A Preliminary result on the rGO functionalization as counter-electrode in dye-sensitized solar cells (DSSC)

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Abstract. In the effort of replacing Platinum (Pt) based counter-electrode (CE) for reducing fabrication cost in the dye-sensitized solar cell (DSSC), we synthesized rGO powder from graphite bar (commercially available) using modified Hummer’s method with an introduction of microwave irradiation. rGO was attached to the FTO surface by dissolving it in the solvent with the addition of ethyl cellulose (ES) following by two-step annealing process. rGO solution was deposited by spin coating technique with different thickness namely 1 layer rGO (A1), 5 layer rGO (A2), 10 layer rGO (A3) and 15 layer rGO (A4) followed by an annealing process, and the reference cell was assigned as A5 (using Pt). From the thin film resistance measurement using the four-probe method and conductivity calculation, the conductivity decreased as the rGO layer becomes thicker, namely from (0.58 to 0.42, 0.07 and 0.03) S/cm for A1, A2, A3, and A4 in consecutive order. From the photovoltaic measurement, we found that the utilization of rGO as a catalyst in CE increased the efficiency of the cell from 3.82% (A5) to 4.52% (A1). Furthermore, increasing the thickness of rGO layer from A1 (2.1 µm) to A2 (10.5 µm) also increased the efficiency from 4.52% to 5.89%, further increasing on the layer thickness A3 (21 µm) to A4 (31.5 µm) reduced the conversion efficiency to 2.57% and 0.33%. The highest conversion efficiency achieved for the cell with 10.5 µm thickness of CE, specifically A2. Further investigation of the influence of CE thickness and conductivity to the internal parameters of the DSSC must be done in order to gain a much better understanding of this result.

1. Introduction

Nowadays, research on dye-sensitized solar cells (DSSC) focusing on the quest for optimizing photovoltaic performances of the cells. As we know that DSSC is built by four components including metal oxide semiconductor deposited on top of the conductive substrate, the sensitized dye attached on metal oxide conductor, the redox couple electrolyte and the counter-electrode (CE). Many research has been done for the perfection of each constituent components, which mostly reported works regarding metal oxide semiconductor [1, 2, 3, 4, 5, 6], dye sensitizer [7, 8, 9] and redox couple electrolyte [10, 11] and very little publication related with CE especially in the effort for replacing Platinum (Pt) as the main catalyst in DSSC’s CE. This may be correlated with the stable properties of Pt including high electrical conductivity, high chemical catalytic activity to induce iodide/triiodide redox reaction.
CE has three important roles in DSSC [12], (i) as the catalyst that boosts the completion process, where the oxidized redox couple is reduced by accepting electrons at the surface of the CE, and a process where the oxidized dye is reduced by collecting electrons via ionic transport materials in solid-state DSSCs. (ii) As a positive electrode of primary cells, it collects electrons from an external circuit and transmits them into the cell. (iii) As the mirror, which reflects unabsorbed light from the cell back to the cell to enhance sunlight harvesting capability of the cell [12, 13]. Based on these function, CE must high catalytic activity, high conductivity, high reflectivity, low-cost, high surface area, porous nature, optimum thickness, chemical and electrochemical stability, chemical corrosion resistance and good adhesivity with conductive substrate [12].

To date, the highest efficiency of DSSC is achieved with the cell utilizing Pt as the catalyst in CE, due to its high electrical conductivity, excellent electro catalytic activity and high electrochemical stability [14]. However, owing to its noble properties along with its scarcity that limits the possibility for mass production of DSSCs and its practical application, has open up possibilities for other materials as the replacement of Pt. Several attempts have been made with the utilization of carbon-based materials such as carbon black [15], activated carbon [16], carbon nanotubes [17] and graphene [18, 19].

Among others, graphene with its high transparency [16, 20], good electrochemical stability and high conductivity [21] has emerged as new potential material for replacing Pt as the catalyst in CE. However, until now it still very hard to obtain single layer structure of graphene, and therefore in this work we presented our preliminary result on the utilization of graphene in its reduced form (reduced graphene oxide/rGO) as the catalyst in DSSC. rGO was synthesize using modified Hummer's method with the introduction of a microwave in the annealing process.

2. Methods

2.1. Reduced graphene oxide (rGO) preparation

2.1.1. Graphene oxide (GO) preparation. GO preparation was following the same method that already reported elsewhere based on modified hummers method re-described in [22, 23]. The graphite bar was crashed until smooth and strained using 200 mesh filter to form homogeneous graphite powder. 2 gr of graphite powder was mixed 98 ml of 98% Sulphuric Acid (H2SO4) and vigorously stirred for four hours in the ice bath environment at 0°C temperature. During the stirring process, 8 gr of Potassium Permanganate (Kmno4) and 4 gr of Sodium Nitrate (NaNo3) was added very slowly into the mixture until the color of the solution turned into blackish green. The temperature then slowly raised to 35°C for 24 hours. The color of the suspension slowly turned to light brown, and the suspension became more viscous. 200 ml of distilled water slowly added into the suspension while stirred for one hour, where the color changed into dark brown and became golden yellow with the addition of 15 ml of Hydrogen Peroxide (H2O2). The suspension was then precipitated for 24 hours to separate the liquid phase and solid phase. The solid phase was washed with 10 ml Hydrochloric Acid (HCl) 37% and distilled water several times until the pH neutralized, dried in the oven at 110°C for 12 hours. 40 mg of the resulting graphite oxide was then diluted into 40 ml of distilled water, stirred overnight and sonicated with the frequency of 53 KHz for 120 minutes.

2.1.2. GO reduction. 10 ml HCl 37% added to the pre-prepared GO solution, to form an acidic environment. 1.6 gr of Zinc powder then added to the GO solution and let for 16 hours. The mixture then stirred for one hour, and 10 ml HCl 37% was added again to remove the Zn particles that did not react in the solution, washed with distilled water until the pH of the solution was neutralized and dried in the oven at 110°C for 12 hours. The resulted rGO powder then subsequently dried in the microwave with 800 Watt power for two minutes with five seconds delay at every 30 seconds. The utilization of
microwave in the drying process to produce homogeneous heat in relative very short time for speeding up the reduction time [22].

2.2. DSSC fabrication

The materials and preparation methods for fabricating DSSCs here were basically the same as reported in [24], the active materials used in this work were cis-bis(isothio-cyanato)bis(2,2’-bipyridyl-4,4’-dicarboxylate) ruthenium(II)-bis-tetrabutylammonium (N719 dye, Solaronix), TiO₂ pastes (Ti-Nanoxide, Solaronix), platinum (Pt) colloidal solution (Platisol, Solaronix). Fluorine-doped SnO₂ glass (FTO, surface resistivity = 15Ω/ per square) were used as electrode substrates. All materials were used as received. The complete DSSC samples were made also by the same fabrication method as reported in our previous work [25, 26]. The electrodes were separated by a separator (Surlyn® of 50 µm thickness). The active area of each cell was 0.5 cm x 0.5 cm.

The counter electrode (CE), prepared as follow, rGO powder was mixed with ethyl cellulose (1:1) in weight with the addition of terpineol, stirred for 24 hours. The mixture then deposited on top of FTO and spin coated with rotating speed of 1000 rpm for 30 seconds. The resulting thin film then experienced two-step annealing process, the first one was in the hotplate at 250°C for 5 minutes, and the second one was in the furnace at 500°C for 30 minutes. All the steps were repeated to make thickness variation of (1, 5, 10 and 15) layers.

2.3. Characterization

The resistance of the rGO layer was measured by using Four-Probe Method (FPM) at the bias voltage of 9 Volt. The thickness of one layer rGO was determined using SEM. The EDS measurement was conducted for one layer rGO to make sure the attachment of rGO on top of FTO conductive substrate. The results are shown in figure 1 (a) and (b). rGO was attached to the FTO conductive substrate, with the existence of 26% carbon atom (C), and 49.18% oxygen atom (O) (figure 1a). The estimated thickness of A1 sample which is one layer rGO is 2.1 µm (figure 1b). Since the resulting rGO layer seems to have a homogeneous thickness, so for other samples A2, A3, and A4, we calculated their thickness based on the result for A1, resulting in a thickness of (10.5, 21, and 31.5) µm respectively.

3. Results and discussions

3.1. Thickness measurement and rGO attachment confirmation using SEM-EDS

Characterization utilized SEM-EDS was conducted in order to measure the thickness of one layer rGO and reassure the attachment of rGO on top of FTO conductive substrate. The results are shown in figure 1 (a) and (b).

3.2. Electrical properties of rGO thin film

Electrical properties of rGO thin film were characterized by its conductivity value. The conductivity was calculated from equation (1),

\[ \sigma = \frac{1}{\rho} \]  

Resistivity (ρ) of the sample was obtained from equation (2),

\[ \rho = \left( \frac{V}{I} \right) t \ln 2 \]  

Where t is the thickness of the thin film and the resistance \( R = \frac{V}{I} \) of the sample was measured with the four-point probe method. The results are tabulated in table 1.
Figure 1. EDS result of one layer rGO on top of FTO substrate (a), and the cross section of one layer rGO (b)

Table 1. The tabulated parameters for calculating conductivity of rGO thin film

| Sample | t (µm) | R (Ω) | V (Volt) | I (A) | ρ (Ω.cm) | σ (S/cm) |
|--------|--------|-------|----------|-------|----------|----------|
| A1     | 2.1    | 11666.7 | 0.35    | $3\times10^{-3}$ | 1.69    | 0.58     |
| A2     | 10.5   | 3200   | 0.32    | $10\times10^{-5}$ | 2.32    | 0.42     |
| A3     | 21     | 9250   | 0.37    | $4\times10^{-5}$ | 13.4    | 0.07     |
| A4     | 31.5   | 12666.7 | 0.38    | $3\times10^{-5}$ | 27.6    | 0.03     |

The conductivity of the rGO layer decreases 27.5%, 87.9% and 94.8% with the increasing of layer thickness from 1 layer (A1) to 5 layers (A2), 10 layers (A3) and 15 layers (A4) in consecutive order. (table 1). The reducing of conductivity might be caused by the amount of ethyl cellulose exist as the thin films getting thicker.

3.3. Photovoltaic characteristics

The photovoltaic characteristics were investigated by current density (I-V) measurement using solar simulator Newport AM 1.5 with the light intensity of 100 mW/cm², the result and the tabulated parameters were shown in figure 2. The cells made in this research have structure configuration of FTO/TiO$_2$/dye/electrolyte/rGO/FTO for A1, A2, A3 and A4, and FTO/TiO$_2$/dye/electrolyte/Pt/FTO for A5 as the reference cell.

The current-density ($J_{sc}$) and open circuit voltage ($V_{oc}$) of the DSSC cells employing rGO as counter electrode shows dependency on electrode thickness. One layer rGO (A1) with 2.1 µm thickness showed an overall conversion efficiency of 28.8% higher than Pt-based CE as the reference cell (A5), which is mostly contribution from its open-circuit voltage ($V_{oc}$) value since A1 has lower current-density ($J_{sc}$) compared to A5 (figure 2, table 2). At this point, lower $J_{sc}$ may correspond with the fact that 2.1 µm thickness is too thin to provide sufficient catalytic activity to efficiently restore iodide (I$^-$) from triiodide (I$_3^-$), and therefore the photo-induced electrons tend to recombine with I$_3^-$, which lowers photocurrent [19]. By increasing the thickness of the rGO layer (A2), $J_{sc}$ increases 34.7%, which indicated that the CE now has sufficient catalytic activity to accelerate diffusion of I$^-$ ion in order to recreate I$^-$ ions for dye regeneration. Further increasing of rGO thickness reduces the $J_{sc}$.
as much as 64.5% and 95.3% for A3 and A4 respectively. $J_{sc}$ reduction with the increasing of rGO layer thickness due the fact that thicker layer will increase diffusion resistance, and eventually slower its diffusion, since the I$_3^-$ ion must diffuse further into the layer to reach the conductive substrate, and on its way, it may recombine with photo-induced electrons, enhancing the possibilities for recombination process.

![Figure 2. J-V curves of the dye-sensitized solar cell utilizing rGO as the catalyst in counter-electrode](image)

**Table 2.** Photovoltaic characteristics of DSSC utilizing rGO as a catalyst in counter-electrode

| Sample | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (Volt) | Fill Factor (%) | Efficiency ($\eta$) (%) |
|--------|----------------------|----------------|----------------|-----------------------|
| A1     | 12,39                | 0,74           | 53,60          | 4,92                  |
| A2     | 16,71                | 0,70           | 50,33          | 5,89                  |
| A3     | 5,92                 | 0,70           | 61,92          | 2,57                  |
| A4     | 0,78                 | 0,61           | 57,53          | 0,33                  |
| A5     | 12,51                | 0,70           | 43,65          | 3,82                  |

Utilization of one layer rGO in A1 augment $V_{oc}$ value as much as 5.7% compared to Pt-based CE in A5. Further increasing of rGO layer thickness, decreases $V_{oc}$ as much as 5.4% from A1 to A2 and A3 respectively, and 17.5% from A1 to A4, where reduced $V_{oc}$ at large thickness might be due to the depletion of I$_3^-$ toward the positive side of the cell [19].
4. Conclusions
We have successfully synthesized rGO from graphite bar using modified Hummer's method with the introduction of microwave irradiation in the reduction process and deposited it on top of FTO conductive substrate with a two-step annealing process. We found that when the rGO layer was too thin (~2.1 µm), the DSSC cell showed lower Jsc compared to Pt-based CE which indicates poor electrochemical activity. Increased CE thickness up to 5 times layering with rGO (10.5 µm) showed the optimum performance of 5.89% overall conversion efficiency, attributed to increased surface area and formation of micro-pores, which led to enhancement of electrochemical activity. The overall conversion efficiency significantly dropped with further increasing on rGO-based CE thickness, which might due to the increase of diffusion resistance of I$_3$- ions to the outer electrode.

References
[1] Sengupta D, Dasa P, Mondal B and Mukherjee K 2016 Renewable and Sustainable Energy Reviews 60 356
[2] Raj CC and Prasanth R 2016 Journal of Power Sources 317 120
[3] Zhang Q and Cao G 2011 Nano Today 6(1) 91
[4] Goh GKL, Lee HQ, Huang TJ and Hui BTT 2014 Journal of Solid State Chemistry 214 17
[5] Prabakar K, Kim MSW-Y and Kim H 2011 Materials Chemistry and Physics 125(1) 12
[6] Asdim K, Manseki TS and Yoshida T 2014 New Journal of Chemistry 38 598
[7] Vougioukalakis GC, Philippopoulos A and Stergiopoulos T 2010 Coordination
[8] Jei S, Zhaofei C and Cheng Z 2012 Dyes and Pigments 95(2) 244
[9] Wang J, Sero-IM, Pan Z, Zhao K, Zhang H, Feng Y, Yang G, Zhong X and Bisquert J 2013 J. Am. Chem. Soc 135(42) 15913
[10] Nogueira AF, Longo C and De Paoli MA 2004 Coordination Chemistry Reviews 248(13-14) 1455
[11] Wang ZS, Sayama K and Sugihara H 2005 J. Phys. Chem. B 109(47) 22449
[12] Wu J, Lan Z, Lin J, Huang M, Huang Y, Fan L, Luo G, Lin Y, Xie Y and Wei Y 2017 Chem. Soc. Rev 46 5975
[13] Wu J, Yan L, Tang Q, Yue G, Lin J, Huang M and Meng L 2014 Sci. Rep 4 4028
[14] Lu MN, Chang CY, Wei TC and Lin JY 2016 Journal of Nanomaterials 2016
[15] Murakami TN, Ito S, Wang Q, Nazeeruddin MK, Bessho T, Cesar I, Liska P, Humphry-Baker R, Comte P and Pechy P 2006 J. Electrochem. Soc 153 A2255
[16] Imoto K, Takahashi K, Yamaguchi T, Komura T, Nakamura J-I and Murata K 2003 Sol. Energy Mater. Sol. Cells 79 459
[17] De Filpo G, Nicoletta FP, Ciliberti L, Formoso P and Chidichimo G 2015 J Power Sources 274 274
[18] Roy-Mayhew JD, Bozym DJ, Punckt C and Aksay IA 2010 ACS Nano 4 6203
[19] Gong J, Zhou Z, Sumathy K, Yang H and Qiao Q 2016 Journal of Applied Physics 119(13) 135501
[20] Kavan L, Yum JH and Graetzel M 2012 ACS Appl. mater. Interfaces 4(12) 6999
[21] Bonaccorso F, Colombo L, Yu G, Stoller M, Tozzini V, Ferarri A-C, Ruoff RS and Pellegrini V 2015 Science 347(6217) 1246501
[22] Agusu L, Ahmad LO, Anggara D, Alimin, Mitsudo S, Fujii Y and Kikuchi H 2018 Journal of Physics Conf. Series 1011 012012
[23] Agusu L, Ahmad LO, Alimin, Nurdin M, Herdianto, Mitsudo S and Kikuchi H 2018 IOP Conf. Series. Material Science & Engineering 367 012002
[24] O'Regan B and Gratzel M 1991 *Nature* **353**(6346) 737
[25] Arsyad Waode S, Herman, Prijamboedi B and Hidayat R 2018 *Ionics* **24**(3)
[26] Arsyad Waode S, Januari A, Jumalia, Ilmawati WS, Usman I and Hidayat R 2018 *Journal of Nonlinear Optical Physics & Materials* **27**(2) 1850019

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