Asian Journal of Chemistry; Vol. 26, No. 5 (2014), 1321-1323

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.17220

# Optimization Study of Graphene Oxide Synthesis with Improvement of C/O Ratio†

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AJC-14761

The present study was aimed to clarify detailed conditions of vigorous solid-state reaction as conventional method for graphene oxide. For optimization study, the effects of an initial concentration of $KMnO_4$ (0.75-7.5 % w/v), reaction temperature (0-120 ºC) and an incubation time (1-48 h) were investigated. The obtained graphene oxide was characterized by Fourier transform infrared spectroscopy, X-ray diffraction spectroscopy, energy dispersive X-ray spectroscopy and scanning electron microscope (SEM) techniques. From the results, the optimum conditions for graphene oxide production were consisted of 4.5 % w/v $KMnO_4$ at 80 ºC for 6 h. IR spectrum showed the characteristic peaks at wave number ($cm^{-1}$) of 3367 (O-H), 1719 (C=O), 1224 and 1049 (C-O). Energy dispersive X-ray spectroscopy of the graphene oxide revealed the improved C/O ratio of 1.10, indicating more polar functional groups bound on the surface of graphene oxide due to the increasing oxidation by $MnO_4^-$. The amorphous graphene oxide was obtained as confirmed by XRD pattern. Additionally, SEM image showed drastically differences in the surfaces between graphene oxide and its graphite powder, depicting a graphene oxide's smooth surface compared with that rough multilayer graphite powder. It could, thus, be gained a crucial factor affecting the graphene oxide synthesis from graphite powder under the optimized method.

**Keywords: Graphite powder, Graphene oxide, Energy dispersive X-ray spectroscopy, Scanning electron microscope.**

## INTRODUCTION

Graphene oxide (GO) is a water-soluble nanomaterial prepared through extensive chemical attack of graphite to introduce oxygen-containing defects in the graphite stack. Graphene oxide sheets are composed of planar, graphene-like aromatic domains of random sizes interconnected by a network of cyclohexane like units in chair conformation which are decorated by hydroxyl, epoxy and carbonyl groups. These functional groups in graphene oxide impart water solubility to the individual sheets and removal of such groups resulted in flocculation and precipitation[1].

Functionalization of graphene oxide can fundamentally change their chemical and physical properties. The resulting chemically modified graphene oxide could then potentially become much more adaptable for almost limitless applications. There are many ways in which graphene oxide can be functionalized, depending on the desired application and amount of functional group on the surface of graphene oxide. For instance, the functionalizations of graphene oxide with polyhedral oligomeric silsesquioxane[2], 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide and N-hydroxysuccinimide[3], *p*-phenylene diamine[4], N-(trimethoxysilylpropyl)ethylenediamine triacetic acid[5], ethylenediamine[6], 9-(4-aminophenyl) acridine[7] and 2-amino-4,6-didodecylamine-no-1,3,5-triazine[8] were reported.

Currently, graphene oxide preparation is relied on Hummers' method using $KMnO_4$, $NaNO_3$ and $H_2SO_4$ under vigorous solid-state reaction. The C/O ratio obtaining from this method is substantially high. However, an optimum condition for higher C/O ratio of the graphene oxide is still limited. In this work, we reported an improvement of C/O ratio in graphene oxide by an optimization condition of the Hummers' method[9].

## EXPERIMENTAL

Sodium nitrate ($NaNO_3$), sulfuric acid ($H_2SO_4$, 98 %) and hydrogen peroxide ($H_2O_2$, 30 %) were purchased from Ajax FineChem Pty Ltd. Potassium permanganate ($KMnO_4$) and graphite powder (< 20 µm, synthetic) were purchased from Carlo Erba and Sigma-Aldrich, respectively. All chemicals were used as received without further purification.

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†Presented at The 7th International Conference on Multi-functional Materials and Applications, held on 22-24 November 2013, Anhui University of Science & Technology, Huainan, Anhui Province, P.R. China

Attenuated total reflectance-Fourier Transform infrared (ATR-FTIR) spectroscopic measurements were performed on TENSOR 27 system Fourier Transform infrared spectrometer (Bruker, Germany). X-ray diffraction spectroscopy (XRD) was conducted with a D8ADVANCE system (Bruker, Germany). Surface morphological images and EDX spectrum were taken by a HITACHI S-3000N scanning electron microscope (SEM, Hitachi Co. Ltd., Japan).

**Optimum conditions for graphene oxide preparation and characterization:** Graphene oxide was prepared from graphite powder (GP) by a sequential oxidation process with strong oxidants including $H_2SO_4$, $KMnO_4$, 30 % $H_2O_2$ and $NaNO_3$, respectively. In a typical synthesis, 3 g of graphite powder was added to cold (0 ºC) 300 mL of 98 % $H_2SO_4$ and stirred for 0.5 h. Then, 3.0 g of $NaNO_3$ was added portion-wise to the mixture and kept further stirring for 0.5 h. Subsequently, a solid powder of $KMnO_4$ (0.75-7.5 % w/v) was varied with slowly adding to the mixture, which always kept below 10 ºC in an ice bath. After stirring for 0.5 h, 200 mL of deionized water was then slowly added to the mixture and stirred again for 0.5 h. After that, both temperatures (0-120 ºC) and an incubation time (1-48 h) of the reaction mixture were also optimized and 40 mL of 30 % $H_2O_2$ was slowly added. The mixture solution was centrifuged and washed several times with deionized water until the pH of the filtrate reached neutral. The lyophilized precipitates were obtained. The obtained graphene oxide was characterized by FTIR, XRD, EDX and SEM techniques. The SEM samples were coated with a thin layer of gold before imaging.

## RESULTS AND DISCUSSION

**Optimum conditions of graphene oxide preparation:** In order to find an optimum condition, three crucial factors including concentration of $KMnO_4$, temperature and incubation time, were explored. Firstly, the optimization of concentration of oxidizing agent was performed. The concentration of $KMnO_4$ was varied from 0.75 to 7.5 % w/v (Table-1) at which both of temperature and incubation time was fixed at 100 ºC and 24 h. At low concentrations (0.75 % and 1.5 % w/v of $KMnO_4$) the oxidation was incompletely obtained as revealed by FTIR (Fig. 1). An increment of $KMnO_4$ concentrations to 3.0 and 4.5 % w/v gave a satisfied C/O ratio. It is interesting to note that higher concentrations than 4.5 % w/v, resulted in insignificant differences in the C/O ratio (Table-1). Thus, the 4.50 % w/v $KMnO_4$ was chosen. Next, the effect of temperature was investigated. The reaction temperatures were varied from 0 to 120 ºC using 4.5 % w/v $KMnO_4$ for 24 h. As expected, at lower temperature range the oxidation of graphene oxide was incomplete as revealed by the C/O ratio. At above 40 ºC, the C/O ratios were increased, implying that the oxidation process of graphene oxide preparation was insignificant improvement. The optimal temperature at 80 ºC was chosen. Finally, an effect of incubation time was also investigated with 4.50 % w/v of $KMnO_4$ and at 80 ºC. The C/O ratios were not improved during 1 and 3 h oxidation. Using longer incubation period from 6 to 9 h gave the improvement of the C/O ratio. However, the incubation time longer than 24 h resulted in the insignificant increment of the C/O ratios. The optimum conditions for graphene oxide synthesis were thus obtained consisting of 4.5 % w/v $KMnO_4$ at 80 ºC for 6 h. It is evident that the C/O ratio of the graphene oxide product was lowered to 1.10 (C % = 52.40, O % = 47.60), basically implying more polar functional groups bound on the surface of graphene oxide due to the increasing oxidation by $MnO_4^-$. It suggests that an immobilization of multi-functional ligands on the graphene oxide product would be easily carried out. However, solubility of the graphene oxide product with different solvent polarity is further one of the expected outcomes.

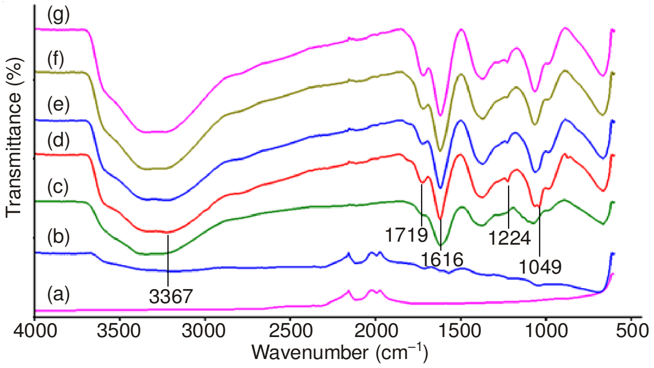

Fig. 1. FTIR spectra of (a) graphite powder and (b)-(g) graphene oxide oxidized with 0.75, 1.5, 3.0, 4.5, 6.0 and 7.5 % w/v $KMnO_4$

Fig. 1 showed the FTIR spectra of graphite powder (a) and the graphene oxides oxidized (b-g) with different concentrations of $KMnO_4$. When using $KMnO_4$ of 4.5-7.5 % w/v, the IR bands at wave number ($cm^{-1}$) at 3367 (O-H), 1719 (C=O), 1224 and 1049 (C-O) were consistently appeared.

**Morphology of graphene oxide:** Morphologies of graphite powder and graphene oxide are shown in Fig. 2(a-b). Graphite powder exhibits a rough surface with multilayer feature. In contrast, an image of graphene oxide appears as a smooth surface one.

TABLE-1
C/O RATIOS IN GRAPHENE OXIDE OBTAINED FROM DIFFERENT EXPERIMENTAL CONDITIONS

| Effect of $KMnO_4$ | | | | Effect of temperature | | | | Effect of incubation time | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $KMnO_4$ conc. (% w/v) | C (%) | O (%) | C/O ratio | Reaction temp. (ºC) | C %) | O (%) | C/O ratio | Incubation time (h) | C (%) | O (%) | C/O ratio |
| 0.75 | 75.08 | 24.92 | 3.01 | 0 | 62.41 | 37.59 | 1.66 | 1 | 61.37 | 38.63 | 1.59 |
| 1.50 | 64.19 | 35.81 | 1.79 | 20 | 61.93 | 38.07 | 1.63 | 3 | 59.76 | 40.24 | 1.49 |
| 3.00 | 62.45 | 37.55 | 1.67 | 40 | 57.97 | 42.03 | 1.38 | 6 | 57.15 | 42.85 | 1.33 |
| 4.50 | 60.07 | 39.93 | 1.50 | 60 | 57.95 | 42.05 | 1.38 | 9 | 57.62 | 42.38 | 1.36 |
| 6.00 | 60.65 | 39.35 | 1.54 | 80 | 56.35 | 43.65 | 1.29 | 12 | 57.63 | 42.37 | 1.36 |
| 7.50 | 60.41 | 39.59 | 1.53 | 100 | 56.60 | 43.40 | 1.30 | 24 | 58.83 | 41.17 | 1.42 |
| – | – | – | – | 120 | 57.62 | 42.38 | 1.36 | 48 | 59.02 | 40.98 | 1.44 |

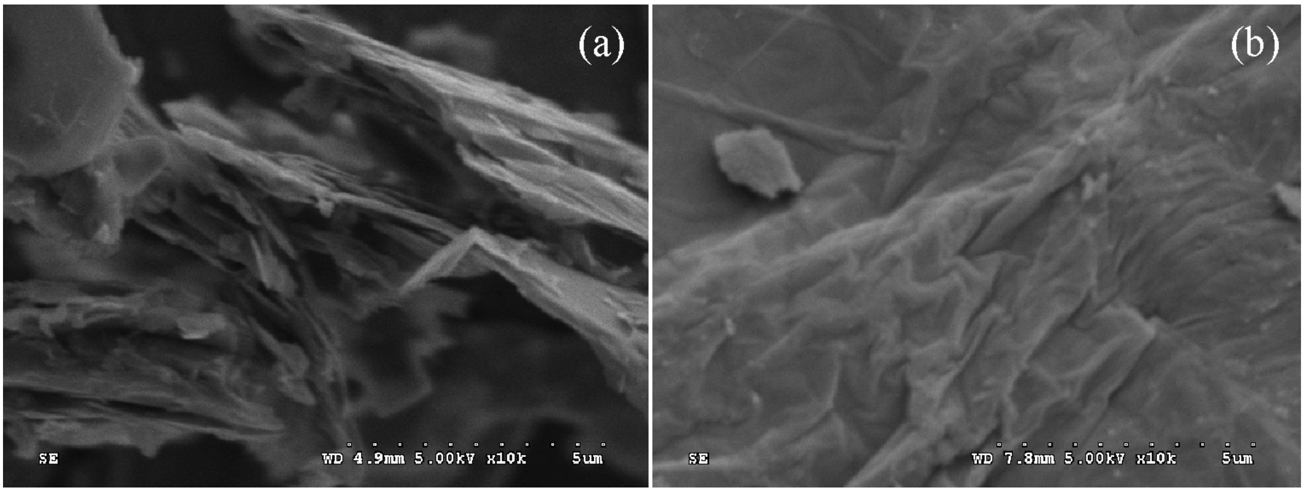

Fig. 2. SEM images of (a) graphite powder and (b) graphene oxide

X-ray diffraction was also employed to evaluate the effects of oxidization on the interlayer distance of graphite. Fig. 3 depicts the XRD patterns of graphite powder and graphene oxide showing their diffraction peaks at 26° and 11° for graphite and graphene oxide, respectively. The graphene oxide was clearly found to be an amorphous material. This is indicating the intense intercalation of graphite during oxidization.

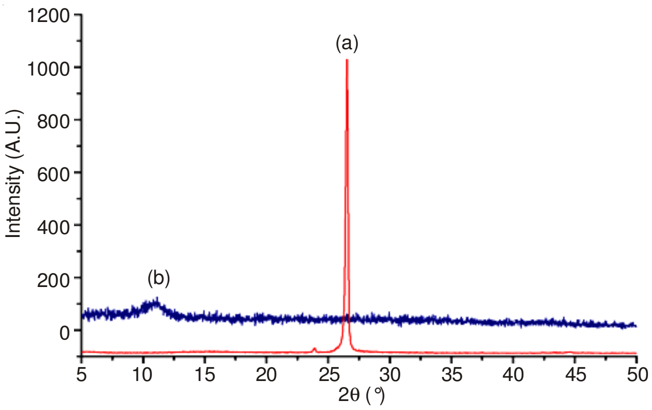

Fig. 3. XRD patterns of (a) graphite powder and (b) graphene oxide

## Conclusion

The optimum conditions for graphene oxide production were consisted of 4.5 % w/v $KMnO_4$ at 80 °C for 6 h. IR spectrum showed the characteristic peaks at wave number ($cm^{-1}$) of 3367 (O-H), 1719 (C=O), 1224 and 1049 (C-O). Energy dispersive X-ray diffraction of the graphene oxide revealed the C/O ratio of 1.10, implying more polar functional groups bound on the surface of graphene oxide due to the increasing oxidation by $MnO_4^-$. The amorphous graphene oxide was obtained as confirmed by XRD pattern. Additionally, SEM image showed drastically differences in the material surfaces between graphene oxide and its graphite powder, depicting the graphene oxide's smooth surface of graphene oxide compared with that rough multilayer graphite powder. Therefore, the C/O ratio could be gained as a criterion factor for the graphene oxide prepared from graphite powder under the optimized method.

## ACKNOWLEDGEMENTS

This research was financially supported by Khon Kaen University and the Ministry of Science and Technology, Bangkok, Thailand.

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