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

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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 °C) 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 °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 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 precipitation¹.

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 silsesquioxane², 1-ethyl-3-(3-dimethyl

aminopropyl) carbodiimide and N-hydroxysuccinimide³, *p*-phenylene diamine⁴, N-(trimethoxysilylpropyl)ethylenediamine triacetic acid⁵, ethylenediamine⁶, 9-(4-aminophenyl) acridine⁷ and 2-amino-4,6-didodecylamine-no-1,3,5-triazine⁸ 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' method⁹.

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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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°C) 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°C 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°C) 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°C 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

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

from 0 to 120°C 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°C , the C/O ratios were increased, implying that the oxidation process of graphene oxide preparation was insignificant improvement. The optimal temperature at 80°C was chosen. Finally, an effect of incubation time was also investigated with 4.50 % w/v of KMnO_4 and at 80°C . 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°C 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 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 ($\text{C}=\text{O}$), 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. ($^\circ\text{C}$)	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 oxidation 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 oxidation.

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 ($\text{C}=\text{O}$), 1224 and 1049 ($\text{C}-\text{O}$). 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.

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