

# Controlled Synthesis and Characterization of rGO Materials by Hydrothermal Method

*Chu Thi Quy, Chu Manh Hung, Bui Thi Hang, Nguyen Duc Hoa\**

*Hanoi University of Science and Technology – No. 1, Dai Co Viet Str., Hai Ba Trung, Ha Noi, Viet Nam*

*Received: July 30, 2018; Accepted: June 24, 2019*

## Abstract

*Oxidative exfoliation followed by chemical reduction is an effective method to synthesize reduced graphene oxide (rGO). However, it is challenging to synthesize large scale high quality rGO by a simple and inexpensive method. In this study, rGO materials were synthesized by a scalable hydrothermal method, where the temperatures were controlled to obtain different morphology and quality of rGO. The morphology and quality of the synthesized rGO were examined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Photoluminescence (PL), and Raman spectroscopy. Results pointed out that the hydrothermal temperatures strongly influenced on the morphology and quality of the synthesized rGO. Material synthesized at 160°C has the highest quality with layered structure of large rGO flakes. The synthesized rGO is potential for sensing and supercapacitor applications.*

Keywords: rGO, Hydrothermal, Morphology, SEM, TEM, PL, Characteristics

## 1. Introduction

Graphitic materials of different forms like graphene and reduced graphene have been extensively studied in recent years [1-3]. Monolayer graphene is excellent for flexible electronic device [1], but it is limited by the challenge in synthesis of large scale and high yield of product [2,3]. Thus it is not suitable for applications those require large amount of materials [4]. In opposite to the monolayer graphene, graphene oxide (GO) and reduced graphene oxide (rGO) can be synthesized by some inexpensive and scalable methods such as mechanical exfoliation [5] or sonication-assisted oxidation [6]. Reduced graphene oxide (rGO) has better metallic properties than those of graphene oxide (GO) after reduction process due to the significant recovery of  $sp^2$  conjugations, as mentioned [7]. Thus rGO can be used in many applications such as gas sensor, supercapacitor, and etc [4]. Synthesis of rGO with ability to control their characteristics, quality and quantity has attracted interests from researcher worldwide due to their massive potential applications [8,9]. Bo et al. [4] reported a method to synthesize rGO using caffeic acid as a reduction agent for sensing and energy storage applications, where the reaction was carried out at 95°C. Hu et al. [10] prepared rGO by reduction of GO using pyrrole for gas sensors. Xu et al. [11] synthesized water soluble rGO from GO using acetylacetone, as both a reducing agent and a stabilizer for adsorption of heavy metal

ions. Munuera et al. [12] prepared rGO by electrochemical exfoliation of graphite in aqueous sodium halide electrolytes for dye adsorption and supercapacitor. It is obviously that the morphology and quality of rGO synthesized by different methods are strongly dependent on the synthetic condition and/or starting precursors [13].

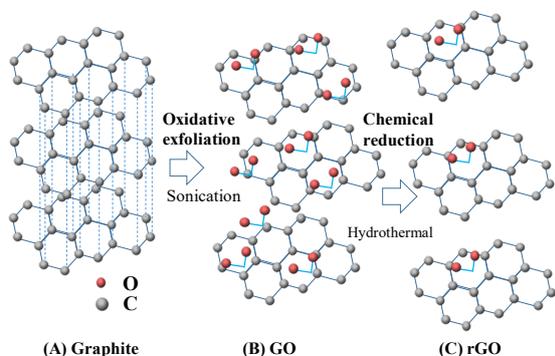
In this study, rGO materials were synthesized by a facile hydrothermal method from modified Hummer's GO using ascorbic acid as reduction agent. We varied the hydrothermal temperatures to control the morphology and quality of the rGO products. The synthesized materials were characterized by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM), Photoluminescence, and Raman spectroscopy.

## 2. Experiments

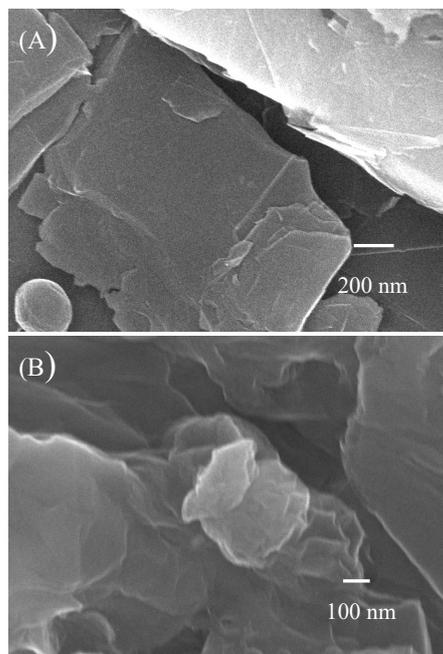
Commercial graphite powders and analytical ascorbic acid were used as precursors for the synthesis of rGO. Process for the synthesis of rGO is shown in Scheme 1. GO was prepared by a modified Hummer method [14]. In a typical synthesis, 0.1 g GO and 1 g ascorbic acid were dispersed in 80 ml deionized water using a sonicator, and then the solution was poured into a Teflon-line autoclave (100 ml capacity) for hydrothermal process. The rGO materials were hydrothermally synthesized at different temperatures ranging from 120 to 180 °C for 1 h to evaluate the effect of synthesis condition on the quality of products. After hydrothermal synthesis, the rGO was found dispersedly and partially precipitation in the solution but not in the hydrogel form. The produced rGO was purified and collected by

\* Corresponding author: Tel.: (+84) 984050213  
Email: hoa.nguyenduc@hust.edu.vn

centrifuging at 10.000 rpm. After drying in an oven overnight at 45 °C, the morphology and crystal structure of the products were characterized using SEM (JEOL JSM-7600F), TEM (JEOL, 2100F), PL and Raman spectroscopy (Renishaw Invia Confocal micro-Raman System).



**Scheme 1.** Diagram of the rGO synthesis: (A) Graphite powders; (B) GO, (C) rGO.



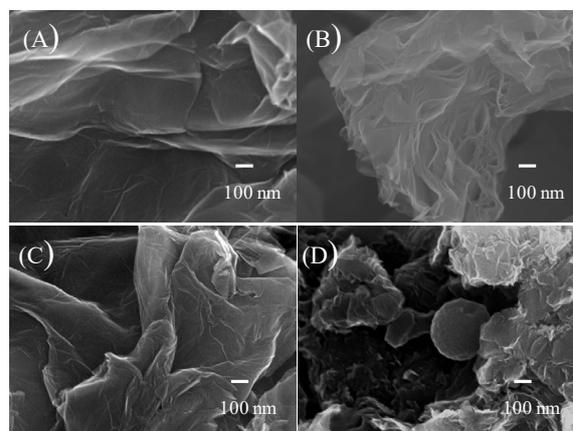
**Fig. 1.** SEM images of the starting (A) graphite powders; (B) GO product

### 3. Results and discussion

Morphology of the starting graphite, GO, and the synthesized rGO was characterized by SEM images. Fig.1(A) shows the SEM images of the starting graphite powders. The graphite powders have the bulky morphology, with an average size of approximately 1  $\mu\text{m}$ . However, after oxidative exfoliation by the modified Hummer's method, the GO materials have a layered structure (Fig.1(B)). The

thickness of the GO layers is very thin of few nanometers; thus, they are curled into granular flakes with scrolled morphology to reduce the surface energy. The morphology of synthesized GO is similar to that reported in ref. [15]. It is believed that during oxidative exfoliation, the oxygen atoms are intercalated into the gaps between graphitic layers [16]. Thereafter, ultra-sonication exfoliates the intercalated GO into layered GO. The GO product obtained after centrifugation and drying has a curvature morphology.

Fig. 2(A-D) shows the SEM images of rGO synthesized at different temperatures. As demonstrated in Fig 2(A), the morphology of rGO synthesized at low temperature of 120°C exhibits curly graphene layers, confirming that the rGO is highly exfoliated. The crumpled structure of rGO is also observed in recent report, explained by the multidirectional compression during synthesis and drying [17]. Morphology of rGO is similar to that of GO, suggesting that the reduction does not significantly alter the physical appearance of the GO films. With increase of hydrothermal temperatures, the obtained rGO products still have layered structures but tended to agglomerate to form bundle of flakes (Fig. 2(B-D)). Upon hydrothermal reduction by ascorbic acid, the interstitial oxygen species are removed from the surface of GO to form rGO [14].



**Fig. 2.** SEM images of rGO synthesized at different temperatures: (A) 120°C; (B) 140°C; (C) 160°C; (D) 180°C.

We selected the sample synthesized at 160°C to further study about their characteristics. TEM image of the rGO synthesized at 160°C shown in Fig.3 demonstrates the ultrathin and flexible structure of the material. The TEM image also suggests that the rGO is homogeneous of few layers thickness [18].

XRD pattern of the rGO synthesized at 160°C (Fig.4(A)) exhibited two broad peaks at  $2\theta=24.1^\circ$  and  $43.4^\circ$ , corresponding to diffraction of the (002), and

(100) planes of rGO, respectively [19]. Fig. 4(B) shows the Raman spectrum of rGO synthesized at 160°C. The Raman spectrum shows two Raman peaks at approximately 1325, and 1571  $\text{cm}^{-1}$ , which were attributed to the active modes of D-, and G-bands, respectively. The D-band is associated to the defect induced peak, whereas the G-band is related to the stretching vibration of all pairs of  $\text{sp}^2$  atoms in both the rings and chains. The relative intensity of the D- and G-bands ( $I_D/I_G$ ) is an estimation of the disorder level in rGO. In case of the synthesized rGO, the ratio  $I_D/I_G$  is less than one, thus confirming the low defect level. The 2D peak at around 2640  $\text{cm}^{-1}$  is attributed to double resonance transitions resulting in the production of two phonons with opposite momentum [6].

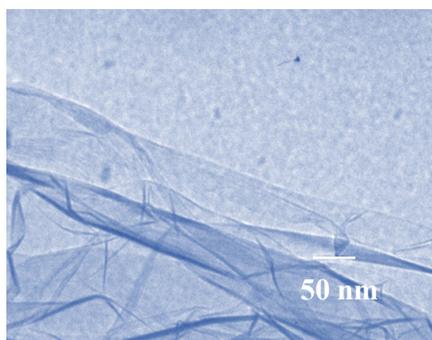


Fig. 3. TEM image of rGO synthesized at 160°C.

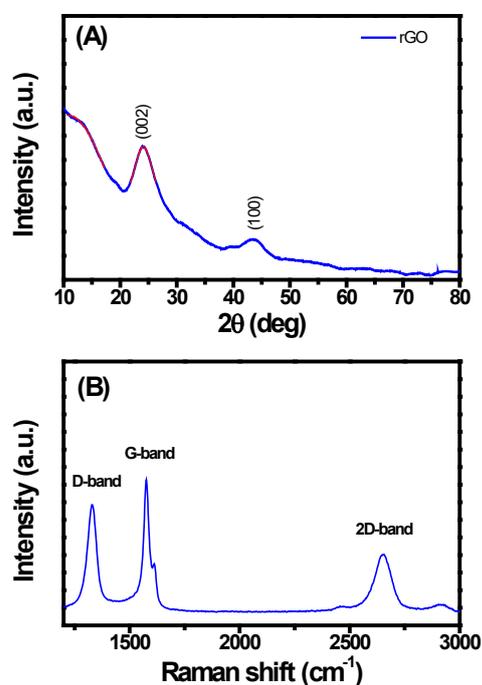


Fig. 4. (A) XRD pattern and (B) Raman spectrum of rGO synthesized at 160°C.

Room temperature photoluminescence spectrum of the rGO synthesized at 160°C is shown in Fig.5. The PL spectrum exhibits a broad peak centered at around 450 nm. It is worth to note that the ideal monolayer graphene is a zero-bandgap semiconductor. However, herein the PL spectrum of rGO shows an asymmetry broad peak. This is caused by the overlapping of multiple peaks. The result is consistent with other report where the bandgap opening was ascribed due to the quantum effect [20].

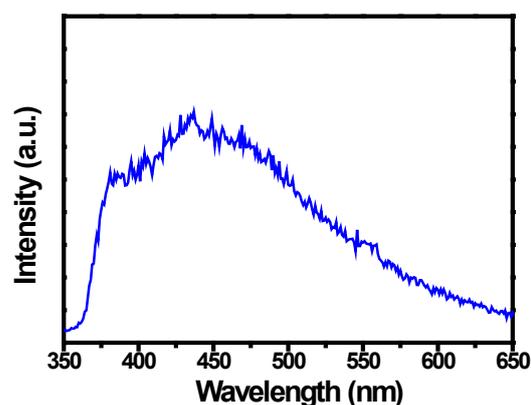


Fig. 5. Photoluminescence spectrum of rGO synthesized at 160°C

#### 4. Conclusion

We have introduced an effective hydrothermal method to synthesize scalable high quality rGO. We also studied the effect of hydrothermal temperatures on the morphology and quality of the rGO materials by TEM, XRD, Raman and PL spectroscopy. We pointed out the sample synthesized at 160°C has the best quality of layered structure with excellent optical properties. The synthesized rGO is of high quality for various applications such as sensing and/or supercapacitor.

#### Acknowledgment

This research was funded by the Vietnam National Foundation for Science and Technology Development (Code: 103.02-2017.15).

#### References

- [1] S.-M. Lee, J.-H. Kim, J.-H. Ahn; Graphene as a flexible electronic material: mechanical limitations by defect formation and efforts to overcome; *Mater. Today*. 18 (2015) 336–344. doi: 10.1016/j.mattod.2015.01.017.
- [2] H. Tan, D. Wang, Y. Guo; Thermal Growth of Graphene: A Review, *Coatings*. 8 (2018) 40. doi:10.3390/coatings8010040.
- [3] T.B. Limbu, J.C. Hernández, F. Mendoza, R.K. Katiyar, J.J. Razink, V.I. Makarov, B.R. Weiner, G. Morell; A Novel Approach to the Layer-Number-

- Controlled and Grain-Size-Controlled Growth of High Quality Graphene for Nanoelectronics; *ACS Appl. Nano Mater.* 1 (2018) 1502–1512. doi:10.1021/acsnm.7b00410.
- [4] Z. Bo, X. Shuai, S. Mao, H. Yang, J. Qian, J. Chen, J. Yan, K. Cen; Green preparation of reduced graphene oxide for sensing and energy storage applications; *Sci. Rep.* 4 (2015) 4684. doi:10.1038/srep04684.
- [5] W. Islamiyah, L. Nashirudin, M.A. Baqiya, Y. Cahyono, Darminto; Sulfuric acid intercalated-mechanical exfoliation of reduced graphene oxide from old coconut shell; in: 2018: p. 20054. doi:10.1063/1.5030276.
- [6] S. Abdolhosseinzadeh, H. Asgharzadeh, H. Seop Kim; Fast and fully-scalable synthesis of reduced graphene oxide; *Sci. Rep.* 5 (2015) 10160. doi:10.1038/srep10160.
- [7] S. Lee, J.-S. Yeo, J.-M. Yun, D.-Y. Kim; Water dispersion of reduced graphene oxide stabilized via fullereneol semiconductor for organic solar cells; *Opt. Mater. Express.* 7 (2017) 2487. doi:10.1364/OME.7.002487.
- [8] N.A. Kumar, S. Gambarelli, F. Duclairoir, G. Bidan, L. Dubois; Synthesis of high quality reduced graphene oxide nanosheets free of paramagnetic metallic impurities; *J. Mater. Chem. A.* 1 (2013) 2789–2794. doi:10.1039/C2TA01036D.
- [9] S. Some, S. Kim, K. Samanta, Y. Kim, Y. Yoon, Y. Park, S.M. Lee, K. Lee, H. Lee; Fast synthesis of high-quality reduced graphene oxide at room temperature under light exposure; *Nanoscale.* 6 (2014) 11322–11327. doi:10.1039/C4NR03009E.
- [10] N. Hu, Z. Yang, Y. Wang, L. Zhang, Y. Wang, X. Huang, H. Wei, L. Wei, Y. Zhang; Ultrafast and sensitive room temperature NH<sub>3</sub> gas sensors based on chemically reduced graphene oxide; *Nanotechnology.* 25 (2014) 25502. doi:10.1088/0957-4484/25/2/025502.
- [11] M. Xu, J. Chai, N. Hu, D. Huang, Y. Wang, X. Huang, H. Wei, Z. Yang, Y. Zhang; Facile synthesis of soluble functional graphene by reduction of graphene oxide via acetylacetone and its adsorption of heavy metal ions; *Nanotechnology.* 25 (2014) 395602. doi:10.1088/0957-4484/25/39/395602.
- [12] J.M. Munuera, J.I. Paredes, M. Enterría, A. Pagán, S. Villar-Rodil, M.F.R. Pereira, J.I. Martins, J.L. Figueiredo, J.L. Cenis, A. Martínez-Alonso, J.M.D. Tascón; Electrochemical Exfoliation of Graphite in Aqueous Sodium Halide Electrolytes toward Low Oxygen Content Graphene for Energy and Environmental Applications; *ACS Appl. Mater. Interfaces.* 9 (2017) 24085–24099. doi:10.1021/acsnm.7b04802.
- [13] X. Wang, X. Wen, Z. Liu, Y. Tan, Y. Yuan, P. Zhang; Rapid and efficient synthesis of soluble graphene nanosheets using N -methyl- p -aminophenol sulfate as a reducing agent; *Nanotechnology.* 23 (2012) 485604. doi:10.1088/0957-4484/23/48/485604.
- [14] L. Van Nang, N.D. Hoa, C. Van Phuoc, C.T. Quy, P. Van Tong, V. Van Quang, N. Van Duy, N. Van Hieu; Scalable Preparation of Graphene: Effect of Synthesis Methods on the Material Characteristics; *Sci. Adv. Mater.* 7 (2015) 1013–1020. doi:10.1166/sam.2015.2171.
- [15] D. Hou, Q. Liu, X. Wang, Y. Quan, Z. Qiao, L. Yu, S. Ding; Facile synthesis of graphene via reduction of graphene oxide by artemisinin in ethanol; *J. Mater.* (2018). doi:10.1016/j.jmat.2018.01.002.
- [16] S.J. Rowley-Neale, E.P. Randviir, A.S. Abo Dena, C.E. Banks; An overview of recent applications of reduced graphene oxide as a basis of electroanalytical sensing platforms; *Appl. Mater. Today.* 10 (2018) 218–226. doi:10.1016/j.apmt.2017.11.010.
- [17] J. Luo, H.D. Jang, T. Sun, L. Xiao, Z. He, A.P. Katsoulidis, M.G. Kanatzidis, J.M. Gibson, J. Huang; Compression and Aggregation-Resistant Particles of Crumpled Soft Sheets; *ACS Nano.* 5 (2011) 8943–8949. doi:10.1021/nn203115u.
- [18] T. Purkait, G. Singh, M. Singh, D. Kumar, R.S. Dey; Large area few-layer graphene with scalable preparation from waste biomass for high-performance supercapacitor; *Sci. Rep.* 7 (2017) 15239. doi:10.1038/s41598-017-15463-w.
- [19] X. Liu, G. Zeng, S. Jiang; One-step synthesis of CdS-reduced graphene oxide composites based on high-energy radiation technique; *Radiat. Phys. Chem.* 119 (2016) 24–28. doi:10.1016/j.radphyschem.2015.09.007.
- [20] J.J. Ding, H.X. Chen, D.Q. Feng, H.W. Fu; Investigation on photoluminescence emission of (reduced) graphene oxide paper; *IOP Conf. Ser. Mater. Sci. Eng.* 292 (2018) 12097. doi:10.1088/1757-899X/292/1/012097.