

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.

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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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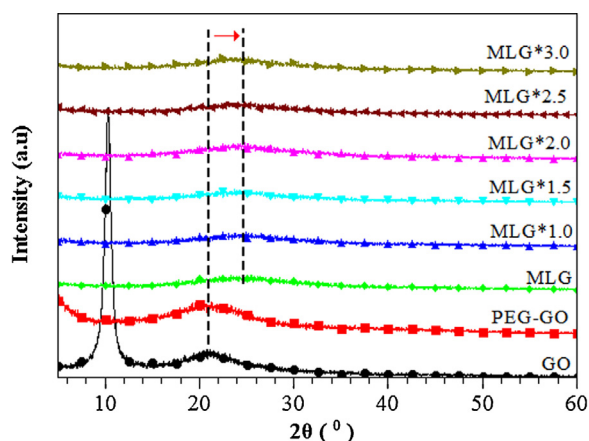


Fig. 1. XRD spectra of GO, PEG-GO, MLG, MLG*1.0, MLG*1.5, MLG*2.0, MLG*2.5 and MLG*3.0 films.

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 ($\approx 100 \mu\text{L}$) 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 $\text{CuK}\alpha$ radiation at a scan rate of $0.025^\circ/0.1 \text{ s}$. 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

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 $2\theta = 10.37^\circ$ and a broad peak at $2\theta = 20.55^\circ$. The sharp peak corresponds to interlayer

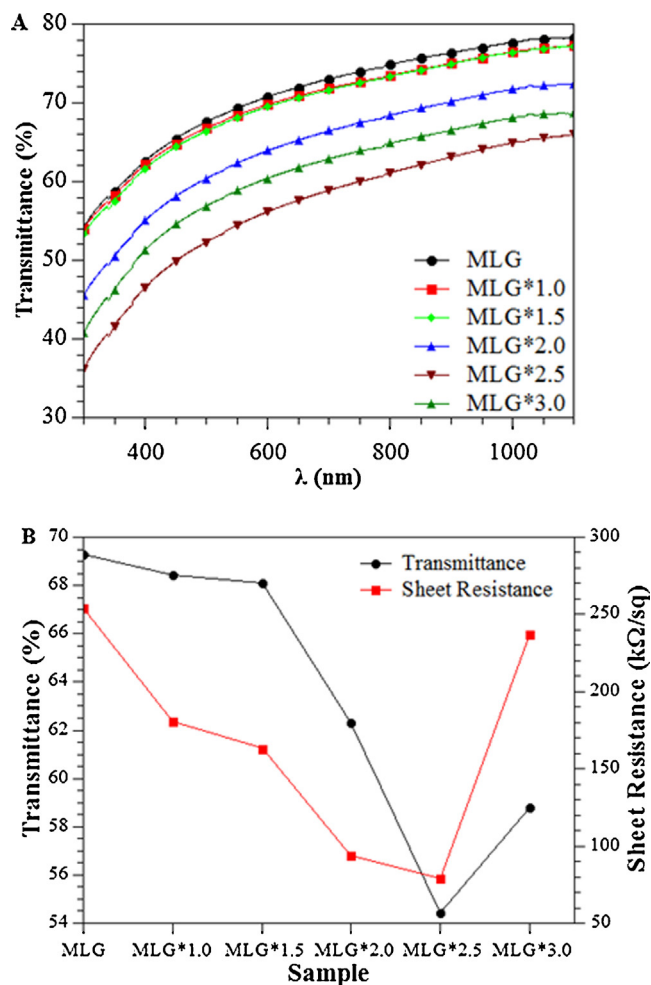


Fig. 2. (A) The optical transmission spectra and (B) the sheet resistance and optical transmittance ($\lambda = 550 \text{ nm}$) of MLG, MLG*1.0, MLG*1.5, MLG*2.0, MLG*2.5 and MLG*3.0 films.

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 $2\theta = 10.37^\circ$ disappeared and the broad peak at $2\theta = 20.55^\circ$ 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 $0.36\text{--}0.37 \text{ nm}$ 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 $\lambda = 550 \text{ nm}$) 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

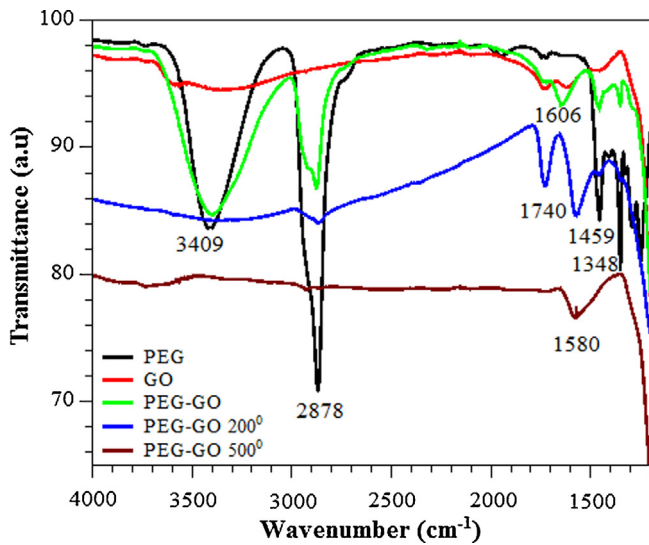


Fig. 3. The FTIR spectra of PEG, GO, PEG-GO, PEG-GO heated at 200 °C and 500 °C.

in Fig. 2B. The lowest sheet resistance of 78.73 k Ω /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 \sim 3409 cm^{-1} is attributed to O–H bonds vibration [17], whereas the strong peaks detected at \sim 2878, \sim 1459 and \sim 1348 cm^{-1} are related to C–H bonds [17]. The typical peaks of PEG at \sim 2878, \sim 1459 and \sim 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 \sim 2878, \sim 1459 and \sim 1348 cm^{-1} reduced significantly after a thermal treatment at 200 °C was given. In addition, two sharp peaks at \sim 1740 and \sim 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 \sim 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

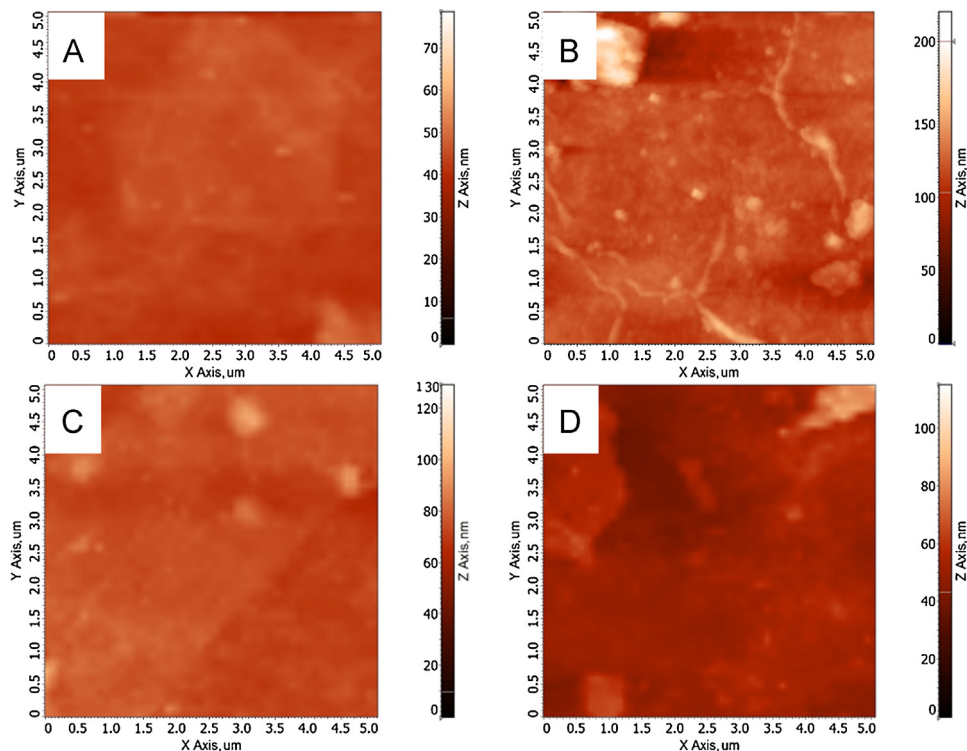


Fig. 4. The AFM images of (A) MLG, (B) MLG*1.0, (C) MLG*2.5 and, (D) MLG* 3.0 films.

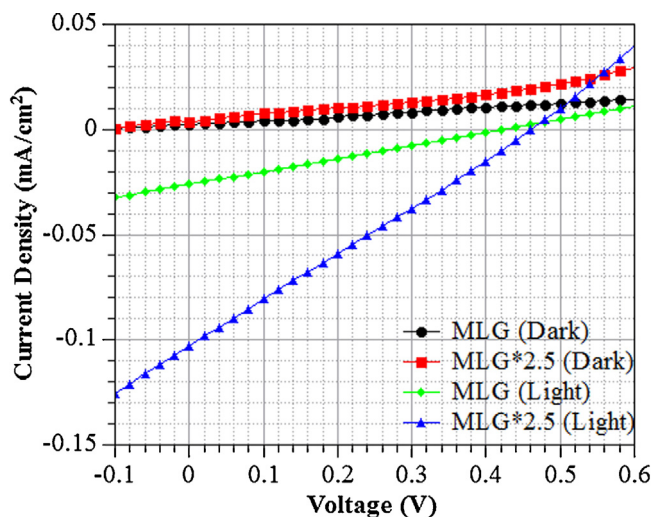


Fig. 5. The J–V characteristic of DSSCs with FTO/ZnO nanorods/electrolyte/MLG/glass and FTO/ZnO nanorods/electrolyte/MLG*2.5/glass structures.

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/cm² are shown in Fig. 5. The DSSC with unmodified graphene film yielded a short circuit current density (J_{sc}) of 0.026 mA/cm², 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/cm², 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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References

- [1] W. Hong, Y. Xu, G. Lu, C. Li, G. Shi, Transparent graphene/PEDOT–PSS composite films as counter electrodes of dye-sensitized solar cells, *Electr. Commun.* 10 (2008) 1555–1558.
- [2] G. Eda, Y.Y. Lin, S. Miller, C.W. Chen, W.F. Su, M. Chhowalla, Transparent and conducting electrodes for organic electronics from reduced graphene oxide, *Appl. Phys. Lett.* 92 (2008) 233305.
- [3] N. Jović, D. Dudić, A. Montone, M.V. Antisari, M. Mitrić, V. Djoković, Temperature dependence of the electrical conductivity of epoxy/expanded graphite nanosheet composites, *Scripta Mater.* 58 (2008) 846–849.
- [4] J.D. Roy-Mayhew, D.J. Bozym, C. Punckt, I.A. Aksay, Functionalized graphene as a catalytic counter electrode in dye-sensitized solar cells, *ACS Nano* 4 (2010) 6203–6211.
- [5] C.M. Weber, D.M. Eisele, J.P. Rabe, Y. Liang, X. Feng, L. Zhi, K. Müllen, J.L. Lyon, R. Williams, D.A.V. Bout, Graphene based optically transparent electrodes for spectroelectrochemistry in the UV–Vis region, *Small* 6 (2010) 184–189.
- [6] B.-S. Kong, H.-W. Yoo, H.-T. Jung, Electrical conductivity of graphene films with a poly (allylamine hydrochloride) supporting layer, *Langmuir* 25 (2009) 11008–11013.
- [7] Y.J. Park, S.Y. Park, I. In, Preparation of water soluble graphene using polyethylene glycol: Comparison of covalent approach and noncovalent approach, *J. Ind. Eng. Chem.* 17 (2011) 298–303.
- [8] J. Zhang, K.H. Au, Z.Q. Zhu, S. O'Shea, Sol–gel preparation of poly(ethylene glycol) doped indium tin oxide thin films for sensing applications, *Opt. Mater.* 26 (2004) 47–55.
- [9] B. Bhattacharjee, D. Ganguli, S. Chaudhuri, Luminescent CdS nanoparticles embedded in polyethylene glycol (PEG 300) matrix thin film, *J. Nanoparticle Res.* 4 (2002) 225–230.
- [10] T. Zhou, F. Chen, K. Liu, H. Deng, Q. Zhang, J. Feng, Q. Fu, A simple and efficient method to prepare graphene by reduction of graphite oxide with sodium hydrosulfite, *Nanotechnology* 22 (2011) 1–6.
- [11] M.I. Ali Umar, C.C. Yap, R. Awang, M. Hj Jumali, M. Mat Salleh, M. Yahaya, Characterization of multilayer graphene prepared from short-time processed graphite oxide flake, *J. Mater. Sci. Mater. Electron.* 24 (2013) 1282–1286.
- [12] M.J. Allen, V.C. Tung, R.B. Kaner, Honeycomb carbon: a review of graphene, *Chem. Rev.* 110 (2009) 132–145.
- [13] H. Hu, Y. Liu, Q. Wang, J. Zhao, Y. Liang, A study on the preparation of highly conductive graphene, *Mater. Lett.* 65 (2011) 2582–2584.
- [14] Z.G. Le, Z. Liu, Y. Qian, C. Wang, A facile and efficient approach to decoration of graphene nanosheets with gold nanoparticles, *Appl. Surf. Sci.* 258 (2012) 5348–5353.
- [15] S.H. Huh, H.M. Ju, S.H. Choi, X-ray diffraction patterns of thermally-reduced graphenes, *J. Korean Phys. Soc.* 57 (2010) 1649–1652.
- [16] C. Van Do, T.T.T. Nguyen, J.S. Park, Fabrication of polyethylene glycol/polyvinylidene fluoride core/shell nanofibers via melt electrospinning and their characteristics, *Sol. Energ. Mater. Sol. C.* 104 (2012) 131–139.
- [17] G. Socrates, *Infrared and Raman Characteristic Groups Frequencies*, 3rd ed., John Wiley & Sons, New York, 1994.
- [18] K.H. Liao, A. Mittal, S. Bose, C. Leighton, K.A. Mkhoyan, C.W. Macosko, Aqueous only route toward graphene from graphite oxide, *ACS Nano* 5 (2011) 1253–1258.
- [19] H.S. Jahromi, H. Taghdisian, S. Afshar, S. Tasharofi, Effects of pH and polyethylene glycol on surface morphology of TiO₂ thin film, *Surf. Coat. Technol.* 203 (2009) 1991–1996.
- [20] G. Wang, X. Shen, B. Wang, J. Yao, J. Park, Synthesis and characterisation of hydrophilic and organophilic graphene nanosheets, *Carbon* 47 (2009) 1359–1364.

- [21] S. Watcharotone, D.A. Dikin, S. Stankovich, R. Piner, I. Jung, G.H. Dommett, G. Evmenenko, S.-E. Wu, S.-F. Chen, C.-P. Liu, Graphene-silica composite thin films as transparent conductors, *Nano Lett.* 7 (2007) 1888–1892.
- [22] J.M. Harris, S. Zalipsky, *Poly(ethylene glycol) Chemistry and Biological Application*, American Chemical Society, Washington, 1997.
- [23] D. Pysch, A. Mette, S.W. Glunz, A review and comparison of different methods to determine the series resistance of solar cells, *Sol. Energ. Mater. Sol. C* 91 (2007) 1698–1706.
- [24] Z. Qin, Y. Huang, J. Qi, Q. Liao, W. Wang, Y. Zhang, Surface destruction and performance reduction of the ZnO nanowire arrays electrode in dye sensitization process, *Mater. Lett.* 65 (2011) 3506–3508.