Reduced Graphene Oxide/Polyaniline Nanocomposite as Efficient Counter Electrode for Dye Sensitized Solar Cells

R Rahmawati¹,³, V Suendo¹* and R Hidayat²

¹Department of Chemistry, Inorganic and Physical Chemistry Research Division, FMIPA, Institut Teknologi Bandung
²Department of Physics, Magnetic and Photonic Physics Research Division, FMIPA, Institut Teknologi Bandung
³Chemistry Education Study Program, FTK, UIN Sunan Gunung Djati Bandung

*vsuendo@chem.itb.ac.id

Abstract. Reduced graphene oxide (rGO) was synthesized using sonication-assisted oxidation of graphite followed by reduction with ascorbic acid as environmentally friendly reductor. The polyaniline was prepared via chemical polymerization of aniline in 0°C. The rGO and polyaniline were blend in three mass compositions of 1:3, 1:1, and 4:1 to produced rGO/polyaniline nanocomposites. The rGO/polyaniline nanocomposites were characterized using Raman spectroscopy, Fourier transform infrared spectroscopy and LCR meter. The rGO sheets as the support materials could provide more active sites for the nucleation of polyaniline, where polyaniline acts as conducting support. The rGO/polyaniline nanocomposites was deposited on synthetic graphite substrate laminated the glass substrate and applied as the counter electrode for efficient dye sensitized solar cells (DSSC). The rGO/polyaniline nanocomposite is an efficient counter electrode because of Pt/TCO free. The usage of rGO/polyaniline nanocomposites film as counter electrode in DSSC was demonstrated. The best performance was obtained for rGO/Polyaniline ratio of 4:1. Here, the optimum short circuit current density (Jsc), the open circuit current (Voc), the fill factor (FF), and the overall conversion efficiency under AM 1.5, 100 mW cm⁻² illumination are 7.853 mA/cm², 0.64 Volt, 47.2% and 2.64%, respectively.

1. Introduction

Dye sensitized solar cells (DSSC) have received much attention due to their low cost, easy fabrication, environmental friendliness, and respectable energy conversion efficiency [1-3]. DSSC consist of several main components n-type semiconductor electrode (photo anode), a sensitizer (dye), a redox couple electrolyte, and a counter electrode (CE) [1]. CE is one of the most important component in DSSC. The role of CE is to transfer electrons from the external circuit back to redox electrolyte which is the mediators for regenerating the sensitizer (dye) after the electron injection and to catalyze the reduction of I³⁻ to I⁻ [1, 4]. A CE material in DSSC should possess a high catalytic activity and stability toward electrolyte. Platinum (Pt) is the most preferred material for CE in DSSC, due to its excellent physical and chemical properties, such as a high electrical and thermal conductivity, catalytic activity toward I³⁻, and corrosion resistance to iodide ions present in redox electrolyte [3-5]. However, because Pt is precious metal, it is high cost and prevented it from being widely used in commercial DSSC. Recently, Pt-free materials with lower cost and good stability have been investigated as counter electrode for DSSC, mainly based on combination carbon materials and conducting polymers [1, 4-6].
Graphene, one of the allotropes of abundantly carbon is one of the most promising materials for application in solar cells. Graphene is possessing high conductivity, great mechanical strength, high carrier mobility, high specific area, and high optical transparency [1-2, 4-6]. However, graphene is not a perfect candidate for a counter electrode in DSSC, because it has limited number of active sites for I$_3$/I$^-$/electro catalysis. Polyaniline is a conducting polymer and has high catalytic activity which has been employed as the counter electrode for DSSC. The combination of graphene and polyaniline are believed as an efficient route [1-6]. The graphene /polyaniline nanocomposite was synthesized using in situ polymerization and deposited on fluorine-doped tin oxide glass has conversion energy efficiency reached 6.09% which is comparable to 6.88% of the cell with Pt counter electrode [2].

In this paper, reduced graphene oxide (rGO) was synthesized using sonication-assisted oxidation of graphite followed by reduction with ascorbic acid as environmentally friendly reductor [7, 8]. The polyaniline was prepared via chemical polymerization of aniline in 0°C [9]. The rGO and polyaniline were blend to produced rGO/polyaniline nanocomposites. The rGO/polyaniline nanocomposites was deposited on synthetic graphite substrate laminated the glass substrate and applied as counter electrode. The counter electrode was the Pt and TCO free, it was low cost, environmental friendly, and efficient.

2. Experimental

2.1. Synthesis of reduced graphene oxide (rGO)

1 g graphite flakes was added to 50 mL concentrated sulphuric acid (97%, Merck) while stirring in ice bath. 3 g potassium permanganate (>99%, sigma Aldrich) was gradually added by maintaining temperature under 10°C. Then, the suspension stirred at room temperature for 25 min followed by 5 min sonication. After repeating the stirring-sonication process for 12 times, the reaction was quenched by addition of 200 mL distilled water. An extra 2h ultrasonic treatment was carried out. After adjusting pH 6 by addition of 1 M sodium hydroxide (>98%, Merck) solution, the suspension was further sonicated for 1h, 10 g of L-ascorbic acid (>99%, sigma Aldrich) was dissolved in 100 mL distilled water and slowly added to the exfoliated graphite oxide suspension at room temperature. The reaction was performed at 95°C for 1h. The resultant black precipitates were washed with 1 M hydrochloric acid (37%, merck) and distilled water to pH 7. Finally, the filtrate was dried to obtain rGO powder.

2.2. Synthesis of polyaniline

Emeraldine salt polyaniline (PANI-ES) was synthesized by chemical oxidation, conventional emulsion polymerization. In two different flask, 9.8 g Ammonium peroxydisulfate (APS) (sigma Aldrich) was dissolved in 100 mL distilled water, in another flask 3.72 g aniline (sigma Aldrich) was dissolved in 100 mL hydrochloric acid (>37%, Merck) 1M. And then, both of flasks was kept out in ethilenglycol bath at temperature 0°C for 1h. APS solution was mixed with aniline solution and kept out at temperature 0°C for 24h. The green precipitates were simply filtered by cellulose filter paper and further were washed with aseton and 1 M hydrochloric acid solution.

2.3. Assembly of rGO/polyaniline nanocomposite film

The rGO and polyaniline were blend in three mass compositions of 1:3, 1:1, and 4:1 to produced rGO/polyaniline nanocomposites. The rGO/polyaniline nanocomposites was deposited on synthetic graphite substrate laminated the glass substrate using screen printing technique, followed by sintering in air at 150°C for 15 min and applied as the counter electrode for efficient dye sensitized solar cells (DSSC).

2.4. Assembly of DSSC

A TiO$_2$ photo anode film were prepared by coating the TiO$_2$ colloid on ITO glass substrate using screen printing technique, followed by sintering in 500°C for 1h. Subsequently, the TiO$_2$ film was soaked in a 0.5 mM N719 (purchased from solaronic, Poland) ethanol solution for 24h. The DSSC was fabricated
by sandwiching liquid electrolyte between a dye sensitized ITO-TiO₂ photo anode and graphene/polyaniline film counter electrode.

Figure 1. Design of DSSC using rGO/PANI nanocomposite CE.

2.5. Other characterizations
Raman spectroscopy measurements were taken using Bruker with a 532 nm laser. FTIR spectra were collected using a Bruker tensor instrument. The solar simulator measurements were taken using ORIEL S013A 100mW/cm² dan Khitley 2400.

3. Results and discussion
Raman spectroscopy is a non-destructive technique in use to study structural change and disorder of graphite, GO, and rGO during the oxidation and reduction steps [7, 8]. As shown in Fig. 2a, graphite has a prominent peak at 1566 cm⁻¹ (G band) which is due to the first order scattering of E₂g mode and two weaker peaks located at 1340 cm⁻¹ and 2687 cm⁻¹ (D and 2D bands, respectively) originated from the second order double resonant process between non-equivalent K point in Brillouin zone of graphene. Structural defects induced by attachment of OFGs to the basal plane of graphene during the oxidation of graphite significantly intensified the D band and up-shifted the G band to 1585 cm⁻¹ in the Raman spectrum of GO. The blue shift of the G band has been attributed to the activation and merging of the Raman –inactive D' band with the G band, the exfoliation of graphite to a single graphene sheet, and the resonation of isolated double bonds at higher frequencies than the G band of graphite [7]. On the other hand, the red shift of G band in Raman spectrum of rGO to 1579 cm⁻¹ was observed that can ascribed to the reduction of GO. The relative intensity of the D and G band (I_D/I_G), which is an estimation of the disorder level in graphene, exhibits a non monotonic behavior. The 2D band is found at around 2697 cm⁻¹ which is in reference with the reported result for the single layer graphene within the experimental accuracy [8].

The FTIR spectrum of graphite, GO and rGO (Fig. 2b) showed various peaks corresponding to different oxygen functionalities verifying successful oxidation of graphite into GO, and reduction of GO to rGO. The broad signal around 3400 cm⁻¹ was due to O-H stretching vibrations and adsorbed water molecules. The peak near 1700 cm⁻¹ is attributed to various skeletal vibrations of C=C aromatic unoxidized graphitic domain. Other prominent signals in the GO’s spectrum which have been attenuated in rGO’s spectrum are 1399 cm⁻¹, and 1071 cm⁻¹ originating from O-H deformation, and the C-O stretching respectively [7, 8].

In Fig. 2c shows the main bands of PANI Raman spectra situated at 1621, 1624, 1491 dan 1505 cm⁻¹ may be attributed to the following: vibration of C=C semiquinonoid ring, and vibration of benzenoid ring. Fig 2d. Shows FTIR spectra of PANI. The main bands situated at 1575, 1490, 1301 and 1138 cm⁻¹ may be attributed to the following vibrations: stretching of C=C in quinoid ring, stretching vibration of C=C benzenoid ring, stretching of C-N secondary aromatic amine, stretching of C=N, respectively [10].
Figure 2. Characterization of graphite, GO, rGO powder, and polyaniline emeraldine salt (a) Normalized Raman spectra of graphite, GO, and rGO. (b) FT-IR spectra of graphite, GO, and rGO.
Graphene is a good electron acceptor. On the other hand, aniline is good electron donor [11]. When polyaniline are blended into graphene sheets, polyaniline can immediately absorb onto the surface of the graphene sheet due to the electrostatic attraction. And then the structure of PANI covering nanosheets forms slowly [12]. During polymerization, graphene sheets acting as the support material can supply a large number of active sites for nucleation of PANI, where polyaniline acts as conducting support [12, 13]. Fig. 3 shows characterization of rGO/PANI nanocomposites film using Raman spectroscopy (Fig. 3a) and FTIR spectroscopy (Fig. 3b). The Raman spectra of rGO/PANI nanocomposites film 4:1, 1:1, and 1:3 (Fig. 3a) exhibit similar signals to that rGO, the D-band and G-
band still in same positions. But, the G-band of rGO/PANI nanocomposites film of 4:1, 1:1, and 1:3 have the shoulder. The broader shoulder showed by rGO/PANI nanocomposites film 1:3, apparently as a result of influence coming from PANI. Therefore, Raman spectra results confirm the formation of PANI nanocomposites coating on the surface of graphene sheet. Fig. 3b shows FTIR spectras of rGO/PANI nanocomposites film 4:1, 1:1, and 1:3. FTIR spectras of rGO/PANI nanocomposites film 1:1, and 1:3 have similar signals to the PANI, but the rGO/PANI nanocomposites film 4:1 has similar signal to the rGO. The spectra of FTIR depends on the composition of the composites.

Fig. 4 shows rGO/PANI nanocomposites conductivity. In Fig. 4a, rGO has typically as semiconductor. Fig. 4b shows that by introducing graphene into PANI matrix, the conductivity increases with increasing graphene content. The highest conductivity achieved by rGO/PANI nanocomposite of 4:1. Based on the graph (Fig. 4b), the rGO/PANI nanocomposites have typically as conductor, conductivity decreases with increasing frequency. Homogeneous PANI coating on the surface of graphene sheets increases both conductivity, and thus is preferred for the enhancement of the electrocatalytic performance as a counter electrode for DSSC [2].

![Gráfico 3. Caracterización de nanocomposites film (a) Raman spectra of rGO/PANI nanocomposites film of 4:1, 1:1, and 1:3.](image_url)
Figure 3 (Cont.). Characterization of rGO/PANI nanocomposites film (b) Normalized FT-IR spectra of rGO/PANI nanocomposites film of 4:1, 1:1, and 1:3.

The photocurrent-voltage curve of DSSC with rGO/PANI nanocomposites are compared in Fig. 5. The best performance of rGO/PANI nanocomposites counter electrode achieved by rGO/PANI of 4:1 with photoconversion efficiency 2.65%, mainly due to highest fill factor 0.472. The PCE increased with the increase in mass composition of rGO. The derived photovoltaic parameters, such as the open-circuit voltage ($V_{OC}$), the short circuit current density ($J_{SC}$), the fill factor (FF) and the photoconversion efficiency (PCE) are summarized in Table. 1. Thus, the as-prepared rGO/PANI nanocomposites is good candidate as the counter electrode in DSSC.

Figure 4. rGO/PANI nanocomposites conductivity (a) conductivity of rGO.
Figure 4 (Cont.). rGO/PANI nanocomposites conductivity (b) conductivity of rGO/PANI 4:1, 1:1, and 1:3.

Figure 5. I-V curve of DSSC based on rGO/polyaniline nanocomposites counter electrode.

Table 1. photovoltaic parameters of DSSC with rGO/PANI CEs.

| Films       | PCE (%) | FF  | Voc (Volt) | Jsc (mA/cm²) |
|-------------|---------|-----|------------|--------------|
| rGOPANI1:3  | 1.04    | 0.463| 0.6        | 3.359        |
| rGOPANI1:1  | 2.01    | 0.446| 0.637      | 6.351        |
| rGOPANI4:1  | 2.64    | 0.472| 0.64       | 7.853        |

4. Conclusions
The best performance was obtained for rGO/Polyaniline ratio of 4:1. Here, the optimum short circuit current density (Jsc), the open circuit current (Voc), the fill factor (FF), and the overall conversion efficiency under AM 1.5, 100 mW cm⁻² illumination are 7.853 mA/cm², 0.64 Volt, 47.2% and 2.64%, respectively.

References
[1] Shalini S, Balasundaraprabhu R, Prasanna S, Mallick T A, and Senthilarasu S 2015 Renewable
and Sustainable Energy Reviews 51 p 1306-1325.

[2] Singh E and Nahwa H S 2015 Science of advanced Materials 7 p 1863-1912.

[3] Janani M, Srikrishnarka P, Nair S V and Nair A S 2015 J. Mater. Chem. A 3 p 17914-17938.

[4] Hardin B E, Snaith H J and McGehee M 2012 Nature Photonics 6 p. 162-169.

[5] Konwer S, Gogoi J P, Kalita A, Dolui S K 2011 J. Mater Sci: Mater Electron 22 p. 1154–1161.

[6] Baniasadi H, Ramazani A, Mashayeksakhan S and Ghaderine F 2014 Synthetic Metals 196 p. 199-205.

[7] Wang G, Zhuo S and Xing 2012 Materials Letters 69 p. 27-29.

[8] Konwer S 2016 J.Mater Sci: Mater Electron 27 p. 4139-4146.

[9] Harish C, SreeHarsha V S, Santhos C, Ramachandran R, Saranya M, Mudallar T V, Govardhan K and Grace N A 2012 Advanced Science, Engineering and Medicine 4 p. 1-9.

[10] Goswami S, Maiti U N, Maiti S, Nandy S, Mitra M K and ChattoPadhyay K K 2011 ScienceDirect:Carbon 49 p. 2245-2252.

[11] Sun H, Luo Y, Zhang Y, Li D, Yu Z, Li K and Meng Q 2010 J. Phys. Chem. C 114 p. 11673–11679.

[12] Lee J W, Ramasamy E, Lee D Y and Song J S 2009 ACS.Applied Materials and Inter 4 p. 114-120.

[13] He B, Tang Q, Wang M, Chen H and Yuan S 2014 ACS Applied Materials and Interfaces 6 p. 8230-8236.