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One-Pot Synthesis of Graphene—Γ-Fe2O3 Composite Through Hydrolysis in A Glycol Medium

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Abstract- A composite comprising graphene and γ-Fe2O3 nanoparticles can be prepared in a glycol medium by a one-pot synthesis starting from graphite oxide, GO, and FeCl3.6H2O. The precursors were dispersed in 1,2-propanediol along with urea as the hydrolysing agent and n-octylamine as the capping agent and the mixture was refluxed. Fe3+ ions undergo hydrolysis to give γ-Fe2O3 nanoparticles and GO gets reduced by glycol simultaneously leading to the formation of graphene—γ-Fe2O3 composite.

Keywords- Graphene—γ-Fe2O3 composite, one-pot synthesis, propylene glycol, hydrolysis.

I. INTRODUCTION

Graphite oxide (GO), a derivative of graphite, has oxygenated graphene sheets covered with epoxy, hydroxyl, and carboxyl groups [1-2]. This increases the spacing between the sheets and reduces interaction between sheets, because of which it is readily dispersible in aqueous as well as organic media leading to the complete delamination of GO into individual graphene oxide sheets [3]. The exfoliation of GO under appropriate treatment opens up the possibility of incorporating guest species in the interlayer, such as nanoparticles due to the large surface area and the presence of oxygenated functional groups on the basal planes and on the edges of the GO [1-2] which also act as the nucleation centre for the nanoparticles to bind.

The composite will have the combined properties of the two components. GO or the GO based nanocomposites can further be reduced to G or G based nanocomposites to retain the graphitic properties such as high thermal and electrical conductivity [4-8], excellent mobility of charge carriers [9], a large specific surface area [10] and good mechanical stability [11] and transport properties [4] in the composite material. There are many reports in the literature on the preparation of graphene–nanoparticle composites [12-13].

Among nanoparticles, superparamagnetic iron oxide nanoparticles are important due to their application in high density magnetic storage devices, ferrofluids, catalysis and magnetic refrigeration systems. They are also useful in various biomedical applications such as magnetic carriers for targeted drug delivery, magnetically mediated hyperthermia, separation of biochemical products and contrast enhancement agent for magnetic resonance imaging [14-17]. However, due to the anisotropic dipolar attraction, these nanoparticles tend to aggregate, losing specific properties associated with single-domain particles. Therefore, they are dispersed in a suitable matrix where the interparticle interactions are minimal [18-19]. Matrices in which the nanoparticles are dispersed can also manipulate the overall properties of the nanoparticles and the composite formed will have unusual properties. The present work reports the synthesis of superparamagnetic γ-Fe2O3 nanoparticles within the graphene sheets. GO powder was first dispersed in propylene glycol through sonication, to which iron (III) chloride along

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with urea and n-octylamine were added. Under reflux conditions FeCl3 undergoes hydrolysis to γ-Fe2O3 and graphite oxide undergoes reduction to graphene resulting in G—γ-Fe2O3 nanocomposite.

II. EXPERIMENTAL

Preparation of GO

GO was prepared from purified natural graphite by the method reported by Hummers and Offeman [19]. In a typical experiment, 1 g of graphite powder was added to 23 cm3 of cooled (0º C) concentrated H2SO4. 3 g of KMnO4 was added gradually with stirring and cooling, so that the temperature of the mixture was maintained below 20 º C. The mixture was then stirred at 35 º C for 30 min. 46 cm-3 of distilled water was slowly added to cause an increase in temperature to 98 º C and the mixture was maintained at that temperature for 15 min. The reaction was terminated by adding 140 cm-3 of distilled water followed by 10 cm-3 of 30% H2O2 solution. The solid product was separated by centrifugation, washed repeatedly with 5% HCl solution until sulfate could not be detected with BaCl2, then the suspension was dried in an oven at 60 º C to obtain GO.

Preparation of G—γ-Fe2O3 nanocomposite

250 mg of GO, 2 g of FeCl3.6H2O, 1.35 g of urea, 2.75 cm3 of n-octylamine and 1.5 cm3 of water were added to 50 cm3 of 1,2-propanediol and the mixture was refluxed 14 h. The product obtained was separated by centrifugation, washed thoroughly with isopropyl alcohol, followed by water and finally with acetone. The sample was dried at 60 ºC in a hot air oven.

Leaching of γ-Fe2O3 from G—γ-Fe2O3 nanocomposite

About 20 mg of the composite was soaked in 20 cm3 of concentrated HCl for 24 h. The greenish yellow supernatant was discarded. The black solid settled was washed repeatedly with distilled water and finally with acetone. The sample was dried in air at 60 º C.

III. CHARACTERIZATION

All the samples were characterized by powder X-Ray diffraction (PANalytical X-pert Pro fitted with a secondary graphite monochromator, CuKα radiation, 2° 2θ/min) and infrared spectroscopy (Nicolet IR200 FTIR spectrometer, KBr pellet, 4 cm-1 resolution).

IV. RESULTS AND DISCUSSION

The powder X-ray diffraction (PXRD) patterns of as prepared GO and the G—γ-Fe2O3 composite are shown in Figure 1. In the pattern of GO (Figure 1a) the intense peak at 2θ = 9.9 ° corresponds to the 002 reflection of GO. The basal spacing is 8.9 Å, which is much larger than that of pristine graphite and is due to the introduction of oxygen containing functional groups on the graphite sheets. The G—γ-Fe2O3 composite (Figure 1b) shows peak due to the cubic phase of γ-Fe2O3, maghemite (JCPDS PDF: 39-1346).

The crystallite size of the γ-Fe2O3 nanoparticles in the composite is calculated from the line broadening using Scherrer formula, $D = 0.9\lambda/\beta\cos\theta$, where D is the average crystallite size, λ is the wavelength of X-rays used, β is the full line width at half maximum intensity (FWHM) and θ is the Bragg angle. The crystallite size of γ-Fe2O3 nanoparticles in the composite is ~7 nm.

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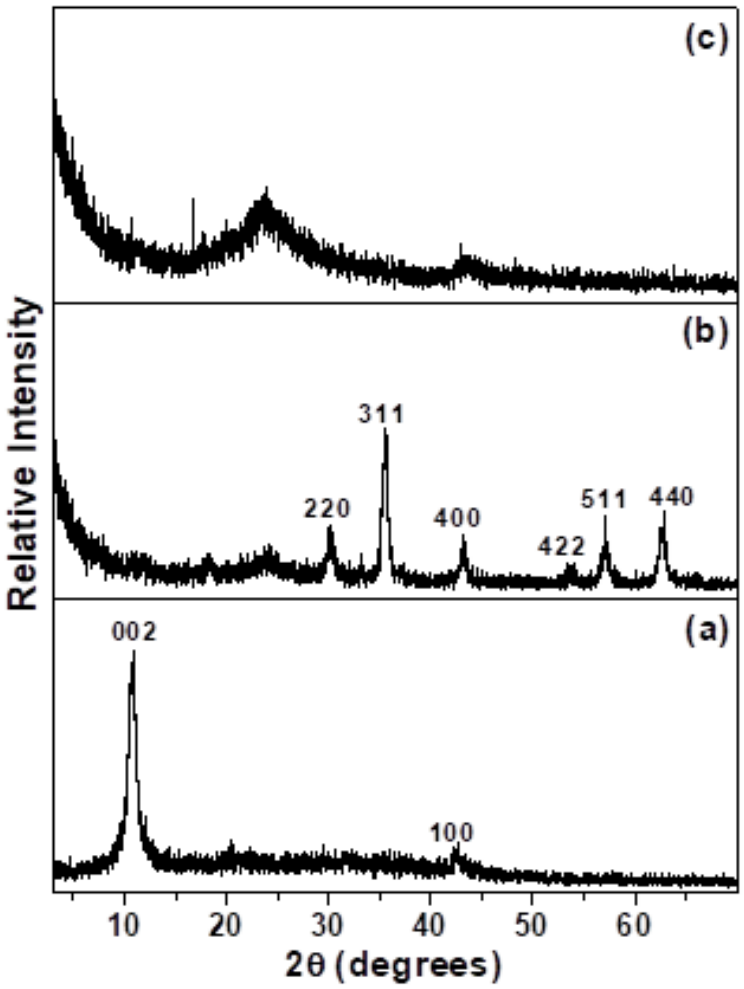

Figure 1. PXRD patterns of GO (a), G—γ-Fe2O3 composite (b) and the product obtained upon acid leaching of the composite (c)

To verify whether the initial GO has undergone reduction to graphene sheets during the hydrolysis and that reduced GO is present in the composite along with the nanoparticles, the composite was soaked in acid to leach out the inorganic matter. Figure 1c is the PXRD pattern of the product obtained upon acid leaching the composite. Here we observe a graphite related broad peak around 2θ = 23.7° (d = 3.8 Å) and no γ-Fe2O3 peaks as the leaching process had removed all the γ-Fe2O3 nanoparticles. A slight increase in basal spacing value of graphite obtained could be due to the incomplete reduction of GO.

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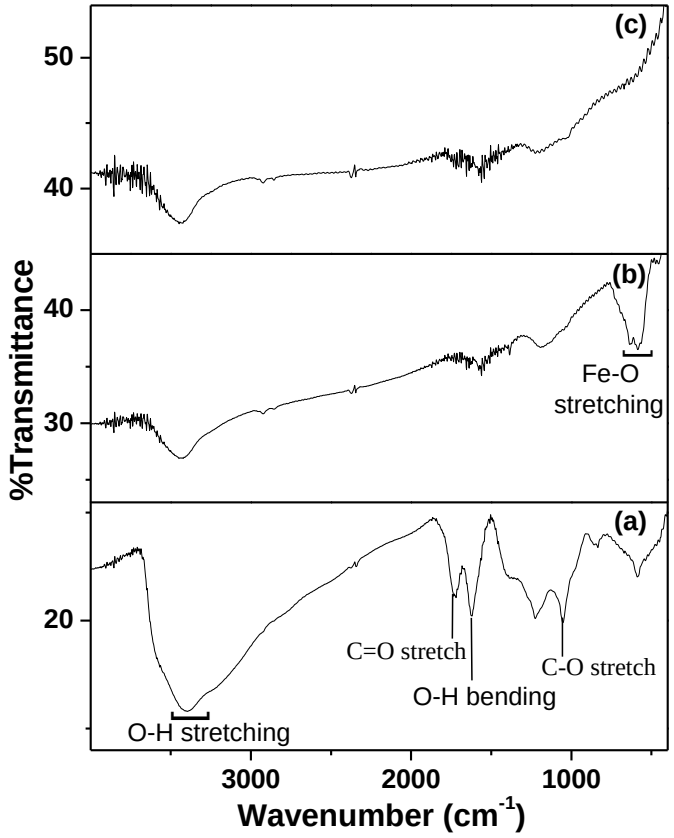

Figure 2. IR spectra of GO (a) G—γ-Fe2O3 nanocomposite (b) and the product obtained upon acid leaching the composite (c)

The IR spectrum of GO (Figure 2a) shows absorption bands due to O—H stretching and O—H bending vibrations at 3415 and 1620 cm-1 respectively. C=O stretching vibrations are observed at 1727 cm-1 and absorption due to C—O stretching at 1052 cm-1. Occurrence of these bands confirms the presence of oxygen containing functional groups on the edges and the basal planes of graphite sheets due to the oxidation of graphite. In the spectrum of the G—γ-Fe2O3 composite (Figure 2b) these bands are either absent or diminished in intensity suggesting that the GO has undergone reduction during the reaction. The Fe—O stretching vibration (609 cm-1) confirms the presence of γ-Fe2O3 in the composite. The acid leached sample (Figure 1c) shows a spectrum similar to that of the composite except that the Fe—O stretching absorption is missing.

V. CONCLUSIONS

When a mixture of GO and ferric chloride was refluxed in a glycol in the presence of hydrolysing agent hydrolysis of ferric ions and reduction of GO occur simultaneously to give G—γ-Fe2O3 composite. Magnetism studies and microscopic characterization of the composite obtained are underway.

REFERENCES

1. A. Lerf, H. He, M. Forster, J. J. Klinowski, Phys. Chem. B 102, 1998, 4477.
2. H. Y. He, J. Klinowski, M. Forster, A. Lerf, Chem. Phys. Lett. 287, 1998, 53–56.

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3. O. C. Compton, Son Binh T. Nguyen, Small 6, 2010, 711.
4. A. A. Balandin, S. Ghosh, W. Z. Bao, I. Calizo, D. Teweldebrhan, F. Miao and C. N. Lau, Nano Lett., 8, 2008, 902.
5. J. N. Hu, X. L. Ruan, Y. P. Chen, Nano Lett., 9, 2009, 2730.
6. I. Jung, D. A. Dikin, R. D. Piner, R. S. Ruoff, Nano Lett., 8, 2008, 4283.
7. W. T. Zheng, Y. Min Ho, H. Wei Tian, M. Wen, J. L. Qi, Y. A. Li, J. Phys. Chem. C 113, 2009, 9164.
8. J. Yan, T. Wei, Bo Shao, Z. Fan, W. Qian, M. Zhang, F. Wei, Carbon 48, 2010, 487.
9. K. I. Bolotin, K. J. Sikes, Z. Jiang, M. Klima, G. Fundenberg, J. Hone, P. Kim, H. L. Stormer, Solid State Commun. 146, 2008, 351.
10. S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, R. S. Ruoff, Carbon 45, 2007, 1558.
11. C. Lee, X. Wei, J.W. Kysar, J. Hone, Science 321, 2008, 385.
12. Gil M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth, Rolf Mülhaupt, J. Am. Chem. Soc.131, 2009, 8262.
13. A. Cao, Z. Liu, S. Chu, M. Wu, Z. Ye, Z. Cai, Y. Chang, S. Wang, Q. Gong, Y. Liu Adv. Mater. 22, 2010,103.
14. A. H. Morrish, The principles of magnetism, Wiley, New York, (1996) Chapter 7.
15. G. D. Stucky, J. MacDougall, Science 247, 1990, 669.
16. L. Gunther, In magnetic properties of fine particles, J. L. Dormann, D. Fiorani, (Eds.), Elsevier, Amsterdam (1992) p213.
17. A. E. Berkowitz, In Nanomaterials, Synthesis, properties and applications, A. S. Edelstein, R. C. Cammarata, (Eds.), Institute of Physics publishing, Bristol 1996, p569.
18. P. García-Acevedo, M. A. González-Gómez, Á. Arnosa-Prieto, L. de Castro-Alves, Y. Piñeiro, J. Rivas Adv. Sci. 10, 2023, 2203397.
19. N. Maniotis, M. Gitsou, M. Maragakis, Journal of Magnetism and Magnetic Materials, 617, 2025, 172843.
20. W. S. Hummers, R. E. Offeman, J. Am. Chem. Soc. 80, 1958, 1339.