

Characteristics of Thermally Reduced Graphene Oxide Thin Film as DSSC Counter Electrode

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Abstract. We report characteristics of reduced graphene oxide (RGO) as a counter electrode for dye-sensitized solar cell (DSSC). The RGO thin films were prepared on FTO (Fluorine-doped Tin Oxide) substrates and followed by a reduction process. The RGO film was used as a counter electrode in a DSSC device, with a structure of FTO/TiO₂/ruthenium dye/mosalyte/RGO/FTO. UV-Vis measurements show an increasing absorption spectrum of RGO film after thermal reduction process and the FT-IR spectrum confirms a removal of the oxygen containing groups after thermal reduction process. The efficiency (η) of the DSSC that applied RGO film as a counter electrode is 0.96%.

1. Introduction

Graphene is attracting a lot of attention due to its promising properties for electronic devices [1-4]. The high optical transmittance (~97.7%) and good conductivity of graphene made it as an excellent candidate for transparent conductive electrodes [5,6]. A low cost method involving thermal reduction of graphene oxide (GO) has attracted considerable attention. However, there are many intercalated impurities, such as carboxyl and hydroxyl groups, embedded in the reduced graphene oxide that must be removed through reduction processes prior to use.

Dye-sensitized solar cell (DSSC) that is a promising alternative to conventional silicon or compound semiconductor solar cells [7]. The basic DSSC structure consists of dye that adhered to nanocrystalline TiO₂ photoanode, an electrolyte solution, and Pt counter electrode [8]. The role of counter electrode is catalyzing the reduction of the redox species in the electrolyte that used as a mediator in regeneration of dyes after electron injection [7]. Pt is commonly used in as counter electrode. Recently, carbon materials have been considered as candidates of counter electrodes for DSSC [9]. In this work we study a reduction method using thermal heating of graphene oxide (GO) obtain graphene-like that known as reduced graphene oxide (RGO) and then used it as a DSSC counter electrode.

2. Experiments

Thin films of GO were prepared from 4 mg/ml GO dispersed in water (Graphenea). The GO dispersion was sonicated (Branson 1800 Series) for 1 hour at room temperature for exfoliation prior to use. The GO dispersion was deposited on FTO substrate by using spincoating technique (Chemat Technology Spin-coater KW-4A) at 1000 rpm for 30 second and dried at 30 °C to remove residual



solvent. In order to obtain reduced graphene oxide (RGO) films, the GO films were thermally reduced by heating at 200°C for 1 hour.

The RGO film was then used as counter electrode in DSSC, with a structure of FTO/TiO₂/ruthenium dye/mosalyte/RGO/FTO. Besides a DSSC with RGO counter electrode (DSSC_{RGO}), we also prepared a DSSC with GO as counter electrode (DSSC_{GO}), and a DSSC with Pt counter electrode (DSSC_{Pt}) as a control. For DSSC assembly, the TiO₂ mesoporous was created by coating titania paste Ti-Nanoxide T/SP (Solaronix SA) on FTO substrate using screen printing technique and continued by sintering at 500°C for 30 minutes to convert anatase to rutile phase. In order to trap incident light, the Ti-Nanoxide MC/SP (Solaronix SA) was coated on FTO/TiO₂-mesoporous with the same deposition and sintering procedure. The FTO/TiO₂ was then immersed overnight in N719 dye solution. The dye solution was prepared from N719 and chenodeoxycolic acid with ratio of 1:10 that dissolved in ethanol. After dye immersion, the FTO/TiO₂/N719 was washed using acetonitrile to remove residual dye particles. *Surylin* (solaronix SA) 25 μm thicknesses was used as spacer between photoanode and counter electrode. Mosalyte as ionic liquid (solaronix SA) was injected through the hole at the counter electrode and then sealed with a transparent tape to avoid leaking.

RGO film was characterized by Ultra-violet Visible spectroscopy (T70+ UV/Vis Spectrometer PG Instrument, Ltd) and Fourier Transform Infrared spectroscopy (FT-IR Shimidzu). The DSSC performances were characterized by using DC voltage (Yokogawa GS200) integrated with digital multimeter (Yokogawa 7555) under 36.5 mW/cm² light irradiation. Device efficiency was calculated from ratio of maximum power of the device (P_{max}) and light power irradiation (P_{light}), while P_{max} is obtained from an open circuit voltage (V_{oc}), a short circuit current density (J_{sc}), and a fill factor (FF).

3. Results and Discussion

The prepared GO films have yellow-brown color and when they have been converted to RGO, the films become grey-black color. The UV-Vis absorbance spectrum of GO film was changed after thermal reduction process as shown in Figure 1. Since the FTO substrate absorbs light in the wavelength region of 200-300 nm, the absorption peak of GO and RGO films could not be identified in the spectra. An absorption difference between FTO and the GO film indicate a presence of GO layer on the FTO substrate. The absorbance spectrum of GO film was increased after thermal reduction process indicates that the RGO film more conductive compare to the GO film. It is related to a recovery of conjugated bonds due to a thermal reduction process that removed oxygen functional group on the GO film.

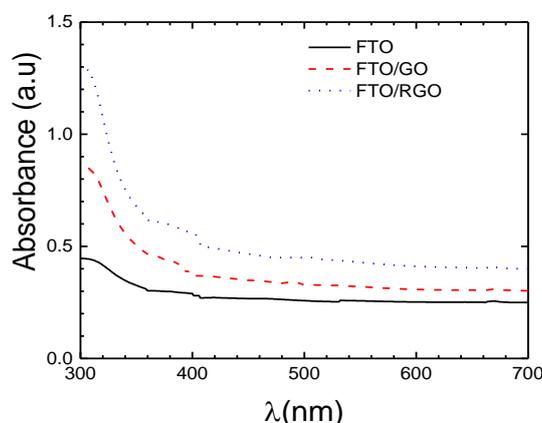


Figure 1. Thermal reduction process has increased UV-Vis absorption spectra of GO film, bared FTO substrate (solid line), FTO/GO film (dashed line), and FTO/RGO film (dotted line).

Figure 2 shows the FT-IR spectra of the GO film (solid line) and the RGO film (dashed line). From the figure it is obvious that thermal reduction process has removed some oxygen containing groups. The intensity of hydroxyl O-H group at 3400 cm^{-1} are considerably reduced and C=C vibration at 1600 cm^{-1} are significantly increased. However, several carboxyl and carbonyl C=O groups at 1735 cm^{-1} , carbonyl 1430 cm^{-1} , epoxy C-O at 1270 cm^{-1} , alkoxy C-O at 1042 cm^{-1} are only reduced and still remained on the RGO film, The increasing of C=C vibration intensity indicates a recovery of conjugated bonds in the RGO film. This result is in-line with the increasing of UV-Vis absorption of RGO film. Some remaining oxygen functional groups still appeared on the RGO film suggest that an improvement of reduction process is still needed.

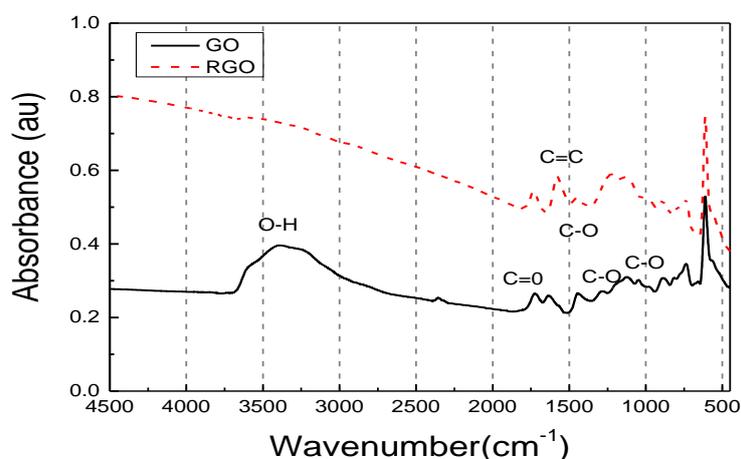


Figure 2. FT-IR Spectra of GO film (solid line) and RGO film (dashed line) shows a removal of several oxygen functional groups after at 200°C for 1 hour.

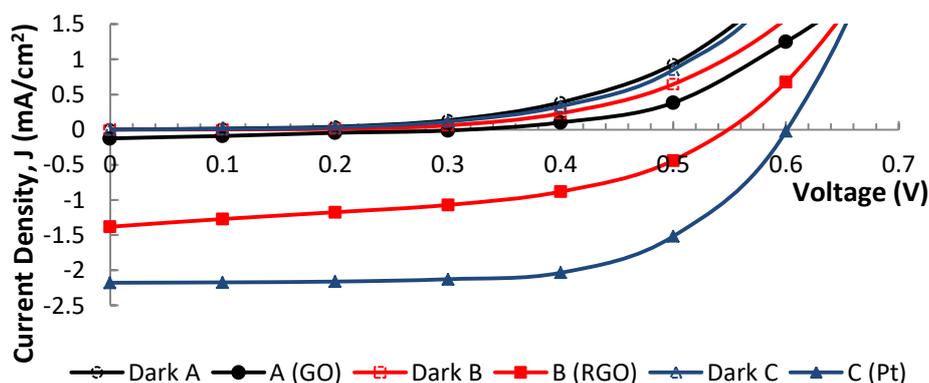


Figure 3. Photocurrent density-voltage (J-V) curves of DSSC with varied counter electrode, GO (circle), RGO (square), and Pt (triangle).

Figure 3 shows J-V curves of DSSC with varied counter electrode (CE), namely DSSC_{Pt} , DSSC_{RGO} and DSSC_{GO} . The photovoltaic parameters of J_{sc} , V_{oc} , FF of the DSSC were extracted from J-V curves and η was calculated, and all results are shown in Table 1. We found that the DSSC with RGO film as counter electrode has a better performance compared to the GO film. This result implies that a thermal reduction process was reduced the oxygen functional groups and it contributes to the changes of insulating state of GO film become semiconducting state of RGO film. The photocurrent density was significantly increased from 0.12 mA/cm^2 in the device with GO film as counter electrode to 1.38

mA/cm² in the device with RGO film. The change indicates that there is an increment of charge transfer inside the cell. Besides, the value of V_{oc} and FF were also increased from 0.3 volt to 0.58 volt and from 29% to 44%, respectively. Increasing of V_{oc} and FF actually attributed to a better interfacing between all layers inside the cell. Performance differences between DSSC that employed GO and RGO film as counter electrode, are mainly influenced by amount of oxygen impurities. Our experimental results show that DSSC_{Pt} that employ Pt as counter electrode still has better performance compare to the DSSC_{RGO} and DSSC_{GO}. Since the FTIR spectra of the RGO film confirm an existence of remained oxygen functional group, it is expected that an improvement of thermal reduction process can further reduce the oxygen content of RGO film. With an improvement of RGO film quality, the performance of DSSC that employed RGO film as a counter electrode can be further enhanced.

Table 1. Photovoltaic parameters of DSSC with structure of FTO/TiO₂/N719dye/CE/FTO using various counter electrode.

Counter Electrode (CE)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	η (%)
GO	0.30	0.12	29	0.03
RGO	0.58	1.38	44	0.97
Pt	0.60	2.18	64	2.30

4. Conclusions

Thermal reduction process of GO film at 200°C for 1 hour can convert the material into RGO that has less oxygen content. The RGO film can be used as a DSSC counter electrode although its performance still below the one that employed Pt as a counter electrode. The efficiency of DSSC with RGO film as counter electrode that has $V_{oc} = 0.58$ volt, $J_{sc} = 1.38$ mA / cm², and FF = 44% is $\eta = 0.96\%$. Since the oxygen functional group contained in the RGO still can be reduced by improving reduction process, the efficiency of DSSC with RGO counter electrode can be improved.

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