °C, respectively. Here the sintering temperature was kept fixed at 45 min. In order to compare the performances of DSSCs with RGO based composite counter electrodes similar DSSCs were also fabricated using Pt counter electrodes and tested.

Electrochemical impedance spectroscopy (EIS) measurements were also performed on DSSCs using a Metrohm Autolab Potentiostat/Galvanostat PGSTAT 128 N with FRA 32 M Frequency Response Analyzer (FRA) covering the frequency range between 1 MHz and 0.01 Hz. The measurements with the DSSCs were carried out under the illumination of 100 mW cm⁻² using the same solar simulator that was used for J-V



Fig. 1. Steps used in the fabrication process of RGO/SnO2/PANI counter electrode.

measurements.

3. Results and discussion

A DSSC counter electrode is expected to possess a good electrocatalytic activity, good electronic conductivity and high specific surface area providing more reaction sites for iodide/tri-iodide ion reduction. Traditional used platinum counter electrode has both the electrocatalytic activity and electronic conductivity. In the present case, while RGO provides the required electro-catalytic activity, PANI, being an electronically conducting polymer, will increase the electronic conductivity by supplementing the electronic conductivity already possessed by the FTO substrate glass. SnO₂, in addition to acting as a binder, also provides electronic conductivity and its nanoporous structure will provide more specific surface area for the iodide/tri-iodide reaction. Therefore, a combination of these three components would provide the optimized features needed for a DSSC counter electrode.

3.1. Structural analysis

The FTIR spectra of pristine RGO, SnO_2 , PANI and the RGO/ SnO_2 /PANI composite are shown in Fig. 2(A). As seen from this figure some differences can be observed in the FTIR spectra of these materials. The

FTIR spectrum of pristine RGO is shown in Fig. 2(A) curve (a). According to this spectrum, the small band at 1571 cm^{-1} is due to C=C skeletal vibration of graphene sheets and the broad band from 1000 to 1250 cm⁻¹ is due to the stretching vibrations of the phenolic and carboxylic groups in the RGO (Nethravathi et al., 2009; Wang et al., 2011). The FTIR spectrum of pristine SnO₂ is shown in Fig. 2(A) curve (b). The peaks at 3391 and 1633 cm^{-1} are due to the stretching vibrations of water molecules or hydroxyl groups absorbed at the surface of SnO₂. The band at 625 cm⁻¹ refers to Sn-O stretching modes of Sn-O-Sn (Blessi et al., 2014). The curve (c) in Fig. 2(A) shows the FTIR spectrum of pristine PANI. Peaks at 1603 and 1494 cm⁻¹ are attributed to the C=C stretching of the quinonoid and benzenoid rings, respectively. Also, The peaks at 1296 cm^{-1} can be attributed to C—N stretching, 1126 cm^{-1} to C—O—C stretching and 819 cm⁻¹ to C—H vibration of benzonoid rings confirming the presence of dominant peaks of pure PANI as reported by several groups (Dissanayake et al., 2020; Kumari et al., 2021; Kunteppa et al., 2011). As shown in curve (d), the FTIR spectrum of RGO/SnO₂/ PANI shows the dominant behavior of PANI in the composite. Here, the peaks related to the PANI matrix in RGO/SnO₂/PANI composite have shifted to slightly higher wavenumbers due to π - π interaction and hydrogen bonding between RGO sheets and the PANI polymer backbone (Zhang et al., 2017).

A study on SnO₂-PANI composite by Biswas et al has revealed that



Fig. 2. (A) FTIR spectra, (B) Raman spectra and (C) XRD spectra of RGO, SnO₂, PANI and RGO/SnO₂/PANI composite.

SnO₂ nanoparticles within the polyaniline matrix induced faster relaxation of charge carriers that essentially enhanced the electrical conductivity of the nanocomposite (Biswas and Bhattacharya, 2017). In another study, Diantoro et al have reported that the addition of SnO₂ has significantly increased the electrical conductivity of PANI-SnO₂ films (Diantoro et al., 2018). Structure and properties of SnO₂ nanoparticles embedded polyaniline (PANI) have been studied by Sun et al (Sun et al., 2012) using X-ray diffraction (XRD), Fourier transform infrared (FT-IR), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). In their studies, the The XRD pattern suggested that PANI did not modify the crystal structure of SnO2 while the FT-IR spectrum has shown that PANI has successfully composited with the nanostructured SnO₂. TEM analysis showed that the SnO₂ nanoparticles with a diameter of 15 nm were embedded well in the porous PANI. Conductivity analysis indicated that the SnO₂/PANI nanocomposites had a higher conductivity than that of the pure SnO₂ nanopowders (Diantoro et al., 2018). These observations show that the SnO₂-PANI composite is a better material to be used it as a CE material in DSSCs.

The Raman spectra of pristine RGO, SnO₂, PANI and RGO/SnO₂/ PANI composite are showed in Fig. 2(B). According to the curve (a) of Fig. 2(B), pristine RGO exhibits two major bands. The first band at 1354 cm^{-1} (D band) is related to the defects and disorder in the hexagonal graphitic layers. The second band at 1591 cm^{-1} (G band) is related to the vibration of sp²-bonded carbon atoms in a 2-dimensional hexagonal lattice. The ratio of intensities of D and G bands (I_D/I_G) is 1.06, which is higher than 1.0 indicating that the degree of disorder is relatively large (Du et al., 2015; Mohamed et al., 2018). According to the curve (b) of Fig. 2(B), the peaks at ~ 572 cm⁻¹ is due to A_{2u} transverse optical phonon mode of tin oxide. Also Raman peaks at ~ 629 cm⁻¹ (A_{1g}) corresponds to symmetric Sn–O stretching mode, $\sim 681 \text{ cm}^{-1} (A_{2u})$ corresponds to longitudinal optical phonon modes and \sim 777 cm⁻¹ (B_{2g}) represents asymmetric Sn-O stretching vibration of tin oxide (Mahmoud et al., 2019; Subramaniam et al., 2018). However, in the composite material, only the peak at 572 cm⁻¹ peak appeared corresponding to the transverse optical phonon mode of tin oxide.

For pristine PANI, C-H bending deformation in the benzenoid ring at 1162 cm⁻¹, C—N + stretching at 1335 cm⁻¹, C—N stretching vibration at 1480 cm⁻¹, C—C stretching of quinoid at 1595 cm⁻¹ are observed in curve (c). According to curve (d) of Fig. 2(B), the Raman spectrum of RGO/SnO₂/PANI composite is almost similar to pristine PANI indicating the presence of dominant Raman active modes in the material. However, it is observed that the peaks are slightly red-shifted in the composite material. Generally, similar Raman features are exhibited by pure PANI and composites of PANI with other carbon structures especially when the content of RGO is low compared to PANI like in the present case. Furthermore, a peak shift towards low wavenumbers for a RGO/SnO₂/PANI composite compared to pure PANI can be attributed as due to the strong π - π electronic interaction between RGO and PANI (Mitra et al., 2015; Zhang et al., 2017).

Fig. 2(C) exhibits the XRD pattern of pristine RGO, SnO₂, PANI and the prepared composite materials of RGO/SnO2/PANI mixture. From curve (a), a broader peak of RGO can be observed at $2\theta = 24.39^{\circ}$ which corresponds to the (002) plane of RGO (Pathak et al., 2019). The XRD patterns of the pristine SnO_2 are illustrated in curve (b). The peaks at 2θ $= 26.51^{\circ}, 33.85^{\circ}, 37.83^{\circ}, 51.72^{\circ}, 65.54^{\circ}$ and 71.34° correspond to (110), (101), (200), (211) and (301) planes of SnO₂, respectively. All these strong diffraction peaks are consistent with a tetragonal crystalline SnO₂ phase and also in agreement with the results reported by Liu et al also (Liu et al., 2015). According to the curve (c) of Fig. 2(C), the pristine PANI exhibits one sharp peak centered around 25.10° accompanied by other two low intensity peaks with their position at 20.08° and 15.29°, corresponding to (200), (020) and (011) semi-crystalline planes of PANI in its emaraldine salt form, respectively (Zhang et al., 2017). The XRD pattern of the RGO/SnO₂/PANI composite is shown by curve (d) of Fig. 2(C). Here, the narrow and sharp diffraction peak centered at 26.43° are clearly due to the contributions from (002) plane of RGO, (110) crystal plane of SnO₂ and (200) plane of PANI. In addition, small peaks at 33.75° , 37.60° , 51.60° , 61.62° and 65.16° provide further evidence of the presence of SnO₂ in the composite sample. Therefore, from these XRD patterns, it can be confirmed that the starting materials RGO, SnO₂ and PANI are present in the composite without apparent structural changes. Similar XRD results have been reported by other groups for the SnO₂/PANI complex (Zhang et al., 2017). Above observations are further confirmed by the SEM and TEM results described in the next section.

3.2. Morphological analysis

Fig. 3(a)–(c) shows the SEM surface images of pristine RGO, pristine PANI and RGO/SnO₂/PANI composite respectively. The SEM image of RGO micrograph (Fig. 3(a)) exhibits a fluffy and wrinkled RGO morphology with many stacking layers, quite similar to the SEM images reported by Le et al (Le et al., 2018). In the SEM image shown in Fig. 3(b) PANI can be seen to be existing in cauli-flower shape morphology which is quite similar to the SEM images reported by Jin-Feng et al (Cui et al., 2014). SEM image in Fig. 3(c) exhibits a mixture of RGO and PANI, but small SnO₂ nanoparticles cannot be seen by SEM. However, TEM images confirmed the existence of SnO₂ nanoparticles and that will be discussed later. Fig. 3(d) shows the cross-section image of RGO/SnO₂/PANI composite counter electrode with a thickness of about 9.8 μ m.

The morphology and the structure of RGO/SnO₂/PANI composite were studied using high resolution transmission electron microscopy (HR-TEM), and the results are shown in Fig. 4.

It can be observed that from TEM images shown in Fig. 4(a) and (b), the size of a RGO sheet is less than 3 μ m and small aggregates of SnO₂ and PANI are decorated over the plane of wrecked RGO sheets. The lattice fringes of SnO₂ nanoparticles with the particle size less than 20 nm are clearly visible and the lattice spacing of d = 0.338 nm for the (110) crystal plane (Fig. 3(c)). In a study of the structure and morphology of SnO₂ nanoparticles embedded polyaniline (PANI) by Sun et al (Sun et al., 2012) the TEM analysis has shown that the SnO₂ nanoparticles had a diameter of 15 nm and were embedded well in the porous PANI structure. In the present work, as shown in Fig. 4(d), the profile of the composite material confirms the above lattice spacing of SnO₂ nanoparticles. This has been further confirmed by the XRD data of pristine SnO₂. The most intense XRD peak at 26.51° (110) gives the dspacing of 0.334 nm which is very close to d-spacing from the HR-TEM image of the SnO₂ nanoparticles.

The surface components of the prepared RGO/SnO₂/PANI composite were confirmed by TEM-EDX mapping analysis. As shown in the Fig. 5, the presence of SnO₂ and PANI over the RGO sheets can be confirmed. Fig. 5(a) shows the selected area of the RGO/SnO₂/PANI composite and Fig. 5(b)-(f) shows the elemental mapping of C, O, N and Sn. These elements can be seen homogeneously distribute over the RGO sheets. According to elemental analysis in Fig. 5(f), elements shows that the amounts of C, O, N and Sn are 78.24 %, 21.72 %, 0.01 % and 0.03%, respectively.

3.3. Photovoltaic performance

The current density–voltage (*J-V*) characteristics of the fabricated DSSCs employing different counter electrodes were studied under light irradiation of 100 mW cm⁻². Fig. 6(a) shows the *J-V* curves of RGO CEs based DSSCs at different sintering temperatures of CEs and Table 1 shows the photovoltaic performance of DSSCs prepared with these RGO CEs. DSSCs with RGO CEs sintered at 250 °C for 45 min exhibited the highest efficiency of 4.48 %. This optimum sintering temperature may depend on the type of binder used, the nature and the amount of the material used.

Fig. 6(b) and the Table 2 shows the variation of photovoltaic performance with the RGO amount used to prepare RGO based CEs. Here, for the optimization of the RGO amount, the sintering temperature and



Fig. 3. FE-SEM images of (a) surface of pristine RGO, (b) surface of pristine PANI, (c) surface of RGO/SnO₂/PANI composite, (d) cross section of RGO/SnO₂/PANI composite counter electrode.

time was kept fixed at 250 °C and 45 min. CE made with 15 mg of RGO showed the best performance with improved short-circuit current density (J_{sc}) probably due to the optimum thickness to act as a electrocatalytic material as the CE.

In order to estimate the optimum amount of SnO₂ in the RGO based CE, the amount of SnO₂ used in the composition was varied by keeping the amount of RGO fixed at 15 mg as optimized previously. The sintering temperature was kept constant at 250 °C and sintering was carried out for for 45 min. Table 3 shows the variation of photovoltaic performance with the amount of SnO₂ colloid solution added to make RGO/SnO₂ composite CEs.

It can be seen from Fig. 6(c) and Table 3, that the power conversion efficiency of DSSC has increased with the added amount of SnO_2 colloidal in to the CE. It can be seen from the Fig. 6(c) and the Table 3, the performances of the DSSC have increased when the amount of SnO_2 is increased in the composition up to 1.0 ml and then started decreasing with the further addition of SnO_2 amount. It was observed that by adding SnO_2 into the RGO, the adhesion of RGO to the FTO glass substrate could be improved significantly.

Fig. 6(d) shows the variation of *J*-*V* characteristics of the DSSCs fabricated with composite RGO/SnO₂/PANI CEs having different weight ratios of PANI and RGO. Weight ratio between PANI and RGO was varied from 1:0 to 1:10. Table 4 summarizes the corresponding photovoltaic parameters of DSSCs made with these composite CEs. For clarity, a few selected *J*-*V* graphs corresponding to 0, 2, 4, 6, 8 and 10 wt ratios of PANI added systems are included in Fig. 6(d).

According to Fig. 6(d) and Table 4, the efficiency of the DSSCs made with RGO/SnO₂/PANI composite increases with increasing the weight ratio of RGO: PANI from 0 to 4 and then starts to decrease with further addition of PANI.

According to Tables 2, the highest solar cell efficiency shown by CE with only RGO is 4.70% whereas according to Table 3, the highest solar cell efficiency shown by the RGO/SnO₂ composite CE is 6.25%. After

incorporating the PANI conducting polymer into the composite, all the photovoltaic parameters of the DSSCs have shown impressive improvements. The highest J_{sc} and the V_{oc} exhibited by the DSSC with optimized RGO/SnO₂/PANI composite CE were 18.60 mA cm⁻² and 708.00 mV respectively with corresponding efficiency of 7.92%. This increase of photovoltaic performance due to PANI by increasing J_{sc} , V_{oc} and FF could very likely be due to the increase in electronic conductivity and electrocatalytic activity of the PANI added composite material. The addition of PANI remarkably enhanced the overall efficiency of DSC by 27%. It should be noted that the open-circuit value (V_{OC}) is determined by the change in the redox potential of electrolyte whereas the catalytic activity of CE towards electrolyte is responsible for the fill factor (FF) value.

Fig. 7 shows the variation of the efficiency with the RGO to PANI weight ratio. As seen from the figure the efficiency enhances due to the incorporation of PANI up to the RGO to PANI ration of 1:4 and then then decreases with the further addition of PANI, showing that excessive amount of PANI is unfavorable for photovoltaic activity.

It was observed that at these high PANI concentrations the CE film was cracked and sometimes get detached from the FTO glass substrate, leading to lower DSSC performance and low values of FF.

The enhanced performance of the DSSC is evidently due to the favorable nanostructure of the optimized $RGO/SnO_2/PANI$ composite CE. Based on the SEM and TEM characterization results, it can be concluded that in the new $RGO/SnO_2/PANI$ composite CE, SnO_2 nanoparticles and PANI are homogeneously dispersed in RGO sheets. This type of composite three-component structure has proved to be superior to that of pristine RGO, SnO_2 or PANI used individually as DSSC CEs in terms of electrical conductivity, catalytic activity and structural stability and improve the performance of DSSCs. The other important factors are the specific surface area and the nano-porous structure of the new CE material as reported by Liu et al in relation to Li⁺ ion battery anodes (Liu et al., 2016). The novel composite structure is found to be very



Fig. 4. TEM images of (a) and (b) for SnO₂ and PANI decorated RGO sheets with two different magnifications, (c) HR-TEM image of RGO/SnO₂/PANI composite and (d) profile of HR-TEM image.

important for the distribution of the electrolyte within the CE and for fast ionic diffusion needed for the fast electrochemical re-dox reaction. With further addition of SnO_2 and PANI to the RGO sheets after the optimum DSSC efficiency point, photovoltaic performance has started to reduce possibly due to the aggregation of SnO_2 and PANI effectively reducing the active specific surface area of the CE and thereby limiting the rate of re-dox reaction at the CE. Therefore, the structural stability, porosity with high specific surface area and good electrical conductivity of the optimized RGO/SnO₂/PANI composite appears to be the crucial factors for improved performance of the DSSC.

Liu et al has reported a high specific surface area of 167.2 m² g⁻¹ for their RGO/SnO₂/PANI composites used as Li + ion intercalation material in a Li + ion battery. The pore size distributions in their samples calculated through the Barret-Joyner-Halenda (BJH) method had shown that SnO₂ nanoparticles were highly microporous, which partially

accounts for its high specific surface area, compared to the RGO sample which had only very few macropores. (Liu et al., 2016). Therefore, in the present work also, we can expect our RGO/SnO₂/PANI composite structure when used as a counter electrode in a DSSC to improve the trapping of liquid electrolyte in the porous structure and increase the number of available sites for the re-dox reaction and hence enhance the rate of electro-catalytic activity.

Since the Pt deposited by sputtering method has been regarded as the most effective CE for DSSCs, the performances of the DSSCs fabricated with the RGO/SnO₂/PANI composite CE and the CE fabricated with the sputtered layer of Pt on FTO substrate were compared. The photovoltaic performances and parameters of these DSSCs are shown in Fig. 7 and tabulated in Table 5 respectively.

As it can be seen from the Table 5 the DSSC with the $RGO/SnO_2/$ PANI composite CE developed in this work exhibits the best power



Fig. 5. TEM-EDX mapping of RGO/SnO₂/PANI composite by EDX spectroscopy, (a) selected area of EDX mapping, elemental distribution of (b) carbon, (c) oxygen (d) nitrogen and (e) tin, (f) elemental analysis graph with details.

conversion efficiency of 7.92 %, which is quite close to that of the DSSC with the Pt CE (8.50 %). In order to further improve the performance of DSSC made with RGO/SnO₂/PANI composite CE, the TiO₂ photoanaode was treated with TiCl₄ immersing the photoanode in an aqueous solution of 0.04 M TiCl₄ at 70 °C for 30-minutes prior dye adsorption. As it is well known, TiCl₄ increases the surface roughness and the specific surface area and thereby increases the amount of dye adsorption by the photoanode. This can also improve the interconnections between the smaller TiO₂ particles and bigger particles and create additional pathways for electrons to reach the conducting layer of the FTO substrate. (Nath et al., 2015).

As it is evident from the Table 5 and curve (c) in the Fig. 8, the DSSC fabricated with TiCl₄ treated photoanode and the optimized CE showed an excellent and comparable power conversion efficiency of 8.68% with respect to the power conversion efficiency of the DSSC fabricated with conventional Pt CE having 9.22%.

3.4. Electrochemical impedance spectroscopy (EIS) analysis of DSSCs

To study the interfacial charge transfer processes of the DSSCs made with the RGO/SnO₂/PANI composite CE, EIS measurements were done under the same light illumination as in the I-V characteristics. A typical Nyquist plot of a DSSC has three semicircles in high, intermediate and low frequency regions. Fig. 8(B) and (D) shows the Nyquist plots of DSSCs made with the new composite CE and Pt CE and also without and with TiCl₄ treatments of the TiO₂ photoanodes. According to the limitations in the range of frequencies of the instrument used in this study, Fig. 8(B) and (D) exhibit only two visible semicircles in the Nyquist plots of DSSCs (Dissanayake et al., 2017; Liu et al., 2016).

The charge transfer resistance values were obtained by fitting the impedance parameters with an equivalent circuit model as shown in the inset of Fig. 8(B) and 8(D) by using NOVA software. The smaller semicircle in the high frequency region is attributed to the electrochemical resistance at the CE/electrolyte interface (R_{1CT}). The large semicircle is attributed to the charge transfer resistance at the TiO₂ photoanode/ electrolyte interface (R_{2CT}). The series resistance (R_s), is attributed to the combination of charge transfer resistance of FTO/TiO₂ interface, the series resistance of FTO/CE interface and resistance of the external circuit. All the EIS parameters are extracted from the equivalent circuit and tabulated in the Table 6.

As it is evident from the Table 6, even though the DSSC fabricated with the Pt CE showed the lowest values for all the interfacial



Fig. 6. Current density-voltage characteristics of DSSCs with (a) pristine RGO CEs sintered at different temperatures, (b) pristine RGO CEs with different amounts of RGO used, (c) RGO/SnO₂ CEs with different SnO₂ amounts and (d) RGO/SnO₂/PANI composite CEs with RGO:PANI wt % ratio.

Photovoltaic parameters of DSSCs made with RGO CEs sintered at different temperatures for 45 min.

CE composition	Sintering temperature	J _{sc} /mA cm ⁻²	V _{oc} / mV	FF %	Efficiency %
RGO	150 °C	$\begin{array}{c} 15.30 \\ \pm \ 0.10 \end{array}$	$509.9 \\ \pm 1.2$	36.91 ± 0.22	$\textbf{2.87} \pm \textbf{0.04}$
	200 °C	$\begin{array}{c} 14.90 \\ \pm \ 0.20 \end{array}$	560.1 ± 1.3	$\begin{array}{c} 45.60 \\ \pm \ 0.25 \end{array}$	$\textbf{3.80} \pm \textbf{0.08}$
	250 °C	14.30 + 0.10	673.6 + 1.6	46.47 + 0.34	4.48 ± 0.06
	300 °C	14.20 + 0.10	$\frac{1}{660.5}$ + 1.4	45.48 + 0.28	4.26 ± 0.07
	350 °C	$\begin{array}{c} 14.40 \\ \pm \ 0.20 \end{array}$	$\begin{array}{c} 581.9 \\ \pm \ 1.8 \end{array}$	$\begin{array}{c} 46.98 \\ \pm \ 0.30 \end{array}$	$\textbf{3.94} \pm \textbf{0.05}$

resistances, DSSC fabricated with the optimized RGO/SnO₂/PANI composite CE are comparable with them. The lowest $R1_{CT}$ value of 4.80 Ω can be seen for the Pt/electrolyte interface. The (RGO/SnO₂/PANI) CE /electrolyte interface shows higher $R1_{CT}$ value of 15.28 Ω . This could be due to the higher resistivity of the composite CE compared to Pt.

Generally, the power conversion efficiency and the fill factor of DSSCs made with Pt-based CEs exhibit better photovoltaic performance

Table 2

Photovoltaic	parameters	of	DSSCs	based	on	RGO	CEs	with	different	RGO
amounts sint	ered at 250 °	Ca	ind used	d to pre	par	e the	CEs.			

CE composition	Amount of RGO used (mg)	J _{sc} ∕mA cm ^{−2}	V₀c∕ mV	FF %	Efficiency %
RGO sintered at 250 °C	5	16.60 ± 0.30	$567.0 \\ \pm 1.1$	$\begin{array}{c} 30.42 \\ \pm \ 0.32 \end{array}$	$\textbf{2.86} \pm \textbf{0.10}$
	10	$\begin{array}{c} 14.30 \\ \pm \ 0.20 \end{array}$	$\begin{array}{c} 673.6 \\ \pm \ 1.3 \end{array}$	46.47 ± 0.24	$\textbf{4.48} \pm \textbf{0.08}$
	15	15.90 ± 0.20	707.3 ± 1.2	41.79 ± 0.28	4.70 ± 0.08
	20	$\begin{array}{c} 12.40 \\ \pm \ 0.10 \end{array}$	$\begin{array}{c} 730.4 \\ \pm \ 1.0 \end{array}$	$\begin{array}{c} 41.05 \\ \pm \ 0.30 \end{array}$	$\textbf{3.72}\pm\textbf{0.05}$

compared to the DSSCs made with the composite CE, very likely due to the high electrical conductivity and high electro-catalytic nature of Pt. A lower $R_{\rm s}$ corresponds to a higher conductivity of the catalytic CE and better fill factor of the DSSC.

Fig. 8(D) shows the Nyquist plots of DSSCs made with TiCl₄ treated TiO₂ photoanode and Table 6(c) and (d) summarizes all the corresponding EIS parameters obtained by fitting the spectra with the equivalent circuit diagram, shown in the inset of the figure. It can be

Photovoltaic parameters of DSSCs made with RGO/SnO2 composite CEs with added amounts of SnO2 colloidal solution.

CE composition	RGO amount used (mg)	SnO ₂ amount used (ml)	$J_{\rm sc}/{ m mA~cm^{-2}}$	V _{oc} / mV	FF %	Efficiency %
RGO/SnO ₂ sintered at 250 °C	15	0	15.90 ± 0.10	$\textbf{707.3} \pm \textbf{1.2}$	41.79 ± 0.42	$\textbf{4.70} \pm \textbf{0.08}$
		0.5	15.70 ± 0.20	643.7 ± 1.3	52.52 ± 0.20	5.31 ± 0.09
		1.0	16.80 ± 0.20	655.9 ± 1.1	56.66 ± 0.25	6.25 ± 0.09
		1.5	16.40 ± 0.30	$\textbf{675.4} \pm \textbf{1.2}$	50.97 ± 0.28	5.64 ± 0.05

Table 4

Photovoltaic parameters of DSSCs made with RGO/SnO₂/PANI composite CEs with added amounts of PANI wt% relative to RGO weight.

RGO:PANI wt ratio	J _{sc} /mA cm ⁻²	V _{oc} / mV	FF %	Efficiency %
1:0	16.80 ± 0.20	655.9 ± 1.1	56.66 ± 0.25	6.25 ± 0.09
1:1	$\textbf{17.10} \pm \textbf{0.10}$	$\textbf{676.9} \pm \textbf{1.4}$	58.98 ± 0.23	6.83 ± 0.07
1:2	17.20 ± 0.30	$\textbf{674.8} \pm \textbf{1.0}$	62.26 ± 0.14	7.22 ± 0.15
1:4	18.60 ±	708.0 ±	63.13 ±	7.92 ± 0.09
	0.10	1.3	0.10	
1:6	$\textbf{17.80} \pm \textbf{0.30}$	691.1 ± 1.1	60.01 ± 0.45	$\textbf{7.38} \pm \textbf{0.08}$
1:8	$\textbf{17.40} \pm \textbf{0.20}$	$\textbf{672.4} \pm \textbf{1.4}$	55.63 ± 0.23	6.51 ± 0.07
1:10	15.50 ± 0.30	$\textbf{664.6} \pm \textbf{1.3}$	58.39 ± 0.24	$\textbf{6.02} \pm \textbf{0.12}$



Fig. 7. Variation of DSSC efficiency with RGO:PANI weight % in the RGO/SnO $_2$ /PANI composite counter electrode.

Table 5

Photovoltaic parameters of DSSCs made with $RGO/SnO_2/PANI$ composite CE and Pt CE with and without $TiCl_4$ treated TiO_2 photoanode.

Photoanode	CE Composition	J _{sc} ∕mA cm ^{−2}	V _{oc} / mV	FF %	Efficiency %
TiO ₂	(a) RGO/ SnO ₂ /PANI (b) Pt	$\begin{array}{c} 18.60 \\ \pm \ 0.10 \\ 17.00 \\ \pm \ 0.20 \end{array}$	$708.0 \\ \pm 1.3 \\ 769.2 \\ \pm 1.0$	$\begin{array}{c} 63.13 \\ \pm \ 0.10 \\ 64.93 \\ \pm \ 0.20 \end{array}$	$\begin{array}{c} 7.92\pm0.09\\ 8.50\pm0.07\end{array}$
TiCl₄ treated TiO2	(c) RGO/SnO ₂ / PANI (d) Pt	$\begin{array}{c} 19.20 \\ \pm \ 0.10 \\ 17.80 \\ \pm \ 0.10 \end{array}$	$728.2 \\ \pm 1.1 \\ 762.6 \\ \pm 1.2$	$\begin{array}{c} 62.12 \\ \pm \ 0.10 \\ 67.94 \\ \pm \ 0.10 \end{array}$	$\begin{array}{l} 8.68\pm0.08\\ 9.22\pm0.08\end{array}$

seen clearly in Fig. 8(D) and the Table 6, that the R_s value is enhanced after the TiCl₄ treatment. This may be due to the increase in crystalline defect concentration of the photoanode. However, the R_{1CT} and R_{2CT} values are slightly decreased compared to the photoanode without TiCl₄ treatment. As expected, 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 (M. Sharif et al., 2019; Nath et al., 2015).

3.5. Cyclic voltammetry analysis

In order to study the electrochemical behaviors of RGO, RGO/SnO₂, RGO/SnO₂/PANI and Pt CEs, cyclic voltammetry (CV) measurements were carried out on them.

Cyclic voltamograms of each CE type were recorded using a iodide based liquid electrolyte with the scan rate of 20 mV s⁻¹ by applying a sweep potential between -0.5 V and 1.2 V (vs Ag/AgCl). Ag/AgCl electrode was used as the reference electrode and Pt rod was used as the counter electrode in CV measurements. CEs made with RGO, RGO/SnO₂, RGO/SnO₂/PANI and Pt were used as the working electrodes one at a time with the active surface area of 1.0 cm^2 . Two distinctive sets of peaks related to oxidation and reduction reactions were observed in the cyclic volatmmograms of each type of CE structure. Cyclic voltammograms obtained for above CEs are shown in Fig. 9(A) and the important parameters extracted from them are tabulated in Table 7.

The negative side of the Y-axis in cyclic voltammogram is assigned to the reduction reaction and the positive side is assigned to the oxidation reaction corresponding to the Eqs. (1) and (2) given below (Mohan et al., 2019; Sun et al., 2018).

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

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

The catalytic activity of the CE is quantitatively described by the peak current densities (J_{ox} and J_{red}) and the peak-to-peak separation (ΔE_p) of the potential difference between the reduction and oxidation peaks of the redox couple ($2I_3^-/I^-$). Superior electro-catalytic behavior of the CE is indicated by a higher peak current density and a lower ΔE_p value, although, the electrical conductivity of the CE material is directly correlated with the oxidation and reduction peak current. It can be seen that the RGO/SnO₂ composite CE has anodic peak current density (J_{ox}) of 0.98 mA cm⁻², which is higher compared to the value of 0.53 mA cm⁻² obtained for the pristine RGO CE, illustrating that improved catalytic activity of the RGO/SnO2 composite CE towards the tri-iodide reduction compared to that of the pristine RGO CE. The RGO/SnO₂/ PANI composite CE shows the highest J_{ox} value of 1.10 mA cm⁻² which corresponds to the highest J_{sc} value of 19.2 mA cm⁻² of the DSSC fabricated with this CE. In comparison, the J_{ox} obtained for the Pt CE is 0.67 mA cm⁻². Similar enhancement in J_{0x} were reported by Mohan et al. (Mohan et al., 2019) and He et al. (He et al., 2014) for the composite CEs made from RGO with different structures of PANI. Similarly, as depicted in Table 7, Jred of RGO/SnO2 CE was slightly higher (-0.67 mA cm⁻²) compared to that of the pristine RGO CE. For the RGO/SnO₂/ PANI composite CE the highest J_{red} value obtained is -1.24 mA cm⁻¹ This may be due to the thicker porous structure of the RGO/SnO₂/PANI layer with higher effective specific surface area compared to the Pt and other two composite CEs.

Generally, the magnitude of the peak-to-peak separation (ΔE_p) , which is the difference between the anodic and cathodic peak potentials, is correlated with the electrocatalytic ability of the CE and lower ΔE_p values are associated with superior electrocatalytic ability as already mentioned earlier. According to the values shown in Table 7, the RGO/SnO₂/PANI composite CE has the lowest ΔE_p value of 0.20 V, which is better than that of Pt CE (0.21 V). The RGO/SnO₂ composite electrode



Fig. 8. (A) Current density vs photovoltage characteristics of DSSCs with RGO/SnO₂/PANI composite CE and Pt CE, (B) EIS spectra of the DSSC made with two different CEs, Platinum and RGO/SnO₂/PANI composite, (c) current density vs photovoltage characteristics of DSSCs with TiCl₄ treated TiO₂ photoanode and Pt CE, RGO/SnO₂ /PANI composite CE, (b) EIS spectra of the DSSCs made with TiCl₄ treated TiO₂ photoanode and two different counter electrodes.

 $R_{\rm s}$, $R1_{\rm CT}$ and $R2_{\rm CT}$ data extracted from EIS spectra of Fig. 8(B) and Fig. 6(D) using the equivalent circuit model for DSSCs fabricated with and without TiCl₄ treatment of TiO₂ photoanode and different types of counter electrodes used in this work.

Photoanode	CE Composition	Rs (Ω)	$R1_{ m CT}\left(\Omega ight)$	$R2_{ m CT}\left(\Omega ight)$
TiO ₂	(a) RGO/SnO ₂ /PANI	25.00	15.28	38.80
	(b) Pt	13.20	4.80	23.51
TiO ₂ treated with TiCl ₄	(c) RGO/SnO ₂ /PANI	45.80	13.60	26.18
	(d) Pt	14.80	3.15	22.14

has an intermediate ΔE_p value of 0.32 V which is lower than that of pristine RGO CE (0.52 V). Therefore, from this CV study, it can be clearly seen that the incorporation of catalytically active PANI in RGO/SnO₂ composite CE can significantly enhance the oxidation and reduction kinetics of triiodide ions. Additionally, the area inside the curve has also increased for the RGO/SnO₂/PANI composite CE which could be due to the electrochemical double layer capacitive behavior shown by high effective surface area of the RGO based composite (Mohan et al., 2019).

The ΔE_p value of the CV measurements was obtained from the peakto-peak separation of oxidation-1 and reduction-1 peaks. Peak positions for calculation of ΔE_p were identified by the numerical values of the current density values, and not by using the graph especially due to the oxidation-1 peak is not clearly visible in the graph.

To find the relationship between increased active sites and diffusion of iodide in the RGO/SnO₂/PANI composite CE, Randles-Sevcik theory mentioned by Eq. (3) can be used.

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

where, J_{Red} is the peak current density of reduction-1 (RED-1) (mA cm⁻²), *K* is a constant (2.69 × 10⁵), *n* (=2) is the number of electrons involved in the charge transfer process, *A* is the area of the electrode (cm²), *C* is the bulk concentration of triiodide species (mol⁻¹ L⁻¹), D_n is the diffusion coefficients of triiodide ions and *v* is the applied scan rate. The calculated diffusion coefficients of triiodide ions at different counter electrodes are listed in Table 7. According to the results in Table 7 the highest value of the diffusion coefficient, 13.31×10^{-5} cm² s⁻¹, was obtained for the RGO/SnO₂/PANI composite CE. The highest J_{ox} and J_{Red} values and smallest $E_{\text{PP}} \Delta E_{\text{P}}$ value and highest D_n value for RGO/SnO₂/PANI CE demonstrate the highest electrocatalytic activity of the composite counter electrode. The RGO/SnO₂ composite CE also showed a relatively higher D_n value of 3.95×10^{-5} cm² s⁻¹ compared to the



Fig. 9. (A) Cyclic voltammograms of (A) RGO, RGO/SnO₂ and RGO/SnO₂/PANI composite CEs, and (B) RGO/SnO₂/PANI counter electrode for 20 cycles at a scan rate of 20 mVs⁻¹.

Table 7					
Electrochemical parameters of different	nt counter	electrodes	obtained	from	C/
measurements.					

Counter Electrode	J _{Ox} /mA cm ⁻²	J _{Red} /mA cm ⁻²	${\Delta E_{ m p}}/{V}$	$D_n (\times 10^{-5})/ \text{ cm}^2 \text{ s}^{-1}$
RGO	0.53	-0.66	0.52	3.83
RGO/ SnO ₂	0.98	-0.67	0.32	3.95
RGO/ SnO ₂ /PANI	1.10	-1.24	0.20	13.31
Pt	0.67	-0.52	0.21	2.38

pristine RGO CE (3.83×10^{-5} cm² s⁻¹) and the lowest D_n value was obtained for the Pt CE due to lowest J_{red} value. These results support the presence of enhanced active sites in the RGO/SnO₂/PANI matrix capable of reducing I_3^- ions and accelerating the charge transfer within the RGO/SnO₂/PANI composite CE (He et al., 2014; Mohan et al., 2019).

In order to examine the electrochemical stability of the RGO/SnO₂/ PANI composite CE, preliminary studies were carried out by obtaining cyclic voltammograms with for 20 cycles with the same scan rate of 20 mVs⁻¹, and results are shown in Fig. 9(B). As it can be seen from the curve's noticeable changes in the peak positions cannot be seen. Therefore, RGO/SnO₂/PANI composite CE seems to be a good candidate to be used in DSSCs as a counter electrode.

3.6. Electrochemical analysis of counter electrodes (CEs) by EIS and Tafel plots

To understand the charge transfer process at the counter electrode/ electrolyte interface, Electrochemical Impedance Spectroscopy (EIS) experiments were carried out for two different counter electrodes with symmetrical dummy cells fabricated with two identical electrodes with active cell area of 1.0 cm^2 . The Nyquist plots obtained are shown in Fig. 10(A) and the corresponding Randles circuit used to fit the Nyquist curves is present in the inset of the graph. Due to the poor clarity of the Nyquist plot taken with the Pt CE, an enlarged plot is shown in the inset of the Figure. The typical Nyquist plot shows a well-defined semicircle with a half curve. This semicircle can be attributed to charge transfer resistance (R_{ct}) and the corresponding constant-phase element of the electrolyte/electrode interface. The other part of the curve represents the Nernst diffusion impedance (Z_w) of the electrolyte. The series resistance (R_s), mainly composed of the bulk resistance of the CE material, the resistance of the FTO layer and the contact resistance of the FTO/electrode, is also included in the equivalent circuit and can be obtained from the intercept on the real axis (He et al., 2014; Sun et al., 2018). Herein we mainly focus on the R_s and R_{ct} values that corresponds to the RGO/SnO₂/PANI composite CE and Pt CE as listed in Table 8.

According to the Table 8 the $R_{\rm s}$ and $R_{\rm ct}$ values for RGO/SnO₂/PANI CE are 24.30 Ω and 23.50 Ω respectively, which are much higher than those for Pt CE (2.45 Ω , 1.01 Ω . The low $R_{\rm ct}$ means that the Pt CE facilitates the transfer of electrons, thereby improving the photovoltaic performance of DSSCs compared to the composite CE.

The Bode plot obtained from EIS measurement also provides more information about the reaction speed of I_3^- reduction at the counter electrode/electrolyte interface. Fig. 10(B) shows the Bode plots for the symmetric cells with two different CEs. The electron lifetime (τ) can be calculated using the Eq. (4),

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

Here f_{max} is the peak frequency in the Bode phase plot (Di et al., 2018; He et al., 2015). τ values for the two different CEs are listed in Table 8. Generally, a smaller τ value represents a faster reaction process of I_3^- reduction. The lower τ value of 13.01 µs obtained for Pt CE compared with the value of 97.52 µs obtained for the RGO/SnO₂/PANI CE confirms the relatively better electrocatalytic activity of the Pt CE.

Additionally, Tafel polarization studies can be used to evaluate the catalytic activity of the newly developed CE. 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 where the voltage is a linear function of log *J*. The curve at low potential region is the polarization zone arising from the electrochemical reactions.

The exchange current density (J_0) is 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 (Xu et al., 2020). 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. The J_0 can be calculated from the polarization region, while J_{lim} can be measured from the diffusion. The magnitude of J_0 represents the rate of the



Fig. 10. (A) Nyquist plots, (B) Bode phase plots and (C) Tafel polarization curves for symmetric cells with RGO/SnO₂/PANI composite CE and Pt CE.

 Table 8

 Electrochemical parameters of different electrodes extracted from EIS measurements and Tafel plot measurements.

Counter electrode	$R_{\rm s}(\Omega)$	R _{ct} (Ω)	τ/μs	log J ₀ /mA cm ⁻²	log J _{lim} /mA cm ⁻²
RGO/ SnO ₂ / PANI	24.30	23.50	97.52	1.00	1.80
Pt	2.45	1.01	13.01	1.81	1.93

reduction of triiodide ions at the catalytically active surface of CE. Therefore, the J_0 is directly correlated with the number of active catalytic sites present in the CE (Mohan et al., 2019). Table 8 summarizes the J_0 and J_{lim} values for the RGO/SnO₂/PANI composite and Pt CEs. As shown in Fig. 10(C) and Table 8, the values of J_0 are 1.00 mA cm⁻² for the RGO/SnO₂/PANI CE and 1.81 mA cm⁻² for the Pt CE. These values are also in general agreement with the relationship between R_{ct} and J_0 expressed 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 Eq. (5), J_0 is inversely proportional to $R_{\rm ct}$ and therefore, the results obtained from EIS and Tafel Plots agree with each other; that is the higher J_0 and $J_{\rm lim}$ are in agreement well with lower resistance in result of EIS measurements done for CEs (Wei et al., 2019b). The low log J_0 value of 1.00 mA cm⁻²

for the RGO/SnO₂/PANI composite CE represents a lower conductivity in comparison with the Pt CE (1.81 mA cm⁻²). Du et al. (Du et al., 2015) and Wei et al. (Wei et al., 2019b) have also reported the similar J_0 and J_{lim} values for Pt CE as estimated in this study. Similar values for Pt counter electrodes were also observed by Du et al (1.2 mA cm⁻²) (Du et al., 2015) and Wei et al (2.0 mA cm⁻²) (Wei et al, 2019b)

However, form this study one can conclude that RGO/SnO₂/PANI composite CE has a great ability to trigger the reduction of triiodide ions at the electrolyte/CE interface though it cannot outperform the Pt CE. The photovoltaic performance of the DSSCs made with the RGO/SnO₂/PANI composite CE and the Pt CE is in agreement with results obtained from CV, EIS and Tafel polarization measurements.

A comparison of efficiencies of several DSSCs fabricated with RGO based CEs, reported by other groups in the literature with their preparation methods, sintering temperatures and the type of the electrolyte used is given in Table 9. Efficiencies of the DSSCs based on Pt CE in these studies are also shown for comparison. Results of the present work based on RGO/SnO₂/PANI CE are included in the last row. To the best of our knowledge, there are no previously published reports on the performance of DSSCs made with this novel and low-cost RGO/SnO₂/PANI composite counter electrode.

In a study on the development of composite anode materials for lithium-ion batteries, a comparison of the specific surface areas of SnO₂, RGO/SnO₂ and RGO/SnO₂/PANI composites has shown that out of these three materials RGO/SnO₂/PANI composite had the highest specific surface area of 167.2 $m^2 g^{-1}$ compared to other two materials. Also, the electronic conductivity of RGO/SnO₂/PANI composite was greatly enhanced compared to pure SnO₂ and RGO/SnO₂ (Liu et al., 2016). In

Comparison of the performance of RGO based counter electrodes reported in literature with the present work.

CE material	Binder	Preparation method	Sintering temperature	η of DSSC made with RGO CE (%)	η of DSSC made with Pt CE (%)	Redox Electrolyte	Ref & Year
RGO	Poly ethylene glycol	Doctor-blade method	450 $^\circ\text{C/5}$ min	Grinded RGO- 7.19 Ultrasonicated RGO- 5.31	7.76	Г/І3	-
PANI/ Graphene	N/A	Aniline-graphene polymerized and CV	Dried at 60 °C for 24 h	7.7 %	N/A	I ⁻ /I ₃ ⁻	(He et al., 2014)
RGO/SnO2	N/A	N/A	200 °C/12 h	6.78	7.22	Γ/I_3	(Du et al., 2015)
PANI/RGO	N/A	Tape casting method	Dried at 60 °C for 10 min	3.02	3.70	Γ/I_3	(Mohamed et al., 2018)
PANI NT/ RGO	Nafion	Doctor blade method	80 °C	5.47	5.54	I'/I ₃	(Mohan et al., 2019)
GO/SnO_2	N/A	Doctor blade method	Dried at 60 °C for 30 min	4.57	N/A	I ⁻ /I ₃ ⁻	(Mahmoud et al., 2019)
RGO/SnO ₂ / PANI	Triton X-100	Spray method	250 °C/45 min	8.68	9.22	Γ/Ι ₃ -	This work

another similar study where the composite structure was prepared by anchoring SnO_2 nanoparticles on PANI nanosheets@RGO layers, it was established that this three component structure not only enhanced the electronic conductivity of the electrode, but also lead to stabilize and enhance its electrochemical performance by providing more reactive sites on the surface (Liang et al., 2011). Similarly, in the case of the DSSCs fabricated with the RGO/SnO₂/PANI composite counter electrodes in this work, we can anticipate a similar environment where the redox reactions become faster and more efficient due to the enhanced electronic conductivity, improved electrocatalytic activity and the increased number of redox reaction sites.

4. Conclusion

In summary SnO₂ nanoparticles and PANI decorated RGO based composite counter electrodes were successfully fabricated by using a simple spray technique for applications in dye-sensitized solar cells. This low-cost preparation method was used to fabricate a porous composite structure with improved interconnections and pathways for improved electrocatalytic effect for triiodide ion reduction at the CE. The power conversion efficiency of pristine RGO CE was increased from 4.70% to 6.25% by introducing SnO₂ nanoparticle to the RGO matrix. This improvement in efficiency can be associated with the increased porous structure of the composite and the improved adhesion due to the presence of SnO₂. After introducing the PANI conducting polymer to the RGO/SnO2 matrix the performance of DSSCs was further enhanced reaching an efficiency value as high as 7.92%. After the TiCl₄ treated TiO₂ photoanode was used, the maximum power conversion efficiency of the RGO/SnO₂/PANI composite CE based DSSC was 8.68%, which is 94% of the efficiency of 9.22% obtained for the control DSSC made with Pt CE and TiCl₄ treated photoanode. The optimized composite CE structure demonstrated the best photovoltaic performance combined with low charge transfer resistance and good efficient electron transport. According to the CV measurements, EIS and Tafel plots for symmetrical CEs, the composite structure exhibits excellent electrocatalytic activity towards the reduction of tri-iodide ions at the electrolyte/CE interface. The study presented here shows that the new RGO/SnO2/PANI composite CE to be a strong candidate for the fabrication of low cost 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 providing research support under Sri Lanka-Pakistan

collaboration grant No. NSF-PSF/ICRP/2017/EA&ICT/04.

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