One-step synthesis of mesoporous silica–graphene composites by simultaneous hydrothermal coupling and reduction of graphene oxide

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Abstract. Silica–graphene oxide composites were synthesized by hydrothermal method with simultaneous functionalization and reduction of graphene oxide (GO) in the presence of mesoporous silica. Two types of silica were used in the study, mesoporous synthetic silica (MSU-F) synthesized by sol-gel method and mesoporous mineral silica (meso-celite) from pseudomorphic synthesis. The infrared spectra of the composites showed the disappearance of the carboxyl peak at 1735 cm^{-1} which could be due to the reduction of the $-\text{COOH}$ group. The enhancement of the band at 1385 cm^{-1} is attributed to the vibration of the $\text{Si}-\text{O}-\text{C}=\text{O}$ moiety formed by reaction of the $-\text{COOH}$ group of GO and the silanol ($\text{Si}-\text{OH}$) of silica. The Raman spectra of the composites show a diminished intensity ratio of D to G band indicating that GO was reduced to graphene sheets. The TEM images demonstrate the coupling of silica to GO surface revealing dense loading of silica on GO in planar structure.

Keywords. Graphene; graphene oxide; mineral silica; silica; mesoporous silica; hydrothermal reduction.

1. Introduction

Graphene has become very popular in the field of materials science due to its novel electrical properties among other things. Graphene oxide (GO) is one starting route to produce large amounts of graphene. GO contains a wide range of oxygen functional groups both on the basal planes and the edges. The reactive oxygen functional groups of GO include epoxy, carboxylic acid and hydroxyl which can be chemically modified to produce homogeneous colloidal suspensions in various solvents (Park *et al* 2009). In the study by Park *et al* (2009), GO sheets were chemically cross-linked with polyallylamine (PAA) via the epoxy groups of GO. An aqueous colloidal suspension of chemically cross-linked GO was generated. Covalent functionalization of graphene sheets with polyvinyl alcohol (PVA) through direct esterification and through acyl chloride derivative was done by Salavagione *et al* (2009). Reduction of GO in PVA-functionalized GO was attained by addition of hydrazine. They have successfully modified graphene by esterification using the carboxylic acid groups in GO and the hydroxyl groups in PVA.

In this current study, GO was both successfully functionalized and reduced by mesoporous silica via direct esterification reaction. Exploiting the functional groups of GO such as hydroxyl and carboxylic acid and the

silanol ($\text{Si}-\text{OH}$) and siloxane ($\text{Si}-\text{O}-\text{Si}$) groups in silica for the formation of the $\text{Si}-\text{O}-\text{C}$ bond has not been reported yet. The possible suggested routes for the reaction are shown below:

Previous studies on silica demonstrated that the silanol groups in mesoporous silica can be esterified. Kimura *et al* (1998) used layered polysilicate and kanemite to react with alcohols and Mitamura *et al* (2001) performed organic esterification of the interlayer silanol groups of H-magadiite with various aliphatic alcohols. The silanol groups of silica can react with alcohols until silicic ester groups are formed. Ballard *et al* (1961) studied the esterification of various alcohols and silanol from finely divided amorphous silica of different surface area. They reported that the active $\text{Si}-\text{O}-\text{Si}$ bonds on the surface can probably react with alcohol to form more silanol groups as shown in the following reaction.

Here we report the novel method of the simultaneous coupling and reduction of GO. The use of mesoporous silica for surface modification of GO provides an ordered pore network. This unique feature of mesoporous silica extends its use in many applications such as in drug delivery, biosensing and electrochemical sensing (Fowler *et al* 2004; Vallet-Reg *et al* 2007). The GO-silica com-

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posites may find possible applications in the development of sensor, supercapacitor device or as support for catalysts and others.

2. Experimental

2.1 Preparation of graphene oxide sheets

Graphene oxide sheets were prepared by a modified Hummers' method from natural graphite flakes (NGS Naturgraphit GmbH, Germany) adopted from Su *et al* (2010). In brief, 2 g of graphite flakes was mixed with concentrated H_2SO_4 (12 mL) and kept at 80 °C for 4–5 h. The solution was cooled to room temperature and then sonicated in a water bath for 2 h. The mixed solution was then diluted with 500 mL of deionized (DI) water and left overnight. The solution was filtered under vacuum using a Whatman filter paper to obtain the pre-oxidized graphite flakes. The product was washed with distilled water and dried at room temperature overnight. The pre-oxidized graphite flakes were put into 120 mL concentrated H_2SO_4 (GR ACS EMD), with added KMnO_4 (15 g) in an ice bath, and stirred at room temperature for 2 h. The solution was diluted with DI water (250 mL), stirred for 2 h, and then added to 0.7 L of DI water. Shortly thereafter, 20 mL of H_2O_2 (CCI ACS Grade, 30%) was added into the mixture, and the color changed to light yellow. After aging overnight, it was filtered and washed with distilled water. To remove residual metal ions, it was slurried in 1:10 HCl solution and then centrifuged and dried at room temperature.

2.2 Pseudomorphic synthesis of meso-celite

About 0.61 g of cetyltrimmonium bromide (CTAB) was dissolved in 6 mL of a 0.7 M solution of NaOH. One gram of diatomaceous earth (Celite 545, Jade Scientific) was then added and the suspension was stirred at room temperature for a further 30 min. After this time, the reaction mixture was incubated at 100 °C for 3 days. The product was filtered and washed with distilled water, then dried for 24 h at room temperature. Calcination was performed by heating the solid to a temperature of 540 °C at a rate of 1 °C/min.

2.3 Mesoporous silica MSU-F (Silapore F 110810)

Mesoporous silica was prepared by the method of Kim and Pinnavaia (2003). In brief, surfactant solution was prepared by stirring P123 in 1 M acetic acid and 10 mL water for 2 h. 1, 3, 5-trimethyl benzene was added to the mixture and allowed to age under ambient conditions. The microemulsion formed was added with sodium silicate and NaOH in water and placed in a mechanical

shaker bath for 24 h. The reaction mixture was then heated at 100 °C at different time intervals. It was then filtered, dried and calcined at 600 °C for 4 h to ensure complete removal of the surfactant.

2.4 Preparation of GO-silica composite

The GO-silica was prepared by reacting different ratios of GO and silica. One mL of concentrated H_2SO_4 was added and the solution was refluxed for 24 h at 100 °C. The GO-silica was filtered and washed with distilled water and dried at room temperature.

2.5 Characterization

A drop of the sample (graphite, GO, silica and GO-silica) was placed on Holey Carbon Films 300 mesh copper grids and was characterized by transmission electron microscopy (JEOL JEM-100CX II Electron Microscope) with an accelerating voltage of 100 kV. Raman spectroscopic measurements (Horiba Jobin Yvon LabRam Aramis) were conducted at room temperature with an excitation wavelength of 532 nm. Infrared spectra were collected with the Mattson Galaxy Series FTIR 5000 using the KBr pellet standard method and scanned at 4 cm^{-1} resolution. All samples were characterized by powder X-ray diffraction using a Bruker Davinci Diffractometer ($\text{CuK}\alpha$ radiation = $\lambda = 1.5418 \text{ \AA}$). Surface area analysis of Celite and Meso-Celite was performed with a Micromeritics ASAP 2010 Analyser (Micromeritics Instrument Corporation, Norcross, GA). The samples were outgassed under vacuum and 150 °C for 24 h prior to analysis.

3. Results and discussion

3.1 Preparation and characterization of GO

In this study, GO was prepared via the modified Hummer's method which uses a combination of potassium permanganate and sulfuric acid. The GO obtained by Hummer's method contains a wide range of oxygen functional groups both on the basal planes and the edges. The reactive oxygen functional groups of GO include epoxy, carboxylic acid and hydroxyl which can be chemically modified to produce homogeneous colloidal suspensions in various solvent (Park *et al* 2009). The infrared spectra of GO revealed the presence of oxygenated groups. Figure 1 shows bands at 3423 and 1630 cm^{-1} characteristic of water and 1718 cm^{-1} for carbonyl (C=O) stretching frequency.

The GO produced was partially oxidized as shown in the XRD pattern in figure 2. The (002) diffraction line of graphite (d -spacing 0.34 nm at 26.05°) broadens.

A unique band for the graphene oxide appears at 10.89° . This corresponds to a d -spacing or interlayer distance between sheets of approximately 0.81 nm that is due to interlamellar water trapped between hydrophilic graphene oxide sheets (Park *et al* 2009). Similar results were observed by Salavagione *et al* (2009) when they synthesized their GO using Hummer's method. A thickness of 4.4 nm for GO sheets was estimated using the Scherrer equation (4). Ju *et al* (2010) and Grayfer *et al* (2011) also employed the Scherrer equation to estimate the thickness of graphene. A monolayer of GO has a thickness of about 0.8 nm (Guo *et al* 2010). This indicates that the GO that we obtained was, on an average, a multilayer one of approximately six sheets.

$$\text{Scherrer equation: } t = (0.9\lambda)/(B\cos\theta), \quad (4)$$

where t is the thickness; $\lambda = 1.54 \text{ \AA}$; B the difference in angles at half maximum $= (2\theta_{\text{high}} - 2\theta_{\text{low}}) \times \pi/180$ (radians).

Figure 3 shows the Raman spectrum of graphite showing a single peak at 1530 cm^{-1} assigned to the G band. GO shows two broad bands: the D band at 1350 cm^{-1} and a G band at 1585 cm^{-1} . The prominent D band for GO clearly indicates the presence of structural imperfections induced by the attachment of hydroxyl and epoxide groups on the carbon basal plane (Eda *et al* 2008). A weak and broad 2D peak appears $\sim 2700 \text{ cm}^{-1}$ (not shown) and is another indication of disorder as the result of an out-of-plane vibration mode. These strong G, D, and 2D bands are very similar to previous results of graphene oxide characterization (Stankovich *et al* 2007; Guo *et al* 2010).

Figure 4(a) shows the TEM image of GO sheets which have thin layer morphology. This is due to the partial delamination caused by oxidation of graphene. In contrast, the TEM image of graphite (figure 4b) depicts a

thicker textural morphology indicating stacking of several layers of graphite sheets.

3.2 Pseudomorphic synthesis of meso-celite

The raw diatomite is industrially beneficiated before its commercial utilization to remove impurities and improve its utilization. The commercial diatomite used in this study was celite and when it was subjected to pseudomorphic synthesis, it was called meso-celite. Pseudomorphic synthesis involved the development of micelle-templated silicas. The self-assembly of surfactant aggregates and mineral species can be controlled to provide stable mesoporous materials with extremely narrow pore-size distributions.

TEM was performed on aqueous dispersions of celite and meso-celite. At the same magnification, figure 5(b) revealed the presence of a mesostructured layer on the surface of meso-celite. On the other hand, celite showed only a smooth surface and the absence of a mesostructure (figure 5a).

The mesoporosity of celite before and after pseudomorphic synthesis was characterized further by N_2 adsorption. In comparison with celite, where a mesoporous structure was not well-evolved, meso-celite structure exhibited enhanced N_2 adsorption. This indicates an increase in surface area, from $24 \text{ m}^2/\text{g}$ of celite to $31 \text{ m}^2/\text{g}$ of meso-celite.

3.3 GO-silica composite

The dispersibility of GO-silica composite in H_2O and CCl_4 was observed to be different. The composite was more homogeneously dispersed in H_2O than in CCl_4 , indicating its increased hydrophilicity. Another observation is the color of the GO before and after hydrothermal (reflux) treatment, which dramatically changed from brown color GO to black reduced GO. This was visual confirmation of the reduction of GO to graphene.

The IR spectra of the composite (GO-meso-celite and GO-MSU-F) in figure 1 reveals the appearance of the 1385 cm^{-1} peak. This band is assigned to Si-O-C=O (Arkles and Peterson Jr 1981) which could have formed when $-\text{COOH}$ from GO reacted with the $-\text{SiOH}$ from silica. The band intensities at 807 and 475 cm^{-1} which correspond to Si-O stretching of silanol were found to be present in the composites. These changes in the IR peaks confirm the successful functionalization of GO with silica. The following are reported works on functionalization of GO via the carboxyl group and they demonstrate decrease in intensity or disappearance of the 1700 cm^{-1} peak: Zhang *et al* (2010) modified GO with poly(*N*-vinylcarbazole) and Park *et al* (2009) cross-linked GO with polyaniline amine.

The disappearance of the carboxyl group at 1735 cm^{-1} was also observed in figure 1. Such occurrence was

Figure 1. Comparison of IR spectra for GO, silica and GO-silica (GO-meso-celite and GO-MSU-F) composites.

Figure 2. Powder XRD patterns of GO, graphite and composite showing broadening of (002) peak indicating that GO was oxidized and exfoliated. XRD peaks for composite show presence of both phases: GO at 11° and 26° and silica at 20°–23°.

Figure 3. Raman spectra of GO, graphite and GO-silica. Intensity ratio of D to G decreased in composite indicating that reduction of GO occurred.

Table 1. XRD data of GO and GO-silica

Sample	Angle (2θ)	d -spacing (nm)
GO	26.08°	0.350
	10.89°	0.815
GO-MSU-F	26.20°	0.349
	11.50°	0.772
GO-meso-celite	26.29°	0.339
	11.53°	0.767

reported in the work of Lin *et al* (2010) when the carboxyl and carbonyl groups of GO dispersed in two solvents, H₂O and dimethylformamide (DMF), decomposed at 100 and 150 °C, respectively.

The XRD patterns of the GO-silica in figure 2 confirmed the presence of both phases (GO and silica) in the composites, GO-MSU-F and GO-meso-celite. XRD peaks at 20°–23° are attributed to silica while peaks at 11 and 26° are for GO. The XRD of the GO-silica samples has a slight shift in the (002) peak maximum from 26.08° in GO to 26.20° and 26.29° (see table 1) in GO-MSU-F and GO-meso-celite, respectively. This shift in the interlayer spacing might be caused by the reduction of the graphene oxide sheets, where the reduction allows the reduced graphene oxide sheets to pack tighter (smaller interlayer distance between sheets) than the less-reduced counterpart (Park *et al* 2009). Furthermore, these decreased values confirm the reduction of the GO sheets to graphene. Occurrence of other XRD peaks may be due to the presence of residual oxygen and hydrogen indicating incomplete reduction of GO sheets to graphene. Hence the reduced graphene sheets obtained here are not pure but chemically modified to a certain extent (Nethravathi and Rajamathi 2008).

As shown in figure 3, the Raman spectra of GO and GO-silica composite differ from GO, the G band of the composites are shifted from GO appearing at 1556 cm⁻¹ for GO-meso-celite and 1573 cm⁻¹ for GO-MSU-F. This

Figure 4. TEM images of GO (a) and graphite (b) showing thicker textural morphology for graphite than GO.

Figure 5. TEM images of (a) MSU-F, (b) meso-celite and (c) celite. This shows that mesopores were introduced into celite.

observation is attributed to graphitic ‘self-healing’ similar to what was observed in the sharpening of the G peak in heat treated graphite (Konstantin *et al* 2008). The D band was also shifted relative to the 1348 cm^{-1} of GO: it is at 1356 cm^{-1} for GO-meso-celite, 1365 cm^{-1} for GO-celite and 1390 cm^{-1} for GO-MSU-F. For the composites, GO-

MSU-F and GO-meso-celite, the D band is absent, but for the GO-celite, it remains. According to Su *et al* (2010) once the GO is reduced, the ratio of the intensity of D and G bands, $I(D)/I(G)$, will decrease with decreasing disorder in graphitic structures. These changes are characteristic of reduced GO sheets, where the reduced graphene

Figure 6. TEM image: (a) GO-MSU-F; (b) GO-meso-celite; (c) GO-celite. It shows dense loading of silica on GO.

oxide sheets pack tighter (smaller interlayer distance between sheets) compared with the GO counterpart (Park *et al* 2009).

TEM images of the composites are shown in figure 6. In contrast to the smooth planar morphology of GO (figure 4a), planar sheets are revealed in figure 6(b and c), with the characteristic rough texture of the silica mesopore (compare with figure 5b). The edges of the plates of GO are evident in the images particularly in the thinly stacked regions. The dense loading of silica particles are seen on the GO surface possibly forming a layered planar structure (Zhang *et al* 2010).

4. Conclusions

The coupling of silica to GO and the partial reduction of GO were demonstrated and confirmed by characterization techniques such as IR, Raman, XRD and TEM. The synthesis route for the hydrothermal reaction of GO and silica could be via the $-\text{COOH}$ from the basal plane of GO and the $-\text{SiOH}$ of the silica. It was also illustrated that meso-celite and MSU-F, which are both mesoporous, reduced the GO better than Celite as shown in the Raman

spectra. TEM images suggest that a silica-layered planar structure was formed in the composite. This could indicate that silica can act as a spacer to prevent the direct restacking of GO sheets. These composites may find applications in the development of sensor, supercapacitor device, or as support for catalysts, and others.

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References

- Arkles B C and Peterson Jr W R 1981 US Patent 4,276,421
- Ballard C C, Broge E C, Ile R K, St John D S and Mcwhorter R 1961 *J. Phys. Chem.* **65** 20

- Eda G, Fanchini G and Chhowalla M 2008 *Nature Nanotechnology* **3** 270
- Grayfer E D, Fedoroy V E, Nazarov A S, Makotchenko V G and Kim S J 2011 *J. Mater. Chem.* 2011 **21** 3410
- Guo Y, Guo S, Ren J, Zhai Y, Dong S and Wang E 2010 *ACS Nano* **4** 4001
- Ju H M, Choi S H and Huh S H 2010 *J. Korean Phys. Soc.* **57** 1649
- Kang S M, Park S, Kim D, Park S Y, Ruoff R S and Lee H 2011 *Adv. Funct. Mater.* **21** 108
- Kim S S, Pauly T R and Pinnavaia T J 2000 *Chem. Commun.* 1661
- Kim S S and Pinnavaia T J 2003 *Chem. Mater.* **15** 11
- Kimura T, Kuroda K and Sugahara Y 1998 *J. Porous Mater* **5** 127
- Konstantin N R, Prud'homme K, Ozbas B, Ilhan A, Aksay A, Schniepp H C and Car R 2008 *Nano Lett.* **8**
- Kou L and Gao C 2011 *Nanoscale* **3** 519
- Lin Z, Yao Y, Li Z, Liu Y, Li Z and Wong C 2010 *J. Phys. Chem.* **C114** 14819
- Mitamura Y, Komori Y, Hayashi S, Sugahara Y and Kuroda K 2001 *Chem. Mater.* **13** 3747
- Nethravathi C and Rajamathi M 2008 *Carbon* **46** 1994
- Park S, An J, Jung I, Piner R, An S J, Li X, Velamakanni A and Rouff R S 2009 *Nanolettts* **9** 1593
- Park S, Dikin D, Nguyen S and Ruoff R S 2009 *J. Phys. Chem.* **C113** 15801
- Salavagione H, Gomez M A and Martinez G 2009 *Macromolecules* **42** 6331
- Stankovich S, Dikin D A, Piner R D, Kohlhaas K A, Kleinhammes A, Jia Y, Wu Y, Nguyen S T and Ruoff R S 2007 *Carbon* **45** 1558
- Su CY, Xu Y, Zhang W, Zhao J, Liu A, Tang X, Tsai C H, Huang Y and Li L J 2010 *ACS Nano* **4** 5285
- Vallet-Reg M, Balas F and Arcos D 2007 *Angew. Chem. Int. Ed.* **46** 7548
- Zhang L S, Guo Y G, Jiang L Y, Wan L J, Yan H J, Wang W D, Wang W and Song W G 2010 *Mater. Chem.* **20** 5462
- Zhang B, Chen Y, Zhuang X, Liu G, Yu B, Kang E, Zhu J and Li Y 2010 *J. Polym. Sci.: Part A: Polym. Chem.* **48** 2642