

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

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Received: 14 August 2012 / Accepted: 20 September 2012 / Published online: 29 September 2012
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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 $\text{CuK}\alpha$ radiation at a scan rate of $0.025^\circ/0.1$ 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

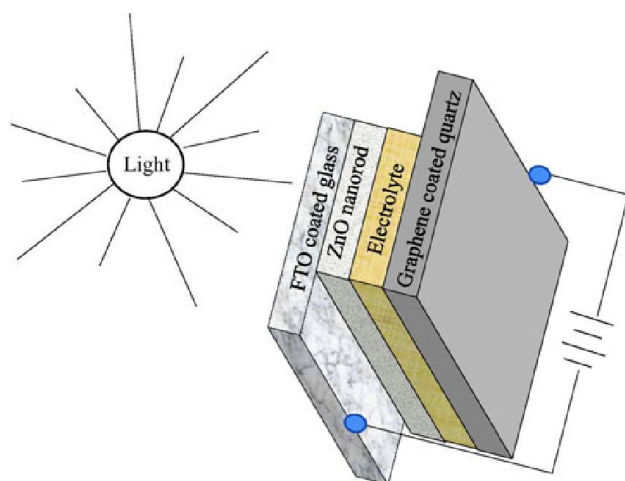


Fig. 1 The DSSC device with FTO/ZnO nanorods/electrolyte/multilayer graphene structure

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 $2\theta = 26.55^\circ$, 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 $2\theta = 9.975^\circ$, 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

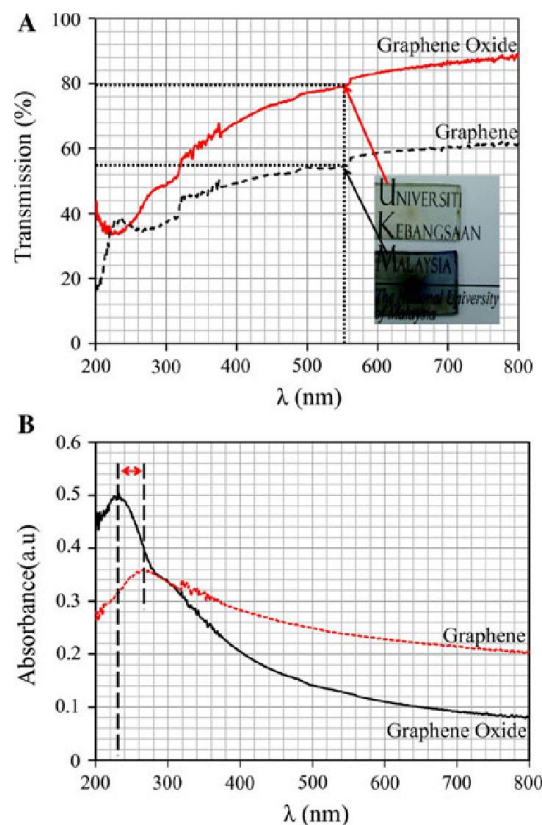


Fig. 2 a and b are the transmission and absorption spectra of GrO and multilayer graphene deposited on quartz substrates, respectively. The inset picture in (a) shows a photograph of corresponding GrO and multilayer graphene

carboxyl (COOH) to graphite oxide [17, 19]. In addition, there was a weak diffraction peak at $2\theta = 22.275^\circ$, 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 ($2\theta = 25.30^\circ$) 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.

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/cm². A typical DSSC exhibited a short circuit current density (J_{sc}) of 0.17 mA/cm², an open circuit voltage (V_{oc}) of 0.46 V, and a fill factor (FF) of

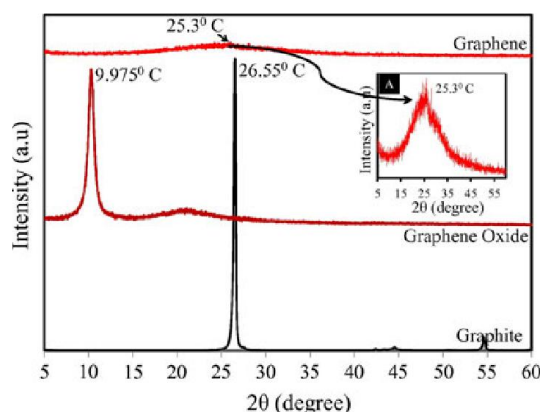


Fig. 3 The XRD spectra of graphite, GrO film and multilayer graphene. The inset shows the enlarged XRD spectrum of multilayer graphene

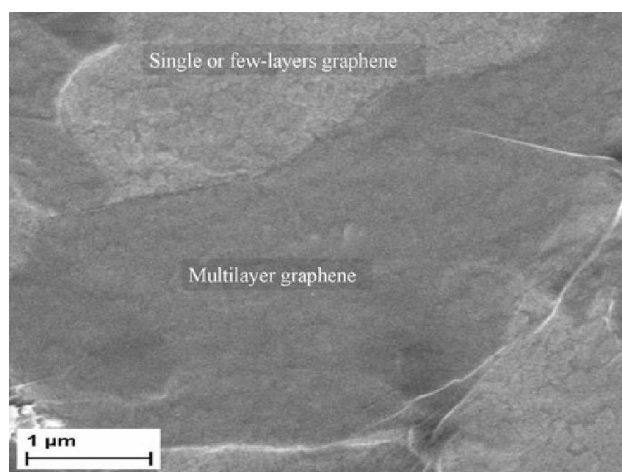


Fig. 4 FESEM image of multilayer graphene

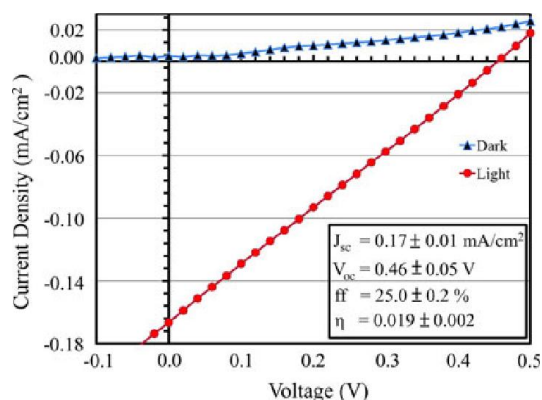


Fig. 5 *J*–*V* characteristic of DSSC cell (inset: the data of photovoltaic parameter)

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/cm², 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/cm², 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.

Acknowledgments This work has been carried out with the financial support of Malaysian Ministry of Higher Education (MOHE), under the Research funding ERGS/1/2011/STG/UKM/02/62. Authors would like to acknowledge Fitri Yenni, Siti Khatijah, Riski Titian Ginting, Eng Liang Lim, and Nasehah Syamin Sabri for their contribution in this work.

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