Microwave Hydrothermal Synthesis of Reduced Graphene Oxide: Effects of Microwave Power and Irradiation Time

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Abstract. Reduced graphene oxide has been synthesized by one-pot microwave assisted hydrothermal method. Effects of microwave power and irradiation time to its crystal structure and electrical conductivity were investigated. Here, graphene oxide, firstly, were synthesized by modified hummers method and subsequently mixed with Zn as a reducing agent. Then it was transferred to modified domestic microwave oven (800 watts) with glass distiller equipment for completely reduction process. Three different power levels (240, 400, 630 watts) and two cases of irradiation times (20 and 40 minutes) were treated. XRD study shows that irradiation time variation is more effective than the variation of power level. Power level of 270 watts and for 40 minutes microwave irradiation are enough for producing estimated bilayer rGO with graphene interlayer of ~0.4 nm. Bilayer graphene and water molecule (~0.3 nm) may vibrate the same manner and perhaps they are accepting the same temperature. Graphene seems to be re-arranged in unspecified way among the thermal pressure, temperature gradient and/or water surface tension between graphene and water induced by microwave, in order to achieve thermal equilibrium throughout the system. The electrical conductivity rGO/PVA (60/40 %w) paper are ranging from 15.6 to 43.4 mS/cm.

1. Introduction

Graphene, two dimensional single layer graphite carbon lattice, has evoked much attention due to its unusual electronic, thermal and mechanical properties [1-6]. During the last decade, many approaches have been formulated for the preparation of graphene, including micromechanical methods [7], epitaxial growth [8], the ultrasonic exfoliations of graphite [9], chemical vapor deposition (CVD) [10], and the chemical reduction of graphene oxide (GO). Among them, the chemical reduction of graphene oxide was considered as a promising method for large-scale production of graphene. It involves conversion of the resulting graphite oxide to graphene oxide (GO), exfoliation process, and the subsequent reduction of GO.

Graphene can be reduced by different ways such as chemical, thermal, electro-chemical, hydrothermal, microwave, gamma ray and photo reductions. As for chemical reduction, different kinds of chemicals have been utilized to reduce GO. In many cases, strong reducing agents such as hydrazine monohydrate, hydroquinone, sodium borohydride, and hydrohalic acid have been used as the reducing
agents [11-14]. However, these chemicals may harm the environment or be cost-prohibitive when used in the large-scale industry. Moreover, graphene layers tend to agglomerate and form graphitic structures when strong chemicals are used. Recently, a significant interest has been directed to use metals (Fe, Al, Zn) as reduction agent of GO [15-17]. Nevertheless, metal particles may remain as impurities and need more treatment to remove it completely.

While conventional thermal treatment has been well-recognized method for reduction of graphene by removing oxygen functionalities from the surface of GO [18], the unconventional thermal method using a microwave as thermal source can rapidly reduce graphene oxide. Microwave irradiation to dry powder of GO was recently found to effectively reduce GO in several seconds [19]. Microwave heating tend to be more effective to reduce GO in lower temperature and shorter period compare to reduction process by the conventional heating. In addition, microwave hydrothermal method was also provide excellent property compare to conventional hydrothermal technique since the microwave device can deliver electromagnetic wave energy homogeneously entire the wet chemicals [20].

In this study, we investigate effect of microwave power and interaction time to the performance of rGO using a modified domestic 2.4 GHz microwave oven as the hydrothermal reactor. Graphene oxide was firstly synthesized using, a wet chemical, hummers method. Then, it was rigorously mixed with Zn for 30 minutes and transferred to glass container that was connected water cooled condenser for microwave irradiation.

2. Experimental sections

2.1 Synthesis of GO

GO was prepared by the oxidation of graphite powder (Sigma Aldrich), without pre-treatment, according to modified hummers method re-described in [21]. Typically, a 2 g of graphite powder was added, under stirring, to 98 mL of concentrated H2SO4 in ice bath. Under robust agitation, KMnO4 (8.0 g) and 4 gram NaNO3 were added slowly, colors of suspension changed to dark green at the end. Stirring process was continued for additional 24 h where temperature was raised to ~35°C, color changed from green purple to be light brown. Then, aquades (200 mL) was added slowly to the suspension for about 1 h. Here, colors changed to be dark brown. Additional 15 mL H2O2 was added slowly to the suspension, turning the color of the solution to yellow. After that, the mixture was centrifuged, filtered, washed with 10 ml HCl 37% and several times with aquades to remove the remaining metal ions. The resulting solid, graphite oxide was dried in air at 105°C for 12 h. The resultant graphite oxide was then diluted to 200 mL of aquades, stirred overnight and then it was sonicated for 120 min at 53 kHz.

2.2 Microwave hydrothermal reduction of GO

Reduction process of GO involved addition of Zn and irradiation of microwave energy. A 0.6 g of Zn was mixed in water based GO dispersion, and subsequently added by, under stirring, 50 mL of hydrochloric acid for another 30 minutes. Then, it was exposed to electromagnetic wave radiation in the domestic microwave oven at different powers (240, 400, and 560 watt) and duration (20 and 40 minutes). Sample names and treatment condition were summarized in Table 1. Here, sample names A, B, C, D, E, and F were corresponding for condition of microwave power-irradiation time: 240 W-20 minutes, 400 W-20 minutes, 560 W-20 minutes, 240 W-40 minutes, 400 W-40 minutes, and 560 W-40 minutes, respectively. At the end, to remove the remaining Zn, solution was finally washed several times with HCl and aquades until pH = ~7. The reduced graphene oxide (rGO) was collected by centrifugation to remove the unexfoliated graphite.
2.3 Characterization
Crystalline structure and phase purity of the as-prepared rGO were examined using powder X-ray diffraction (XRD). XRD pattern was recorded with graphite-monochromated Cu-Kα (γ = 1.54056 Å) radiation on Rigaku RINT UltimaII ranging from 10° to 70° (2θ) with a scanning speed of 2° per minute. The surface morphology of the resulting products were investigated by a scanning electron microscopy (SEM) TESCAN. Fourier transforms infrared spectroscopy (FTIR) spectra were recorded on a Fourier transform infrared spectrometer (Bruker Vertex V70). Electrical conductivity was studied using a four point probe measurement where the electrode spacing was 1.0 mm.

3. Results and Discussions

Figure 1 shows XRD spectrum of as-prepared rGO at different conditions (powers and irradiation times). In the case of microwave irradiation time is 20 minutes, peaks of 002 crystal plane of rGO are 19.45°, 19.13°, and 20.28°, corresponding to power of 240 W, 400 W, and 560 W, respectively. Peak tends to shift to the left by increasing microwave power, indicating the decrease of calculated inter-layer distance from 0.456 nm to 0.438 nm (see Figure 2a). By contrast, peak is drifted to the bigger diffraction angle (Figure 1b), namely layer-by-layer stacking distance is changing from 0.41 nm to 0.43 nm, if the power is adjusted from 240 W to 560 W and the interaction time is 40 minutes. The inter-layer or layer-by-layer stacking distance (d) was calculated by using the well-known Bragg’s law nλ = 2d sinθ. Here, the wavelength, λ is 0.15406 nm.

![Figure 1. XRD diffraction spectrum of the as-prepared rGO](image1)

![Figure 2. Inter layer distance and stacking thickness](image2)
The stacking thickness of graphene layers can be estimated from (002) diffraction peak of XRD data [23, 24] using the Scherrer formula

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  

where \( k \) is a constant value (0 < \( k < 1 \)) and \( \beta \) is the full-width of half maximum. Here, \( k = 0.89 \) was used in all calculation. Number of layers was estimated from \( N = (D + d)/d \).

For irradiation of only 20 minutes, a rapidly decreasing of stacking thickness of layered rGO from 0.69 nm to 0.54 nm as the microwave power raising has been observed from XRD data. However, when irradiation period is about 40 minutes the stacking thickness is very slightly altered by changing the microwave power. An interesting phenomenon found in estimation of number of layered graphene, in all cases a bilayer graphene was found, except in case of power level of 240 W and irradiation of 20 minutes, the three layers graphene is exist. It seems that, in this case, packets of bilayer graphene are favorably formed in the water under irradiation of microwave power. The fact that bilayer graphene with interlayer distance of 0.4 nm is very similar to the size of water molecule (~0.3 nm) in the ‘eyes’ of a very long wavelength of microwave, bilayer graphene and water molecule are vibrating in the same manner and perhaps they are accepting the same temperature, even though the graphene and water molecule have different dielectric constant. Graphene may be re-arranged in ‘unspecified’ way among the thermal pressure, temperature gradient and/or water surface tension between graphene and water induced by microwave, in order to achieve thermal equilibrium through out the system [21]. Although, high densification, smaller size, and less pores have been specified as the microwave effect or non-thermal effect on the sintering process of materials compared to the conventional heating at the same temperature, the mechanism responsible for such effect is still unclear. The physics of the microwave processing of materials had remained unexplored and hence these complex phenomena are ‘less understood’.

Water dispersion test in Figure 3 shows that dispersion can be prevented almost in the same period for all samples. It confirms existing of the same layers of graphene in all samples processed in different powers and irradiation times.

**Figure 3.** Dispersion test of graphene in water where graphene are proceeded by irradiation of (a) 20 minutes and (b) 40 minutes. In all cases, microwave power 240, 400, and 560 W are applied.
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Table 1. Electrical conductivity of PVA/rGO (40:60 %w)

| Power (W) | Irradiation time (minutes) | Conductivity (S/cm) |
|-----------|----------------------------|---------------------|
| 240       | 20                         | 0.026               |
| 400       | 20                         | 0.041               |
| 560       | 20                         | 0.033               |
| 240       | 40                         | 0.036               |
| 400       | 40                         | 0.043               |
| 560       | 40                         | 0.016               |

Electrical conductivity of PVA/rGO (40:60 %w) paper are shown in Table 1. Conductivity is ranging from 0.016 S/cm (560 W, 40 minutes) to 0.043 S/cm (400 W, 40 minutes). In electrical conductivity consideration, processing of graphene using microwave, the power should be no more than 400 W. Morphology of PVA/rGO paper using rGO processed by microwave irradiation at 400 W and 40 minutes are shown in Figure 4. It has micrometer scale of pores (Figure 4a) and morphology of clumped graphene layers are shown in Figure 4b.

FTIR spectra confirm reduction of graphene seen in Figure 5. In the spectrum, the peaks located at 3424 and 1087 cm\(^{-1}\) are attributed to the stretching vibration of hydroxyl groups. A very weak interaction peak at 1720 which corresponds to stretching vibration of C=O, can be assigned to a complete reduction of graphene oxide. More importantly, the shifting peak at around 1573 cm\(^{-1}\) (in-plane vibration of C=C) by changing processing condition by microwave are the strong indication of interaction between graphene layer and microwave radiation.

Figure 4 SEM image of PVA/rGO (40:60 %w) paper, (a) low magnification and (b) high magnification.
Figure 5. FTIR spectrum of pVA/rGO paper processed at different microwave power and irradiation time of 20 minutes

4. Conclusion

Hydrothermal synthesis of reduced graphene oxide by utilization of microwave irradiation has been demonstrated where effect of microwave power and irradiation time to the crystal structure of graphene are investigated. XRD study shows that irradiation time variation is more effective than varying the power level. A 270 watts and 40 minutes of microwave irradiation are enough for producing the bilayer graphene with graphene interlayer of ~0.4 nm. The electrical conductivity rGO/PVA (60/40 %w) layers are ranging from 15.6 to 43.4 mS/cm. Processing graphene should use power not more than 400 W in order to reach high electrical conductivity.

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