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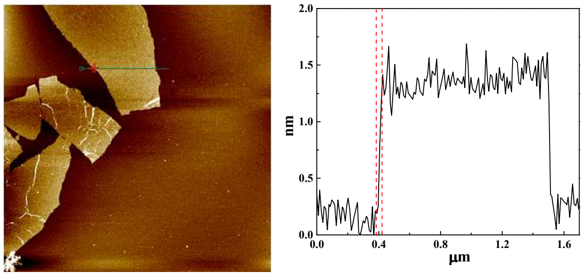

A fast and facile microwave-assisted method was developed for preparing GO.

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Cite this: DOI: 10.1039/c0xx00000x

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COMMUNICATION

Fast and facile microwave-assisted synthesis of graphene oxide nanosheets

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

A fast and facile approach is developed to convert graphite into graphene oxide (GO) with the aid of microwave irradiation. The GO product is characterized with various techniques. In comparison with the traditional Hummers route, the new method greatly shortens reaction time and is more environmentally friendly.

Graphene, which is a two-dimensional honeycomb lattice plane film composed of carbon atoms with sp^2 hybrid orbital, has drawn a great deal of attention due to its remarkable physicochemical properties such as a large specific surface area,[1,2] high carrier concentration and mobility,[3] and excellent optoelectronic properties.[4] This makes graphene an interesting object of fundamental research and a promising material for prospective practical applications in catalysis,[5-7] biosensors [8-11] and water purification.[12]

Recently, several methods were developed to prepare graphene, including micromechanical exfoliation of graphite,[13] chemical vapour deposition,[14] and direct liquid-phase exfoliation of graphite.[15,16] However, the most widely used approaches of preparing graphene are based on chemical, thermal and/or photochemical reduction of graphene oxide (GO), which is obtained from the oxidative exfoliation of graphite oxide. GO possesses different properties from graphene due to the covalent functionalization by oxygen-containing groups. GO sheets are strongly hydrophilic and can generate stable and homogeneous colloidal suspensions in aqueous and various polar organic solvents due to the electrostatic repulsion between the negatively charged GO sheets, which makes them easy to process.[17] In general, GO may be synthesized by Brodie,[18] Staudenmaier,[19] and Hummers methods.[20] All these methods involve the oxidation of graphite to various levels. Brodie and Staudenmaier methods require a combination of potassium chlorate ($KClO_3$) and nitric acid (HNO_3) to oxidize graphite, and the Hummers method involves a long-time treatment of graphite with potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$) and sulfuric acid (H_2SO_4). After the oxidizing procedure, GO sheets are obtained by exfoliating the oxidized graphite through sonication in aqueous solution. It is certain that these methods are time-consuming and harmful to the environment because of the use of concentrated oxidizing agents and the generation of toxic gases NO_2, N_2O_4, and/or ClO_2.

Herein, we report an ultrafast and facile method for the microwave-assisted preparation of GO. The GO product obtained by this new method is named M-GO. Our findings make it possible to fabricate mostly monolayer GO materials through low-cost facile processing techniques, which involve a microwave treatment to shorten the reaction time to several minutes. The process eliminates the steps that involve toxic or dangerous materials, and is very easy to operate and scalable.

The new method typically involves the following procedures. Concentrated H_2SO_4 (10 mL) was added to a mixture of graphite flakes (0.1 g, SP1 graphite, purchased from American Bay Carbon (Bay City, MI)) and $KMnO_4$ (0.9 g) in a 500 mL three-neck flask. After the mixture was stirred for 5 min, it was placed in a microwave cavity. The microwave oven (XiangHu, XH-300A) was then operated at a power of 250 W, in 30-s cycles for a total reaction time of 150 s. At the end of each cycle, the flask was placed in an ice bath for cooling down rapidly. Finally, 15 mL of 30% H_2O_2 was dropwise added, and the reaction was carried out for about 2 min with stirring. The mixture was centrifuged at 13000 rpm for 10 min (Heraeus Multifuge X1) and the supernatant was decanted away. The solid was washed 3 times in succession with 5% HCl, and then with deionized water until the solution pH was close to neutral. In each wash step, the mixture was centrifuged 13000 rpm for 10 min and the supernatant was again discarded. The obtained product was dispersed in 100 ml water with stirring for 5 min. Only a few of black graphite particles were precipitated at the bottom of the beaker. After the black graphite particles were removed, the suspension was exfoliated further by ultrasonication for 0.5 h, and used as a stock of M-GO suspension in water.

Typical transmission electron microscopic (TEM) images of M-GO were presented in Fig. 1. A low-magnification TEM micrograph (Fig. 1(a)) showed the M-GO sample was in the form of monolayer sheets with sizes upto micrometers (in width). The M-GO sheets exhibited a relatively sharp border and statistical TEM analysis indicated that their average size was about 5 μm. In addition, M-GO sheets showed crumpled wave-like shape, which is the intrinsic nature of graphene. Such crumpled structure allows the sheet to have no scrolling.[21] The high resolution TEM micrograph (Fig. 1(b)) clearly showed that the border of the GO sheets were usually scrolled and partially folded at their edges.

As shown in Fig. 2a, X-ray diffraction (XRD) patterns of graphite, H-GO and M-GO were obtained, where H-GO was obtained with a modified Hummers method. The graphite exhibited a single well-defined peak at 2θ=26.4° with an interlayer space of ~0.337 nm, corresponding to (002) plane. For

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H-GO and M-GO, this peak completely disappeared and a peak of the (002) crystalline plane was observed at 10.2° with an interlayer space of ~0.86 and 0.87 nm, respectively. The XRD data show the transformation of the interlayer spacing (d_{002} spacing) from 0.337 to 0.87 nm, which is a clear indication of the transformation from graphite to GO. The distance between consecutive carbon layers is increased for GO due to the introduction of oxygen-containing functional groups to the carbon basal plane.[22] Compared with H-GO, the peak of M-GO is sharper. It indicates that the thickness of GO with microwave condition is more uniform.

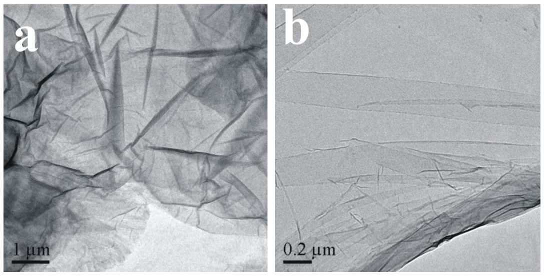

Fig. 1. TEM images of M-GO with different magnifications.

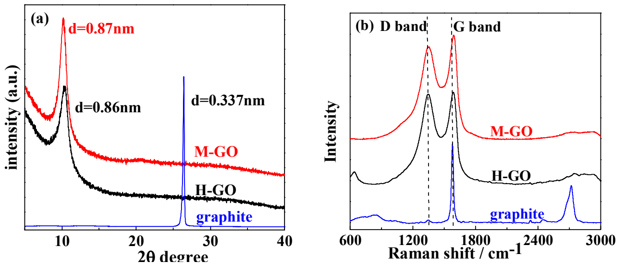

Fig. 2. (a) XRD patterns and (b) Raman spectra of graphite, H-GO and M-GO.

Raman spectra were obtained to characterize the structure of H-GO, M-GO and graphite. As shown in Fig. 2b, H-GO and M-GO yielded grossly similar Raman spectra. Both H-GO and M-GO Raman spectra exhibited G peaks at ~1588 cm^{-1} and D peaks at ~1347 cm^{-1}, which are characteristic of GO. The broadening and the shift of G line to higher frequency and the appearance of a broad D band point to intense formation of structural defects and dramatic break up of the original graphite domains, which is in a good agreement with the crystalline changes deduced from the XRD data. This high density of defects in GO is due to the large abundance of oxygenated functional groups that disrupt the planar sp^2 structure.[23] In addition, The intensity ratio of D to G band (I_D/I_G) is correlated to the in-plane crystal domain size. The ratio of I_D/I_G was decreased from 0.97 for H-GO to 0.90 for M-GO. This indicates that the size of the sp^2 domains of M-GO is larger with less defects, being in favour of reduction of GO. Fourier transform infrared (FT-IR) spectra were also recorded (Fig. 3a). Both H-GO and M-GO had similar IR characterizations: the bands at 1726, 1400, 1221 and 1054 cm^{-1} corresponded to C=O (COOH) stretching vibration, O-H deformation vibration, C-O (epoxy) and C-O (alkoxy) stretching vibration, respectively. The band at 1605 cm^{-1} was C=C (C-C) stretching vibration.[12,24] The broad band at 3412 cm^{-1} was considered as the vibration of O-H and/or water molecules. UV/vis absorption spectra were shown in Fig. 3b. The λ_{max} value of M-GO, corresponding to $\pi \rightarrow \pi^*$ transitions (conjugation), was almost the same as that (~230 nm)of H-GO, being well consistent with that previously reported for GO.[25] Similarly, a shoulder peak occurred at ~300 nm for both M-GO and H-GO, which was attributed to $n \rightarrow \pi^*$ transitions of the carbonyl groups. All the spectroscopic characterization results suggests that M-GO are very similar to H-GO in structure.

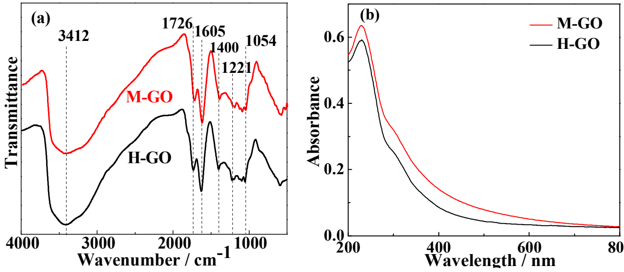

Fig. 3. (a) FT-IR and (b) UV/vis absorption spectra of H-GO and M-GO.

Atomic force microscopy (AFM) characterization is a direct method of quantifying the thickness of the exfoliated GO. As shown in Fig. 4, the cross-sectional view of the typical AFM image of M-GO indicated that the average thickness of M-GO sheets was about 1.1 nm, suggesting a successful exfoliation of graphite down to individual GO sheets under the microwave conditions. It is known that the basal planes of the graphene sheets in GO are decorated mostly with epoxide and hydroxyl groups, in addition to carbonyl and carboxyl groups.[26] Therefore, GO is expected to be thicker than a pristine graphene sheet with a well-known thickness of 0.34 nm. Moreover, it is somewhat larger than the inter layer spacing of GO (0.87 nm) measured by XRD. The reason is that oxygen-containing functional groups disrupt the original conjugation and introduces lattice defects to result in folds and distortions of the sheets.[22]

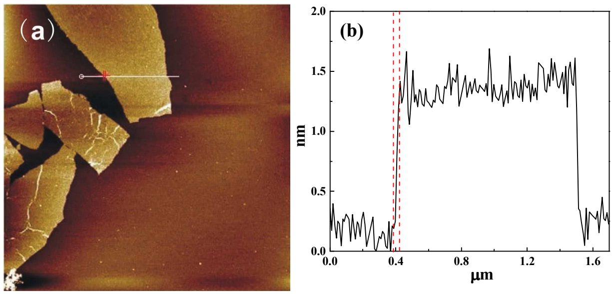

Fig. 4. (a) Tapping mode AFM image and (b) height profile of M-GO.

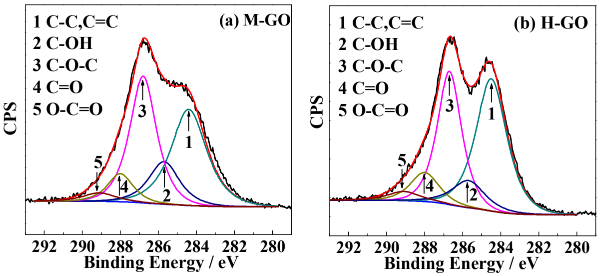

Fig. 5. Deconvolution of the C1s XPS peak of (a) M-GO and (b) H-GO.

As shown in the X-ray photoelectron spectroscopic (XPS) survey scan in Fig. 5, The meticulous deconvolution of the C1s XPS spectra of H-GO and M-GO samples gave five components at 284.4, 285.7, 286.7, 288, and 289.1 eV, corresponding to C=C/C-C in aromatic rings, C-OH, C-O-C (epoxy), C=O, and COOH (carboxyl) groups, respectively.[24] These results show

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clearly that the microwave irradiation process has introduced oxygenated functional groups into the graphene surface, which may be similar to the result by traditional Hummers' method. From the XPS analysis, we obtained the percentages of C and O elements and O/C atomic ratio on the surface of H-GO and M-GO samples. The O/C atomic ratio of H-GO and M-GO was 0.49 and 0.53, respectively.

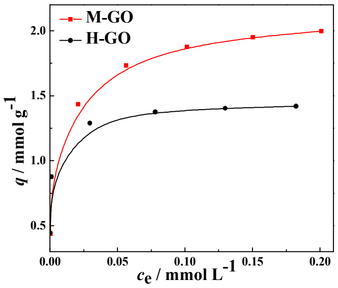

Fig. 6. Adsorption isotherms of MB on H-GO and M-GO.

The adsorption of methyl blue (MB) on H-GO and M-GO are compared in Fig. 6. The maximum adsorption capacities of H-GO and M-GO were obtained as 1.42 and 2.02 mmol g^{-1} (Table 1), respectively. The enhanced adsorption capacity of M-GO may be due to more adsorption sites provided by the increased oxygen-containing functional groups on M-GO.

Table 1. Maximum adsorption capacity (q_m) and Langmuir constant (K_L) for adsorption of MB on H-GO and M-GO

Adsorbents	q_m (mmol g^{-1})	K_L(L $mmol^{-1}$)	R^2
H-GO	1.42	703	0.999
M-GO	2.02	195	0.997

In conclusion, we presented an ultrafast and facile method to prepare GO from graphite by microwave irradiation. The new method had significant advantages over Hummers' method and other traditional chemical oxidation methods. The new method yielded GO having a higher degree of oxidation with an oxygen/carbon atomic ratio of 0.53. The reaction time was shortened to several minutes in the new approach, being much shorter than that required in Hummers' method (about 5 h). The control of the reaction temperature in the new method was also much simplified, in contrast to the three special temperature control steps in Hummers' method. Moreover, the preparation with the new method did not generate toxic gases such as NO_2 and N_2O_4 because the use of nitrate was eliminated. Therefore, the new method is environmentally friendly, and it will greatly helpful for the large-scale production of GO.

Acknowledgements

This work was supported by the National High Technology Research and Development Program of China (863 Program) (Grant No. 2012AA06A304) and the National Science Foundation of China (Grant Nos. 21177044 and 21377169).

Notes and references

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Preparation of H-GO by Hummers method.[15] In brief, concentrated H_2SO_4 (46 mL) was added to a mixture of graphite flakes (1 g) and $NaNO_3$ (1 g) in a 250 mL beaker. The mixture was stirred for 0.5 h in an ice bath at 5 °C. $KMnO_4$ (6 g) was added slowly in small portions to keep the temperature below 5 °C, being followed by stirring for 2 h. Then the mixture was heated up to 35 °C and stirred for 2 h. After that, 46 mL of deionized water was gradually added into the solution. The reaction temperature was raised to 98 °C. After it was maintained at 98 °C for 15 min, the heat was removed. Additional water (100 mL) and 30% H_2O_2 (20 mL) were added. The mixture was centrifuged and washed with deionized water sequentially. The obtained product was dispersed in water, exfoliated through ultrasonication for 1 h, and used as a stock of H-GO suspension in water.

Batch adsorption experiments. The adsorption experiments were performed on a shaker at a shaking speed of 160 rpm. The aqueous solutions of MB at concentrations of 0.027-0.321 mmol L^{-1} were separately added to 100-mL conical flasks with seals. A given amount of H-GO or W-GO suspension (60 mg L^{-1}) was added into the solution. The total solution volume was rapidly adjusted to 50 mL by adding water. At given time intervals, aliquots of the suspension (about 1 mL) were sampled. After the suspension was immediately centrifuged at a high speed of 16000 rpm on Hettich EBA21 to remove the solids, the concentration of MB in the supernatant was analyzed by measuring its absorbance at its adsorption maximum wavelength on a UV-Vis spectrophotometer (CARY 50 Scan). The amount of phenolic compounds at equilibrium was calculated with eq. (1),

$$q_e = \frac{(c_0 - c_e)}{m} V \qquad (1)$$

where q_e (mmol g^{-1}) is the equilibrium adsorption capacity of the adsorbent, c_0 and c_e (mmol L^{-1}) are the initial and final concentrations of MB in solution, V is solution volume, and m is the mass of the used H-GO or M-GO.

Characterization. TEM images were obtained on a TECNAI G2 20U-Twin electron microscope, using an accelerating voltage of 200 kV. XPS analysis was conducted on a VG Multilab 2000 spectrometer (Thermo Electron Corporation) with Al Kα radiation as the exciting source (300W). The binding energies were corrected according to C 1s line at 284.6 eV. After subtracting the Shirley-type background, the core-level spectra were decomposed into their components with mixed Gaussian-Lorentzian (20:80) shapelines using the CasaXPS software. FT-IR spectra were measured on a Bruker VERTEX 70. Raman spectra were measured on a confocal laser micro-Raman spectrometer (Thermo Fischer DXR, USA) equipped with a diode laser of excitation of 532 nm (laser serial number: AJC1200566). AFM study was performed by means of Veeco DI Nanoscope Multi Mode-8 SPM system. XRD pattern was obtained on a diffractometer with Cu Kα radiation (PANalytical B.V. X'Pert PRO), operated at 40 mA and 40 kV.

1 K. Geim and K. S. Novoselov, Nat. Mater., 2007, 6, 183-191.
2 S. Park and R. S.Ruoff, Nat. Nanotechnol, 2009, 4, 217-224.
3 S. V. Morozov, K. S. Novoselov, F. Schedin, D. Jiang, A. A. Firsov and A. K. Geim, Phys. Rev. B, 2005, 72, 201401-1-4.
4 F. Bonaccorso, Z. Sun, T. Hasan and A. C. Ferrari, Nat. Photonics, 2010, 4, 611-622.
5 R. Leary and A. Westwood, Carbon, 2011, 49, 741-772.
6 D. Chen, H. B. Feng and J. H. Li, Chem. Rev., 2012, 112, 6027-6053.
7 F. X. Jiang, Z. Q. Yao, R. R. Yue, Y. K. Du, J. K. Xu, P. Yang and C. Y. Wang, Int. J. Hydrogen Energy, 2012, 37, 14085-14093.
8 W. R. Yang, K. R. Ratinac, S. P. Ringer, P. Thordarson, J. J. Gooding and F. Braet, Angew. Chem. Int. Ed., 2010, 49, 2114-2138.
9 L. M. Lu, O. Zhang, J. K. Xu, Y. P. Wen, X. M. Duan, H. M. Yu, L. P. Wu and T. Nie, Sens. Actuators B, 2013, 181, 567-574.
10 Y. S. Gao, J. K. Xu, L. M. Lu, L. P. Wu, K. X. Zhang, T. Nie, X. F. Zhu and Y. Wu, Biosens. Bioelectron., 2014, 62, 261-267.
11 P. P. Zhang, X. Y. Zhang, S. Y. Zhang, X. Lu, Q. Li, Z. Q. Su and G. Wei, J. Mater. Chem. B, 2013, 1, 6525-6531.

RSC Advances Accepted Manuscript

12 X. B. Wang, S. S. Huang, L. H. Zhu, X. L. Tian, S. H. Li and H. Q. Tang, Carbon, 2014, 69, 101-112.
13 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang and Y. Zhang, Science, 2004, 306, 666-669.
14 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, 2009, 457, 706-710.
15 W. C. Du, J. Lu, P. P. Sun, Y. Y. Zhu and X. Q. Jiang, Chem. Phys. Lett., 2013, 568–569, 198-201.
16 W. C. Du, X. Q. Jiang and L. H. Zhu, J. Mater. Chem. A, 2013, 1, 10592-10606.
17 J. P. Zhao, S. F. Pei, W. C. Ren, L. B. Gao and H. M. Cheng, ACS Nano, 2010, 4, 5245-5252.
18 B. C. Brodie, Ann. Chim. Phys., 1860, 59, 466-472.
19 L. Staudenmaier and Ber. Deut., Chem. Ges., 1898, 31, 1481-1487.
20 W. S. Hummers and R. E. Offeman, J. Am. Chem. Soc., 1958, 80, 1339.
21 I. Janowska, K. Chizari, O. Ersen, S. Zafeiratos, D. Soubane and V. D. Costa, Nano Res., 2010, 3, 126-137.
22 A. M. Abdelkader, I. A. Kinloch and R. A. W. Dryfe, Chem. Commun., 2014, 50, 8402-8404.
23 K. N. Kudin, B. Ozbas, H. C. Schniepp, R. K. Prud'homme, I. A. Aksay and R. Car, Nano Lett., 2008, 8, 36-41.
24 P. G. Ren, D. X.Yan, X. Ji, T. Chen and Z. M. Li, Nanotechnology, 2011, 22, 055705.
25 D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z.Z Sun, A. Slesarev, L. B. Alemany, W. Lu, and J. M. Tour, ACSnano, 2010, 4, 4806-4814.
26 J. F. Shen, Y. Z. Hu, M. Shi, X. Lu, C. Qin, C. Li, and M. Ye, Chem. Mater., 2009, 21, 3514-3520.

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