



## Pt-free spray coated reduced graphene oxide counter electrodes for dye sensitized solar cells



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### ABSTRACT

Graphene oxide (GO) was synthesized using a modified Hummers method and was reduced by using focused sunlight to obtain solar reduced graphene oxide (SRGO). GO and SRGO are then used as Pt-free counter electrode materials in dye sensitized solar cells (DSSCs). GO and SRGO counter electrodes were prepared by a simple spray coating method to produce homogeneous electrode layers. The DSSCs with GO and SRGO counter electrodes exhibited an overall power conversion efficiencies of ~3.4 and ~4%, respectively. Cyclic voltammetry and electrochemical impedance spectroscopy reveal that the DSSC with SRGO counter electrode exhibits higher electro-catalytic activity and lower charge transfer resistance at the electrode/electrolyte interface (in comparison to the DSSC with GO) resulting in higher conversion efficiency. Moreover, the microstructural features of SRGO are found to be suitable for its improved interaction with the liquid electrolyte and the enhanced electro-catalytic activity at its surface.

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### 1. Introduction

Grätzel cells or Dye Sensitized Solar Cells (DSSCs) (O'Regan and Grätzel, 1991; Grätzel, 2003; Imalka Jayawardena et al., 2013) are expected to challenge the performance of Si based solar cells and compete for a significant market share in next generation solar cells. This is owing to their good performance even under diffuse light (Cornaro and Andreotti, 2013), lower production costs, innate solution processability which allows easy fabrication of large area cells, and excellent unit price per performance metric which allows them to gain grid parity. A DSSC typically consists of a photo-anode, an electrolyte with redox species (such as iodide/tri-iodide ( $I^-/I_3^-$ ) in an organic solvent), and a counter electrode (CE). The anode consists of a transparent conducting oxide (TCO) coated glass substrate with a layer of mesoporous network of wide band gap metal oxide semiconductor, such as  $TiO_2$ , which is sensitized with a suitable dye. The redox couple in the electrolyte works as a mediator which transfers electrons from the cathode to the oxidized dye molecules (Wu et al., 2015).  $I^-$  ions reduce the sensitizer

and oxidize to  $I_3^-$  ions while the monovalent  $I^-$  ions are recovered at the cathode.

Commonly, platinum coated TCO glass substrate is used as the CE because of platinum's high catalytic activity and resistance to corrosion due to the electrolyte. However, due to platinum's high cost and low corrosion resistance to the iodide based electrolytes (Koo et al., 2006; Agresti et al., 2015), scientists have investigated alternative CEs and redox couple electrolytes other than iodide/tri-iodide ( $I^-/I_3^-$ ). These alternative electrolytes, such as anion doped PEDOT (Xia et al., 2008), have assisted in producing stable solid state DSSCs. Instead of Pt, a number of carbon based materials (Janani et al., 2015) including graphene related materials (Choi et al., 2011; Wang and Hu, 2012; Gong et al., 2012; Yeh et al., 2014; Zhu et al., 2015; Huo et al., 2016) have been tested as alternative CE materials which exhibited excellent conductivity and high electro-catalytic activity. Even though the efficiencies of DSSCs with graphene related materials (graphene obtained through electrophoretic deposition (Choi et al., 2011) and graphene with incorporation of  $SiO_2$  nanoparticles (Gong et al., 2012)) as CE materials are high (5.69% (Choi et al., 2011) and 4.04% (Gong et al., 2012)), the fabrication of devices involve complex process steps and therefore require optimization of a number

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of process parameters. In another important work (Yeh et al., 2014) the efficiency of DSSC with photothermal reduced graphene oxide (P-rGO) as CE was 7.62%, the method used for fabricating the final CE may not be suitable for realizing large area CEs. In the case of graphene based composites as CE materials in DSSCs, it is difficult to understand and control the electrochemical activity at the electrode/electrolyte interface. However, graphene ink (Casaluci et al., 2016) spray coated on FTO substrates was recently used as a CE in fabricating large-area DSSC modules via the spray coating technique. In this case, the electrochemical activity at the electrode/electrolyte interface could be easily explained. Additionally, using a CE composed of graphene nanoplatelets (GNP), in the structure FTO/Au/GNP, produced a DSSC with a record efficiency of over 14% (Kakiage et al., 2015), outperforming a similar FTO/Pt CE DSSC. In both cases, the electrolyte was a cobalt(III/II) tris(1,10-phenanthroline) complex ( $[\text{Co}(\text{phen})^{3+/2+}]$ ) transition metal redox couple system with  $\text{TiO}_2$  electrodes co-photosensitized with a strongly anchored alkoxy-silyl-dye (ADEKA-1) and a carboxy-organic dye (LEG4).

On the contrary to the above mentioned works, in this work we have demonstrated an easy fabrication process of robust DSSCs with graphene oxide (GO) and solar reduced graphene oxide (SRGO) as CE materials and nanocrystalline  $\text{TiO}_2$  photo-anode. The novel points of this work are: (i) integrating an excellent photo-anode (Susmitha et al., 2015) into DSSC, (ii) easy and renewable method of preparing CE materials without any metallic layer or in composite form, (iii) spray coating of CE materials facilitating the fabrication of large area CEs, (iv) energy conversion efficiency of  $\sim 4\%$  (without using Pt or any CE material in composite form), comparable to the values exhibited by DSSCs with graphene composites and (v) owing to the innate nature of the CE materials used in this work, the electrochemical activity at the electrode/electrolyte interface could be easily explained.

## 2. Experimental details

### 2.1. Preparation of nanocrystalline $\text{TiO}_2$ photo-anode

Photo-electrodes were fabricated by following a previously reported procedure (Susmitha et al., 2015) which is briefly given here for convenience. As-procured fluorine-doped tin oxide (FTO) conducting glass plates ( $7 \Omega/\text{square}$ , TCO22-7, Solaronix) were cleaned with a detergent solution and then rinsed sequentially with Millipore water, absolute ethanol and 2-propanol (Merck, Germany) to remove organic and other particulate contaminants. FTO glass plates were then dried under a nitrogen purge. Nanocrystalline titanium dioxide ( $\text{TiO}_2$ , anatase phase) layer was coated onto the FTO glass plates and then sintered. In order to make sure that the  $\text{TiO}_2$  layer has a good mechanical contact with the conducting FTO glass substrate,  $\text{TiO}_2$  coated plates were treated with a 40 mM titanium tetrachloride ( $\text{TiCl}_4$ ) solution at  $70^\circ\text{C}$ . A 43T mesh screen was used to produce  $\sim 12 \mu\text{m}$  thick  $\text{TiO}_2$  film using commercial 18 nm  $\text{TiO}_2$  colloidal paste (18NR-T, Dyesol) after sintering at  $500^\circ\text{C}$  for 30 min. Another 90T mesh screen was used to produce  $\sim 6 \mu\text{m}$  thick film of 200 nm scatter  $\text{TiO}_2$  paste (WER2-O, Dyesol). A post-deposition  $\text{TiCl}_4$  treatment was then undertaken, before sintering further at  $500^\circ\text{C}$  for 30 min. While cooling the electrodes to around  $110^\circ\text{C}$ , the electrodes were stained in purified cis-bis (isothiocyanato) bis (2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II)-bis-tetrabutylammonium dye solution (0.3 mM, N719), prepared in a mixture of tert-butanol/acetonitrile (1/1 v/v), for 18 h under dark conditions. The photo-electrode was subsequently withdrawn from the solution and rinsed twice with anhydrous acetonitrile to remove any unan-

chored dye molecules on the surface of the  $\text{TiO}_2$  film. The plates were finally dried under nitrogen purge.

### 2.2. Fabrication of GO and SRGO CEs

GO and SRGO were prepared using previously reported procedures (please see supporting information (SI) for details) (Gedela et al., 2015). 1 mg of GO (or SRGO) was then dispersed in 1 mL of iso-propanol (Merck, Germany) and the resultant solution was ultrasonicated for 30 min prior to spray coating the entire volume with a spray gun at 1 mL/min using pure  $\text{N}_2$  gas. To inject the electrolyte into the test cells, holes (0.1 mm diameter) were drilled into the FTO glass plates using a micro-tipped drill (DREMEL 300) with a diamond coated micro-drill bit. The FTO glass was washed sequentially with diluted detergent, 0.1 M HCl solution in ethanol, Millipore water, absolute ethanol and finally cleaned with iso-propanol in a sonicator for 30 min. The cleaned FTO glass substrate was placed on a hotplate at  $180^\circ\text{C}$  and the entire 1 ml of GO (or SRGO) solution was spray coated using a 0.3 mm micro-tip needle spray gun at  $1 \text{ mL min}^{-1}$  using pure  $\text{N}_2$  gas. The temperature  $180^\circ\text{C}$  was used during spray coating to ensure the evaporation of the solvent and good adhesion of the GO (or SRGO) to the FTO substrate. The heat treatment to a moderate temperature of  $380^\circ\text{C}$  after the coating is to increase the porosity of GO (or SRGO) for enhancing the adsorption of the electrolyte for improvement in electrochemical activity, which in turn enhances the efficiency of the DSSC. The spray coated GO or SRGO FTO glass substrate was then heated in a furnace at  $380^\circ\text{C}$  for 30 min to obtain FTO/GO and FTO/SRGO CEs.

### 2.3. Fabrication of DSSCs

The photo-anodes and CEs were assembled using thermal adhesive (25  $\mu\text{m}$ , Surlyn, Solaronix) as a spacer to produce a sandwich cell. The liquid electrolyte was prepared by mixing 1-butyl-3-methylimidazolium iodide (BMII, 0.5 M), lithium iodide (LiI, 0.1 M), Iodine ( $\text{I}_2$ , 0.05 M), guanidinetiocyanoate (GuNC, 0.1 M), and tert-butylpyridine (tBP, 0.5 M) in acetonitrile. The prepared electrolyte was injected through the hole drilled through the CE, before the holes were sealed with a cover glass using Surlyn. The fabricated DSSCs (Table 1) have an active area of  $\sim 0.36 \text{ cm}^2$ .

### 2.4. Electrochemical characterization and DSSC testing

Cyclic-voltammetry was used to understand  $\text{I}^- - \text{I}_3^-$  redox reaction occurring in the  $\text{LiClO}_4$  (0.1 M)/LiI (5 mM)/ $\text{I}_2$  (0.5 mM)/acetonitrile electrolyte solution at the CEs. A potentiostat (CHI608E instrument) in a three electrode configuration was used to measure the current at a scan rate of  $10 \text{ mV s}^{-1}$ . An  $\text{Ag}/\text{Ag}^+$  electrode (0.01 M  $\text{AgNO}_3$  in acetonitrile) was used as the reference electrode, and the  $\text{TiO}_2/\text{dye}$  complex was used as the working electrode. Electrochemical impedance spectroscopy (EIS) was performed in the frequency range of 0.1 Hz to 100 kHz on an electrochemical workstation (IVIUMSTAT, IVIUM technologies b.v.) at 10 mV and respective open circuit voltage.

To check the solar photovoltaic performance of the fabricated DSSCs, the current density-voltage characteristics were measured under the illumination of Xe arc solar simulator (PEC-L01, Pecell

**Table 1**  
Photo- and counter- electrode configurations.

Photo-electrode	Counter electrode	Cell name
FTO/ $\text{TiO}_2$ /N719	FTO/GO	GO-DSSC
FTO/ $\text{TiO}_2$ /N719	FTO/SRGO	SRGO-DSSC

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