REPUBLIK INDONESIA
KEMENTERIAN HUKUM DAN HAK ASASI MANUSIA

SURAT PENCATATAN
CIPTAAN

Dalam rangka pelindungan ciptaan di bidang ilmu pengetahuan, seni dan sastra berdasarkan Undang-Undang Nomor 28 Tahun 2014 tentang Hak Cipta, dengan ini menerangkan:

Nomor dan tanggal permohonan : EC00201983902, 26 November 2019

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Kewarganegaraan : Indonesia

Jenis Ciptaan : **Karya Tulis (Artikel)**

Judul Ciptaan : **Effect Of Graphite Oxide Solution Concentration On The Properties Of Multilayer Graphene**

Tanggal dan tempat diumumkan untuk pertama kali di wilayah Indonesia atau di luar wilayah Indonesia : 31 Desember 2013, di Selangor

Jangka waktu pelindungan : Berlaku selama hidup Pencipta dan terus berlangsung selama 70 (tujuh puluh) tahun setelah Pencipta meninggal dunia, terhitung mulai tanggal 1 Januari tahun berikutnya.

Nomor pencatatan : 000171827

adalah benar berdasarkan keterangan yang diberikan oleh Pemohon.
Surat Pencatatan Hak Cipta atau produk Hak terkait ini sesuai dengan Pasal 72 Undang-Undang Nomor 28 Tahun 2014 tentang Hak Cipta.

a.n. MENTERI HUKUM DAN HAK ASASI MANUSIA
DIREKTUR JENDERAL KEKAYAAN INTELEKTUAL

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Effect of graphite oxide solution concentration on the properties of multilayer graphene

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Effect of Graphite Oxide Solution Concentration on the Properties of Multilayer Graphene

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Abstract. This paper reports the influence of graphite oxide (GO) solution concentration on the optical and electrical properties of multilayer graphene (MLG) films. Graphene oxide (GrO) films were deposited on the glass substrates by spin coating aqueous solutions of GO with different concentrations (7, 8, 9, 10 and 11 mg/ml). The GrO films were then thermally reduced at temperature of 500^0C in argon flow for half an hour to form MLG films. Both the transmittance and sheet resistance decreased with the GO concentration from 8 mg/ml to 9 mg/ml, possibly due to thicker and uniform coverage of MLG over the substrate. However, the transmittance and sheet resistance increased rapidly as the GO concentration reached 11 mg/ml, which can be attributed to poor film quality. The MLG film obtained at concentration of 10 mg/ml showed the highest transmittance/sheet resistance ratio with 69 % transmittance and sheet resistance of 292 ± 63 kΩ/sq. The optimum MLG film was utilized as counter electrode in dye sensitized solar cells based on ZnO nanorods.

Keywords: Dye sensitized solar cells; sheet resistance; transmittance.
PACS: 68.65.Pq; 78.67.Wj; 81.05.uf; 81.20.Ka

INTRODUCTION

For the past two decades, graphene has been attracting attention due to its good electrical property and high optical transmission [1-5]. Graphene as a monolayer of carbon in two dimensional honeycomb lattices can be easily prepared by reduction of graphene oxide (GrO) [6-8]. Hummers method is a famous, low cost and simple technique to obtain large quantity of graphite oxide (GO) which can be exfoliated to form GrO film [9].

It is well known that both sheet resistance and transmittance of graphene film decrease with film thickness. Weber at al. reported that the transmittance of 24 nm-thick graphene film at 300 nm is ~55 % which is much lower than that of 8 nm-thick graphene film (~80 %) [10]. Meanwhile, graphene film should be made thicker to minimize the boundaries between individual graphene sheets which normally result in higher sheet resistance [11]. The thickness of the graphene film could be controlled by manipulating the GO solution concentration or coating cycle [12]. This present work reports the effect of GO solution concentration (7, 8, 9, 10 and 11 mg/ml) on the optical and electrical properties of multilayer graphene (MLG) films. The highest transmittance to sheet resistance ratio of MLG film was obtained at GO concentration of 10 mg/ml. The corresponding MLG film has been successfully applied as transparent counter electrode in dye sensitized solar cell (DSSC).

EXPERIMENTAL

The procedures to produce GO flake using modified Hummers method were described elsewhere [13]. The GO flakes were dissolved in deionized water at various concentrations of 7, 8, 9, 10, and 11 mg/ml by sonication for 20 min followed by stirring for 2 hours. Then, the resultant solution was spin-coated on the glass substrates to form GrO films. Next, the GrO films were annealed at 500^oC in argon flow for half an hour to form MLG films.

Halo DB-20 UV-Vis spectrophotometer was used to investigate the optical transmission of MLG films. The sheet resistance of MLG films was characterized by four point probe measurement using Keithley 2401 source

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meter. Lastly, DSSC consisted of ZnO nanorod arrays as photoanode and optimum MLG as counter electrode with an iodine electrolyte was fabricated as shown in FIGURE 1. The ZnO nanorod arrays were grown on FTO glass substrates following the method described elsewhere [14-15]. The DSSC with active area of 0.23 cm^2 was characterized by current–voltage measurement under 100 mW/cm2 simulated AM 1.5 G sunlight using Keithley 237 source measurement unit.

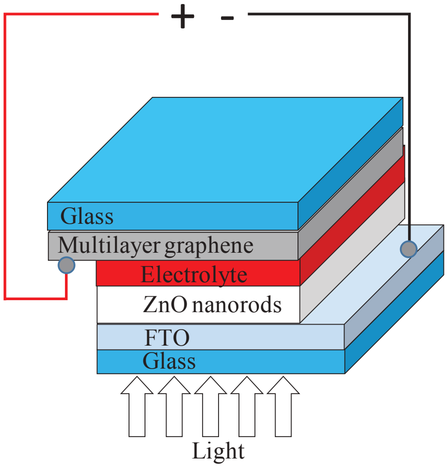

FIGURE 1. The DSSC with ZnO nanorods/electrolyte/MLG structure.

RESULTS AND DISCUSSION

The optical transmission spectra of MLG films prepared at different GO concentrations are shown in FIGURE 2. It can be clearly seen that the transmittance decreased significantly from 69-71 % (λ=550 nm) to 62 % when the GO concentration increased from 7-8 mg/ml to 9 mg/ml. This can be explained by the formation of thicker MLG film and uniform coverage of MLG over the substrate. However, the transmittance started to increase as the GO concentration further increased to 10 and 11 mg/ml due to poor film quality. The crack and void can be clearly observed from the photograph of the corresponding MLG films deposited from concentrated solution (FIGURE 3).

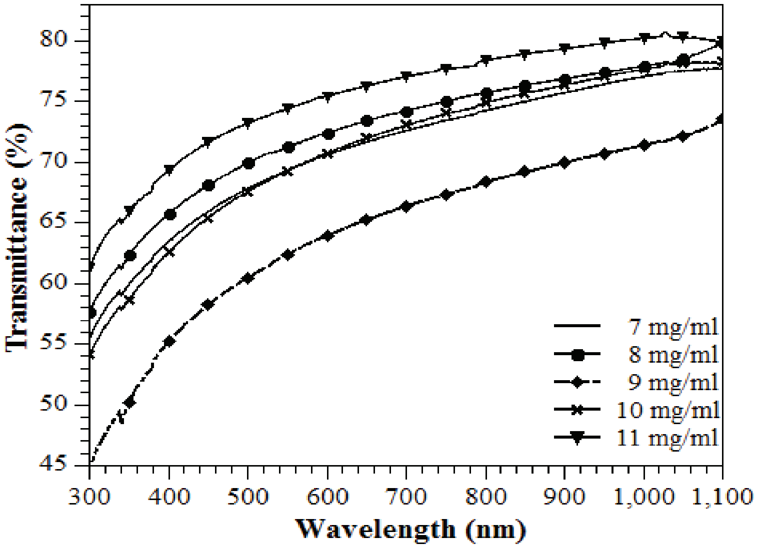

FIGURE 2. The optical transmission spectra of MLG films prepared at different GO concentrations.

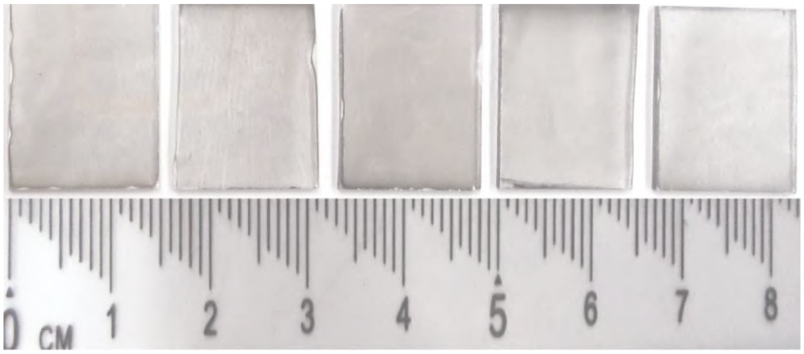

FIGURE 3. The photograph of MLG films prepared at GO concentrations of 7, 8, 9, 10, and 11 mg/ml (from left to right).

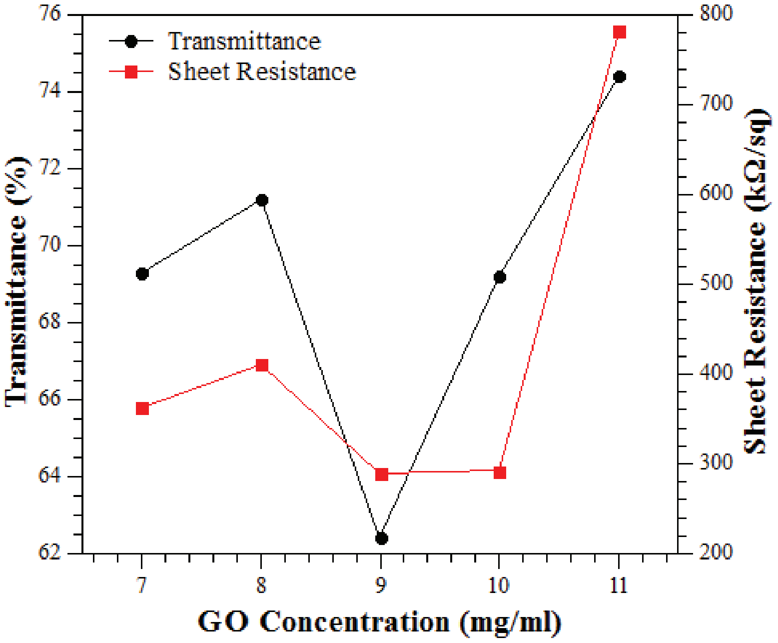

FIGURE 4. The transmittance and sheet resistance of MLG films as a function of GO concentration.

TABLE (1). The transmittance and sheet resistance of MLG films prepared at various GO concentrations

Concentration (mg/ml)	Transmittance (T, %)	Sheet Resistance (SR, kΩ/sq)	T/SR
7	69.3	362.14 ± 49.44	0.19
8	71.2	410.09 ± 35.69	0.17
9	62.4	289.79 ± 12.81	0.22
10	69.2	291.95 ± 63.07	0.24
11	74.4	781.96 ± 299.7	0.10

FIGURE 5 shows the current density–voltage (J–V) graph of DSSC constructed with 10 mg/ml MLG film as counter electrode in dark and under illumination of a simulated AM 1.5 G sunlight at 100 mW/cm^2. The DSSC showed power conversion efficiency (PCE) of 0.0027 % with short circuit current density (Jsc) of 26 µA/cm^2, open circuit voltage (Voc) of 0.42 V, and fill factor (FF) of 25 %. It should be noted that the present PCE was smaller than that of a similar DSSC with MLG as counter electrode reported recently because the substrate and thermal reduction temperature are different [13].

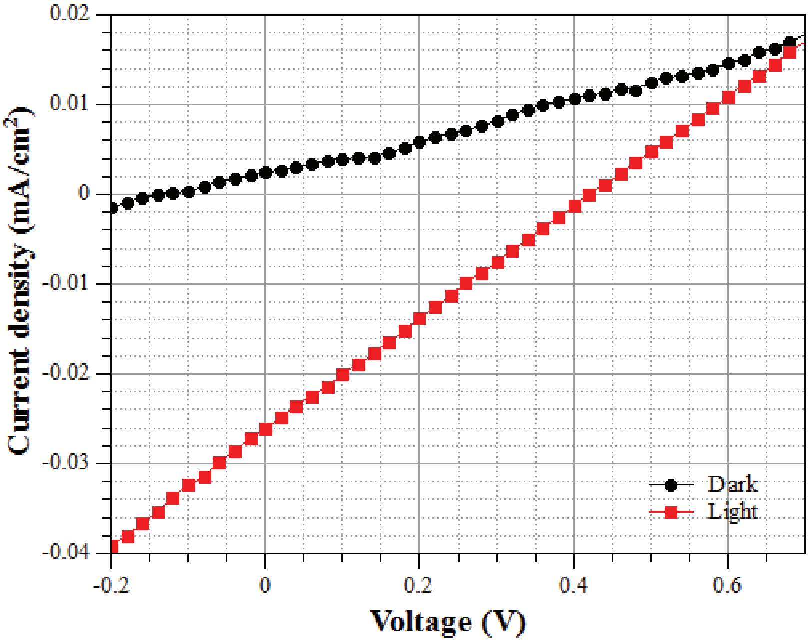

FIGURE 5. The J–V characteristic of DSSC in dark and under illumination.

CONCLUSION

The effect of GO solution concentration on the optical and electrical properties of MLG films has been investigated. The transmittance and sheet resistance decreased when the GO concentration increased from 8 mg/ml to 9 mg/ml as a result of formation of thicker MLG film and uniform coverage of MLG over the substrate. Further increase in GO concentration to 11 mg/ml results in higher transmittance and sheet resistance due to poor film quality. The MLG prepared at GO concentration of 10 mg/ml which showed the highest transmittance to sheet resistance ratio was studied as a transparent counter electrode in DSSC. The DSSC yielded Jsc of 26 µA/cm^2, Voc of 0.42 V, and FF of 25 %, resulting in PCE of 0.0027 %.

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This work has been carried out with the financial support of the Malaysian Ministry of Higher Education (MOHE), under the Research funding ERGS/1/2011/STG/UKM/02/62. The authors would like to thank Fitri Yenni Naumar, Siti Khatijah Md. Saad, Riski Titian Ginting, Eng Liang Lim for their contribution in this work and Mr. Zailan Bin Mohd Yusof in XRD characterization.

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SURAT PENCATATAN
CIPTAAN

Dalam rangka pelindungan ciptaan di bidang ilmu pengetahuan, seni dan sastra berdasarkan Undang-Undang Nomor 28 Tahun 2014 tentang Hak Cipta, dengan ini menerangkan:

Nomor dan tanggal permohonan : EC00201983903, 26 November 2019

Pencipta

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Kewarganegaraan : Indonesia

Jenis Ciptaan : **Karya Tulis (Artikel)**

Judul Ciptaan : **Effect Of Growth Temperature On ZnO Nanorod Properties And Dye Sensitized Solar Cell Performance**

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a.n. MENTERI HUKUM DAN HAK ASASI MANUSIA
DIREKTUR JENDERAL KEKAYAAN INTELEKTUAL

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Conference Paper

Effect of Growth Temperature on ZnO Nanorod Properties and Dye Sensitized Solar Cell Performance

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Abstract Nanostructure of semiconductor materials zinc oxide (ZnO) is widely used in fabrication of solar cell devices. The performance of such devices is strongly depending on the nanostructures of the thin films used. In this paper reports the effect of growth temperature during synthesis of one-dimensional (1-D) anatase ZnO nanorod arrays through hydrothermal process facing their structure, morphology, and optical properties. The ZnO nanorod was first synthesized use the solution concentration and time fixed at 0.04M and 1 hour. The growth temperature were varied from 70, 80, 90 and 100 °C. The effect of growth temperature on the structural, morphology, and optical absorption of ZnO nanorod were studied by using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and UV–vis spectroscopy. The regularity, diameters, heights, and surface densities of the ZnO nanorods were increased with the growth temperature.The optimum results of FESEM characterizations showed that the grown ZnO nanorods have diameters of 64.14 ± 8.3 nm, heights of 363.72 ± 34 nm and surface densities of 182 numbers/μm^2 which was obtained at temperature of 90 °C. The optimum ZnO nanorod film was utilized as photo anode in dye sensitized solar cells. The DSSC yielded Jsc of 0.86 mA/cm^2, Voc of 0.49 V, and FF of 38 %, resulting in PCE of 0.16 %.

Keywords: growth temperature, one-dimensional, ZnO nanorod array, DSSC

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1. Introduction

Research efforts on one dimensional (1-D) ZnO nanostructures such as nanorod still have high interest rates since a few decades ago because it has unique properties for many applications such as sensor, solar cell, electronics devices and etc.[1]. Numbers of scientific papers related on the ZnO nanostructure whether fundamental or practical application has become the evidence of their popularity. One of the main aspects in this research is to synthesize the ZnO nanorod with regular rod, small diameter, higher, and optimum of their surface densities but also an improved quality of their optical and electronic properties. Tian, Voigt [2] mention the extended and oriented nanostructures are desirable for many applications. Besides, the direct fabrication of

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complex nanostructures with controlled crystalline morphology, orientation and surface architectures remains a significant challenge.

Previously, oriented carbon nanotubes and ZnO nanorod shave been prepared by high-temperature vacuum deposition techniques. However, this method makes the structure of ZnO becomes damaged and increase the preparation cost. A variety of methods have been reported for fabricating arrays of aligned ZnO nanostructure, including vapour phase transport, metal organic chemical vapour deposition (MOCVD),and hydrothermal processes. However, vapour-phase transport and MOCVD usually require single-crystal substrates and high operation temperature.

In this paper, ZnO nanorod was provided through a hydrothermal process and the effect of the temperature during preparation step to their properties and DSSC performance is also investigated. This research is expected to find the lowest temperature to produce a better ZnO nanorod and applied of them on DSSC device with better performance and low cost.

2. Experimental

ZnOnanorods arrays were prepared on FTO glass substrates which were pre-coated with ZnO nanoparticles using hydrothermal process. ZnOnanorods which first seed layers prepared by alcohothermal process which contain of zinc acetate (Zn $(H_3COO)_{2.}$ H2O) (98%, Sigma Aldrich) in ethanol to form ZnO seeded-substrate. The ZnO seeding substrate was subject to annealing at 350 °C in air for an hour and followed by immersing them in closed vial containing zinc nitrate hexahydrate (99%, Sigma Aldrich) and hexamethyl-tetramine (99%), Sigma Aldrich) in DI water. Next, the final concentration of that solution was maintained at 0.04 M and then inserts them in heating drying oven with various temperature such as 70, 80, 90 and 100^{o}C for 1 hour. The detail of the ZnOnanorods preparation processes has been described very well elsewhere [3, 4]. The resultant ZnOnanorod were characterized by X-Ray diffraction (XRD), Halo DB-20 UV-Vis spectrometer, and Carl Zeiss Supra 55VP field emission scanning electron microscopy (FESEM) to investigate their composite-structure, optical absorbance properties and morphology as well. Besides, the current (J)–voltage (V) curve of cell underactive area of 0.23 cm^{2}was recorded by a Keithley model 237 measurement, which were presented in the "Result and discussion "section.

ZnOnanorod will be used as photo anode in dye sensitized solar cells (DSSC). Installation of a DSSC solar cell device was made by clamp the photo anode with counter electrode and put insulating material between of them. Furthermore, the electrolyte is injected into the active area to make the DSSC device can work to convert sunlight coming through photo anode to become electric current. The DSSC performance of the solar cell with active area of 0.23 cm^2 was investigated by current–voltage measurement under 100 mW/cm^2 simulated AM 1.5 G sunlight using Gambry 1000 interface measurement unit.

The electrolyte used is s standard iodolyte. Dye solution prepared by dissolving 7.0 mg powder dyes N-179 in 20 ml of ethanol to a concentration of 0.3 mM. The counter electrode was used of 40 μl a liquid plastisol which in-situ coated on the FTO substrate

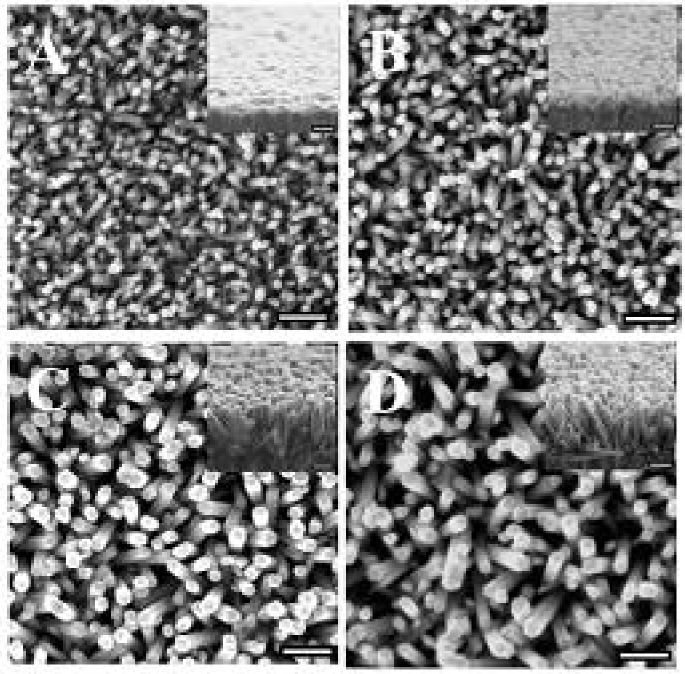

Figure 1: FESEM image variations in temperature (A) to 70, (B) 80, (C) 90 and (D) 100 ° C with scale bar 200 nm. The inset picture in each image shows a cross-sectional FESEM micrograph of the corresponding image (scale bar in 200 nm).

at 2000 rpm for 30 seconds. The same step was repeated up to 3 times on each substrate where each of them heated at 100 ° C for 10 minutes. Next, that substrate was annealed at 450^o C for 1 hour. Prior to the installation of solar cell devices do, photoanode consisting of ZnOnanorod grown on FTO soaked into 20 ml of N-719 dye solution with a concentration of 0.3 mM, for 2 hours. This immersion is carried out in a dark room, as N-719 is very sensitive and unstable under light radiation, photo anode left to dry in the air and kept so in this process photo anode is not exposed to light.

3. Result and discussion

The ZnONanorods has been successfully synthesized by using hydrothermal process. Fig. 1A shows the ZnOnanorods FESEM image on FTO grown at 70^{o}C followed by annealing at 350^{o}C for 1 h. In this case, the ZnOnanorod has not been formed perfectly. Meanwhile, by increase of grown temperature to 80^{o}C causes the ZnONanorod has been start to grow on the FTO substrate with average diameter about 33.69 nm (see Fig. 1B). Furthermore, this average diameter increases to 64.14 nm when it was grown at 90^{o}C with a uniform size and regular form as shown in Figure 1C. Lastly, the increase in the growth temperature to 100^{o}C even made a reduced the average diameter to 55.64 nm with irregular and not uniform size.

Fig 2. shows the XRD peaks of ZnOnanorods which was prepared by using a variety of grown temperature. This it found that the S70 sample XRD peaks observed are too weak which mean the growth processes has not occurred properly at this temperature. Nanorod growth started to grown with better form in samples S80 and S90. The sample

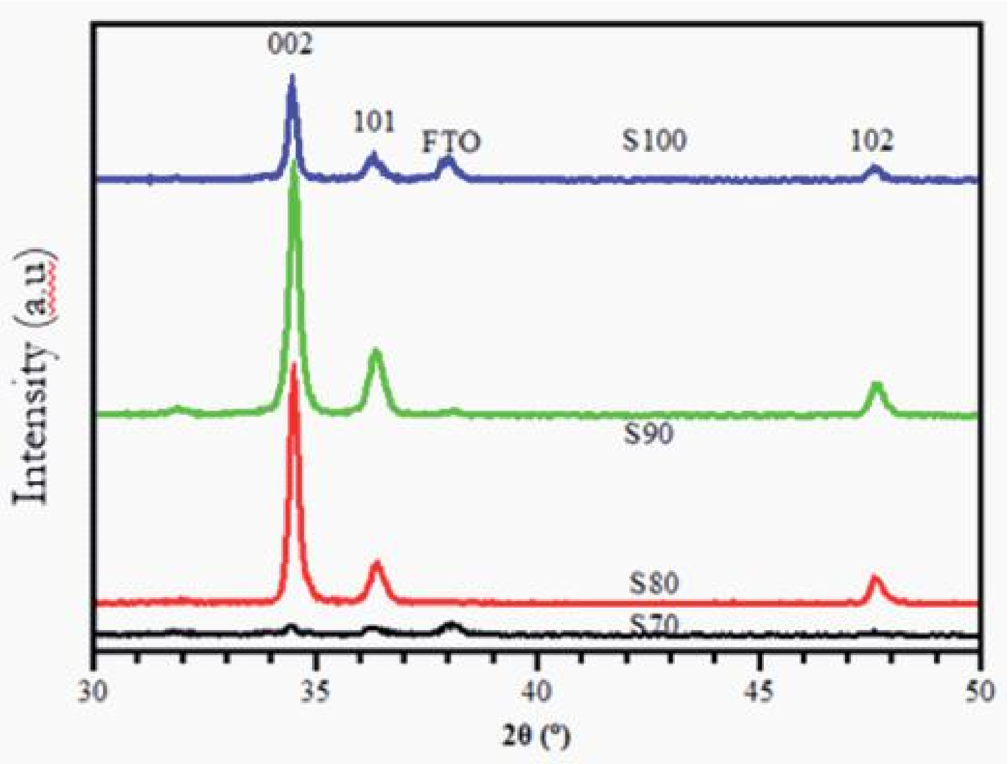

Figure 2: XRD spectra of ZnO nanorods at grown temperature of 70, 80, 90 and 100^{o}C..

Label Samples	Voc (mV)	Jsc (mA/cm^2)		PCE (%)	FF (%)
S80	0.44	0.40		0.06	0.34
S90	0.49	0.86		0.16	0.38
S100	0.47	0.71		0.12	0.35

Table 1: DSSC performance parameters of ZnO nanorod grown at the growth temperature variations.

S100 shows the higher and there are additional peaks of FTO substrate. This means that, the growing process began to fail because of the water solvent boiling begins at a temperature of 100°C. As can be seen from these spectra, 3 main peaks namely at 2θ= 34.50, 36.50, and 47.80 where obtained. According to JCPDS file: No. 84-1286 for ZnO the peak was shown above associated with plane of (002), (101), and (110) phase. It was found that only the ZnO peak was detected in those spectra, showing the preparation step does not affect the impurities occurred. Besides, the border peaks show the formation of ZnO nanostructure, which good accordance with previous report [1, 5]. The intensity of the ZnO (002) increases and the peak width decreases with the growth processing time increased.

Figure 3 shows the current density–voltage (J–V) graph of DSSC constructed with plastisol as counter electrode under illumination of a simulated AM 1.5 G sunlight at 100 mW/cm^2. A typical DSSC exhibited a short circuit current density (Jsc) of 0.16 mA/cm^2, an open circuit voltage (Voc) of 0.49 V, and a fill factor (FF) of 38% which was obtain at sample S90. The detail of the DSSC parameter of the sample was described at table 1.

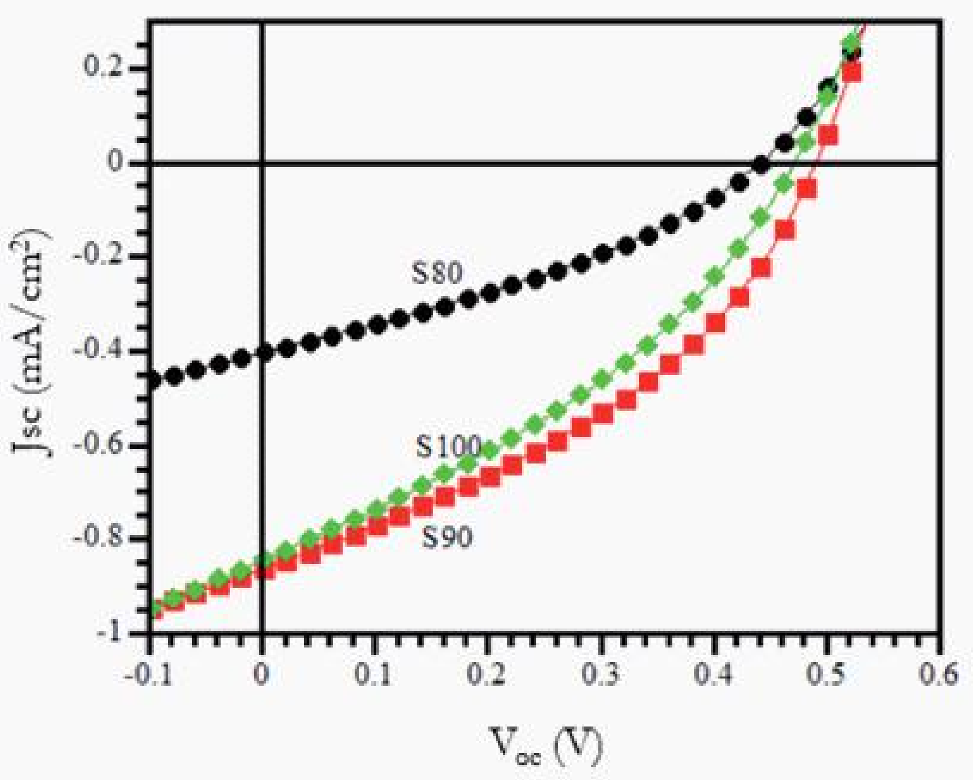

Figure 3: JV curve of a solar cell DSSC devices ZnO nanorod in bright conditions by varying the growth temperature.

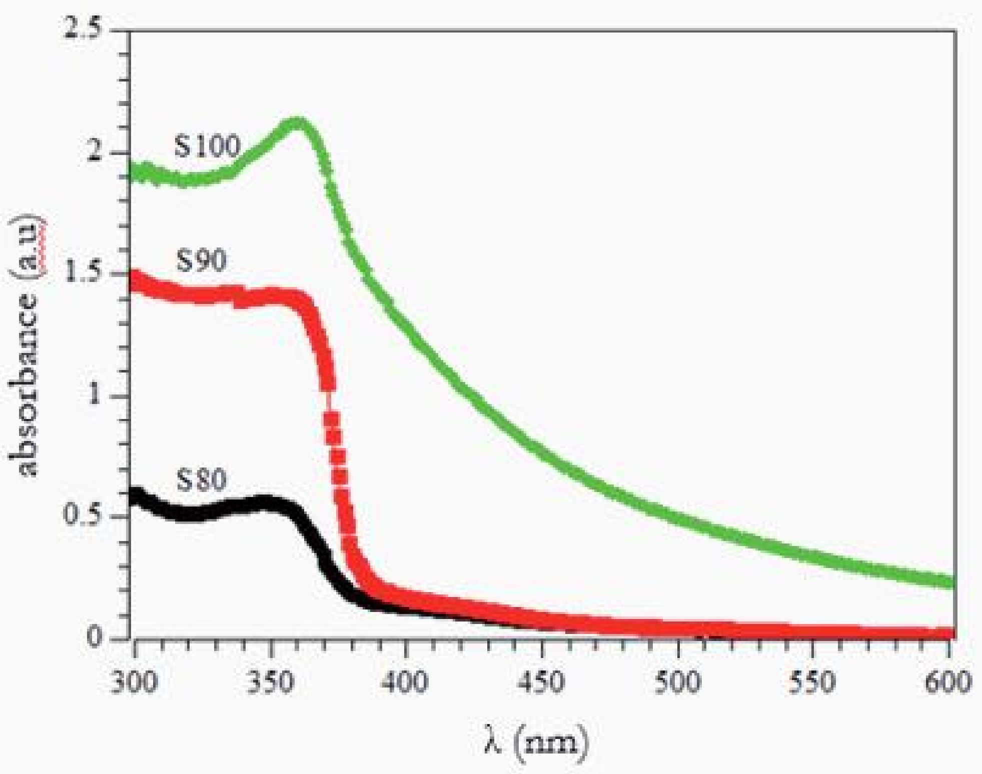

Figure 4: The optical absorption spectrum of ZnO nanorod grown by varying the growth temperature.

Fig 4 shows the optical absorption spectrum of ZnOnanorod grown with the growth temperature variations. The optical absorption of sample S80 and S90 is the same as the optical absorption variations sample first. While the S100 has the highest intensity of the sample, which corresponds to the sample has the highest elevation nanorod. Optical absorption for the S100 has a shoulder that is shaped like a top, which may be due to sample density nanorod has a small, high altitude that makes it easy to apply thermal vibrations of optical radiation

4. Conclusion

The study on the implementing of ZnONRs parameter at various growth temperatures have been performed. The broad peak, and clearly XRD spectra confirm the effect of ZnO nanorods formation. The best photovoltaic performance of DSSC with platisol as a counter electrode which exhibited the J_{sc} of 0.86 mA/cm^2, V_{oc} of 0.49 V, and FF of 38 %, resulting the PCE of 0.16 % was obtained at ZnONRs which prepared at growth period of 1h, growth temperature of at 90^{o}C.

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SURAT PENCATATAN

CIPTAAN

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Nomor dan tanggal permohonan : EC00201983904, 26 November 2019

Pencipta

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Kewarganegaraan : Indonesia

Pemegang Hak Cipta

Nama : **Dr. Marjoni Imamora, M.Sc**

Alamat : Perumahan Dobok Indah Blok C No.3 Lima Kaum Batusangkar, Batusangkar, Sumatera Barat, 27211

Kewarganegaraan : Indonesia

Jenis Ciptaan : **Karya Tulis (Artikel)**

Judul Ciptaan : **Formation Of Gold-coated Multilayer Graphene Via Thermal Reduction**

Tanggal dan tempat diumumkan untuk pertama kali di wilayah Indonesia atau di luar wilayah Indonesia : 15 Mei 2013, di Bangi, Selangor

Jangka waktu pelindungan : Berlaku selama hidup Pencipta dan terus berlangsung selama 70 (tujuh puluh) tahun setelah Pencipta meninggal dunia, terhitung mulai tanggal 1 Januari tahun berikutnya.

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Formation of gold-coated multilayer graphene via thermal reduction

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ABSTRACT

The gold-coated multilayer graphene was obtained by simultaneous thermal reduction of gold ions and graphene oxide blend film under argon flow for an hour. The effects of thermal reduction temperatures (200 °C, 400 °C, and 500 °C) on the structural, optical, and electrical properties of gold-coated multilayer graphene were studied by using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), UV–vis spectroscopy, and four point probe measurement. The optical transmittance increased and the sheet resistance decreased with the thermal reduction temperature. The highest optical transmission of 66% and the lowest sheet resistance of 78.3 kΩ/sq were obtained at thermal reduction temperature of 500 °C.

1. Introduction

Indium tin oxide (ITO) and fluorine-doped tin oxide (FTO), with good transparency and high conductivity at room temperature [1], have been widely used as transparent electrode in solar cell application [2–5]. Recently, the research interest has focused on graphene which can serve as alternative transparent electrode due to its high electrical conductivity [2,3], high optical transmission [6], chemical stability, low cost [7], and availabilty [8,9]. However, efforts to further improve its properties through simple, cheaper, and environmental friendly methods still remain a great challenge to researchers.

Multilayer graphene (MLG) has been obtained through thermal reduction of graphene oxide (GrO) film prepared by chemical route using the modified Hummers method in previous work [9]. However, the properties of resultant MLG are strongly dependent on the synthesis protocol [10]. The presence of functional groups during graphite oxide (GO) flake preparation could change the electronic-structure [11] and high energy induced by ultrasonic agitation during GrO preparation could damage its lattice-structure [12]. Besides, point defects and wrinkles could be formed during GrO thermal reduction [13]. All those factors contribute to lower optical transmittance and higher sheet resistance.

Kim et al. reported that spin coating of gold(III) chloride ($AuCl_3$) solution on graphene film leads to 77% decrease in sheet resistance and only 2% decrease in optical transmittance [14]. The decrease in sheet resistance is due to p-doping of graphene by reduction of gold ion to gold particle. However, the reduction of sheet resistance in multilayer graphene layer is not significant as compared to that in single or two layers graphene. Meanwhile, Le et al. demonstrated that gold nanoparticles-coated graphene could be obtained by adding gold(III) chloride hydrate ($HAuCl_4$) to the GrO aqueous solution followed by chemical reduction of GrO and gold ion by using polyelectrolyte (PDDA) as reducing agent and stabilizer [15].

It is well known that gold chloride tetrahydrate ($HAuCl_4 \cdot 3H_2O$) could be decomposed to gold particle when heated at and above 200 °C [16]. In addition, thermal reduction is also considered as one of most famous techniques to produce graphene from graphene oxide film [17]. In this work, a simple approach to simultaneously reduce the graphene oxide and gold ion by applying heat treatment at different temperatures was explored. The X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) results confirm that graphene oxide and gold ion have been successfully reduced and gold-coated multilayer graphene (Au-MLG) was obtained. The optical transmittance of Au-MLG increased whereas the sheet resistance decreased with the thermal reduction temperature.

2. Experimental

GO flake was prepared by using the modified Hummers method and the synthesis details were described elsewhere [9]. The typical gold-coated graphene oxide (Au-GrO) films preparation step is shown below: GO flake was dissolved in 0.01 M

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aqueous solution of $HAuCl_4 \cdot 3H_2O$ (99.999%, Sigma-Aldrich) at a concentration of 10 mg ml^{-1}. The solution underwent sonication for 30 min and followed by stirring for an hour. Then, the solution was spin-coated on quartz substrates to obtain Au-GrO films by using Chemat Technology KW-4A spin-coater. The Au-GrO films were then annealed at 200 °C, 400 °C, and 500 °C in argon atmosphere for an hour to form Au-MLG. The resultant samples were then denoted as Au-MLG2, Au-MLG4, Au-MLG5 for thermal reduction temperatures of 200 °C, 400 °C, and 500 °C, respectively.

The optical transmission characterization of Au-GrO and Au-MLG films was carried out by using Halo DB-20 UV–vis spectrophotometer. The crystal-structure was characterized by using Bruker D8 Advanced X-ray diffractometer with CuKα radiation at a scan rate of 0.025°/0.1 s. The morphology of the samples was obtained by using Zeiss Supra 55VP field emission scanning electron microscope (FESEM) at an acceleration voltage of 3 kV. Lastly, the sheet resistance was obtained via four point probe measurement using Keithley 2401 source meter.

3. Results and discussion

The XRD spectra of Au-GrO and Au-MLG films are shown in Fig. 1. A sharp peak at $2\theta=9.82°$ corresponding to interlayer distance of C–C of 0.90 nm was observed in the XRD spectrum of Au-GrO. A weaker peak at $2\theta=20.55°$ shows the incomplete oxidation and intercalaction of graphite [9]. It is interesting to note that another two peaks at $2\theta=38.19°$ and 44.40° associated with (111) and (200) planes of anatase phase of gold, respectively can be identified (JCPDS file no. 00-004-0784). This indicates that some of the Au^{3+} ions could be reduced to Au^0 particles without any thermal treatment. It has been reported that Au^{3+} ions could be easily reduced on the graphene to form Au^0 particles as described by the following reaction [14]:

$$AuCl_4^{-}+3e \rightarrow Au^0+4Cl \quad (1)$$

This reduction process is possible since the oxidation of graphite is incomplete in present work. In addition, some Au^0 particles could also be produced on sonication via the following reactions [18]:

$$H_2O \rightarrow H^{*}+{}^{*}OH \quad (2)$$

$$AuCl_4^{-}+3H^{*} \rightarrow Au^0+4Cl^{-}+3H^{+} \quad (3)$$

After thermal reduction at 200 °C, the sharp peak at $2\theta=9.82°$ disappeared and a broad peak at $2\theta=22.05°$ corresponding to the interlayer distance of C–C of 0.404 nm was detected, suggesting removal of functional groups such as hydroxyl (OH), epoxy (C–O–C) and carboxyl (COOH) from Au-GrO film [9,15,19,20]. The interlayer distance of C–C decreased further to 0.396 nm ($2\theta=22.90°$) and 0.394 nm ($2\theta=23.05°$), at temperatures of 400 °C and 500 °C, respectively, indicating more functional groups could be removed at higher temperature. Two peaks corresponding to (111) and (200) planes of gold became more pronounced at temperatures of 200 °C and 400 °C. This is due to the thermal decomposition of $HAuCl_4 \cdot 3H_2O$ to Au when the heating temperature reached 200 °C according to the following reaction [16]:

$$HAuCl_4 3H_2O \xRightarrow{100^{\circ}C} AuCl_3 \xRightarrow{160^{\circ}C} AuCl \xRightarrow{200^{\circ}C} Au \quad (4)$$

Since Au-MLG heated at 500 °C had the smallest number of remaining functional groups, gold ions were reduced more uniformly on the graphene. As a result, well distributed and smaller size of gold was formed as evidenced by the broadened XRD peak of gold plane.

Fig. 2 shows the optical transmission spectra of Au-GrO, Au-MLG2, Au-MLG4, and Au-MLG5 films. The transmittance of Au-GrO film reduced significantly from 75% ($\lambda=550$ nm) to 53% when the film was heated at 200 °C as a result of partial restoration of conjugated C═C bonds in the graphene structure [21]. In contrast to pristine graphene, increasing the thermal reduction temperature did not lead to decrease in optical transmittance, but to an increment. A valley at around 650 nm in the optical transmission spectra of Au-MLG2 and Au-MLG4 films could be related to plasmonic band of aggregative states of gold nanoparticles [22]. On the other hand, a valley at around 550 nm corresponding to plasmonic band of ordinary gold nanoparticles was observed in the optical transmission spectra of Au-MLG5 film. This suggests that the gold particles tended to aggregate together at lower thermal reduction temperature. A more complete decomposition of $AuCl_3$ and reduction of gold aggregations lead to increase in transmittance with thermal reduction temperature due to lesser scattering effect.

Fig. 3 shows the typical FESEM images of Au-MLG films prepared at thermal reduction temperature of 400 °C and 500 °C. The particle size of gold on Au-MLG4 film was larger than that on Au-MLG5 film, providing further evidence for the formation of gold aggregate at lower thermal reduction temperature. The Au-MLG5 film was also flatter than the Au-MLG4 film probably due to inhibition of wrinkle formation by Au nanoparticles. In addition, it can be seen that more Au particles were formed on the wrinkles, which is well in line with other report [14].

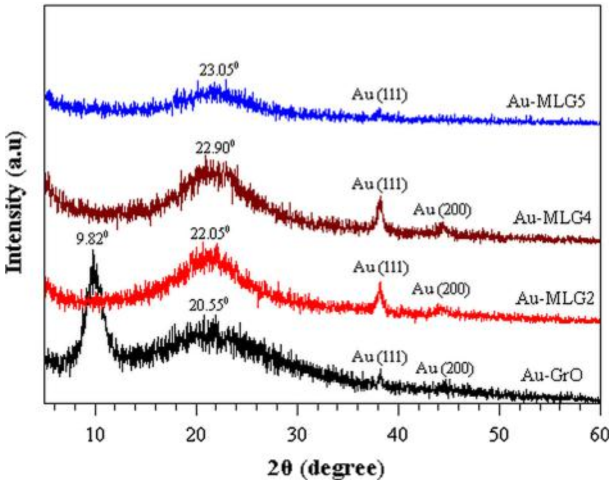

Fig. 1. The XRD spectra of Au-GrO, Au-MLG2, Au-MLG4, and Au-MLG5 films.

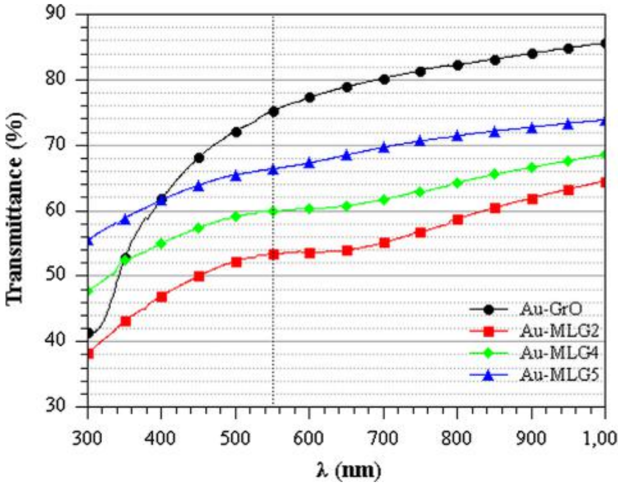

Fig. 2. The optical transmission spectra of Au-GrO, Au-MLG2, Au-MLG4, and Au-MLG5 films.

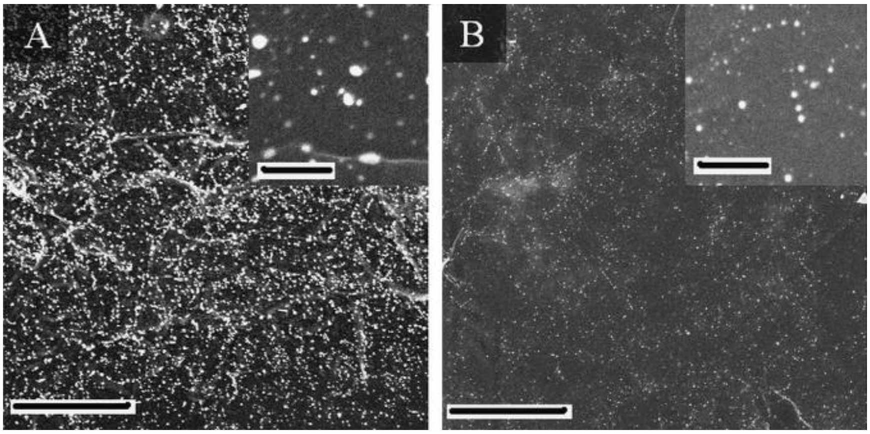

Fig. 3. FESEM images of (A) Au-MLG4 and, (B) Au-MLG5 (scale bar $=2$ μm). The insets show the respective enlarged FESEM images (scale bar $=200$ nm).

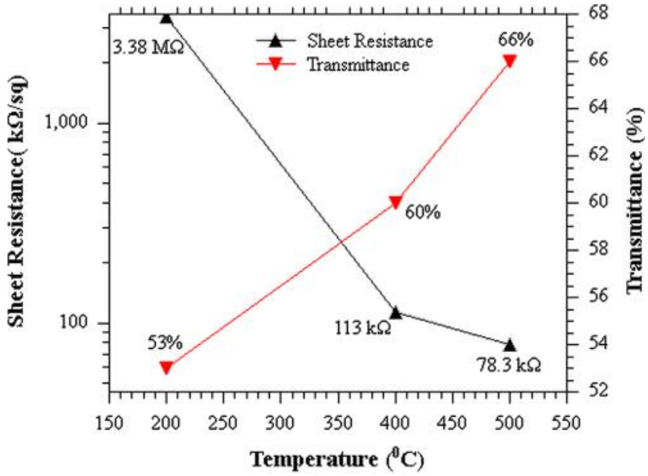

Fig. 4. The sheet resistance and optical transmittance ($\lambda=550$ nm) of Au-MLG films as a function of thermal reduction temperature.

Fig. 4 shows the sheet resistance and optical transmittance ($\lambda=550$ nm) of the Au-MLG films prepared at different thermal reduction temperatures. The optical transmittance increased whereas the sheet resistance decreased as the thermal reduction temperature increased. The optimum optical transmittance of 66% and sheet resistance of 78.3 kΩ/sq were achieved at thermal reduction temperature of 500 °C. The decrease in sheet resistance is mainly attributed to restoration of larger portion of conjugated C═C bonds in the graphene structure at higher temperature [21]. It is also worth noting that the sheet resistance of Au-MLG heated at 500 °C was slightly smaller than that of MLG (91.6 kΩ/sq) heated at the same temperature (Ali Umar, MI, unpublished data). It is believed that p-doping of graphene by gold ions [14] and creation of direct conductive path between graphene sheets connected by the gold particles [23] contribute to the reduction in sheet resistance.

4. Conclusions

The effects of thermal reduction temperature on the structural, optical, and electrical properties of Au-MLG films have been investigated. The graphene oxide and gold ions have been successfully reduced to form Au-MLG film at and above 200 °C. The optical transmittance of Au-MLG films increased with the thermal reduction temperature as a consequence of more complete decomposition of $AuCl_3$ and reduction of gold aggregations. Meanwhile, the reduction in sheet resistance with thermal reduction temperature is mainly ascribed to restoration of conjugated C═C bonds in the graphene structure. The highest optical transmittance of 66% and the lowest sheet resistance of 78.3 kΩ/sq were obtained at thermal reduction temperature of 500 °C.

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CIPTAAN

Dalam rangka pelindungan ciptaan di bidang ilmu pengetahuan, seni dan sastra berdasarkan Undang-Undang Nomor 28 Tahun 2014 tentang Hak Cipta, dengan ini menerangkan:

Nomor dan tanggal permohonan	:	EC00201983905, 26 November 2019
Pencipta		
Nama	:	**Dr. Marjoni Imamora, M.Sc**
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Kewarganegaraan	:	Indonesia
Pemegang Hak Cipta		
Nama	:	**Dr. Marjoni Imamora, M.Sc**
Alamat	:	Perumahan Dobok Indah Blok C No.3 Lima Kaum Batusangkar, Batusangkar, Sumatera Barat, 27211
Kewarganegaraan	:	Indonesia
Jenis Ciptaan	:	**Karya Tulis (Artikel)**
Judul Ciptaan	:	**The Effect Of Spin-coated Polyethylene Glycol On The Electrical And Optical Properties Of Graphene film**
Tanggal dan tempat diumumkan untuk pertama kali di wilayah Indonesia atau di luar wilayah Indonesia	:	21 Juni 2014, di Bangi, Selangor
Jangka waktu pelindungan	:	Berlaku selama hidup Pencipta dan terus berlangsung selama 70 (tujuh puluh) tahun setelah Pencipta meninggal dunia, terhitung mulai tanggal 1 Januari tahun berikutnya.
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The effect of spin-coated polyethylene glycol on the electrical and optical properties of graphene film

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ABSTRACT

This paper reports the modification of electrical and optical properties of graphene film by spin coating polyethylene glycol (PEG) solution onto the graphene oxide film followed by thermal reduction process. The PEG solution was deposited onto the graphene oxide film at different spin coating speeds (1000, 1500, 2000, 2500 and 3000 rpm). The introduction of PEG at appropriate spin coating speed results in lower sheet resistance and optical transmittance, probably due to better alignment and stacking of the graphene sheets. It is interesting to find that the dye sensitized solar cell with PEG-modified graphene film as counter electrode showed 4 times increase in power conversion efficiency as compared to that with unmodified graphene film.

1. Introduction

Graphene film composed of single or multilayer graphene (MLG) has been considered to be a potential replacement for expensive platinum which serves as a transparent counter electrode in dye sensitized solar cell (DSSC) application due to its good electrical conductivity, high optical transmittance [1,2], and low cost [3]. However, it has been reported that for the same optical transmittance, the sheet resistance of graphene film is much larger than that of platinum [4]. This could be due the poor interconnection between the separated graphene sheets which limits the electronic conduction across the sheets. Although a thicker graphene film can be deposited to ensure the individual graphene sheets are connected to each other and hence lower sheet resistance, the optical transmittance will decrease accordingly [5].

Kong et al. reported that the electrical conductivity of reduced graphene oxide (RGO) film increased by 120% after undergoing poly(allylamine hydrochloride) (PAH) treatment [6]. The PAH molecules which attached to the edge of RGO sheets played a role to connect the separated RGO sheets. However, due to the hydrophobicity of RGO, the penetration of hydrophilic PAH solution into the RGO layer is limited. Similar to PAH, Park et al. proposed that chemical cross-linking between multi carboxyl (COOH) groups situated at the edge of graphene oxide (GO) sheet and two terminal hydroxyl (OH) groups of polyethylene glycol (PEG) could be formed [7]. In addition, the PEG solution has been reported to have a weak reducing effect on GO [8,9].

In view of the interaction between PEG and GO, the PEG solution was spin-coated directly onto the GO film and followed by heat treatment in the present work. In contrast to PAH treatment on RGO layers, better penetration of PEG solution into the interlayer of GO can be expected since both of them are hydrophilic [6]. Besides, thermal reduction method was used to transform the PEG-modified GO film into conducting graphene film rather than chemical reduction approach which normally involves toxic and strong reducing agent such as hydrazine monohydrate [10]. The effects of spin coating speed (1000, 1500, 2000, 2500 and 3000 rpm) on the electrical and optical properties of PEG-modified graphene films were studied. The sheet resistance and optical transmittance both decreased as the spin coating speed was increased from 1000 to 2500 rpm, after which both of them started to increase. The PEG-modified graphene film with the lowest sheet resistance of 78.73 kΩ/sq was

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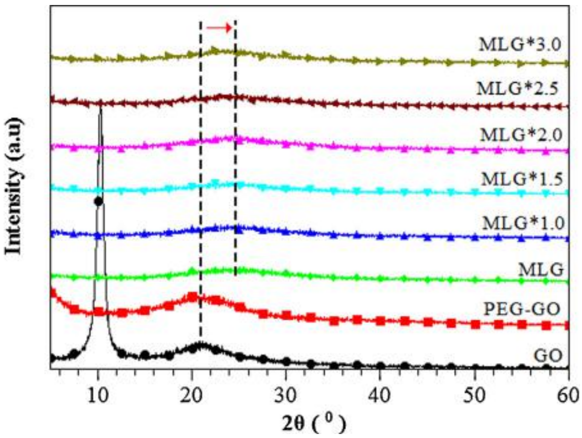

Fig. 1. XRD spectra of GO, PEG-GO, MLG, MLG*1.0, MLG*1.5, MLG*2.0, MLG*2.5 and MLG*3.0 films.

applied as counter electrode in DSSC and the corresponding DSSC showed 4 times increase in power conversion efficiency (PCE) as compared to the DSSC with unmodified graphene film.

2. Experimental

The graphite oxide flakes were prepared by using modified Hummers' method and the detailed procedures can be found elsewhere [11]. The graphite oxide flakes were dissolved in deionized water at a concentration of 10 mg/ml. The solution was sonicated for 30 min and followed by stirring for 2 h. Then, the solution was spin coated on glass substrate at 3500 rpm for 30 s to obtain GO film. This is followed by spin coating of PEG 200 (molecular weight of 200 g/mol) on the GO film at different speeds, namely 1000, 1500, 2000, 2500, and 3000 rpm. The same volume of PEG 200 (≈100 μL) was dropped on the samples during the spin coating process. Lastly, the PEG-modified GO films were annealed at 500 °C in argon atmosphere for half an hour to form conducting graphene films. The graphene film consisted of MLG as reported previously [11]. The samples were denoted as MLG*1.0, MLG*1.5, MLG*2.0, MLG*2.5, and MLG*3.0 for spin coating speeds of 1000, 1500, 2000, 2500, and 3000 rpm, respectively.

The crystal structures of the samples were characterized by using Bruker D8 Advanced x-ray diffractometer with CuKα radiation at a scan rate of 0.025 °/0.1 s. The optical transmission of the samples was investigated by using Halo DB-20 UV–Vis spectrophotometer. On the other hand, the sheet resistances were obtained via four point probe measurement using Keithley 2401 source meter. The Fourier Transform Infrared Spectroscopy (FTIR) of the samples was investigated by using Perkin Elmer 400 FTIR-NIR spectrometer. The surface morphology of the samples was investigated by using NT-MDT Ntegra Prima atomic force microscope (AFM) at room temperature. Lastly, DSSCs consisting of ZnO nanorods arrays as photoanode and graphene film as counter electrode with iodine electrolyte were fabricated. The photovoltaic performance of DSSCs with unmodified and PEG-modified graphene films was investigated by current–voltage measurement under 100 mW/cm^2 simulated AM 1.5 G sunlight using Keithley 237 source measurement unit.

3. Results and discussion

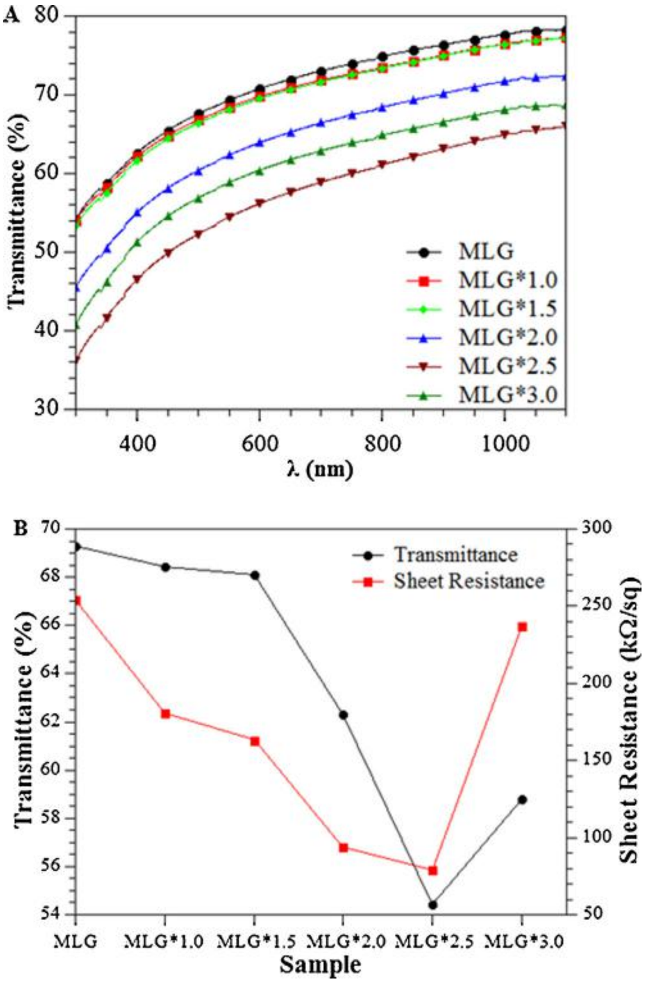

Fig. 2. (A) The optical transmission spectra and (B) the sheet resistance and optical transmittance (λ = 550 nm) of MLG, MLG*1.0, MLG*1.5, MLG*2.0, MLG*2.5 and MLG*3.0 films.

The XRD spectra of GO, PEG-GO, MLG, MLG*1.0, MLG*1.5, MLG*2.0, MLG*2.5 and MLG*3.0 films are shown in Fig. 1. The XRD spectrum of GO film consisted of a sharp peak at $2\theta = 10.37°$ and a broad peak at $2\theta = 20.55°$. The sharp peak corresponds to interlayer distance of around 0.83 nm, whereas the broad peak indicates the incomplete oxidation and intercalation of graphite [11]. It is interesting to note that the sharp peak at $2\theta = 10.37°$ disappeared and the broad peak at $2\theta = 20.55°$ shifted to 22.05° (interlayer distance of 0.42 nm) when the GO film was coated with PEG. This suggests that most of the water molecules and some functional groups such as OH, epoxy (C—O—C) and COOH [10,12–14] have been removed from the PEG-modified GO film before the thermal reduction process. The interlayer distance decreased further to 0.36–0.37 nm after the thermal reduction process as a consequence of removal of more functional groups at higher temperature [15]. In addition, there is no significant interlayer distance variation among the samples after the thermal reduction process, implying the PEG located in between the GO sheets has been completely removed and the degree of GO reduction was similar [16].

Fig. 2A shows the optical transmission spectra of unmodified graphene film and graphene films modified with PEG at different spin coating speeds. The optical transmittance (at λ = 550 nm) of the graphene film only decreased slightly from 70% to 69% and 68% when the PEG was spin coated at speeds of 1000 and 1500 rpm, respectively. The optical transmittance decreased significantly to 54% when the spin coating speed reached 2500 rpm. However, further increase in spin coating speed to 3000 rpm results in higher optical transmittance (59%). The sheet resistance of the samples exhibited the similar trend to the optical transmittance as shown

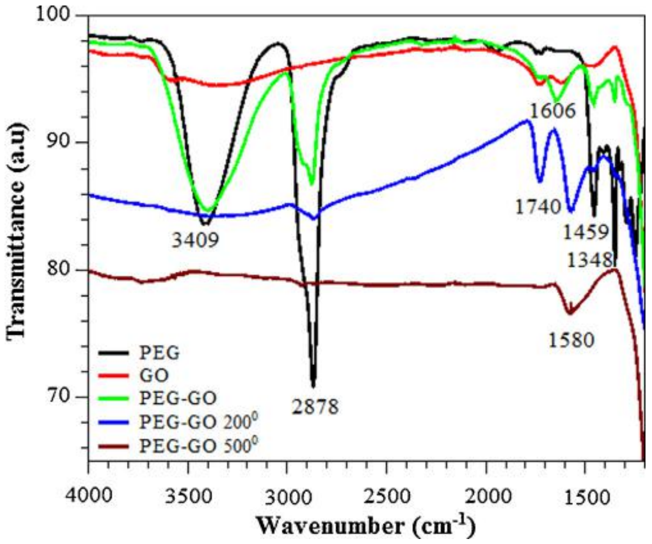

Fig. 3. The FTIR spectra of PEG, GO, PEG-GO, PEG-GO heated at 200 °C and 500 °C.

in Fig. 2B. The lowest sheet resistance of 78.73 kΩ/sq was achieved at spin coating speed of 2500 rpm.

In order to understand the reason behind the changes of optical transmittance and sheet resistance upon PEG modification, FTIR and AFM measurements were carried out. The FTIR spectra of pure PEG, GO, PEG-GO, and PEG-GO heated at 200 °C and 500 °C are shown in Fig. 3. In the FTIR spectrum of pure PEG, the broad peak at ~3409 cm^{-1} is attributed to O—H bonds vibration [17], whereas the strong peaks detected at ~2878, ~1459 and 1348 cm^{-1} are related to C—H bonds [17]. The typical peaks of PEG at ~2878, ~1459 and 1348 cm^{-1} also appeared in the FTIR spectrum of PEG-GO, indicating the PEG has been successfully incorporated into the GO film. It is interesting to note that the intensity of characteristic peaks of PEG at ~2878, ~1459 and 1348 cm^{-1} reduced significantly after a thermal treatment at 200 °C was given. In addition, two sharp peaks at ~1740 and ~1580 cm^{-1} corresponding to C=O stretching of ester linkages and benzene ring vibration of C=C bonds [17], respectively, are clearly observed. This suggests that OH groups of PEG have been connected to COOH groups of GO and the GO has been partially reduced to form graphene film [18]. However, as the thermal reduction temperature was further increased to 500 °C, only a broad and weak peak at ~1580 cm^{-1} due to C=C bonds is observed which implies that the reduction of GO was almost complete and no PEG residual was found. It is believed that thermal reduction at 500 °C could gasify and completely eliminate the PEG from the GO film, which is in agreement with previous report [19]. It has been reported that the ionic conduction characteristic of hydrated PAH which serve as intermediate material between individual graphene sheets contributes to the improved conductivity of RGO film [6]. Since the PEG has been completely removed from the film at 500 °C in the present case, the role of PEG in reducing the sheet resistance should be different from that of PAH.

The typical AFM images of MLG, MLG*1.0, MLG*2.5 and MLG*3.0 films are shown in Fig. 4. It can be clearly observed that the surface of MLG*1.0 was rougher than that of MLG. The root mean square (RMS) roughness of MLG*1.0 (15.6 nm) was larger than that of MLG film (10.9 nm). The PEG could penetrate into the interlayer of GO sheets due to their similar hydrophilic property when the solution was dropped onto the GO film [20]. It is possible that the realignment of mobilized GO sheets occurred due to the centrifugal force generated during the spin coating process [21]. At relatively low spin coating speed (1000 rpm), smaller centrifugal force made less PEG solution to be scattered away from the GO film, hence resulting in larger agglomeration of PEG [22]. The elimination of agglomerates of PEG during the thermal reduction process causes the resulting graphene film to become rougher and have more wrinkles. However, it should be noted that the sheet resistance of MLG*1.0

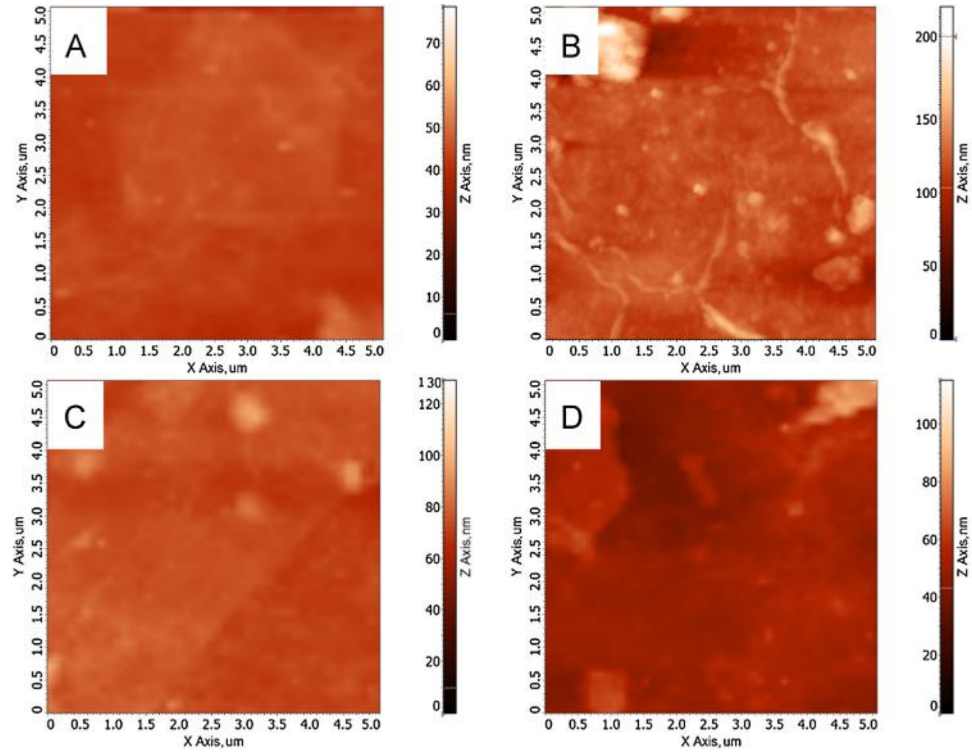

Fig. 4. The AFM images of (A) MLG, (B) MLG*1.0, (C) MLG*2.5 and, (D) MLG* 3.0 films.

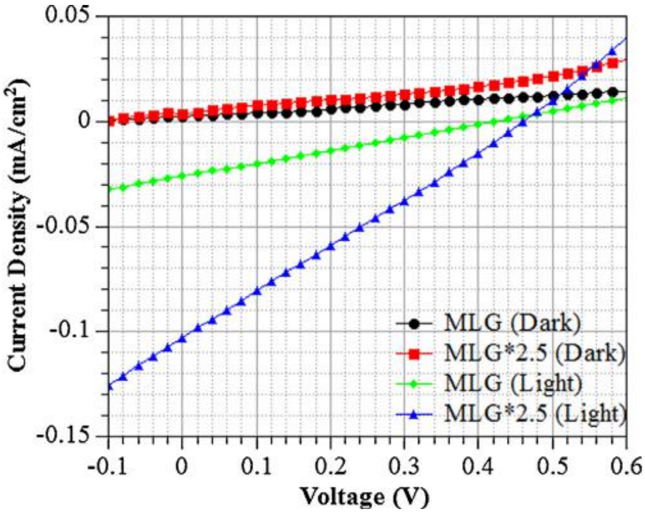

Fig. 5. The J–V characteristic of DSSCs with FTO/ZnO nanorods/electrolyte/MLG/glass and FTO/ZnO nanorods/electrolyte/MLG*2.5/glass structures.

film was still lower than that of MLG (Fig. 2B). The removal of ester linkage between OH groups of PEG and COOH groups at the edge of GO sheets at high thermal reduction temperature could result in stacking of GO sheets. The stacking of graphene sheets leads to decrease in the number of sheet-to-sheet junctions. The electrons can move faster across the interconnected graphene sheets, hence resulting in smaller sheet resistance. Furthermore, the increase in portion of graphene film with stacking structure enhances both the light absorption and reflection, which leads to decrease in optical transmission [5]. The graphene film became smoother, as indicated by the decrease in RMS roughness to 11.3 nm, when the spin coating speed was increased to 2500 rpm. The stronger centrifugal force at high spinning speed not only leads to less agglomeration of PEG, but also better alignment and stacking of the graphene sheets as evidenced by the lowest values of sheet resistance and optical transmittance. Even though the MLG*3.0 film (RMS roughness of 10.1 nm) was smoother than the MLG*2.5 film, the sheet resistance of the former was higher. It is believed that the role of PEG solution in promoting better interconnection between graphene sheets was minimized due to the relatively high centrifugal force.

The PEG-modified graphene film (MLG*2.5) with the lowest sheet resistance and unmodified graphene film were used as counter electrode in DSSCs. The corresponding current density–voltage (J–V) curves in dark and under illumination of a simulated AM 1.5 G sunlight at 100 mW/cm^2 are shown in Fig. 5. The DSSC with unmodified graphene film yielded a short circuit current density (J_{sc}) of 0.026 mA/cm^2, an open circuit voltage (V_{oc}) of 0.42 V, and a fill factor (FF) of 25%, resulting in PCE of 0.0027%. On the other hand, the PCE of the DSSC with MLG*2.5 film increased significantly to 0.012% with a J_{sc} of 0.10 mA/cm^2, a V_{oc} of 0.44 V and an FF of 27%. As expected, the significant increase in J_{sc} and PCE could be correlated with the reduction of sheet resistance of the graphene film upon PEG modification [23]. Despite the very low PCE, better photovoltaic performance could be achieved by adding dyes to the ZnO nanorods which enlarges the wavelength range of light absorption [24].

4. Conclusions

The effects of spin coating speed on the electrical and optical properties of PEG-modified graphene films have been successfully investigated. The sheet resistance and optical transmittance decreased with the spin coating speed up to 2500 rpm, after which both of them began to increase. The decrease of sheet resistance and optical transmittance upon PEG modification could be attributed to the better alignment and stacking of the graphene sheets. The PCE of DSSC with the lowest sheet resistance PEG-modified graphene film as counter electrode increased by 4 times as compared to that with unmodified graphene film. The PEG modification has been demonstrated to a valuable and simple approach to improve the electrical and optical properties of graphene film.

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SURAT PENCATATAN

CIPTAAN

Dalam rangka pelindungan ciptaan di bidang ilmu pengetahuan, seni dan sastra berdasarkan Undang-Undang Nomor 28 Tahun 2014 tentang Hak Cipta, dengan ini menerangkan:

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Pencipta

Nama : **Dr. Marjoni Imamora, M.Sc**

Alamat : Perumahan Dobok Indah Blok C No.3 Lima Kaum Batusangkar, Batusangkar, Sumatera Barat, 27211

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Kewarganegaraan : Indonesia

Jenis Ciptaan : **Karya Tulis (Artikel)**

Judul Ciptaan : **Characterization Of Multilayer Graphene Prepared From Short Processed Graphite Oxide Floke**

Tanggal dan tempat diumumkan untuk pertama kali di wilayah Indonesia atau di luar wilayah Indonesia : 29 September 2012, di Bangi, Selangor

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DIREKTUR JENDERAL KEKAYAAN INTELEKTUAL

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Characterization of multilayer graphene prepared from short-time processed graphite oxide flake

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Abstract Multilayer graphene has been prepared by thermal reduction of graphene oxide film. The graphite oxide flake was first synthesized by using modified Hummers method with a relatively small amount of oxidizing agent and short-time processing at ambient temperature. The graphite oxide flake was dispersed in deionized water and deposited on quartz substrates to form graphene oxide film. The red shift of absorption peak and decrease of interlayer distance as interpreted from the X-ray diffraction spectrum indicate the formation of multilayer graphene. The resultant multilayer graphene has been successfully used as counter electrode in FTO/ZnO nanorods/electrolyte/multilayer graphene dye sensitized solar cell.

1 Introduction

Graphene, a nanoscale carbonized material in the two-dimensional lattice, has become an interesting subject for researcher in the world for the past two decades [1]. The high surface area graphene which can be produced at low cost and obtained easily, has been found useful in several applications such as solar cell [2–5], transistor [6], battery [7], sensor [8], etc. The new modification efforts in preparation of large scale graphene film through simple, fast and cheap process still remain great challenging. Various methods in preparation of graphene have been reported, such as chemical vapor deposition [9], molecular beam epitaxy [10] and chemical route by exfoliation of graphite [11–14]. Among those methods, the use of the chemical route, particularly the Hummers method, is preferable because it is simple, cheap and large scale graphite oxide (GO) flake can be produced.

It is well known that GO can be produced by treating the graphite with strong oxidizing agents such as potassium permanganate ($KMnO_4$) in concentrated sulfuric acid (H_2SO_4) [4, 15–17]. Normally, an ice bath system is needed during $KMnO_4$ addition to reduce overheating and possibility of explosive condition [4, 15, 16]. Meanwhile, reaction temperature or time can be increased to enhance the degree of oxidation of graphite [4, 16, 17]. A previous study has shown that decreasing the amount of oxidizing agent or oxidation time could lead to partial oxidation and incomplete exfoliation of graphite, resulting in formation of multilayer graphene oxide structure instead of ordinary graphite oxide [18]. Graphene can be produced through reduction of graphene oxide (GrO) film using three various techniques, namely chemical technique by using hydrazine (N_2H_2) [19], physical technique by using a thermal reduction through annealing treatment and combination both of them [4]. Among those reduction techniques, thermal reduction is most commonly used because it is simple, environmental friendly and impurity materials can be effectively removed from the graphene film. It has been observed that the electrical conductivity of multilayer

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graphene was much higher than that of graphene by using the same reduction method [18]. Therefore, it is suggested that the utilization of high amount of oxidizing agents and thermal controlling is not required if high electrical conductivity multilayer graphene is desired.

Platinum has been widely used as counter electrode in dye sensitized solar cells (DSSCs) [20]. Since platinum is an expensive material, the researchers have started exploring cheaper alternative materials to replace the platinum particularly the carbonized materials such as carbon nanotubes [8, 9] and graphene nanocomposite [5]. However, the use of pristine graphene as a counter electrode in DSSCs has rarely been reported. Therefore, it seems desirable to investigate the potential of multilayer graphene for use as a counter electrode in DSSCs. The present work reports on the preparation of multilayer graphene through thermal reduction of GrO film. The GrO film was formed by using modified Hummers method with a relatively small amount of oxidizing agent and short-time processing. The red shift of absorption peak and decrease of interlayer distance confirm the formation of multilayer graphene. The photovoltaic performance of device with multilayer graphene as counter electrode was comparable to that based on platinum.

2 Experimental procedures

Multilayer graphene was prepared through three steps-processes, namely synthesis of GO flake, deposition of GrO film and thermal reduction of GrO film. 2 g of graphite powder with average particle size of 20 μm (synthetic graphite, Sigma–Aldrich) and 1 g of sodium nitrate ($NaNO_3$, 99 %, Sigma–Aldrich) were placed in a flask which contained 200 ml of sulfuric acid (H_2SO_4, 98 %, J.T. Berck), and the solution was stirred at room temperature. 6 g of potassium permanganate ($KMnO_4$, 99.0 %, Unilab Ajax) was slowly added to the solution over 30 min. Stirring was continued for 3.5 h at room temperature. 300 ml of deionized (DI) water was slowly added to the solution, and stirring was continued for 2 h. Lastly, 160 ml of 5 % hydrogen peroxide (H_2O_2, 30 %, Merck) was added to stop the oxidation process, and the mixture was stirred for 15 min at room temperature. The amount of $KMnO_4$ in H_2SO_4 was relatively small as compared to the conventional Hummers method [15].

To remove the ions of oxidizing agent and other inorganic impurities, the resultant mixture was purified through centrifugation and sonication. Three washing and filtering steps were conducted in 100 ml 5 % H_2SO_4, 100 ml 5 % H_2O_2 and 100 ml 1 M hydrochloric chloride (HCl, 37 %), followed by three times washing processes in 300 ml DI water. After the GO was dispersed and sonicated in DI water, the suspension was centrifuged at 1,500 rpm for 2 min and the supernatant liquid was collected and then the precipitated material was dispersed in DI water again. This process was repeated two times and the collected supernatant liquid was then further centrifuged at 6,000 rpm for 10 min. The precipitation was dried in vacuum oven at 80 °C and at a pressure of −0.08 bar for 12 h to produce GO flake, and subsequently stored in vacuum box for repeatable use.

Next, small amount of GO flake was dispersed in DI water with concentration of 10 mg/ml by sonication. The resultant solution was spin-coated on quartz substrate at 500–1,000 rpm for the first 15 s and followed by 4,500–5,000 rpm for 60 s to produce GrO film. To reduce the GrO film, the sample was annealed at 600 °C in argon for 1 h to produce multilayer graphene. The optical characterization of GrO film and multilayer graphene was carried out by using Perkin Elmer Lambda 900 UV–Vis spectrophotometer. The crystal structures of graphite, GrO film and multilayer graphene were characterized by using Bruker D8 Advanced X-ray diffraction (XRD) with CuKα radiation at a scan rate of 0.025°/0.1 s. The morphology of multilayer graphene was investigated by using Carl Zeiss Supra 55VP field emission scanning electron microscope (FESEM).

In order to investigate the suitability of multilayer graphene as counter electrode in DSSCs, DSSC consisted of ZnO nanorods photoanode and multilayer graphene counter electrode that sandwiched an electrolyte of 0.5 M Li I/0.05 M I2/0.5 M tertbutylpyridine in acetonitrile was assembled as shown in Fig. 1. The ZnO nanorod arrays were grown on FTO glass substrates which were pre-coated with ZnO nanoparticles using a low temperature chemical solution method. ZnO nanorods were grown on the ZnO seeded–substrates by immersing them in a closed vial containing 40 mM zinc nitrate hexahydrate and 40 mM hexamethylenetetramine in DI water at 90 °C for 45 min. The details of the ZnO nanorods synthesis processes were described elsewhere [21]. The photovoltaic performance of the solar cell with active area of 0.25 cm^2 was investigated by current–voltage measurement under 100 mW/cm^2 simulated AM 1.5 G sunlight using Keithley 237 source measurement unit.

3 Results and discussion

Multilayer graphene has been successfully synthesized through thermal reduction of GrO film which was formed from GO by using modified Hummers method. Since the amount of oxidizing agent ($KMnO_4$ in H_2SO_4) was relatively small, ice bath was not required to prevent explosive condition and the whole chemical oxidation was carried out

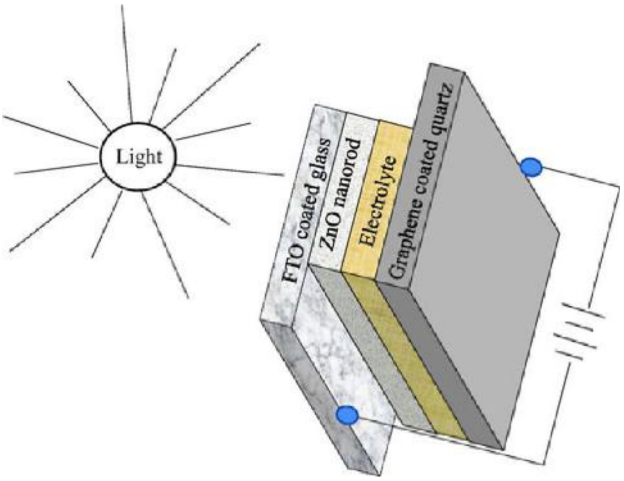

Fig. 1 The DSSC device with FTO/ZnO nanorods/electrolyte/multilayer graphene structure

at ambient condition by using the present modified method. The oxidation time was kept short in the present study to ensure partial oxidation and incomplete exfoliation of graphite, by which multilayer graphene could be formed [18].

The transmission and absorption spectra of GrO film and multilayer graphene deposited on quartz substrates are shown in Fig. 2. The transmittance of GrO film and multilayer graphene gradually decreased with decrease of wavelength in the range of 280–800 nm [4]. In addition, there was a significant transparency difference between the GrO film and multilayer graphene as shown in the inset of Fig. 2a. GrO film had bright yellow in colour and changed to grey after thermal reduction. The GrO film showed a transmittance of 79 % at $\lambda = 550$ nm. After thermal reduction, the transmittance decreased to 54 %, indicating the formation of multilayer graphene since absorbance of each individual graphene layer is approximately 2.3 % [22]. The absorption peaks of GrO and multilayer graphene were found to be 233 and 270 nm, respectively. The relatively large absorption peak wavelength of GrO indicates the incomplete oxidation of graphite [23]. The red shift of absorption to 270 nm suggests that part of conjugated C=C bonds have been restored as a result of thermal reduction [24]. Both of the results are similar to the value reported in the literature [11, 24, 25].

Figure 3 shows the XRD spectra of graphite, GrO film and multilayer graphene. A significant peak occurred in XRD spectrum of graphite at $2\theta = 26.55°$, corresponding to $d_{001} = 0.34$ nm which is also known as interplanar spacing of graphite [16, 19]. After oxidation process, the peak shifted to $2\theta = 9.975°$, resulting in $d_{001} = 0.89$ nm. The increasing of the interlayer distance from 0.34 to 0.89 nm can be attributed to the presence of functional group such as hydroxyl (OH), epoxy (C–O–C), and carboxyl (COOH) to graphite oxide [17, 19]. In addition, there was a weak diffraction peak at $2\theta = 22.275°$, providing further evidence for the incomplete oxidation and intercalation of graphite. After a thermal reduction process at 600 °C for 1 h under argon atmosphere, the atomic distance was reduced to 0.35 nm ($2\theta = 25.30°$) as a consequence of removal of functional groups. Such finding agrees well with the absorption result shown in Fig. 2b. Besides, the broadened and lower intensity of the XRD spectrum of multilayer graphene (inset of Fig. 3) indicates that GrO film has been successfully reduced to form multilayer graphene with different lattice structure of graphite [16]. Figure 4 shows a typical FESEM image of multilayer graphene deposited on substrate. The darker region in the FESEM image indicates the formation of multilayer graphene, whereas the lighter region might correspond to single or few-layers graphene.

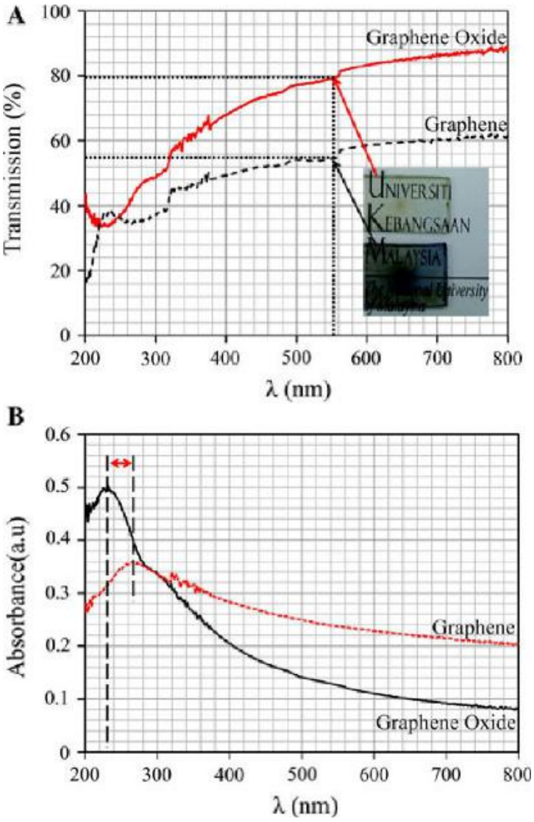

Fig. 2 **a** and **b** are the transmission and absorption spectra of GrO and multilayer graphene deposited on quartz substrates, respectively. The *inset* picture in (**a**) shows a photograph of corresponding GrO and multilayer graphene

Figure 5 shows the current density–voltage (J–V) graph of DSSC constructed with multilayer graphene as counter electrode in dark and under illumination of a simulated AM 1.5 G sunlight at 100 mW/cm^2. A typical DSSC exhibited a short circuit current density (J_{sc}) of 0.17 mA/cm^2, an open circuit voltage (V_{oc}) of 0.46 V, and a fill factor (FF) of

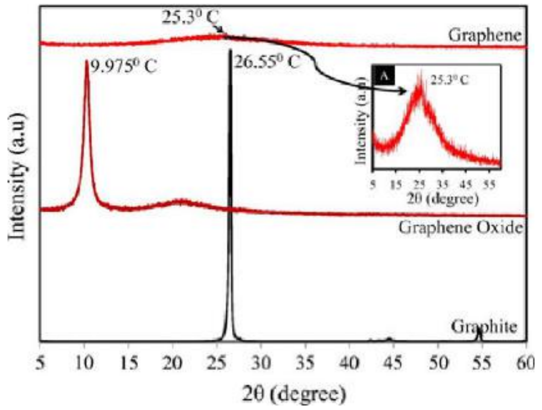

Fig. 3 The XRD spectra of graphite, GrO film and multilayer graphene. The *inset* shows the enlarged XRD spectrum of multilayer graphene

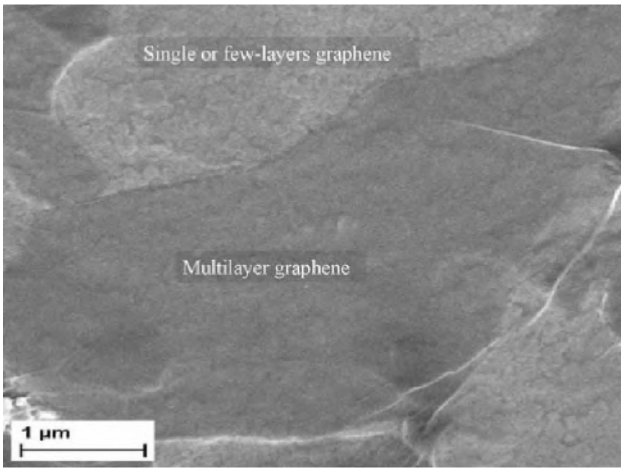

Fig. 4 FESEM image of multilayer graphene

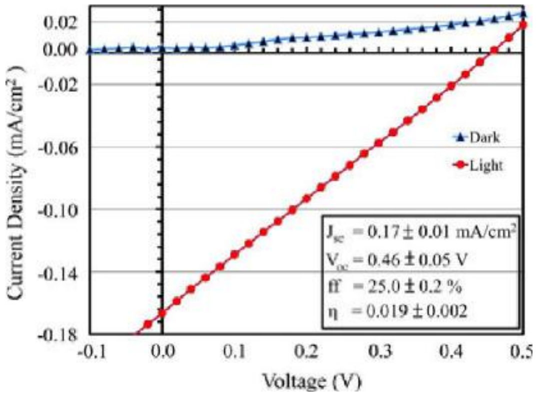

Fig. 5 *J*–*V* characteristic of DSSC cell (*inset*: the data of photovoltaic parameter)

25 %, resulting in a power conversion efficiency (PCE) of 0.019 %. The overall performance of DSSC is given in the inset of Fig. 5. A similar DSSC with platinum as counter electrode which exhibited J_{sc} of 0.28 mA/cm^2, V_{oc} of 0.44 V and FF of 30 % has been reported recently [26]. The photovoltaic performance of the present device was comparable to that of platinum based DSSC, making multilayer graphene a potential candidate for counter electrode application. The small FF value could be attributed to relatively high sheet resistance of multilayer graphene (120 kΩ/sq). Since the multilayer graphene and other experimental variables such as ZnO nanorods property [27], dye coating process [28], and electrolyte selection [3, 29] are far from being optimized, applying the multilayer graphene in optimized DSSC reported elsewhere will surely result in improved photovoltaic performance.

4 Conclusion

GO flake, an initial material for preparation of multilayer graphene, has been successfully produced by using modified Hummers method with relatively small amount of oxidizing agent and short-time processing at ambient temperature. The red shift of absorption peak and decrease of interlayer distance confirm the formation of multilayer graphene through thermal reduction of GrO film. The resultant multilayer graphene has been successfully applied as a counter electrode in DSSC with the structure of FTO/ZnO nanorods/electrolyte/multilayer graphene. The J_{sc}, V_{oc}, FF, and PCE of the DSSC were 0.17 mA/cm^2, 0.46 V, 25 and 0.019 %, respectively. The multilayer graphene has been shown to be a potential replacement for platinum as counter electrode in DSSC.

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SURAT PENCATATAN
CIPTAAN

Dalam rangka pelindungan ciptaan di bidang ilmu pengetahuan, seni dan sastra berdasarkan Undang-Undang Nomor 28 Tahun 2014 tentang Hak Cipta, dengan ini menerangkan:

Nomor dan tanggal permohonan : EC00201983907, 26 November 2019

Pencipta

Nama : **Dr. Marjoni Imamora, M.Sc**

Alamat : Perumahan Dobok Indah Blok C No.3 Lima Kaum Batusangkar, Batusangkar, Sumatera Barat, 27211

Kewarganegaraan : Indonesia

Pemegang Hak Cipta

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Alamat : Perumahan Dobok Indah Blok C No.3 Lima Kaum Batusangkar, Batusangkar, Sumatera Barat, 27211

Kewarganegaraan : Indonesia

Jenis Ciptaan : **Karya Tulis (Artikel)**

Judul Ciptaan : **Effect Of Thermal Reduction Temperature On The Optical And Electrical Properties Of Multilayer Graphene**

Tanggal dan tempat diumumkan untuk pertama kali di wilayah Indonesia atau di luar wilayah Indonesia : 26 Agustus 2016, di New York

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Nomor pencatatan : 000171839

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Effect of thermal reduction temperature on the optical and electrical properties of multilayer graphene

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Abstract Multilayer graphene was prepared by thermal reduction of graphene oxide film at various temperatures (200, 400 and 500 °C) in argon atmosphere for an hour. The graphite oxide was first synthesized by using modified Hummers method and spin coated on quartz substrate to form graphene oxide film. X-ray diffraction, field emission scanning electron microscopy, UV–Vis spectroscopy and four point probe measurement were used to characterize the resultant multilayer graphene. The transmittance and sheet resistance decreased with the thermal reduction temperature. The lowest sheet resistance of 91.6 ± 0.3 kΩ/sq was obtained at temperature of 500 °C, showing almost 100 times improvement compared to that prepared at 200 °C.

1 Introduction

Graphene, a low cost material with a monolayer of carbon in 2D honeycomb lattice with a 0.34 nm thickness [1], has been found useful in solar cell application due to its good electrical and optical transmission properties [2–6]. Especially in dye sensitized solar cells (DSSC) devices, graphene has been used widely as a counter electrode. Graphene in this study is provided by means of chemical method through oxidation of graphite using modified Hummer methods. Hummers method has become a famous technique of graphene oxide preparation because it is a low cost and simple method by which large scale of graphene oxide can be obtained easily [7, 8]. Graphene can be produced via thermal reduction of graphene oxide film deposited on substrate [9]. However, it has been reported that, the sheet resistance of graphene film is much larger than that of platinum for the same optical transmittance [10]. This could be due the poor interconnection with neighboring ones which limits the electronic conduction across the sheets. Although a thicker or multilayer graphene film can be deposited to ensure the individual graphene sheets are connected to each other and hence lower sheet resistance, the optical transmittance will decrease accordingly [11].

Multilayer graphene has been successfully synthesized from graphite oxide prepared by using modified Hummers method with a relatively small amount of oxidizing agent and short-time processing at ambient temperature in previous work [7]. However, the high temperature (600 °C) applied during thermal reduction of graphene oxide is not suitable if the multilayer graphene is to be used as low-cost counter electrode deposited on glass substrate in dye sensitized solar cell application. Therefore, the present work was carried out to investigate the effect of using lower thermal reduction temperature (200, 400, and 500 °C) on the electrical and optical properties of multilayer graphene. The transmittance and sheet resistance of multilayer graphene decreased with the temperature. The lowest sheet resistance of 91.6 ± 0.3 kΩ/sq was obtained at temperature of 500 °C, showing almost 100 times increase as compared to that of 200 °C.

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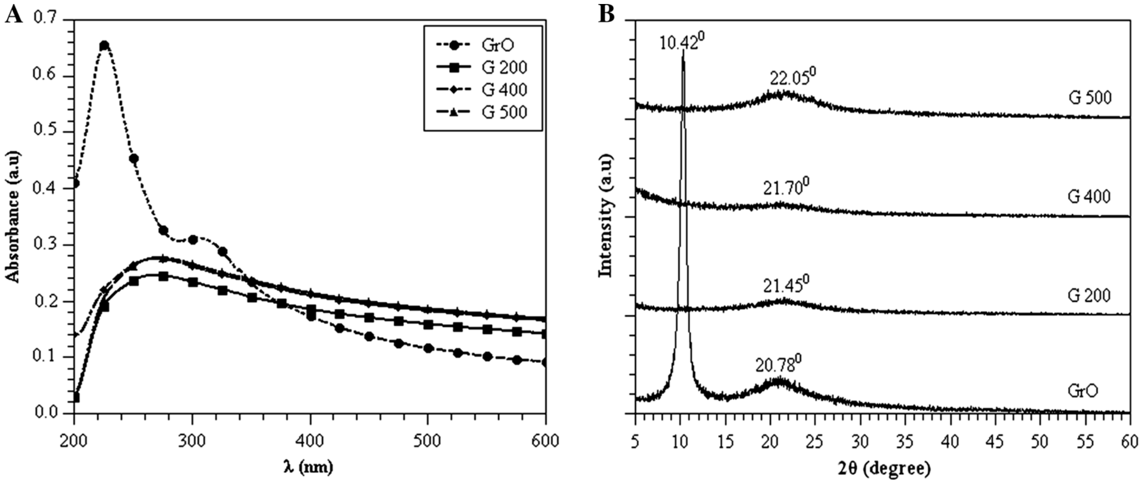

Fig. 1 Absorption (**a**) and XRD (**b**) spectra of graphene oxide and multilayer graphene films prepared at different thermal reduction temperatures

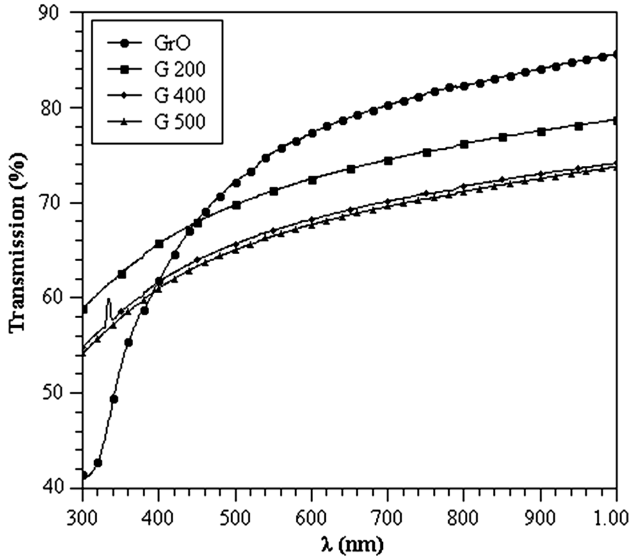

Fig. 2 Transmission spectra of graphene oxide and multilayer graphene films prepared at different thermal reduction temperatures

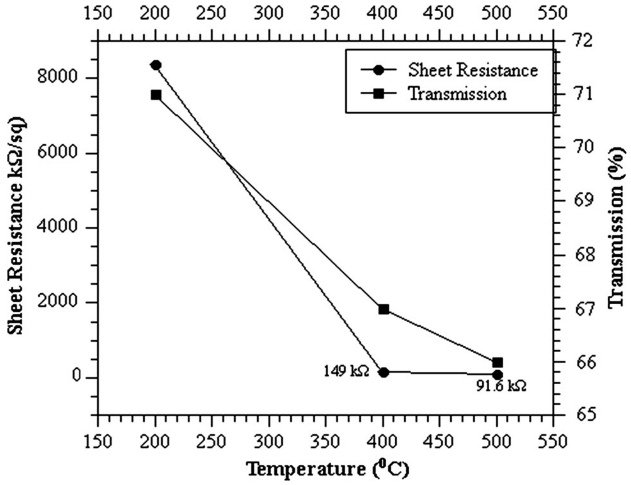

Fig. 3 The sheet resistance and optical transmittance of multilayer graphene films as a function of thermal reduction temperature

2 Experimental

Multilayer graphene was synthesized from graphite oxide prepared by using modified Hummers method [12]. The details of the graphite oxide flake synthesis were described elsewhere [7]. The typical preparation of graphene oxide film is shown below: small amount of graphite oxide flake was dissolved in deionized water at a concentration of 10 mg ml^{-1} by sonication for 30 min followed by stirring for 2 h. Then, the resultant solution was spin-coated by using Chemat Technology Spin-Coater KW-4A on quartz substrates to form graphene oxide film. Next, they were annealed at 200, 400, and 500 °C in argon atmosphere for 1 h to form MLG film. The resultant samples were then denoted as G200, G400, and G500, respectively.

The optical transmission characterization of graphene oxide and multilayer graphene films was carried out by using Halo DB-20 UV–Vis spectrophotometer. The crystal-structure of the films was characterized by using BrukerD8 Advanced X-ray diffraction (XRD) with CuKα radiation at a scan rate of 0.025°/0.1 s. The morphology of the samples was obtained by using Zeiss Supra 55VP field emission scanning electron microscope (FESEM) at an acceleration voltage of 3 kV. Lastly, the sheet resistance of MLG films was studied via Four Point Probe measurement by using Keithley 2401 source meter.

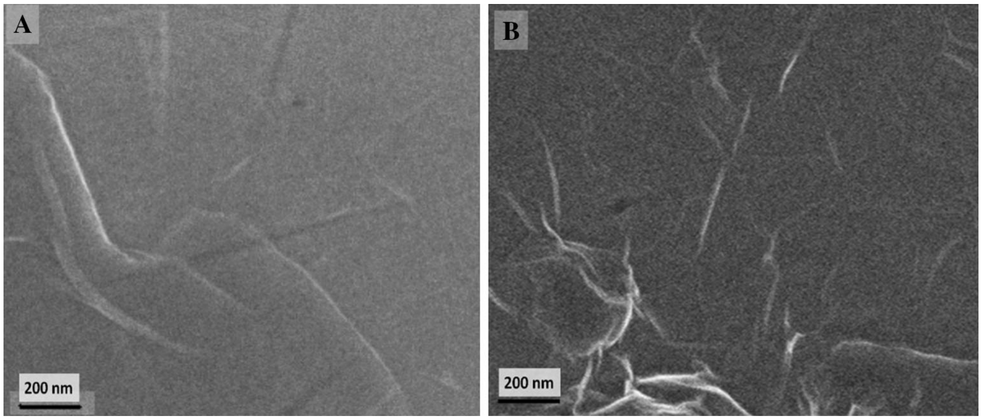

Fig. 4 FESEM images of multilayer graphene prepared at **a** 400 °C, and **b** 500 °C

3 Results and discussion

Optical absorption spectra of graphene oxide and multilayer graphene films prepared at different thermal reduction temperatures are shown in Fig. 1a. It was found that graphene oxide exhibited a maximum absorption peak at 226 nm and a shoulder peak at 310 nm. The absorption peak red-shifted to 270 nm as the thermal reduction temperature increased, indicating part of conjugated C=C bonds have been restored as an effect of heating process applied [7].

X-ray diffraction spectra of graphene oxide and multilayer graphene films are shown in Fig. 1b. A significant diffraction peak at $2\theta = 10.42°$ corresponding to interlayer distance of 0.886 nm was observed in the XRD spectrum of graphene oxide. The weakening of Van der walls force [8, 13] and the presence of functional groups such as hydroxyl, epoxy, and carboxyl during the oxidation step [14–16] contributes to the increase in interlayer distance. In addition, a weak diffraction peak detected at $2\theta = 20.78°$ indicates incomplete oxidation and intercalation of graphite [7]. After thermal reduction at 200 °C, the diffraction peak shifted to $2\theta = 21.45°$, indicating interlayer distance was reduced to 0.411 nm due to the removal of water molecules and functional groups [9]. The interlayer distance decreased further to 0.406 nm and 0.401 nm at temperature of 400 and 500 °C, respectively. The decrease in interlayer distance with thermal reduction temperature suggests more functional groups could be removed at higher heating temperature.

The optical transmission spectra of graphene oxide and multilayer graphene films are shown in Fig. 2. The transmittance of multilayer graphene decreased significantly with increasing thermal reduction temperature. The graphene oxide film showed a transmittance of 79 % at $\lambda = 550$ nm. After thermal reduction, the transmittance decreased to 54 %, indicating the formation of multilayer graphene (±19 layer or 6.46 nm in thickness) since absorbance of each individual graphene layer is approximately 2.3 % [17]. Besides that, the decrease in transmittance could be attributed to partial restoration of conjugated C=C bonds in the graphene structure [18]. Figure 3 shows the optical transmittance at $\lambda = 550$ nm and sheet resistance of the corresponding films as a function of thermal reduction temperature. Both sheet resistance and optical transmittance decreased as the temperature increased. The multilayer graphene prepared at temperature of 500 °C exhibited the lowest sheet resistance of 91.6 ± 0.3 kΩ/sq, almost 100 times improvement as compared to that prepared at 200 °C. The lowest sheet resistance obtained in this work was slightly higher than that obtained from graphene (70 kΩ/sq) with similar transmittance of 65 % [19].

Figure 4 shows the typical FESEM images of multilayer graphene prepared at thermal reduction temperature of 400 and 500 °C. The wrinkle observed in G500 was more significant than that in G400, probably due to escape of more functional groups at higher temperature. Besides, increase in thermal reduction temperature also results in graphene aggregation due to stronger attractive force between layers [20].

4 Conclusions

The effect of thermal reduction temperature on the optical and electrical properties of multilayer graphene has been investigated. The interlayer distance of graphene decreased with the temperature, indicating more water molecules and functional groups were removed. The transmittance and sheet resistance of multilayer graphene decreased with increasing temperature due to partial restoration of conjugated C=C bonds in the graphene structure. The lowest sheet resistance of 91.6 ± 0.34 kΩ/sq was achieved at temperature of 500 °C, exhibiting almost 100 times improvement compared to that of 200 °C.

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