Effects of reduction time on the structural, electrical and thermal properties of synthesized reduced graphene oxide nanosheets

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Abstract. The reduction of graphene oxide (GO) nanosheet is a promising route to produce a stable colloidal dispersion of reduced graphene oxide (RGO) nanosheets in a large scale. The production of RGO nanosheet is one of the important topics in nanotechnology disciplines due to its contribution in various applications, such as the platinum catalyst support in direct methanol fuel cell. Therefore, in this paper, the RGO nanosheets were prepared via highly efficient chemical reduction reaction of exfoliated GO nanosheets using sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) as the reducing agent. Extensive characterizations have been conducted in terms of structural, thermal stability and electrical conductivity properties by means of high-resolution transmission microscopy, the Fourier transform infrared spectroscopy, UV–visible spectroscopy, ^{13}C NMR and four-point probe conductivity measurement. The results indicate that most of oxygen-containing functional groups from GO nanosheets have been removed and the RGO-3 possess greater thermal stability compared to GO nanosheets. The prepared RGO-3 shows the highest electrical conductivity at room temperature which is $\sim 2.0 \times 10^3 \text{ S m}^{-1}$. Based on these analyses, the plausible mechanism of reduction of GO to RGO by sodium oxalate is well proposed.

Keywords. Reduced graphene oxide nanosheets; graphene oxide nanosheets; sodium oxalate; thermal stability; electrical conductivity.

1. Introduction

Direct methanol fuel cell (DMFC) is an energy conversion system that has greater attraction as power sources for electronic device applications. Most of the researchers come with new ideas which focus to enhance the fuel cell's performance and reduce the cost.¹ However, this has been delayed due to the deficiency of catalyst materials. Platinum (Pt) is the most efficient electro-catalyst mainly chosen in fuel cell's application due to its highest catalytic activities compared to the other catalyst.² However, the usage of Pt limits the practical application due to its expensive and less availability in nature.³ These limitations can be resolved by reducing the Pt loading at the electrodes with the use of electro-catalyst support.⁴ The characteristics of good material for electro-catalyst support are it should possess high electrical conductivity, good catalyst interaction and large surface area for high dispersion of Pt catalyst. In recent times, carbonaceous materials were greatly utilized as electro-catalyst support because carbon is an important electrode assembling for maximizing DMFC performance.⁵

Graphene is one of the most promising carbonaceous materials with two-dimensional layer of sp^2 hybridized carbon atom that are arranged in a honeycomb lattice structure.⁶

In recent years, it has received a rising attention in fuel cell research fields and been an important material as it possesses larger specific area,⁷ good mechanical strength,⁸ higher electrical conductivity⁹ and excellent thermal stability.¹⁰ The large-scale production with low cost of producing graphene by the chemical reduction method has been considered to be the most appropriate approach.^{6,11} In recent times, the uses of environment-friendly reducing agents to produce reduced graphene oxide (RGO) nanosheets have been reported, such as pyrrole,¹² L-glutathione,¹³ sodium diphenylamine sulphonate¹⁴ and ascorbic acid.¹⁵ However, its feasibility still requires further evaluations due to some of its drawbacks, such as high in cost, experimentally time consuming and limited applications.¹⁶

In our previous report, it was possible to synthesize graphene nanosheets just via reducing the GO nanosheets by sodium oxalate under heating treatment, which showed satisfying properties as demonstrated via efficient characterizations such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HRTEM) and Raman spectrometry.¹⁷ It was demonstrated that sodium oxalate could reduce the oxygen-containing functional groups, such as epoxy, hydroxyl, carboxyl and carbonyl groups on the surface and at the edge of GO. The outstanding advantage of using sodium oxalate is its high reducibility and less hazardous compared with vigorous

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and poison reducing agents such as hydrazine and sodium borohydride. Therefore, herein, the RGO nanosheets were prepared via chemical reduction of exfoliated GO by sodium oxalate as the efficient reducing agent. The structural, electrical conductivity and thermal stability of the prepared RGO were investigated.

2. Experimental

2.1 Materials

Purified graphite powder was obtained from Superior Graphite Co. Ltd. Sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) (Fisher brand), hydrogen peroxide (H_2O_2 , 35%) and sodium nitrate (NaNO_3) were purchased from Riedel-de Haën. Hydrochloric acid (HCl, 37%) was purchased from RCI Labscan, potassium permanganate (KMnO_4) from COMAK, and concentrated sulphuric acid (H_2SO_4 , 95–97%) from QR&C. All chemicals were of analytical grade and used as-received without further purification.

2.2 Synthesis of GO nanosheets

The GO nanosheet was synthesized through the oxidation of the purified graphite powder via modified Hummers' method.¹⁸ Three grams of NaNO_3 was dissolved in 140 ml of concentrated H_2SO_4 in an ice bath. Then, 15 g of KMnO_4 and 3 g of graphite powder were gradually added into the mixture. The temperature was kept below 20°C under vigorous stirring using a mechanical stir bar for 2 h. The temperature of the mixture was then increased and maintained at 35°C . The mixture was continuously stirred for another 12 h until it turned into a brown paste. After that, 250 ml of deionized water was added into the mixture and stirred for 30 min. Next, 20 ml of 35% H_2O_2 and 800 ml of deionized water were added into the mixture. The stir was continued until the mixture colour changed from brown into brilliant yellow. The mixture was filtered and washed using 1 M HCl and deionized water until the pH of the filtrate became neutral. Lastly, the mixture was dried in oven at 80°C .

2.3 Chemical reduction of GO nanosheet

The RGO nanosheet was synthesized through chemical reduction of exfoliated GO nanosheet according to our previous report.¹⁷ Firstly, 200 mg of solid GO was dispersed in 200 ml of deionized water under ultra-sonication for 3 h by using a high-power ultrasonic pole at 0°C until it turned into a dark-brown GO aqueous colloid. In typical reduction process from GO to RGO, 100 ml of GO colloid was mixed with 40 ml of sodium oxalate solution (0.45 M) in a 250 ml conical flask under vigorous stirring. The final solution was kept at $\pm 95^\circ\text{C}$ for a period of 1/2 h (RGO-1), 1 h (RGO-2) and 2 h (RGO-3). Then, the products were centrifuged

for 20 min at 3000–4000 rpm and washed using deionized water repeatedly. Finally, the products were dried at 80°C in oven.

2.4 Characterization

The FTIR spectra of the samples were obtained using Nicolet 5700 FTIR in the wavelength range of $500\text{--}4000\text{ cm}^{-1}$. The ultraviolet-visible spectra were obtained using Shimadzu UV-visible spectrophotometer (UV-1601 PC) with wavelength of $200\text{--}600\text{ nm}$. The morphology of the synthesized GO and RGO were characterized by HRTEM (FEI TECNAI G2) at acceleration voltage of 200 kV and scanning electron microscopy (SEM, HITACHI TM3000). Thermogravimetric analysis (TGA) was conducted on a Mettler Toledo TGA/SDTA 851 thermal analyzer in a dynamic atmosphere of nitrogen. The samples were heated inside alumina crucible at $10^\circ\text{C min}^{-1}$. ^{13}C NMR (400 MHz) spectra were collected using a Bruker Avance III HD. The electrical conductivity of samples was calculated from the I – V characteristics by the four-point probe method. From the I – V characteristics by the four-point probe method, the resistance of the samples was calculated according to Ohm's law. Therefore, the resistance, resistivity and conductivity of the samples were calculated using the following formula as reported by Sahoo *et al.*¹⁹

$$\text{Resistance} = V/I,$$

$$\text{Resistivity } (\rho, \Omega \text{ cm}) = \pi t / \ln 2(V/I),$$

$$\text{Conductivity } (\sigma, \text{S cm}^{-1}) = 1/\rho,$$

where V is the measured voltage, I the current applied and t the thickness of the sample.

3. Results and discussions

3.1 Plausible reduction mechanism

The possible mechanisms for the reduction of carboxyl and epoxide groups of GO nanosheets using sodium oxalate as the reducing agent have been well established in this study.²⁰ In case of carboxyl groups, the reduction mechanism involves the decarboxylation process which causes the liberation of carbon dioxide (CO_2) under heat treatment as shown in figure 1a. The mechanism of ring opening of epoxide groups in GO is according to the base-catalysed reaction. Since the epoxide groups are very reactive, the strong bases and nucleophiles are necessary to attack and open epoxides which led to relieve the strain of the three-membered ring. In this case, the strong base and nucleophile is hydroxyl group. Figure 1b shows the plausible mechanism of reductive cleavage of epoxide groups in GO with a few steps.

Figure 1. Plausible mechanism for the reduction of (a) carboxyl groups and (b) epoxide groups in GO using sodium oxalate as reducing agent.

3.2 Structural analysis

3.2a FTIR spectroscopy: FTIR analysis was performed to confirm the removal of oxygen-containing groups in the GO

after being reduced by the sodium oxalate. Figure 2 shows the FTIR spectra for the GO, RGO-1, RGO-2 and RGO-3. The GO spectrum shows a broad peak at 3276 cm^{-1} and sharp peak at 1732 cm^{-1} which were attributed to

Figure 2. FTIR spectra for GO (before) and after being reduced by sodium oxalate for 30 min (RGO-1) 1 h (RGO-2) and 2 h (RGO-3).

the O–H stretching and C=O stretching vibration, respectively. Aromatic C=C stretching vibration appearance was confirmed by a peak at 1616 cm^{-1} . The peaks at 1149 and 1047 cm^{-1} were designated to epoxy C–O stretching vibration and alkoxy C–O stretching vibration, respectively; similar to the characteristic peaks as reported by Jin *et al.*¹¹ Overall, the peak intensities were reduced remarkably with the reduction. After the reduction, the peak intensities for oxygen-containing group at 3276 and 1149 cm^{-1} were reduced remarkably, while the peaks at 1732 and 1047 cm^{-1} were significantly weakened for RGO-1 and RGO-2. The peaks at 3276 , 1732 , 1149 and 1047 cm^{-1} were totally disappeared for RGO-3. However, the peak at 1616 cm^{-1} was still available, which indicates that the sp^2 hybridization of C=C bonds have been well-restored. These results suggest that the GO nanosheets have been successfully reduced to RGO nanosheets using sodium oxalate as a chemical reducing agent when the reduction time is prolonged to a certain period.

3.2b UV-vis spectrophotometer: The UV-vis spectra for the GO, RGO-1, RGO-2 and RGO-3 are shown in figure 3. For the GO, there was a strong absorption peak at 230 nm , corresponding to the conjugated aromatic double bonds (C=C) with $\pi\text{--}\pi^*$ transition. Another peak at 301 nm , which was a shoulder band, corresponded to the carbonyl bonds (C=O) with $\text{n--}\pi^*$ transition. After the reduction, a strong absorption peak appeared at around ~ 242 , 249 , and 257 nm for RGO-1, RGO-2, and RGO-3, respectively. Thus, it indicates that the conjugated structure of RGO which is an aromatic C=C bond is well restored upon reduction as similarly

Figure 3. UV-vis absorption spectra of GO aqueous dispersion (before) and after being reduced by sodium oxalate for RGO-1, RGO-2 and RGO-3.

reported by Jin *et al.*¹¹ This is in agreement with the FTIR results.

3.2c ^{13}C NMR spectroscopy: The solid-state ^{13}C NMR spectra were carried out to characterize the reduction of GO by sodium oxalate. ^{13}C NMR spectra of GO and RGO-3 are shown in figure 4a and b, respectively. In the spectrum of GO, it was confirmed that the presence of abundant epoxide and hydroxyl groups that align perpendicular to the basal-plane carbon atoms at 66 and 73 ppm , respectively. There are too small peak of the carbonyl groups (carboxyl) for ^{13}C NMR detection, which are located at the edges of the basal plane. The resonance at 130 ppm belongs to the un-oxidized sp^2 carbons atom. In the spectrum of RGO-3,

Figure 4. Solid-state ^{13}C NMR spectra of (a) GO and (b) RGO-3.

it indicates a significant reduction in the amount of epoxide and hydroxyl groups present with structural change after reduced by sodium oxalate. The peaks of those oxygen-containing functional groups became weaker and smaller. On the other hand, the peaks from the oxygenated and carbonyl

carbons are totally reduced. In addition, the plentiful sp^2 carbons atoms were introduced with the sharper peak in RGO-3 spectra, at around 90–160 ppm, suggesting the formation of graphene materials.^{21,22} RGO-3 has the high intensity of sp^2 carbon network compared to GO. It indicates that the

extensive conjugated carbon sp^2 structure has been recovered in the reduction process.

3.3 Morphological analysis

The surface morphology of the GO and RGO-3 were investigated by using SEM and HRTEM. The surface morphology image of the GO is shown in figure 5a. It showed that a few layers of structure of GO nanosheets were corrugated. Figure 5b shows the surface morphology of the RGO-3 which was observed in the top-view of SEM image. The RGO-3 was observed in figure 5c to have a wrinkled paper-like structure arranged in transparent layer and exhibits a very stable towards the radiation of electron emitted by high-energy electron beam.²² The number of the RGO layers can be identified through their folder edges.²³ The HRTEM images that capture the border of the RGO-3 (figure 5d) showed almost a single layer as indicated by the arrow. Therefore, it was concluded that the produced RGO-3 was likely to be monolayer.

3.4 Thermal stability analysis

The effect of the reduction time on the thermal stability of the GO and RGO-3 were investigated by TGA analysis. The typical TGA curves of the GO and RGO-3 are shown in figure 6a and b, respectively. The TGA curve of the GO exhibited two significant stages of mass loss upon the increase in temperature. The first stage of the mass loss was approximately 43 wt% at the temperature range of 0–300°C, which is due to the loss of remaining oxygen-containing functional groups while the second stage at around 600°C, displayed approximately 97 wt% mass loss which is related to the pyrolysis of the labile oxygen-containing functional groups as well as decomposition of carbon skeleton. In comparison with GO, significantly decreased mass loss was observed for RGO-3 and the TGA curves show a small weight loss in the temperature range from 0 to 600°C due to the efficient removal of oxygen-containing functional groups by using sodium oxalate as the reducing agent. At around 300°C, the mass loss was about 22 wt% for RGO-3. At approximately 600°C, the mass loss became more significant which

Figure 5. Surface morphology of (a) GO, (b) RGO-3 under scanning electron microscopy and HRTEM image of (c) RGO-3 and (d) RGO-3 edges at different magnifications.

Figure 6. Comparison of thermal stability for (a) GO and (b) RGO-3 under TGA analysis.

was about 32 wt% for RGO-3. This suggests that the RGO-3 exhibits greater thermal stability compared to GO due to the removal of labile oxygen-containing functional groups²⁴ which leads to better graphitization and deoxygenation of RGO-3 with the enhanced van der Waals forces between layers.¹¹

3.5 Electrical conductivity analysis (room temperature)

Electrical conductivity (σ) of RGO is the most critical criteria to evaluate the reduction degree and it is governed by its structural properties. In the present work, the conductivity improves with the increase of reduction time. This is due to the removal of the residual oxygen in the RGOs. In our case, the highest value of electrical conductivity was exhibited by RGO-3, which is about $\sim 2.0 \times 10^3 \text{ S m}^{-1}$ compared to RGO-2 and RGO-1. However, GO is an electrically insulating material since most of the carbon atoms in GO are sp^3 hybridized. The existence of many oxygen-containing functional groups breaks the conjugated structure and thus resulting in a decrease of carrier mobility and concentration. The obtained value of electrical conductivity of RGO-3 using sodium oxalate as reducing agent is comparable with that of some other conventional reducing agent like NaBH_4 (0.45 S cm^{-1}),²⁵ hydrazine (22.4 S cm^{-1}),²¹ nascent hydrogen (11.20 S cm^{-1})²⁶ and sodium carbonate (10 S m^{-1}).¹¹ Therefore, it was concluded that the reduction of GO with sodium oxalate can lead to the restoration of electrical properties of the prepared RGO.

4. Conclusion

In this paper, the degree of reduction towards the physico-chemical properties of RGO in terms of structural, thermal and electrical conductivity at different reduction times using sodium oxalate as reducing agent has been reported. The structural analysis confirmed the formation of high-quality RGO-3 with the removal of oxygen-containing

functional groups from the surface of GO. From TGA, RGO-3 is found to be more thermally stable compared to GO. The plausible mechanism of reduction of GO to RGO using sodium oxalate has been well proposed. This produced RGO-3 with high electrical conductivity could be valuable for the practical application as a novel Pt electro-catalyst support in the promising energy conversion system of DMFC. Our future work will describe about the anode platinum-based catalyst by incorporating the graphene nanosheets as the electro-catalyst support for DMFC application.

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