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Fabrication of Graphite/Tin Oxide/Polyaniline Composite Counter Electrode for Application in Dye-Sensitized Solar Cells

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Abstract. Dye-sensitized solar cells (DSSCs) can serve as an alternative to fossil fuels for energy production, with advantages including a simple fabrication process and environmental friendliness. However, the counter electrodes (CEs) of DSSCs are generally fabricated from platinum (Pt), which causes high production costs. Therefore, low-cost alternatives to Pt-based CEs are being sought. Carbon-based materials and conducting polymers offer lower cost, high chemical stability and high electro-catalytic behavior. Although these materials have some drawbacks, composites can function well. In this study, composite CEs consisting of Sri Lankan natural graphite, tin oxide nanoparticles and polyaniline conducting polymer were prepared by spray technique. The CEs were characterized by X-ray diffraction, Raman spectroscopy and scanning electron microscopy, and the excellent catalytic activity of the composite CE was demonstrated by cyclic voltammetry analysis. The composite CE-based DSSCs showed good stability and satisfactory performance compared with Pt CE-based DSSCs.

INTRODUCTION

Dye-sensitized solar cells (DSSCs), first reported by O'Regan and Grätzel in 1991 [1], are a type of electrochemical device that converts solar energy directly into electricity. A typical DSCC structure includes three major components: a dye-adsorbed titanium dioxide (TiO_2) photoanode, a redox electrolyte, and a counter electrode (CE). The CE plays a key role in regulating the performance of a DSSC as a catalyst for the redox couple regeneration and the electron collector from the external circuit.

Generally, platinum (Pt) deposited on fluorine-doped tin oxide (FTO) conductive glass is used as the CE owing to its excellent electro-catalytic activity for the triiodide reduction, high electrical conductivity and good chemical stability. However, because of the high cost and chemical degradation of Pt in the corrosive iodine environment of the DSSC, more cost-effective, electrolyte-resistant and earth-abundant alternatives for CEs are needed for DSSC applications [2].

Various potential alternative materials have been investigated as replacements for Pt in CEs, including low-cost carbon-based materials. However, the development of carbon-based CEs has been hindered by low adhesion to the conducting substrate, which results in low redox performance and low charge-transfer ability, among other problems. To overcome the problems, we developed a CE fabricated by spray technique, using a composite based on Sri Lankan natural graphite. Sri Lankan natural graphite has a good demand owing to its high purity and the high crystallinity required for many high-tech applications.

Our group recently reported on a graphite/SnO_2 composite-based CE for DSSCs [3]. Tin oxide (SnO_2) nanoparticles improved the adhesion of graphite on an FTO-conducting substrate. In the current study, different

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amounts of polyaniline (PANI) conducting polymer were introduced as an additional component in graphite/SnO_2 composite. PANI conducting polymer is widely used for DSSC applications as an electrolyte material [4] and as a CE material [5], owing to its facile synthesis, relatively high electronic conductivity, electro-catalytic activity and low cost.

The photovoltaic performance of DSSCs based on the novel CE was found to be significantly influenced by the addition of SnO_2 nanoparticles and PANI conducting polymer. The power conversion efficiency of DSSCs improved from 4.38% for the pristine graphite-based CE to 5.58% for the graphite/SnO_2 CE. At the optimum composition, the graphite/SnO_2/PANI composite CE was associated with a power conversion efficiency of 6.97%.

METHODOLOGY

Graphite/SnO_2/PANI composite CEs were prepared by spray technique. A spray solution was prepared by mixing graphite, SnO_2 nanoparticles, PANI conducting polymer, acetic acid, Triton X-100 and ethanol. The solution was sonicated for 1 hour before being sprayed on FTO glass substrate kept at 100°C. Finally, the glass substrate was sintered at 250°C for 45 minutes in a muffle furnace.

The photoanode was prepared by applying two successive layers of TiO_2 to conducting glass substrate [6]. For the first layer, P90 TiO_2 powder was mixed with 0.1 M HNO_3 to form a paste. A cleaned FTO glass substrate was then coated with this paste by spin coating technique. For the second layer, a creamy paste was prepared by mixing P25 TiO_2 powder with 0.1 M HNO_3, Triton X-100 and PEG 2000. This paste was doctor bladed onto the P90 TiO_2 layer and sintered at 450°C for 45 minutes to obtain a porous TiO_2 layer. After cooling to room temperature, the photoanode was immersed in Ru N719 dye for 24 hours.

A DSSC was fabricated by sandwiching the liquid electrolyte in between the dye-attached TiO_2 photoanode and the graphite/SnO_2/PANI composite CE. The liquid electrolyte was made by mixing 0.6 M 1-methyl-3-propylimidazolium iodide ionic liquid, 0.03 M iodine, 0.1 M guanidinium thiocyanate, 0.5 M 4-tert-butylpyridine and acetonitrile.

RESULTS AND DISCUSSION

The X-ray diffraction (XRD) spectrum shown in Fig. 1a was obtained for graphite/SnO_2/PANI composite material. The diffraction peaks of crystalline graphite and SnO_2 nanoparticles are clearly distinguishable. The peaks at 2θ = 26.5°, 44.5°, and 54.6° indicate (002), (101), and (004) crystal planes of graphite (JCPDS card no: 75-1621), respectively [7]. The peaks at 2θ = 33.8°, 37.8°, 54.4°, and 65.5° correspond to (101), (200), (211), and (301) planes of SnO_2, respectively (JCPDS card no: 41-1445) [8]. However, peaks corresponding to PANI conducting polymer are not clearly visible as they may overlap with graphite and SnO_2 XRD peaks.

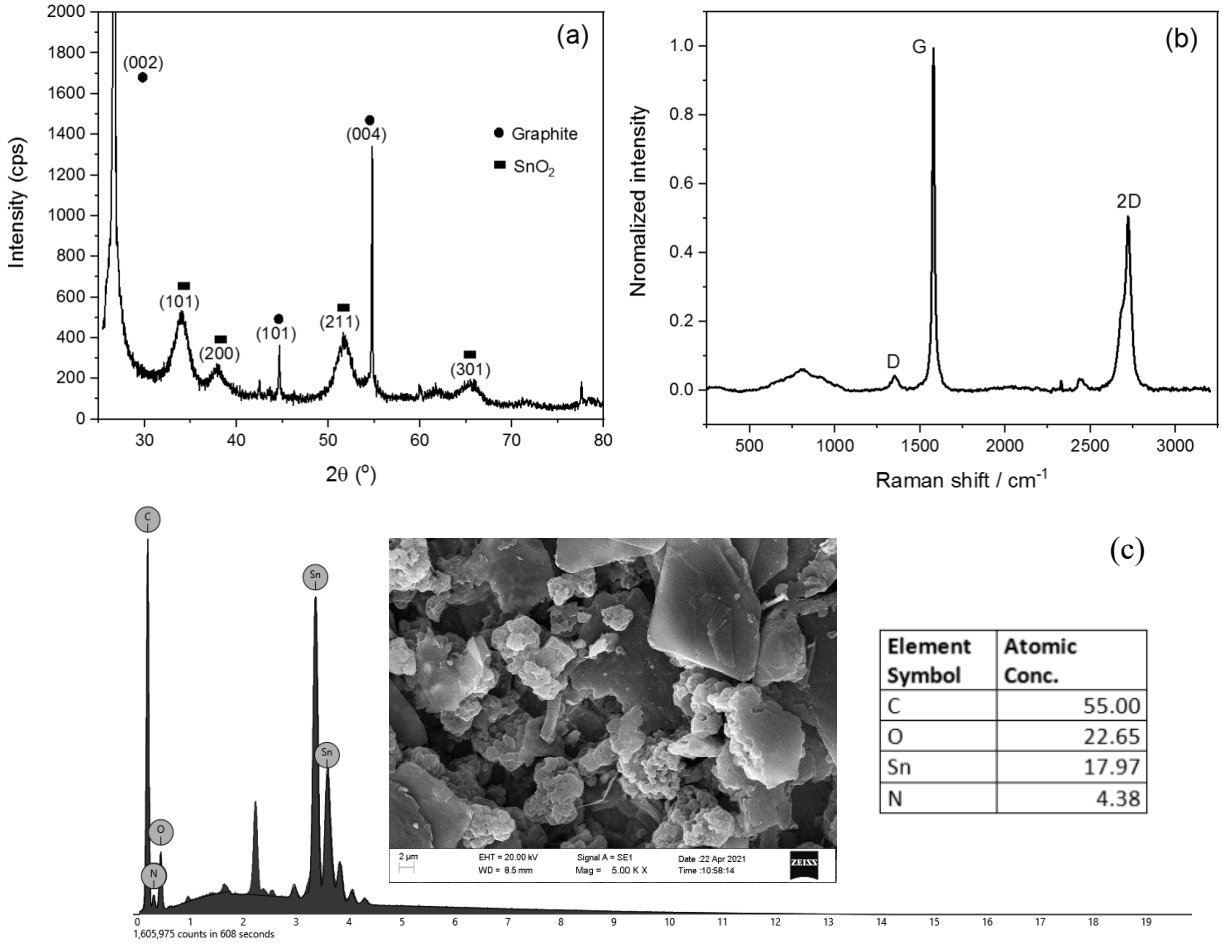
The Raman spectrum of graphite/SnO_2/PANI composite material is presented in Fig. 1b. The major peaks correspond to graphite, which is indicated by a strong G-band at 1,579 cm^{-1} arising from the in-plane C-C bond stretching in the graphitic materials. The G-band is related to the vibration mode of the sp2 graphitic structure. The D-band at 1,352 cm^{-1} corresponds to the degree of disorder, and the 2D-band is assigned to the second order of the D-band in graphite at 2,722 cm^{-1} [9].

Figure 1c exhibits the scanning electron microscopy (SEM) image of surface morphology of the graphite/SnO_2/PANI composite CE. The composite film clearly has a porous structure with good contact for better adhesion onto the FTO glass substrate. The surface components of the prepared graphite/SnO_2/PANI composite CE are further confirmed by the X-ray energy dispersive spectrum (SEM EDS). The inset table shows the amounts in atomic concentration of C, O, Sn, and N as 55.00%, 22.65%, 17.97% and 4.38%, respectively.

The current density-voltage (J-V) characteristics of the fabricated DSSCs with different CEs were studied under light irradiation of 100 mW cm^{-2}. Photovoltaic performance was assessed for a pristine graphite CE, a graphite/SnO_2 composite CE and a graphite/SnO_2/PANI composite CE (Fig. 2a). The CE made of graphite/SnO_2/PANI composite was also compared with the sputtered Pt plate used as a CE. The photovoltaic performances of the DSSCs using the different CEs are summarized in Table 1. Notably, important solar cell parameters, mainly the open circuit voltage (V_{oc}), fill factor (*FF*), and the efficiency, were increased with incorporation of SnO_2 and PANI into graphite. The short circuit current density (J_{sc}) also slightly improved for graphite/SnO_2/PANI composite CE compared to pristine graphite-based CE.

Cyclic voltammetry measurements were performed to investigate the electrochemical behavior of graphite/SnO_2/PANI composite CE. The characteristic plots obtained for the optimized CE were recorded using an

iodide-based liquid electrolyte with the scan rate of 10 mV s^{-1} by applying a sweep potential from −1.0 V to 1.0 V. A silver/silver chloride electrode was used as the reference electrode, and a Pt rod was used as the CE. Each of the prepared composite CEs was used as the working electrode with an active surface area of 1.0 cm^2. Figure 2b shows the cyclic voltammetry analysis graphs for the composite CE and Pt CE. Two distinctive sets of peaks related to oxidation and reduction reactions were observed for both CEs confirming the excellent electro-catalytic activity towards the I^-/I_3^- redox reaction of the electrolyte.



Element Symbol	Atomic Conc.
C	55.00
O	22.65
Sn	17.97
N	4.38

FIGURE 1. (a) XRD and (b) Raman spectra of graphite/SnO_2/PANI composite material. (c) SEM surface image of graphite/SnO_2/PANI composite CE and the EDS mapping graph by EDS spectroscopy (used with the permission of the SEM imaging facility of the Department of Geology, University of Peradeniya, Sri Lanka).

CONCLUSION

We successfully used a spray method to fabricate graphite CEs incorporating SnO_2 nanoparticles and PANI for applications in DSSCs. This simple and low-cost preparation method enabled formation of a porous structure with improved catalytic effect for triiodide ion reduction at the CE. The energy conversion efficiency of the DSSC made with the composite CE was 77% of that of the DSSC with a Pt-based CE under similar conditions.

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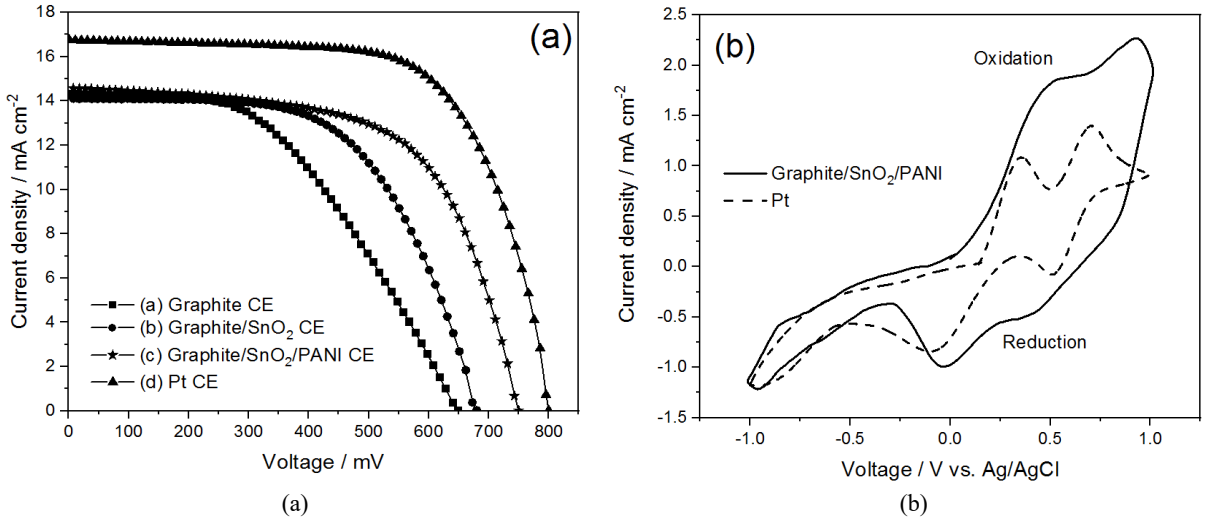

(a) (b)

FIGURE 2. (a) Current density versus photo voltage characteristics of DSSCs with different CEs. (b) The cyclic voltammetry graphs of the graphite/SnO_2/PANI composite CE, in a three-electrode arrangement using a 10 mV s^{-1} scan rate.

TABLE 1. Photovoltaic parameters of DSSCs with different CEs.

Counter Electrode	J_{sc} (mA cm^{-2})	V_{oc} (mV)	*FF* (%)	Efficiency (%)
Graphite	14.30	648.50	47.36	4.38
Graphite/SnO_2	14.10	682.30	59.11	5.58
Graphite/SnO_2/PANI	14.60	753.00	63.41	6.97
Pt	16.80	806.02	66.65	9.02

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