

Scalable Synthesis of Reduced Graphene Oxide using FeSO₄

Kadambinee Sa, Prakash Chandra Mahakul, BVGS Ram Subrahmanyam,
Sunirmal Saha, Jonaki Mukherjee, Pitamber Mahanandia*

*E-mail: pitam@nitrrkl.ac.in

Abstract. We report a simple technique for synthesis of reduced graphene oxide (rGO). In this technique ferrous sulfate (FeSO₄) has been used to reduce the oxygen functional groups from the graphene oxide. The prepared rGOs have been characterized by x-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FTIR), UV-Vis and Raman spectroscopy. The TEM and HRTEM reveal that the prepared rGOs are mostly double layers. This technique can be adopted to prepare rGO in large scale.

Keywords: Graphene oxide, Reduce Graphene Oxide, X-ray diffraction, Raman spectroscopy

PACS: 81.05.ue; 61.48.Gh; 61.05.cp; 82.80.Gk

INTRODUCTION

Since the discovery of Graphene which is one of the allotrope of carbon also a two dimensional single sheet of sp² hybridized carbon atoms has attracted great research interest [1] for synthesis. It's fascinating physical properties have numerous promising applications such as transparent electrode [2], field effect transistors [3,4], electrochemical device [5] and nanocomposites [6]. The physical properties of graphene depend on the method of productions. Various methods such as mechanical cleavage, chemical exfoliation and thermal expansion of graphite, chemical reduction of graphene oxide (GO) [1,7-10] are being used for the synthesis of graphene. Preparation of graphene in large scale is possible by chemical reduction of graphene oxide (GO). The graphene prepared by chemical reduction method are called reduced graphene oxide (rGO). Different reducing agents such as hydrazine and its derivatives, NaBH₄, hydroquinone, hydriodic acid (HI), sulfur containing compounds, metal powders, hydroxylamine and vitamin C have been used to obtain rGOs from GO. But in chemical reduction of GO using hydrazine and its derivatives refluxing is needed throughout the process. Similarly there are very limited journals which are reported about simultaneously both mass scale production and few layer graphene sheet. Barman et al. [11] reported a fast environment friendly and green approach to obtain few-layer graphene by

the almost instantaneous reduction of graphene oxide using Mg ribbons in acidic solution with a hydrogen spill over mechanism. P. Liu et al. [12] demonstrated a green and facile approach to synthesize cost-effective, environmentally friendly, and large-scale production of few layers rGO with Zn powder under acidic condition at room temperature. P. Cui et al. [13] reported a new reducing agent system: hydriodic acid with trifluoroacetic acid, which can chemically convert graphene oxide into monolayer reduced graphene oxide with mass production at temperatures below 0°C in solution. Y. Liu et al. [14] developed ultrafast method to reduce GO with Zn powder in mild alkaline conditions which results in large-scale production of a mixture of single-layered graphene and few-layered graphene. S. Mao et al. [15] reported a one-step approach to prepare single-layer RGO) which also offers the possibility of mass production of RGO. A Malesevic et al. [16] presented the mass production of freestanding FLG by means of MW PECVD. . P. Mahanandia et al. [17] demonstrated an electrochemical technique for the large scale synthesis of high quality few layer graphene sheets (FLGS) directly from graphite using oxalic acid (a weak acid) as the electrolyte. This work demonstrates both large scale production and bi-layer graphene by reduction of GO using FeSO₄ and H₂SO₄.

EXPERIMENTAL

Modified Hummers method [18] has been used for the synthesis of Graphite oxide. In this method 1.0g of graphite powder (GFG: 50) was mixed with 0.5 g of NaNO_3 and 25 mL of concentrated H_2SO_4 . The temperature of the mixture was decreased using an ice bath and stirred for 2 h. Then, 3 g of KMNO_4 was added slowly and continuously stirred for another one hour. The cooling bath was then removed and the mixture was cooled down to room temperature. Then 100 mL of distilled water was added and the temperature was increased to 98°C . After that 300 mL of water was added again and continuously stirred for another one hour and a half. The colour of the mixture turned to mud brown. This mixture was then treated with 10 mL of H_2O_2 to terminate the reaction. The prepared material graphite oxide (GO) was washed many times by distilled water to remove the unwanted ions and acid until it reached the pH value about 7. The product was recovered by filtering and drying in vacuum at 100°C for 3 hours. The as synthesized graphite oxide was dispersed and exfoliated in water by sonication till no particulates were visible with a homogeneous yellowish brown suspension. For obtaining rGO by reducing oxygen functional group from GO, 0.3 gm FeSO_4 was added into 500ml GO suspension and stirred for an hour at 80°C and then 10 ml of sulphuric acid (H_2SO_4) was added. The material was recovered by filtration using a membrane filter and washed by water repeatedly to recover rGO. The as synthesized sample was annealed at 200°C in argon atmosphere. The as-prepared samples were characterized by optical microscopy, field emission scanning electron microscope (FESEM, Nano Nova SEM/ FEI), transmission electron microscopy (TEM), X-ray diffraction (XRD, RIGAKU JAPAN, ULTIMA-IV), Fourier transform infrared spectroscopy (FTIR), UV-Vis spectroscopy and Raman spectroscopy.

RESULTS & DISCUSSION

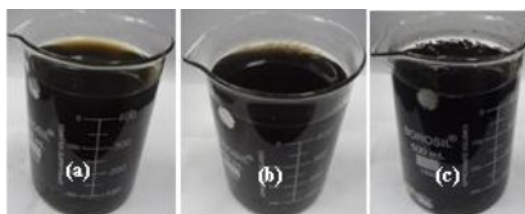


FIGURE 1. (a) $\text{GO}+\text{FeSO}_4$ (b) $\text{GO}+\text{FeSO}_4$ at the time of addition of H_2SO_4 (c) $\text{GO}+\text{FeSO}_4$ after 5min of addition of H_2SO_4 .

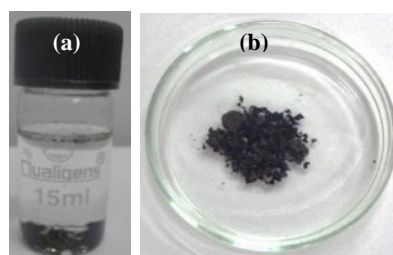


FIGURE 2. Digital images of as-prepared rGO (a) before neutralizing (b) after dried.

Fig.1 (a),(b),(c) are the digital images of $\text{GO}+\text{FeSO}_4$, $\text{GO}+\text{FeSO}_4$ at the time of addition of H_2SO_4 and $\text{GO}+\text{FeSO}_4$ after 5min of addition of H_2SO_4 and Fig.2 (a) and (b) are the digital images of as-prepared rGO before neutralizing and after dried respectively.

Fig.3 (a) shows the XRD pattern of rGO which shows a broad (002) peak at 25° . Due to over stacking of rGO the characteristic diffraction peak is broadening and shift from graphite (that appears at 26.41°). This indicates that the rGOs are exfoliated [19]. The structural characteristics have been investigated by Raman spectroscopy. Fig. 3(b) shows the Raman spectrum of GO and rGO. The major Raman features of the GO are G band 1572 cm^{-1} and D band 1347 cm^{-1} , but in rGO the peaks are shifted to 1587 cm^{-1} and 1350 cm^{-1} respectively. The D peak and G peak are due to the disorder in the carbon lattice and graphitization in rGO. The intensity ratio $I_{\text{D}}/I_{\text{G}}$ of GO and rGO are found to be 1.04 and 1.126.

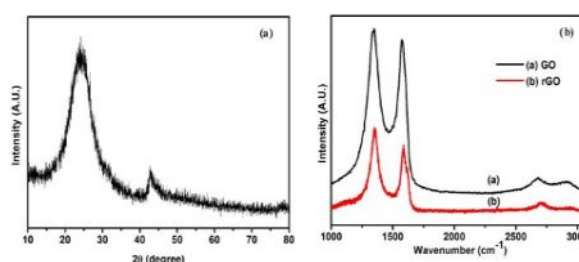


FIGURE 3. (a) XRD pattern of rGO, (b) Raman of as produced GO & rGO

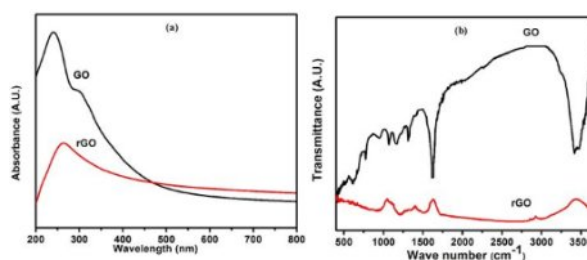


FIGURE 4. (a) UV-Vis (b) FTIR spectra of as produced GO & rGO.

UV-Vis spectrum of GO and rGO are shown in Fig. 4(a). It has been observed that due to π - π^+ absorption band and n - π^+ absorption band GO exhibits peak at 240 nm and 300 nm respectively. But in case of rGO the π - π^+ absorption band shifts to 265 nm which suggest the restoration of structural ordering of C=C conjugation and electronic configuration within the carbon network. The FTIR spectra of GO and as-prepared rGO is shown in Fig.4 (b). The band at 3418 cm^{-1} which is due to vibration of water molecules. The bands at 1169 cm^{-1} and 1069 cm^{-1} which are due to phenolic hydroxyl group and epoxy groups. The peaks at 1634 cm^{-1} is due to the skeletal vibrations of un-oxidized graphitic domains. The peak present at 1634 cm^{-1} is due to the C=C recovery for hexagonal structure as observed in FTIR spectra of rGO. However, few other peaks are with less intensities which indicates that almost all oxygen functional groups during reduction.

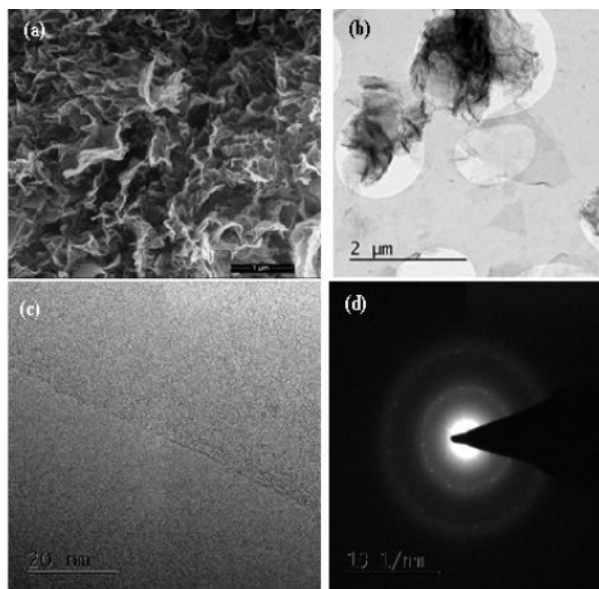


FIGURE 5. (a) SEM, (b) TEM, (c) HRTEM images and (d) SAED pattern of as produced rGO.

Fig.5 (a) shows the SEM images of as produced rGO using FeSO_4 and it shows that sheets are randomly oriented. The TEM and HRTEM images of as-prepared rGO are shown in Fig.5 (b) and (c). From the HRTEM it is observed that the prepared rGOs are mostly is bi-layer in nature. This indicates that the method is very much effective in producing bi-layers rGOs in large scale.

CONCLUSION

In summary we have successfully prepared large scale bi-layer rGO using FeSO_4 . The successful preparation of rGO has been confirmed by XRD, Raman spectroscopy, UV-Vis spectroscopy, FTIR and FESEM and TEM.

REFERENCES

1. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science* **306** 666-669 (2004).
2. X. Wang, L. Zhi and K. Mullen, *Nano Lett.* **8** 323-327 (2008).
3. Y. Zhang, Y. W. Tan, H. L. Stormer and P. Kim, *Nature* **438** 201-204 (2005).
4. S. Gilje, H. Song, M. Wang, K. L. Wang and R. B. Kaner, *Nano Lett.* **7** 3394-3398 (2007).
5. J. S. Bunch, A. M. Zande, S. S. Verbridge, I. W. Frank, D. M. Tanenbaum, J. M. Parpia, H. G. Craighead and P. L. McEuen, *Science* **315** 490-493 (2007).
6. S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen and R. S. Ruoff, *Nature* **442** 282-286 (2006).
7. M. J. McAllister, J. Li, D. H. Adamson, H. C. Schniepp, A. A. Abdala, J. Liu, M. Herrera-Alonso, D. L. Milius, R. Car, R. K. Prud'homme and I. A. Aksay, *Chem. Mater.* **19** 4396-4404 (2007).
8. Z. Juang, C. Wu, C. Lo, W. Chen, Y. Huang, J. C. Hwang, F. Chen, K. C. Leou and C. H. Tsai, *Carbon* **47** 2026-2031 (2009).
9. K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J. H. Ahn, P. Kim, J. Y. Choi and B. H. Hong, *Nature* **457** 706-710 (2009).
10. S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Y. Jia, Y. Wu, S. T. Nguyen and R. S. Ruoff, *Carbon* **45** 1558-1565 (2007).
11. B. K. Barman, P. Mahanandia and K. K. Nanda, *RSC Advances* **3** 12621 (2013).
12. P. Liu, Y. Huang, L. Wang, *Materials Letters* **91** 125-128 (2013).
13. P. Cui, J. Lee, E. Hwang and H. Lee, *Chem. Commun.* **47** 12370-12372 (2011).
14. Y. Liu, Y. Li, M. Zhong, Y. Yang, Y. Wen and M. Wang, *J. Mater. Chem.* **21** 15449 (2011).
15. S. Mao, K. Yu, S. Cui, Z. Bo, G. Lu and J. Chen, *Nanoscale* **3** 2849 (2011).
16. A. Malesevic, R. Vitchev, K. Schouteden, A. Volodin, L. Zhang, G. V. Tendeloo, A. Vanhulsel and C. V. Haesendonck, *Nanotechnology* **19** 305604 (2008).
17. P. Mahanandia, F. Simon, G. Heinrich and K. K. Nanda, *Chem. Commun.* **50** 4613 (2014).
18. V. C. Tung, M. J. Allen, Y. Yang and R. B. Kaner, *Nat. Nanotechnol.* **4** 25 (2009).
19. Y. Liu, Y. Li, M. Zhong, Y. Yang, Y. Wen and M. Wang, *J. Mater. Chem.* **21** 15449 (2011).