



Graphene-Au Film Synthesized from GrO in Au-Aqueous Solution as Counter Electrode For DSSC Application

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Abstract

The study on the optical, electrical properties of multilayer graphene (MLG) obtained by thermal-reduction of graphene oxide (GrO) which was synthesized directly by mixing graphite oxide (GO) flake in 0.005, 0.01, 0.015, and 0.02 M of Au aqueous solution has been successfully performed. The resultant GrO was subjected to an annealing temperature of 200°C, 400°C, 500°C for 1h to obtain MLG, and G-Au_{2x}, G-Au_{4x}, and G-Au_{5x} (x=0.005, 0.01, 0.015, and 0.02). The resultant samples were then characterized using FESEM, UV-VIS, four-point probe measurements to study its morphology, optical, and electrical properties. The transmission G-Au increase and its sheet resistant decrease as an increase of annealing temperature. Besides, the annealing treatment was then achieved of its microstructure which is expected may be used as a counter electrode in solar cell applications. The best DSSC devices with Glass/FTO/ZnO Nanorods/Dye/G-Au_{50.01}/Quartz structures have resulted in current-density, Voc, and solar cell performance of 0.1 mA/cm², 0.42 V, and 0.01%, respectively.

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INTRODUCTION

Good optical properties are necessary for optoelectronics applications, especially in solar cell devices. Indium titanium oxide and fluoro doped tin-oxide (FTO) thin film are the famously use as a transparent electrode in optoelectronic applications because they have good transparency and high conductivity at room temperature (Wu et al., 2008). Graphene as a single layer of carbon in 2D which an exceptional property such as electrical (Gilje et al., 2007; Wang et al., 2009) and optical properties has become a new alternative transparent electrode since founded for almost two decades ago. Nevertheless, it has good transparency but low in conductivity which can be used as an opportunity and challenge. It's peculiar that since it was found that electron mobility in the 2D graphene film exceeding 15.000 m²v⁻¹s⁻¹ (Wang et al., 2009). Thus graphene providing a great chance to explore and develop in terms of low-cost preparation (Hong et al., 2008), modified composition oxidation agent, and doping materials with enhanced an electrical and transparency of graphene (Eda & Chhowalla, 2010).

Generally, graphite oxide (GO) can be produced either a physics technique or a chemical technique. Among them, a chemical technique, especially by the Hummer's method (Hummers & Offeman, 1958) involving graphite oxidation, exfoliation, and reduction is preferable and a famous technique and yielding important step to produce high-quality properties of graphene film, especially optical and conductivity properties. Graphene can be obtained through vapor exposure of hydrazine (Eda & Chhowalla, 2010);

Zhou et al., 2011), thermal-reduction (Choi et al., 2011; Kymakis et al., 2011; Osváth et al., 2007) and combination both of them (Kymakis et al., 2011). Among them, thermal-reduction is very famously applied since the vapor of hydrazine is not sufficient for optimum reduction of the oxide layer (Wu et al., 2008).

Research about the enhanced of optical properties and reduce the sheet resistivity has been reported (Bonaccorso et al., 2010), but almost of the obtained that, sheet resistant increase as an increase of the film transmission (Li et al., 2010). The present paper will be reported on the study of optics, microstructure, and electrical properties as an effect of Au addition during the preparation of graphene oxide film. The resultant properties obtained were compared to the pristine graphene in various annealing treatments with the same composition and applied them as a counter electrode (CE) for DSSC devices.

METHOD

Graphene was prepared from GO which is obtained through modified Hummers-method (Hummers & Offeman, 1958). All the materials used in this research such as graphite powder, sodium-nitrate, sulphuric-acid, potassium-permanganate, hydrogen-peroxide, and hydrochloric-chloride were purchased from Sigma-Aldrich. There is 4 main process in this synthesized namely: oxidation of GO, washing, filtering and drying to produce GO flake. The detail of such process has been explained well in a previous report (Umar & Yap, 2013).

To synthesize the GO-Au film, the GO flake was dissolved in 0.005, 0.01, 0.015, 0.02 M of Au^{+3} aqueous solution, and in DI at a concentration of 10 mg/ml by stirring and sonication. The resultant solution was spin-coated on quartz substrates by using Spin-Coater. Next, the resulting graphite oxide (GrO) film was put in a furnace and annealed the sample at 200°C, 400°C, and 500°C in argon for 1 h to produce graphene film. The obtained graphene film was labeled as an MLG2, MLG4, MLG5, G-Au_{2x}, G-Au_{4x}, and G-Au_{5x}. The detail of that sample was described in Table 1.

Table 1. The list of sample influence in this research.

Nu.	Concentration	Annealing Temperature (°C)	Sample Name
1	10 mg/ml of DI	200°C	MLG2
		400°C	MLG4
		500°C	MLG5
2	x=0.005, 0.01, 0.015, and 0.02 M of Au^{+3}	200°C	G-Au _{2x}
		400°C	G-Au _{4x}
		500°C	G-Au _{5x}

The optical transmittation and morphology of MLG and G-Au films were obtained by using Halo UV-Vis spectrophotometer and Zeiss Supra 55VP FESEM, respectively. The sheet-resistance of the resultant MLG and G-Au film was obtained by Four Point Probe. The current-density-voltage (J-V) of the DSSC was obtained by using the Keithley source meter under illumination by simulated sunlight with an intensity of 100 mW cm² to characterize the device performance (See Fig.1).

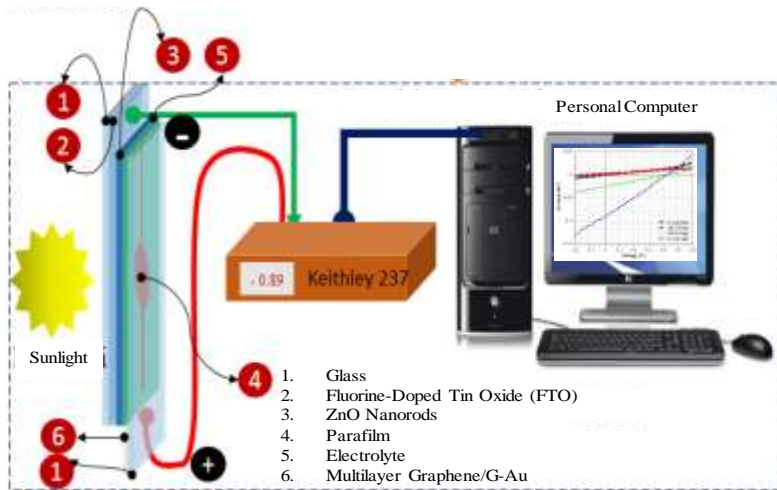


Figure 1. The DSSC array with the structure of Glass/FTO/ZnO Nanorods/electrolyte/MLG or G-Au/Quartz (Marjoni, 2014).

RESULTS AND DISCUSSION

Fig. 2 shows that the graph of sheet resistance and optical transmittance at $\lambda = 550$ nm of G- Au Film at various Au concentration. The complete data for all samples have been summarized in Table 2. From Fig. 2 and Table 2 shows, the G-Au film prepared by using Au solution at 0.01 M succeeded in producing the optimum optical transmittance and lowest sheet resistance film of 68% and 82 ± 39 k Ω /sq respectively. MLG-Au has exhibited a good tunable sheet resistivity comparison with the MLG film where GAu_{5,0.01} which has 82.2 k Ω of sheet resistance and 68% of its transparency has been shown in Table 2. It's the best sheet resistance in this work and also close to the resultant of reference (Eda et al., 2008). It's believed as an effect of gold nanoparticles addition during GrO preparation which has a unique property with highly dependent on their size, structure, and surrounding (Xiao & Qi, 2011).

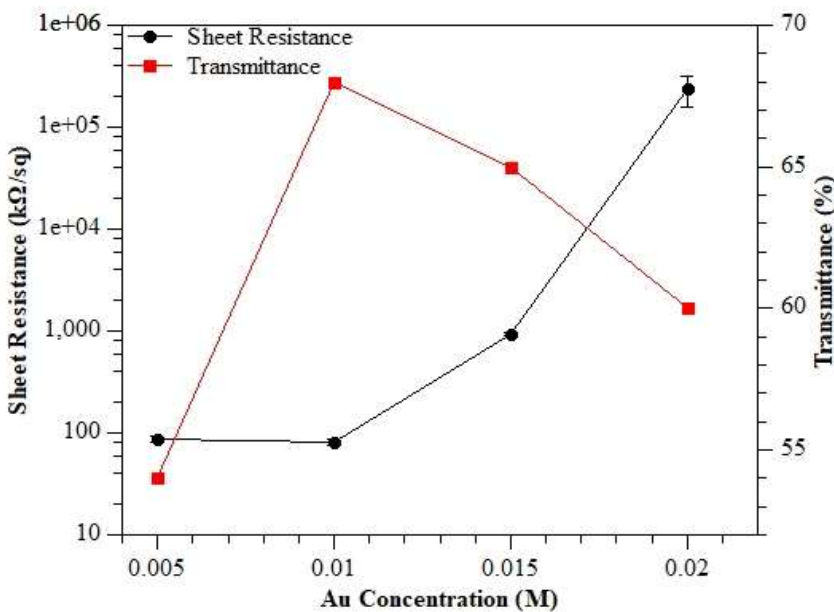


Figure 2. Optical-Transmittance at $\lambda = 550$ nm versus Sheet-Resistance curve of G-Au Film at Various Au Concentration.

Table 2. The Optical-Transmittance and Sheet-Resistance Data of MLG and G-Au Film Prepared at Various Au Concentration.

Sample	Concentration (M)	Optical Transmittance (T) (%)	Sheet Resistance (SR) k Ω /Sq.	T/SR	Ref
MLG	10	69.2	291.95 \pm 63.07	0.24	(Umar et al., 2013)
G-Au _{5x}	0.005	54	86.99 \pm 5.90	0.62	(Marjoni, 2014)
	0.01	68	82.21 \pm 5.3	0.83	
	0.015	65	932.02 \pm 21.7	0.07	
	0.02	60	235718 \pm 75811	0.0003	

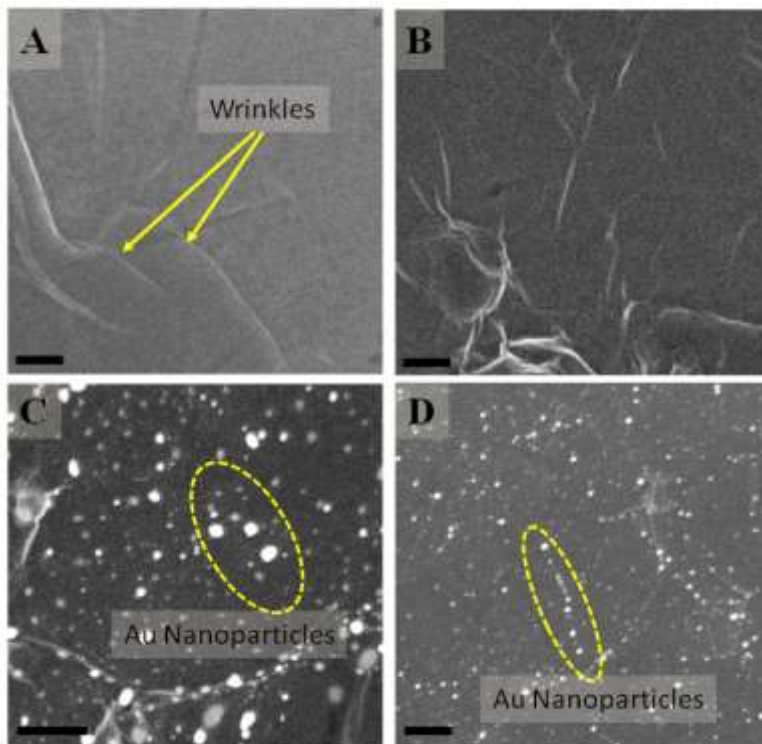
**Figure 3.** FESEM images of MLG annealing at (A) 400°C (B) 500°C, FESEM images of MLG-Au annealing at (C) 400°C, (D) 500°C (scale bar for (A), (B), (D), and (E) in 200 nm).

Fig. 3 shows the micrograph of MLG₄, MLG₅, G-Au_{4.01}, and GAu_{5.01} film obtained by FESEM characterization. The wrinkles in Fig. 3A occurred as a result of the functional layer already separated during the annealing process. Besides, the increasing of the annealing temperature, graphene aggregation effect, and attractive force between layer during thermal reduction (Cuong et al., 2010) also causing the wrinkles/folds to occur in the film (Umar et al., 2017). This phenomenon will make an increasing attenuation coefficient (Li et al., 2010). It's affected by the increase of the white-light absorbing and maintaining a high surface area of the electrode (Cong et al., 2010). The opposite phenomenon occurs, from Fig. 3C and 3D show that the microstructure of G-Au. Small particles in Figure 3C and 3D which are circled in yellow-colored are gold particles that successfully attach to multilayer graphene. It's surprisingly improved optics, and microstructure properties through an increasing of annealing temperature applied. It's

believed as an effect of gold nanoparticles addition during GrO preparation which has a unique property with highly dependent on their size, structure, and surrounding (Xiao & Qi, 2011). Besides, it's also led to smoother and brighter G-Au film with decreasing in light absorption. Au particle arrangement is better and flatter (see Fig. 3D) than Fig. 3C. Besides, it has filled in the blank part in between the graphene layer so that Au nanoparticles have been successfully exhibiting to be a potential material in the achieved of optical properties (Treguer et al., 2008) of graphene film.

The MLG and G-Au_{5,0.01} as the best sheet-resistance and optical transmittance were used as CE in DSSC. Fig. 4 shows the J-V curves of the DSSC device in dark and under the illumination and the photovoltaic parameter is described in Table 3. The DSSC with MLG film as a CE yielded a short circuit current-density (J_{sc}) of 0.03 mA/cm², a V_{oc} of 0.42 V, and a fill-factor (Devi et al., 2011) of 25%, resulting in PCE of 0.0027%. On the other hand, the J_{sc} and PCE of the DSSC with G-Au_{5,0.01} film as a CE increased significantly which is approximately 300 percent. This result shows that Au nanoparticles were successful to achieve photo-current enhancement in multilayer graphene film (Devi et al., 2011). Besides, the significant increase in J_{sc} and PCE could be correlated with the reduction of sheet resistance of the graphene film upon Au addition.

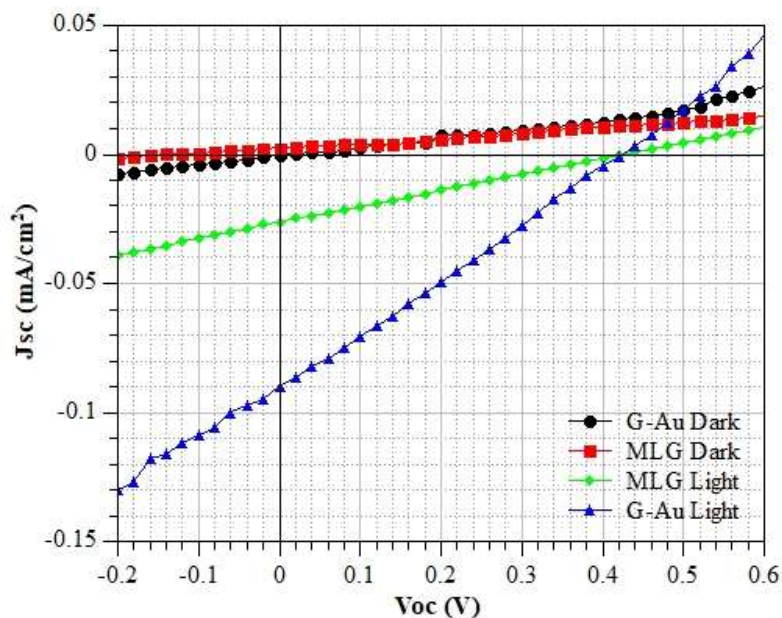


Figure 4. The current-voltage curve of DSSC devices with the structure Glass/FTO/ZnO Nanorods/Dye/MLG or G-Au/Quartz (Marjoni, 2014).

Table 3. The photovoltaic parameters data of DSSC with the structure Glass/FTO/ZnO Nanorods/Dye/MLG or G-Au/Quartz

CE	V_{oc} (V)	J_{sc} (mA/cm ²)	FF(%)	Eff (%)
MLG	0.42	0.03	25	0.003
G-Au5	0.42	0.10	26	0.010

CONCLUSION

The optical properties of MLG have been successfully improved by using aqueous solution surfactant containing 0.01 M Au since GrO preparation. Herein also the transmission spectra of the G-Au_{5,0.01} sample was then increased linearly with annealing temperature. The microstructure of the G-Au sample was also smoother and flatter as a function of annealing treatment. Amazingly, Au nanoparticles addition during GrO

preparation has been successfully enhanced optical, electrical, and microstructure of resultant graphene. It's making Au-nanoparticle very potential material to enhance the electrical and optical properties.

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