Controlled oxidation of graphite to graphene oxide with novel oxidants in a bulk scale

Malgorzata Wojtoniszak · Ewa Mijowska

Received: 27 June 2012 / Accepted: 11 October 2012 / Published online: 30 October 2012 © The Author(s) 2012. This article is published with open access at Springerlink.com

Abstract In this study, a novel method of graphite chemical exfoliation to create graphene oxide (GO) is reported. Here, new oxidants were examined: a mixture of perchloric and nitric acids and potassium chromate. Furthermore, an effect of oxidation time, temperature of oxidation, and ultrasonication on graphite exfoliation degree was investigated. The obtained GOs were next reduced with glucose, used as a reducing agent. Detailed analysis of the materials indicated that when graphite was oxidized for 24 h at 50 °C, 5-layered graphene was prepared. An effect of sonication process was also examined, and it was found to enhance the exfoliation to bilayer graphene. Furthermore, when time and temperature were increased to 48 h and 100 °C, respectively, graphite was exfoliated to single-layer graphene. Therefore, it is believed that the proposed route can be applied for the preparation of graphene or few-layered graphene with defined number of layers upon the process parameters optimization and in a bulk scale. The materials were characterized with atomic force microscopy, Fourier-transform infrared spectroscopy, Raman spectroscopy, and X-ray diffraction.

Keywords Graphite · Chemical exfoliation · Graphene oxide

Introduction

Graphene shows excellent properties, such as high intrinsic carrier mobility (200,000 cm²/V·s), superior thermal conductivity, and excellent mechanical strength and elasticity (Bolotin et al. 2008; Balandin et al. 2008; Lee et al. 2008). Since graphene was isolated in 2004 by Geim and coworkers (2004) using a scotch tape method, there have been many processes developed to produce graphene. Although the mechanical exfoliation of graphite leads to production of high-quality and high-mobility graphene flakes, this method is a time consuming process limited to a small scale production. One of the methods is thermal decomposition of SiC in temperature range between 1,000 and 1,500 °C. Here, Si sublimate from the silicon carbide and leave behind a carbon-rich surface (Hass et al. 2008). This method requires controlling the number of graphene layers, repeatability of large area growths, and interface effects with the SiC substrate (Choi et al. 2010). The second method of graphene synthesis is chemical vapor deposition (CVD). This process is promising in large scale production of graphene. Many papers concerning CVD growth of graphene using different catalysts (Ni, Cu, ZnS, Fe) have been reported (An et al. 2011; Wei et al. 2009; Li et al. 2009; Reina et al. 2009;
Obraztsov 2009). Graphene can be also synthesized via chemical exfoliation of graphite, where interlayer van der Waals forces are eliminated: chemical derivatization, intercalation, thermal expansion, the use of surfactants, and oxidation–reduction (Chakraborty et al. 2008; Lotya et al. 2009; Lee et al. 2008). The most common route to chemically exfoliate graphite is the use of strong oxidants to produce graphene oxide in a first stage. Graphite oxide was first prepared by B.C. Brodie, where it was treated with a mixture of potassium chlorate and nitric acid (Brodie 1859). Later, Hummers and Offeman (1958) used a mixture of sulfuric acid, sodium nitrate, and potassium permanganate to oxidize graphite. Recently, many papers reporting a modification of the Hummers method have been published. For instance, Marcano et al. (2010) used a mixture of sulfuric and orthophosphoric acids and potassium permanganate in the oxidation process, and found it improved an efficiency of the oxidation. This process is still widely investigated for two reasons: (1) it gives an opportunity to produce large scale graphene or few-layered graphene, (2) it has potential to provide the samples with controlled number of graphene layers upon the process parameters optimization.

In this study, novel oxidants of graphite, toward its chemical exfoliation, were examined: a mixture of perchloric and nitric acids and potassium chromate. Furthermore, an effect of oxidation time, temperature of oxidation and ultrasonication in exfoliation degree were investigated. The obtained materials were characterized with TEM, FT-IR, Raman spectroscopy, and XRD.

**Experimental**

**Materials**

Graphite was purchased from Alfa Aesar (synthetic, 99.9995 %, 325 mesh). Perchloric acid, nitric acid, hydrochloric acid, and ethanol were obtained from Chempur. $K_2CrO_4$ was bought from POCH.

**Methods**

Here, three types of graphene oxides (GOs) were prepared. In the first procedure of GO1 synthesis, 1 g of graphite was dispersed in a mixture of perchloric and nitric acids (350 mL, 4:3—volume ratio), and next, $K_2CrO_4$ (6 g) was added. The mixture was then heated to 50 °C and reaction was operated for 24 h. The obtained mixture was next filtrated through polycarbonate (PC) membrane (Whatman 0.2 μm) and washed three times with ethanol (200 mL) and 10 % hydrochloric acid (200 mL) to remove residual metal ions, and finally with distilled water until pH of the solution was 7. Finally, the material was dried in air at 100 °C for 24 h.

In the second method, prior heating a mixture of graphite, perchloric acid, nitric acid, and $K_2CrO_4$, an ultrasonication process was performed for 6 h at room temperature. After oxidation process, the purification, filtration, and drying steps were realized as in the first procedure, and finally GO2 was obtained.

In the third route, the time and the temperature of oxidation process were increased to 48 h and 100 °C, respectively. The sonication, purification, filtration, and drying steps were carried out as in the second procedure to obtain GO3. After the purification process of the each graphene oxide, the content of impurities was determined with thermogravimetric analysis. It was estimated that GO1, GO2, and GO3 contain 0.11, 0.19, and 0.08 wt% of contaminants, respectively (data are not presented here).

Reduced graphene oxide (RGO) was synthesized with glucose using as a reducing agent (Zhu et al. 2010). In a typical procedure, graphene oxides (GO1, GO2, and GO3) were separately dispersed in 50 mL of water (0.5 mg/mL) and ultrasonicated for 2 h. Next, 80 mg of glucose was added to each homogeneous GO dispersion, and the mixtures were stirred for 30 min. Then, 40 μL of ammonia solution was added and reactions were heated to 95 °C, stirring simultaneously for 2 h. Next, the each reaction mixture was filtered through PC membrane (0.2 μm Whatman). The obtained solid material was then washed with water and ethanol (3 times). Finally, the products (RGO1, RGO2, and RGO3) were dried in air at 100 °C for 24 h.

The morphology of the obtained materials was characterized via atomic force microscopy (Nanoscope V MultiMode 8, Bruker). The measurements were done in air under ambient conditions. Raman measurements were performed on an In-Via Raman microscope (Renishaw) with excitation laser wavelengths of 785 nm. Raman spectra were obtained from individual flakes deposited on SiO$_2$/Si wafer (300 nm SiO$_2$) (Liana et al. 2010). The crystallographic
structure of the samples were characterized by XRD analysis (X’Pert PRO Philips diffractometer) using a CuKα radiation. FT-IR absorption spectra were recorded on Nicolet 6700 FT-IR Spectrometer.

Results and discussion

In this study, novel oxidants were used to create chemical exfoliation of graphite. In order to examine the efficiency of oxygen-containing functional groups introduction to carbon lattice, FTIR spectroscopy was used. Figure 1 presents FTIR spectra of GO1, GO2, and GO3. At each spectrum, several typical modes corresponded to oxygen-functional groups are detected. Here, stretching vibration modes of C–O bonds arise at 1,099 cm⁻¹. The peaks between 1,190 and 1,380 cm⁻¹ are related with C–OH stretching vibration (Xu et al. 2008). Deformation vibration modes of O–H groups are observed at 1,431 cm⁻¹ (Stankovich et al. 2006). The bands appeared at 1,635 cm⁻¹ correspond to adsorbed water molecules indicating hydrophilic properties of the material (Paredes et al. 2008). At approximately 1,709 cm⁻¹ C=O stretching vibration of carboxyl groups are detected. The peaks at around 3,430 cm⁻¹ arise from O–H stretching vibration (Wojtoniszak et al. 2012). FTIR spectroscopy confirms successful oxidation. Furthermore, the intensities of the modes between 1,230 and 1,740 cm⁻¹ increased in order of GO1, GO2, and GO3 which suggests an increase of the oxidation efficiency.

For further analysis XRD was used to monitor chemical exfoliation of graphite in a bulk scale. Figure 2 shows XRD patterns of graphite, GO1, GO2, and GO3. XRD pattern of graphite is dominated by single peak at 26.48° corresponding to (002) plane (Liana et al. 2010). After oxidation process, the peak started to vanish, and new peaks arose at 24.28°, 24.78°, and 24.23° in XRD patterns of GO1, GO2, and GO3, respectively. On the basis of Bragg’s law, the interlayer spacing (d₀₀₁) of GO1, GO2, and GO3 is 3.7, 3.6, and 3.7 Å, respectively. It is enhanced compared to that of graphite (3.4 Å) (Fan et al. 2011). In GO2 and GO3 XRD patterns, more distinct decay of the peak at 26.48° is observed. It suggests an enhanced exfoliation of graphite when oxidation was performed with ultrasonication treatment and when a time and a temperature was increased, also confirming the enhanced oxidation effect.

In order to determine the number of graphene layers, the samples underwent the reduction process. For reduced graphene oxide (RGO) preparation, glucose was used as a reducing agent. The obtained
materials (RGO1, RGO2, and RGO3) were analyzed with Raman spectroscopy to characterize their structure, in terms of number of graphene layers and lattice defects. Figure 3 presents Raman spectra of graphite (A), RGO1 (B), RGO2 (C), and RGO3 (D). All spectra exhibit 3 typical modes related to graphite-like structure: a G band, a D band, and a 2D band (Fig. 3, left panel). The G mode at approximately 1,580 cm$^{-1}$ originates from the in-plane vibration of sp$^2$ carbon atoms and is a doubly degenerate phonon mode ($E_{2g}$ symmetry) at the Brillouin zone center (Li et al. 2007). The D band at roughly 1,320 cm$^{-1}$ is a breathing mode of $A_{1g}$ symmetry involving phonons near the $K$ zone boundary (Wilson et al. 2009). The 2D band arises from a two phonon double resonance Raman process (Ferrari and Robertson 2000). The 2D band is a key mode in identification of number of graphene layers. According to its position, shape and intensity, a thickness of graphene may be determined (Ferrari and Robertson 2000; Ni et al. 2008). Charlier et al. (2008) plotted the evolution of the 2D band as a function of layers in single-, bi-, and few-layer graphene. Briefly, a 2D band of bi- and few-layer graphene has 2 components 2D$_1$ and 2D$_2$. Increasing the number of layers leads to a significant increase of the relative intensity of the 2D$_2$ peak and blue shift of the 2D peak. However, a 2D peak of single-layer graphene is composed of a single 2D peak, positioned at roughly 2,600 cm$^{-1}$. Therefore, a Lorentzian
fitting of the RGOs spectra was performed and is presented in Fig. 3 (right panel). Here, 2D band of RGO1 differs from 2D band of graphite, and has two components: $2D_1$ and $2D_2$ with maximal intensity at 2,624 and 2,657 cm$^{-1}$, respectively. It may be attributed to 5-layered graphene. The $2D_2$ peak of
RGO2 decreases in comparison to RGO1. Furthermore, the 2D peak of RGO2 shifts to lower frequencies. These observations suggest the enhanced exfoliation of graphene when sonication was utilized leading to creation of bilayer graphene. It is clearly seen that 2D peak of RGO3 vanishes, and single 2D peak appears at 2,584 cm\(^{-1}\) attributed to single-layer graphene (Ferrari et al. 2006). It is known that a ratio between the intensities of the D and the G bands (\(I_D/I_G\)) determines relative defect content in the carbon lattice (Jorio et al. 2011). Therefore the \(I_D/I_G\) ratios of RGOs spectra were calculated and results are presented in Fig. 4. It is shown that the \(I_D/I_G\) ratio increases in order of RGO1, RGO2, and RGO3. This is related to the formation of vacancies and defects in carbon lattice, such as five- and seven-membered carbon rings, during the reduction process (Schniepp et al. 2006). This means that introduction of more oxygen-functional groups during the oxidation results in formation of more defects and vacancies in the final product—graphene.

To confirm the morphology of RGO1, RGO2, and RGO3, atomic force microscopy was applied. Figure 5 presents topography and height profiles of the prepared nanomaterials. The sizes of graphene flakes ranged from 30 to 70 nm in the each sample. The thickness of RGO1, RGO2, and RGO3 was 2.5–2.6, 1.3, and 1.0–1.1 nm, respectively. It was already reported that the thickness of a single-layer graphene on a substrate SiO\(_2\)/Si with approximately 1 nm rms roughness, would be 0.8–1.2 nm. The enhanced thickness of monolayer graphene may be attributed to the interaction between the sample and the tip (Gupta et al. 2006; Nemes-Ince et al. 2008). In bi- or few-layered graphene, the thickness arises with additional layer and therefore, adding the expected 0.35 nm height corresponding to the native van der Waals inter-layer distance (Soldano et al. 2010). It was concluded that RGO1, RGO2, and RGO3 were composed of 5-layered, bilayer, and monolayer graphene, respectively (Li et al. 2008a, b). This observation is in full agreement with Raman response of the samples.

**Conclusions**

In summary, novel method of chemical exfoliation of graphite was presented. Here, novel oxidants were examined: a mixture of perchloric and nitric acids and potassium chromate, and an effect of oxidation time, temperature of oxidation, and ultrasonication in exfoliation degree were investigated. The presented methodology leads to creation of graphene with controlled number of layers: single-, bi-, and 5-layered graphene in a bulk scale.

**Acknowledgments** The authors are grateful for the financial support of National Science Center, nr 2011/01/N/ST5/02912.

**Open Access** This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

**References**

An H, Lee WJ, Jung J (2011) Graphene synthesis on Fe foil using thermal CVD. Curr Appl Phys 11:S81–S85. doi: 10.1016/j.cap.2011.03.077

Balandin AA, Ghosh S, Bao W, Calizo I, Teweldebrhan D, Miao F, Lau CN (2008) Superior thermal conductivity of single-layer graphene. Nano Lett 8:902–907. doi: 10.1021/nl0731872

Bolotin KI, Sikes KJ, Jiang Z, Klima M, Fudenberg G, Hone J, Kim P, Stormer HL (2008) Ultrahigh electron mobility in suspended graphene. Solid State Commun 146:351–355. doi:10.1016/j.ssc.2008.02.024

Brodie BC (1859) On the atomic weight of graphite. Proc R Soc Lond 10:249–259. doi: 10.1098/rspl.1859.0007

Chakraborty S, Guo W, Hauge RH, Billups WE (2008) Reductive alkylation of fluorinated graphite. Chem Mater 20:3134–3136. doi:10.1021/cm800606q

Charlier JC, Eklund PC, Zhu J, Ferrari AC (2008) Electron and phonon properties of graphene: their relationship with carbon nanotubes. Top Appl Phys 111:673–709

Choi W, Lahiri I, Seelaboyina R, Kang YS (2010) Synthesis of graphene and its applications: a review. Crit Rev Solid State Mater Sci 35:52–71. doi:10.1080/1040403903505036

Fan ZJ, Kai W, Yan J, Wei T, Zhi LJ, Feng J (2011) Facile synthesis of graphene nanosheets via Fe reduction of exfoliated graphite oxide. ACS Nano 5:191–198. doi: 10.1021/nn102339t

Ferrari AC, Robertson J (2000) Interpretation of Raman spectra of disordered and amorphous carbon. Phys Rev B 61:14095–14107. doi:10.1103/PhysRevB.61.14095

Ferrari AC, Meyer JC, Scardaci V, Casiraghi C, Lazzeri M, Mauri F, Piscanec S, Jiang D, Novoselov KS, Roth S, Geim AK (2006) Raman spectrum of graphene and graphene layers. Phys Rev Lett 97:187401–187404. doi:10.1103/PhysRevLett.97.187401

Gupta A, Chen G, Joshi P, Tadigadapa S (2006) Raman scattering from high-frequency phonons in supported \(n\)-graphene layer films. Nano Lett 6:2667–2673. doi: 10.1021/nl061420a
Hass J, De Heer WA, Conrad EH (2008) The growth and morphology of epitaxial multilayer graphene. J Phys Condens Matter 20:323202–323229. doi: 10.1088/0953-8984/20/32/323202

Hummers WS Jr, Offeman RE (1958) Preparation of graphitic oxide. J Am Chem Soc 80:1339. doi:10.1021/ja01539a017

Jorio A, Ferreira EHM, Canc ¸ado LG, Achete CA, Capaz RB (2011) Measuring disorder in graphene with Raman spectroscopy. Phys Status Solidi B 247:2980–2982. doi: 10.1002/pssb.201000247

Lee C, Wei X, Kysar JW, Hone J (2008) Measurement of the elastic properties and intrinsic strength of monolayer graphene. Science 321:385–388. doi: 10.1126/science.1157996

Li ZQ, Lu CJ, Xia ZP, Zhou Y, Luo Z (2007) X-ray diffraction patterns of graphite and turbostratic carbon. Carbon 45:1686–1695. doi:10.1016/j.carbon.2007.03.038

Li D, Mueller MB, Gilje S, Kaner RB, Wallace GG (2008a) Processable aqueous dispersions of graphene nanosheets. Nat Nanotechnol 3:101–105. doi:10.1038/nnano.2007.451

Li X, Wang X, Zhang L, Lee S, Dai H (2008b) Chemically derived, ultrasmooth graphene nanoribbon semiconductors. Science 319:1229–1232. doi: 10.1126/science.1152458

Li X, Cai W, An J, Kim S, Nah J, Yang D, Piner R, Velamakanni A, Jung I, Tutuc E, Banerjee SK, Colombo L, Ruoff RS (2009) Large-area synthesis of high-quality and uniform graphene films on copper foils. Science 324:1312–1314. doi: 10.1126/science.1171245

Liana P, Zhub X, Lianga S, Li Z, Yang W, Wang H (2010) Large reversible capacity of high quality graphene sheets as an anode material for lithium-ion batteries. Electrochim Acta 55:3909–3914. doi:10.1016/j.electacta.2010.02.025

Lotya M, Hernandez Y, King PJ, Smith RJ, Nicolosi V, Karlsson LS, Bligh FM, De S, Wang Z, McGovern IT, Duesberg GS, Coleman JN (2009) Liquid phase production of graphene by exfoliation of graphite in surfactant/water solutions. J Am Chem Soc 131:3611–3620. doi: 10.1021/ja078449u

Marcano DC, Kosynkin DV, Berlin JM, Sinitskii A, Sun Z, Slesarev A, Alemany LB, Lu W, Tour JM (2010) Improved synthesis of graphene oxide. ACS Nano 4:4806–4814. doi: 10.1021/nn1006368

Nemes-Ince P, Osváth Z, Kamarás K, Biró LP (2008) Anomalies in thickness measurements of graphene and few layer graphite crystals by tapping mode atomic force microscopy. Carbon 46:1435–1442. doi:10.1016/j.carbon.2008.06.022

Ni Z, Wang Y, Yu T, Shen Z (2008) Raman spectroscopy and imaging of graphene. Nano Res 1:273–291. doi:10.1007/s12274-008-8036-1

Novoselov KS, Geim K, Morozov SV (2004) Electric field in atomically thin carbon films. Science 306:666–669. doi: 10.1126/science.1102896

Obraztsov AN (2009) Chemical vapour deposition: making graphene on a large scale. Nat Nanotechnol 4:212–213. doi:10.1038/nnano.2009.67

Paredes JI, Villar-Rodil S, Martínez-Alonso A, Tascón JMD (2008) Graphene oxide dispersions in organic solvents. Langmuir 24:10560–10564. doi:10.1021/la801744a

Reina A, Jia X, Ho J, Nezich D, Son H, Bulovic V, Dresselhaus MS, Kong J (2009) Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition. Nano Lett 9:30–35. doi:10.1021/nl801827v

Schneipp HC, Li JL, McAllister MJ, Sai H, Herrera-Alonso M, Adamson DH (2006) Functionalized single graphene sheets derived from splitting graphite oxide. J Phys Chem B 110:8535–8539. doi:10.1021/jp060936f

Soldano C, Mahmood A, Dujardin E (2010) Production, properties and potential of graphene. Carbon 48:2127–2150. doi:10.1016/j.carbon.2010.01.058

Stankovich S, Piner RD, Nguyen SBT, Ruoff RS (2006) Synthesis and exfoliation of isocyanate-treated graphene oxide nanoplatelets. Carbon 44:3342–3347. doi:10.1016/j.carbon.2006.06.004

Wei D, Liu Y, Zhang H, Huang L, Wu B, Chen J, Yu G (2009) Scalable synthesis of few-layer graphene ribbons with controlled morphologies by a template method and their applications in nanoelectromechanical switches. J Am Chem Soc 131:11147–11154. doi:10.1021/ja903092k

Wilson NR, Pandey PA, Beanland R, Young RJ, Kinloch IA, Gong L (2009) Graphene oxide: structural analysis and application as a highly transparent support for electron microscopy. ACS Nano 3:2547–2556. doi:10.1021/nn900994t

Wojtoniszak M, Zielinska B, Kalenczuk RJ, Mijowska E (2012) Photocatalytic performance of titania nanospheres deposited on graphene in coumarin oxidation reaction. Mater Sci Pol 30(1):32–38. doi:10.2478/s13536-012-0008-1

Xu Y, Bai H, Lu G, Li C, Shi G (2008) Flexible graphene films via the filtration of water-soluble noncovalent functionalized graphene sheets. J Am Chem Soc 130:5856–5857. doi: 10.1021/ja800745y

Zhu C, Guo S, Fang Y, Dong S (2010) Reducing sugar: new functional molecules for the green synthesis of graphene nanosheets. ACS Nano 4:2429–2437. doi:10.1021/nn1002387