Drop-coated reduced- GO thin film as counter electrode in DSSC

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Abstract. In the last decade, many researchers have been proved the role of graphene-based material as counter electrode in dye sensitized solar cell (DSSC) system. One of graphene-based material is reduced graphene oxide (rGO) that have been widely used in optoelectronic devices. Based on it, in this work we prepared the rGO thin films and used as counter electrode (CE) in DSSC with FTO/TiO 2/Ru-dye/CE/FTO structure. The rGO thin films were deposited on FTO (Fluorine-doped Tin Oxide) substrates by drop casting technique. The 0.5 and 1.0 mg/ml of rGO powder were dispersed in two kind of solvents which are dimethylformamide (DMF) and l N-methyl-2-pyrrolidinone (NMP) for each concentration. The rGO thin films that produced from two different solvents have a differ visible wavelengths absorbance, although prepared from the same concentration. Form scanning electron microscopy (SEM) observation, the morphology of rGO thin film that prepared using NMP is more homogenous than DMF solvent. This situation may relate to the ability of each solvent in dispersing rGO powder. Fourier Transform Infra-Red spectroscopy was used to identify the presence of certain functional groups both in powder and thin film. The carboxyl group of C-O and C=O is appeared in thin film. The rGO thin film as counter electrode in DSSC was studied from current-voltage (I-V) characteristics. This work revealed that rGO thin film is able to use as alternative counter electrode in Pt-free DSSC since it produced 2.22% in efficiency (under 36.5 mW/cm 2 light irradiation).

1. Introduction

Dye-sensitized solar cell (DSSC) is one of emerging photovoltaic devices that offers a good alternative in solar cell technology. Dye sensitized based solar cell is a device that converts visible light into electricity (charge motion) based on sensitization of wide bandgap semiconductors [1]. DSSC was invented by Brian O’Regan and Michael Gratzel in 1991. Dye-sensitized solar cells (DSSCs) have been considered as a next-generation renewable power source owing to relatively high solar-to-electricity conversion efficiency (ŋ), simple fabrication process, and low cost. The challenging issues for developing DSSC are to achieve high efficiency and to reduce production cost. Recent work for reducing production cost is focusing on replacement of the expensive catalytic Pt layer on counter electrodes (CEs) with other cheaper materials, such as graphite, fullerene, amorphous carbon, active carbon, carbon black, carbon nanotubes and graphene [2].

Graphene is a carbon 2D allotrope composed of a stable hexa-atomic honeycomb structure with a theoretical thickness of only 0.34 nm and has sp 2 hybridized carbons [3]. The high optical
transmittance (~97.7%) and good conductivity of graphene made it as an excellent candidate for transparent conductive electrodes [4]. The most promising path for producing graphene related compounds, from both scale up and cost perspectives, is starting from graphene oxide (GO) obtained by a chemical oxidation method and reduction of oxygen contain by either chemically or thermally process [4]. The reduced graphene oxide (rGO) possesses some oxygen-containing functional groups (~OH, C=O), −COOH and carbonyl groups decorating the periphery of the planes. These functional groups which are exist along surface defects produced during the oxidation of graphene sheets, are believed to be responsible for the electrocatalytic activity [5]. Reduced graphene oxide (rGO) thin film with the thicknesses ~10 nm deposited on Transparent Conducting Oxide (TCO) has a low electrical resistance (~0.84 kΩ/sq), 85% transmittance (λ = 550 nm), conductivity of 1.190 S/cm, high surface-to-volume ratio, high carrier mobility, and high catalytic activity [5-7]. In this work, we investigate the drop-coated rGO thin film to study and to prove graphene material as good alternative counter electrode in DSSC.

2. Experiments
FTO substrates were cleaned with detergent and subsequently washed by ethanol and isopropanol in ultrasonic bath. TiO₂ mesoporous T/SP (Solaronix SA) was deposited twice on FTO by screen printing technique and annealed up to 500°C for 30 minutes. Single layer of TiO₂ MC/SP (Solaronix SA) was also deposited on top of TiO₂ mesoporous with the same technique and annealing treatment as deposition of TiO₂ mesoporous. Dye solution was prepared from ruthenium dye N719 (Solaronix SA) and chenodeoxycholicacid was dissolved in ethanol with 1:10 wt/wt. The FTO/TiO₂ was immersed in dye solution for 24 hours. The FTO/TiO₂/Ru was washed by acetonitrile several times for remove unabsorbed dye particles.

We used DMF (dimethylformamide) and NMP (N-methyl-2-pyrrolidone) to dispersed rGO powder (Graphenea) with concentration 0.1 mg/ml for each solvent. Before deposition of rGO layer, cleaned FTO substrates were treatment previously by dropping the solvent on top of FTO during annealed at 65°-100°C (for DMF) and 100°C (for NMP). Afterward, rGO dispersed solution was drop-coated on prepared FTO and annealed at the same heating temperature according to each solution. Finally, the photoanodes (FTO/TiO₂/Ru) and counter electrode (FTO/rGO) were assembled using thermal adhesive (Surlyn, 25 µm thicknesses) as spacer to construct a sandwich structure (FTO / TiO₂ / dye/ electrolyte / RGO / FTO). The electrolyte (mosalyte, Solaronix SA) was injected via cavity that available in rGO/FTO side’s. The prototype DSSC have an active area approximately of 0.2 cm².

The absorbance spectra of rGO thin film as counter electrode was measured by UV-Visible spectrophotometer. Fourier Transform Infrared (FT-IR) spectroscopy was also carried out to investigate the functional groups of hydroxyl and carbonyl in rGO powder and rGO thin film. The surface morphology and element composition of rGO thin film were analyzed using scanning electron microscope (SEM) and energy dispersive spectrum (EDS). Solar cell performance was characterized by current-voltage (I-V) using DC voltage integrated with digital multimeter under 36.5 mW/cm² light irradiation.

3. Results and discussion
The rGO thin films show high transmittance in visible wavelength, therefore they cannot be distinguished with bare FTO. We measured UV-Vis absorbance spectra from each sample to ensure that the rGO thin film was successfully deposited. Figure 1 shows UV-visible absorption spectra for all samples. The higher absorption of rGO/FTO as compared with bare FTO indicates that rGO thin film has been successfully deposited. The films prepared from NMP dispersion medium has higher absorption than that of DMF dispersion. Figure 2 shows SEM micrograph of FTO/rGO prepared from NMP and DMF. The dark images are identified as rGO sheets, whereas the bright round clusters are
FTO surface. Homogenous rGO layer from regular stacked rGO sheets should have transparent layer. The dark images in figure 2(a) exhibit irregular stacked rGO sheets due to not well dispersed of rGO in DMF. Meanwhile, transparent images of surface in figure 2(b) show that rGO sheets are well dispersed in NMP. This result might be related to higher polarity and solubility of rGO in NMP than that of DMF [8, 9].

**Figure 1.** Absorption spectra for RGO thin films deposited by drop casting technique.

**Figure 2.** SEM micrograph of FTO/rGO thin film prepared from different solvent, (a) DMF and (b) NMP.
Figure 3. FT-IR spectra of rGO powder and thin film dissolved in NMP and DMF.

Figure 3 shows Fourier Transform Infra-red (FTIR) spectra of rGO thin films prepared from DMF and NMP dispersion. All spectra have main functional groups C=O at 1118 cm\(^{-1}\), C=C at 1593 cm\(^{-1}\) and C=O at 1722 cm\(^{-1}\). These spectra are good agreement with other studies [10, 11], indicates that rGO films have been formed.

Figure 4. Photocurrent density-voltage (J-V) curve of DSSC with the structure of FTO/TiO\(_2\)/Ru/mosalyte/rGO/FTO.

Figure 4 shows current density-voltage (J-V) characteristic curves using rGO thin films as counter electrode. J-V curve of DSSC using platinum (Pt) as counter electrode is also plotted for comparison. The solar cell parameters such as open circuit voltage (\(V_{oc}\)), short current density (\(J_{sc}\)), Fill Factor (\(FF\)) and efficiency (\(\eta\)) are tabulated in table 1. \(J_{sc}\) values of devices using rGO-NMP and rGO-DMF are higher than that of Pt as counter electrode, which shows that rGO has higher
catalytic property than Pt. Meanwhile, all devices have comparable $V_{oc}$ values. However, the FF and $\eta$ values of rGO based DSSC are lower than that of Pt. This result is related to higher value of series resistance of rGO thin film due to low quality of the rGO layer. Further optimization of rGO thin film is highly required to improve the performance of DSSC. This study shows that rGO thin film can be used as counter electrode of DSSC.

| Counter Electrode   | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | $P_{max}$ (mW/cm$^2$) | FF (%) | Eff (%) |
|---------------------|--------------|-----------------------|-----------------------|--------|---------|
| rGO-DMF 0.1         | 0.60         | 3.23                  | 0.76                  | 39.22  | 2.08    |
| RGO-NMP 0.1         | 0.58         | 2.96                  | 0.767                 | 44.75  | 2.10    |
| Pt                  | 0.6          | 2.17                  | 0.84                  | 64.43  | 2.3     |

4. Conclusions
The reduced graphene oxide thin films as counter electrode in DSSC with structure of FTO/TiO$_2$/Ru/Mosalyte/rGO/FTO was successfully prepared. The rGO thin films were prepared from dispersed rGO powder in NMP and DMF. The rGO thin film prepared in NMP has more homogenous surface morphology than that of in DMF. The functional groups of rGO do not depend on solvent. The efficiency of devices using rGO thin films as counter electrode are comparable to device using Pt. This result shows that rGO thin film can be used as alternative counter electrode of DSSC.

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