Reduced graphene oxide on the performance of solid-state dye-sensitized solar cell

HH Foong, H Ahmad, CH Ting, CY Ng and HK Jun*

Department of Mechanical and Material Engineering, Lee Kong Chian Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, Sungai Long Campus, Bandar Sg. Long, 43000 Kajang, Malaysia.
*Email: junhkl1@gmail.com

Abstract. Dye-sensitized solar cell (DSSC) is a third generation solar cell which provides a good research platform for future photovoltaic technologies. DSSC can be categorized into two types based on the nature of its electrolyte, namely liquid and solid-state. In general, DSSC with liquid-based electrolyte has risk of electrolyte leakage. Therefore, the utilization of solid-state hole transport materials instead of liquid electrolytes can overcome the leakage issue of liquid-based DSSC. Despite of this advantage, the performance of solid-state dye-sensitized solar cell (SS-DSSC) is low compared to the cell that uses liquid electrolyte. To remedy this, doping with foreign materials is used to enhance the performance of the solar cell. Hence, this work focuses on the effect of reduced graphene oxide (RGO) on the performance of SS-DSSC utilizing TiO2 nanoparticles. The electrode samples were characterized with scanning electrode microscopy, energy dispersive spectroscopy, UV-Visible spectroscopy, IV test, and electrochemical impedance spectroscopy (EIS). By introducing RGO into SS-DSSC, the efficiency and fill factor was improved by at least 15%. Moreover, the presence of RGO increased the electron lifetime with higher recombination resistance as observed from EIS result.

1. Introduction

With the increasing number of world population, the demand for energy will also increase in tandem. The usage of fossil fuels has resulted in fast climate change due to global warming. Therefore, accessing to environmental friendly energy resources has become crucial to cater the increase demand of clean energy. Solar energy is an effective alternative and clean energy source for sustainable development.

Dye-sensitized solar cell (DSSC) is a third generation solar cell where its working principle depends on the photo-excited electron movement from the dye molecules to the external circuit and looping back to the dye molecules through the electrolyte or hole transport layer (HTM) [1]. The entire process occurs under light exposure.

In general, DSSC can be categorized into two types, which are liquid and solid-state (SS) types [2]. Liquid-based DSSC is known to have problems of possible leakage. Therefore, the utilization of solid-state HTM instead of liquid electrolytes can overcome this issue. However, the current performance of solid-state DSSC is low compared to the cell that uses liquid electrolyte. The performance of solid-state cell could be further improved with the incorporation of graphene-based material within the active layer [3].

Graphene based materials that have good electrical, optical, mechanical properties have been used in DSSC as transparent electrode instead of the usual fluorine doped tin oxide as well as used as
photo-anode. Graphene is largely applied in DSSC due to its transparency and stability to visible light [4]. Previous study has shown that graphene could lower the band gap of TiO$_2$ into visible range of wavelength, thus increasing the performance of DSSC [5]. When graphene is added into electrolyte, the performance of DSSC improved due to reduced potential loss (as a result of incompatibility of HOMO level of dye molecule and redox potential of electrolyte) and fast charge transport [3].

On the other hand, reduced graphene oxide (RGO), which is a graphene-like sheets of graphene oxide where its oxygen-containing groups have been discarded, has shown to improve the performance of DSSC when used as counter electrode [6]. In this work, the effect of RGO to the performance of DSSC was investigated. RGO was added into TiO$_2$ paste to form a composite blend for anode electrode application. The properties of the samples were characterized and their performance was assessed. This study is hoped to provide some insight on the effect of RGO to the performance of SS-DSSC since it is not frequently explored.

2. Experimental

2.1. Materials

All materials were procured from Sigma Aldrich, unless otherwise specified. The materials used in this work included conductive fluorine doped tin oxide (FTO) conducting glasses (13 Ω sq$^{-1}$) (Dyesol), titania blocking layer paste (Dyesol), titania paste (DSL 18NR-T) (Dyesol), platinum precursor (Solaronix), RGO (Timesnano), ruthenium dye 535 sensitizer (Solaronix), 2,2',7,7'-tetrakis (N,N-dimethoxyphenylamine)-9,9'-spirobi fluorene (spiro-OMeTAD), chlorobenzene, 4-tert-butylpyridine, lithium bis(trifluoromethylsulfonyl)imide salt (LiTFSI), acetonitrile and ethanol. All chemicals were used as received.

2.2. Methods

Anode electrode was fabricated by firstly spin coating a titania blocking layer at 3000 rpm for 10 s. This was followed by sintering at 450°C for half an hour. After that, a mixture of RGO-TiO$_2$ paste was deposited on top of the sintered layer using doctor blade method. Different RGO-TiO$_2$ compositions were studied: pure TiO$_2$, 0.1 wt% RGO-TiO$_2$, 0.2 wt% RGO-TiO$_2$ and 0.3 wt% RGO-TiO$_2$. The deposited layer was then sintered at 450°C for 30 min. The as prepared anode electrode was soaked overnight in ruthenium dye ethanolic solution for dye attachment.

After dye soaking, the electrode was cleaned. Then 22μL of electrolyte was deposited on top of the dyed RGO-TiO$_2$ layer before spin coating at 2000 rpm for 20 s and left to solidify. The electrolyte consists of 80 mg of spiro-OMeTAD dissolved in 0.5 ml chlorobenzene with 4-tert-butylpyridine and LiTFSI in acetonitrile. The coated anode electrode was then assembled with counter electrode which was coated with thin layer of platinum precursor. The counter electrode was heated at 450°C prior usage.

2.3. Characterization

Anode electrode samples without dye attachment were characterized with Hitachi S-4800 scanning electron microscope coupled with energy dispersive spectroscopy, Cary 100 Conc UV-Vis spectrophotometer and Shimadzu XRD 6000 diffractometer. The performances of the assembled cells were measured with Keithley electrometer under 1 sun illumination. Their impedance responses were recorded with Zive SP1 electrochemical workstation under dark condition bias at open-circuit voltage.

3. Results and discussion

The anode electrodes were first characterized with SEM and EDX in order to confirm the nanostructure size of the active layer. Figure 1 shows the surface morphology of the anode samples under 40,000x magnification. All the images show distinct crystalline structure of TiO$_2$. With addition of RGO, the porosity of the particles TiO$_2$ is observed to have slightly reduced.
The presence of RGO can be confirmed by the increase of carbon element in EDS results. Figure 2 shows the elemental composition of TiO$_2$ sample and 0.3 wt% RGO-TiO$_2$ sample. The higher carbon content in RGO-TiO$_2$ sample indicates that rich carbon substance has been successfully added into the sample; in this case it’s RGO. The carbon atomic content increased from 3.53% for undoped TiO$_2$ sample to 19.72% for 0.3 wt % RGO-TiO$_2$. The crystallinity of the samples was further confirmed with XRD measurement (result not shown here). There’s no appreciable difference in terms of peak intensity and broadening. Other study also confirmed this observation [7]. Thus, the inclusion of up to 0.3 wt% RGO in the TiO$_2$ layer does not change the crystallinity of the TiO$_2$ layer, which is important for the dye anchoring.

The effect of RGO to the light absorbing ability was analyzed with UV-Vis spectrophotometer. Figure 3 shows the visible light absorbance of RGO-TiO$_2$ and undoped TiO$_2$ electrode samples, with and without dye attachment. Only one set of RGO-TiO$_2$ sample is shown (i.e. 0.3 wt% RGO-TiO$_2$) to avoid cluttering of the spectra. It can be observed that the absorption rate is improved with the presence of RGO in dye-sensitized TiO$_2$ sample compared with that without RGO. The effect is prominent in the region of 400-500 nm wavelength. The increased of light absorbance suggests a decreased in band gap. With the inclusion of RGO, it is thought to have improved the diffuse absorption and reflectance properties of TiO$_2$ under visible light.

The effect of doping RGO with TiO$_2$ on the performance of SS-DSSC was further analyzed by characterizing its current density against voltage (J-V) responses. Table 1 shows the J-V results while its corresponding data is shown in Figure 4 (left). Only 0.3 wt% RGO-TiO$_2$ sample is shown as its performance is the highest among the RGO doped samples. On the other hand, the charge transport
kinetic behavior is represented in Nyquist plot (Figure 4, right) and the relevant values are tabulated in Table 1 as well.

**Figure 3.** UV-Vis spectra of TiO$_2$ layer with and without RGO and dye attachment.

**Figure 4.** I-V curves (left) and EIS spectra (right) of DSSC with and without RGO in TiO$_2$ layer. The inset shows the equivalent circuit of the spectra.

**Table 1.** Performance of SS-DSSC with its corresponding internal resistances and constant phase elements values.

| Sample         | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF (%) | $\eta$ (%) | $R_s$ (k$\Omega$) | $R$ (M$\Omega$) | $Q_y$ ($\times 10^{10}$ S.$s^p$) | $Q_a$ (M$\Omega$) | $R_1$ (M$\Omega$) | $Q_y1$ ($\times 10^{-7}$ S.$s^p$) | $Q_a1$ |
|----------------|-----------------------|--------------|--------|------------|------------------|-----------------|-----------------------------------|------------------|------------------|-----------------------------------|-------|
| Pure TiO$_2$   | 5.40                  | 0.25         | 31     | 0.47       | 3.15             | 0.51            | 3.61                             | 0.89             | 0.62             | 1.82                             | 0.60  |
| 0.3 wt% RGO-TiO$_2$ | 5.72               | 0.29         | 38     | 0.55       | 10.47            | 1.07            | 6.48                             | 0.81             | 2.78             | 1.11                             | 0.76  |

The fill factor (FF) of the cells are within the range of 0.3 to 0.4 range which suggests that addition of RGO has negligible effect on it. FF is usually responsive to the series resistance in the solar cell that is generally derived from the resistance of the transparent conducting oxide, electrolyte as well as counter electrode. From Table 1, cell with RGO content has improved short-circuit current density ($J_{sc}$) at the value of 5.72 mA/cm$^2$ compared to normal cell of 5.40 mA/cm$^2$. Consequently, the efficiency of SS-DSSC with RGO is higher than the normal SS-DSSC. The overall performance is low
due to the possible poor contact between the solid-state electrolyte and dye-sensitized TiO$_2$ of the anode electrode as well as counter electrode.

To understand the performance of the devices, the charge transport and recombination properties are analyzed. Such information can be acquired from Nyquist plot where the internal resistance and impedance can be derived from the equivalent circuit corresponding to the device [8]. The equivalent circuit for this SS-DSSC consists of a resistor coupled with two pairs of parallel resistor and constant phase element. From the Nyquist plot, it is apparent that SS-DSSC with 0.3 wt% RGO, the central arc is wider with respect to undoped TiO$_2$ sample. Therefore, with the inclusion of RGO, the electron lifetime and recombination resistance of SS-DSSC are improved, where the product of resistance and true capacitance is higher. This observation is beneficial in designing better and efficient photoanode structure where the addition of RGO has a role as performance enhancer.

4. Conclusion
RGO doped SS-DSSC has been successfully fabricated and investigated. The efficiency of the RGO doped SS-DSSC is higher when compared to undoped device where more than 15% improvement in efficiency was observed. The improved performance is supported by better light absorbance as well as longer electron lifetime of the device. Nevertheless, further study is required to ascertain the limit of the doping amount of RGO in SS-DSSC.

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