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Reducing Graphene Oxide via Hydroxylamine: A Simple and Efficient Route to Graphene

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ABSTRACT: Bulk-scale production of individual graphene sheets is still challenging although several methodologies have been developed. We report here a rapid and cost-effective approach to reduction of graphene oxide (GO) using hydroxylamine as a reductant. We demonstrated that the reduction of GO with hydroxylamine could take place quickly under a mild condition, and the as-produced graphene sheet showed high electrical conductivity, fair crystalline state, and admirable aqueous dispersibility without using any stabilizing reagents. A mechanism for removal of epoxide and hydroxyl groups from GO by hydroxylamine has been proposed. Comparing with other reported methods, the reduction of GO with hydroxylamine should be a preferable route to bulk-scale production of the graphene because it is simple, efficient, and cost-effective.
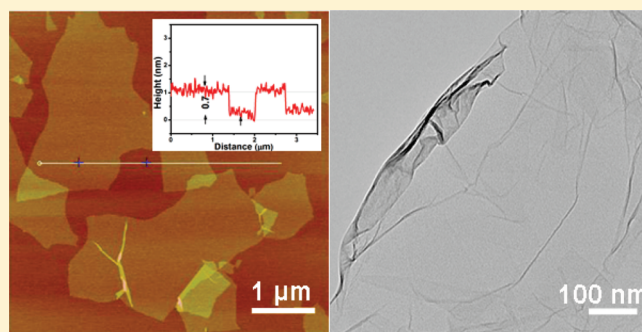
■ INTRODUCTION

Graphene and chemically reduced graphene oxide (CRG) sheets, having single-atomic layered structure and unique mechanical,[1] thermal,[2] and electrical[3] properties, hold great promise for many technological applications.[4−6] The precondition for their practical application is to obtain high-quality individual graphene or CRG sheets in bulk quantity. Approaches including micromechanical[7,8] and ultrasonication-assisted exfoliations of graphite,[9] chemical vapor deposition,[10] epitaxial growth,[11−13] and solution-based chemical reduction of graphene oxide (GO)[14−21] have been explored for this purpose. Among them, the solution-based chemical reduction of GO has been considered as one of the most efficient ways to bulk-scale production of graphene. So far, a number of chemical reductants and corresponding reduction procedures have been developed for the GO reduction. For instance, using hydrazine[18,22,23] or its derivates[24,25] as a reductant, GO sheets suspended in water or organic solvents, such as N,N-dimethylformamide (DMF)[14] and N-methyl-2-pyrrolidinone (NMP),[26] can be reduced rationally to CRG at ambient or under hydro/solvothermal conditions. However, the severe poisonous and explosive characteristics of hydrazine and its derivates require that precautions must be taken when large quantities of hydrazine or its derivates are used.[27] In our previous work, considering the environmentally friendly property and the mild reduction capability, L-ascorbic acid (Vitamin C) was used to the reduction of GO in water, and we found the oxygen-containing groups on GO could be removed considerably.[28] However, the strong reactivity with water and the high price of L-ascorbic acid are the real draw-backs of the method used for producing a large quantity of the CRG in

aqueous dispersion. Other chemicals, such as sodium borohydride,[29] hydroquinone,[30] sodium hydrogen sulfite,[31] hydroiodic acid,[32] and even the bacteria[33] were used for the reduction of GO. For bulk quantity production of high-quality CRG, each of them has its advantages and disadvantages. The key issues in most cases are that the oxygen-functional groups of GO could not be removed thoroughly and thus the conjugate electronic state of graphene could not be restored completely. The as-generated CRG sheets exhibited poorer electrical and mechanical properties than those of the pristine graphene sheets.[16] Additionally, the dispersibility of CRG sheets depends strongly on the capping agents used during the reductions. The progress in this research area has been recently reviewed.[4−6,34−36]

Hydroxylamine (NH_2OH) and its chloride and sulfate salts are commonly used for reducing metal ions, such as Ag^+, Au^{3+}, Pd^{2+}, and Cu^{2+} et al., removing monochloramine, a harmful species in the chlorine-treated water,[37−40] and even in removing oxygen.[41] Hydroxylamine has high reduction capability but weak reactivity with water and other solvents that make it an appropriate reductant for the GO reduction in aqueous suspension. In comparison with hydrazine and its derivates, the most commonly used reductants for GO reduction, hydroxylamine exhibits relatively lower poisonous and explosive properties. The price of hydroxylamine is much lower than that of L-ascorbic acid. These properties render the hydroxylamine an appropriate reductant for preparation of graphene in bulk quantity.

Herein, we describe the reduction of GO in water using hydroxylamine generated in situ through the reaction of hydroxylamine hydrogen chloride ($NH_2OH \cdot HCl$) with ammonia. The reduction extent, the structure including morphology and chemical composition, and the electrical conductivity of the as-produced CRG sheets have been characterized by a variety of complementary methods, including atomic force microscopy (AFM), transmission electron microscopy (TEM) and electron diffraction (ED), scanning electron microscopy (SEM), X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and other spectroscopic measurements. We demonstrated that NH_2OH can reduce GO efficiently and generate a stable aqueous dispersion of CRG without using any polymeric or surfactant stabilizers during the reduction process, which should be beneficial to the practical applications of the CRG.

■ EXPERIMENTAL SECTION

Materials. Graphite (crystalline powders, ∼500 mesh) was purchased from Shanghai Yifan graphite Co., Ltd., Shanghai, China. Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) and sodium nitrate ($NaNO_3$) were obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. $KMnO_4$, concentrated H_2SO_4, and HCl were acquired from Shanghai Lingfeng Chemical Reagent Co., Ltd., Shanghai, China. All of the reagents were used as received.

Preparation and Reduction of GO. GO was prepared from graphite powder through a modified Hummers method as we described in our previous work.[28,42,43] In a typical experiment of the GO reduction with hydroxylamine, 25 mg of $NH_2OH \cdot HCl$, and 200 μL of ammonia aqueous solution (30% in volume) were added into 50 mL, 0.25 mg/mL aqueous suspension of GO in a 500 mL flask. The mixture was heated in a water bath at ∼90 °C; meanwhile the color of the mixture changed from yellowish brown to homogeneous black indicating the reduction took place. The as-generated CRG was separated from the reaction mixture through filtration and washed with ultrapure water for three times.

Characterization. AFM images of GO and CRG were acquired using a Multimode Nanoscope V scanning probe microscopy (SPM) system (Bruker, USA). The commercially available AFM cantilever tips with a force constant of ∼50 N/m and resonance vibration frequency of ∼350 kHz (Bruker, USA) were used. TEM images and selected area electron diffraction (SAED) patterns were acquired using a JEM-2010 transmission electron microscope (JEOL Ltd., Japan) operated at 200 kV. The specimens of TEM were prepared by placing the aqueous suspension (∼0.05 mg/mL) of GO or CRG on the copper grids and dried under ambient conditions. SEM images were obtained on an Ultra 55 scanning electron microscope (Zeiss, Germany). The FTIR spectra were acquired on a EQUINOX 55 FTIR spectrometer (Bruker, Germany). The specimens for FTIR measurement were prepared by grinding the dried powder of GO or CRG with KBr together and then compressed into thin pellets. Raman spectra were recorded on an Invia/Reflrx Lasser Micro-Raman spectroscope (Renishaw, England) with an excitation laser beam wavelength of 514 nm. The powders of GO or CRG placed on a clean SiO_2/Si substrate were used for the Raman measurement. The electrical conductivity of CRG was measured using a SZ-82 digital four-point probe system (Suzhou, China). The X-ray powder diffraction patterns were recorded on
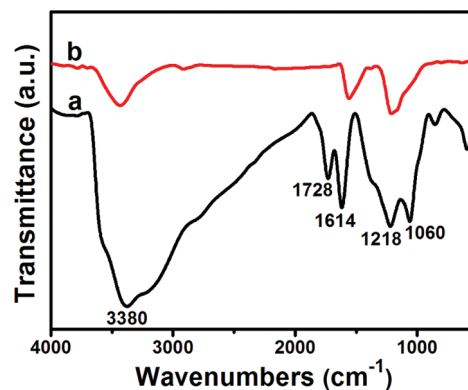

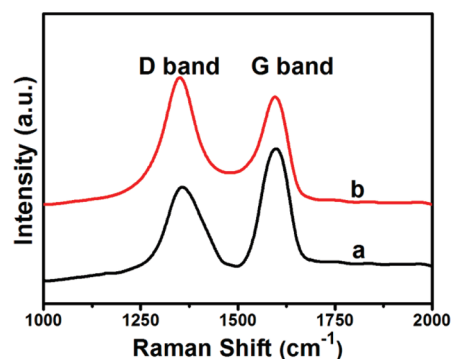**Figure 1.** FTIR spectra of (a) GO and (b) CRG reduced with hydroxylamine for one hour.

Figure 2. Raman spectra of (a) GO and (b) CRG reduced with hydroxylamine for one hour.

a BRUKER-AXS diffractometer (Bruker, Germany) using Cu Kα radiation (λ = 0.154 nm). The X-ray photoelectron spectroscopy measurements were performed on a Axis Ultra DLD spectrometer, (Kratos Analytical, UK) using monochromated Al Kα source at 15 kV.

■ RESULTS AND DISCUSSION

Hydroxylamine (NH_2OH) is generally prepared through the reaction of its salts, such as hydroxylamine hydrochloride, phosphate, or sulfate, with alkali and used instantly.[37,38] In this work, the hydroxylamine was generated by adding the concentrated ammonia aqueous solution to the aqueous solution containing the mixture of GO and hydroxylamine hydrochloride ($NH_2OH \cdot HCl$), and used in situ for the GO reduction. The pH of the reaction mixture was kept above 10, at which the reduction took place efficiently (indicated by the color change of the reaction mixture from the yellowish brown to black) and the as-generated CRG could be suspended stably in the reaction system (water). The reduction process was followed by complementary spectroscopic experiments. Figure 1 shows the typical FTIR spectra of GO before and after the hydroxylamine reduction for one hour. Before the reduction, as shown in part a of Figure 1, the vibration and deformation bands of O—H at 3380, the stretching vibration band of C=O at 1728 cm^{-1}, and the stretching vibration bands C—O of epoxy and alkoxy at 1218 and 1060 cm^{-1} respectively demonstrate that the GO has abundant oxygen containing groups. After one hour reduction, the intensities of the all FTIR peaks correlated to the oxygen
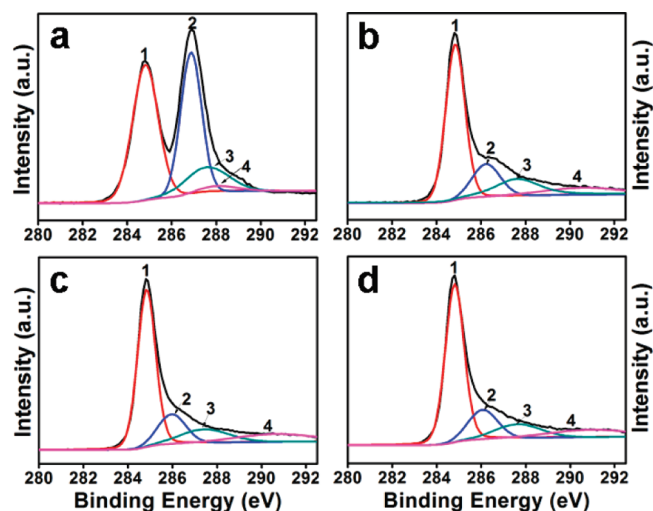
Figure 3. C1s XPS spectra of GO before (a) and after being reduced for 30 min (b), 1 h (c), and 12 h (d). The peaks 1, 2, 3, and 4 correspond to C=C/C−C in aromatic rings, C−O (epoxy and alkoxy), C=O, and COOH groups, respectively.

Table 1. Carbon to Oxygen (C:O) Atomic Ratios of GO and the CRG Reduced via L-Ascorbic Acid, Hydrazine, and Hydroxylamine for Different Reduction Times

reductant	reduction time/h	C:O (atomic ratio)
L-ascorbic acid	0	2.0:1
	24	2.4:1
	48	5.7:1
NH$_2$OH	0	1.9:1
	0.5	6.1:1
	1	9.7:1
NH$_2$NH$_2$[24]	0	2.7:1
	24	10.3:1

containing groups decreased dramatically as shown in part b of Figure 1. The reduction of GO can also be monitored by the variation of the relative intensities of G band at 1596 cm^{-1} corresponding to the first-order scattering of the E$_{2g}$ mode, and D band at 1357 cm^{-1}, arising from a breathing mode of κ-point phonons of A$_{1g}$ symmetry in the Raman spectra of the GO during the reduction.[44] As shown in Figure 2, with the reduction progressing, the ratio of D/G increased gradually, implying that the new domains of conjugated carbon atoms (bonded in sp^2 hybridization) were formed accompanying the removal of the oxygen containing groups.

The reduction extent of the GO by hydroxylamine was characterized further by XPS. Figure 3 shows the C 1s XPS peaks of GO and CRG reduced with hydroxylamine for 0.5, 1, and 12 h, respectively. The spectrum of GO, in part a of Figure 3, can be deconvoluted into four different peaks that correspond to carbon atoms assuming different binding statues. The peaks centered at the binding energies of 284.8, 286.0, 287.6, and 288.2 eV were assigned to the carbon atoms of C=C/C−C in aromatic rings, C−O (epoxy and alkoxy), C=O, and COOH, respectively. With the reduction progressing, the intensities of XPS peaks of the carbon atoms bonded to oxygen decreased rapidly, especially that of C−O (epoxy and alkoxy), indicating most of the epoxide
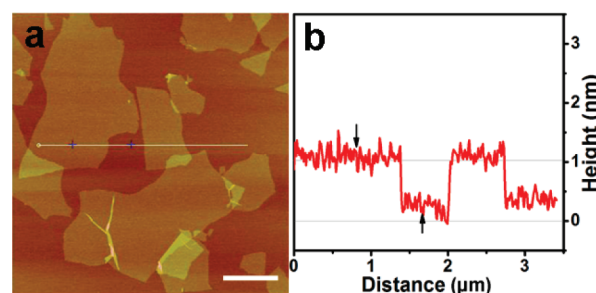

Figure 4. (a) Tapping mode AFM image of CRG sheets deposited on freshly cleaved mica substrate. (b) Height profile of CRG sheets. The scale bar equals 1 μm.
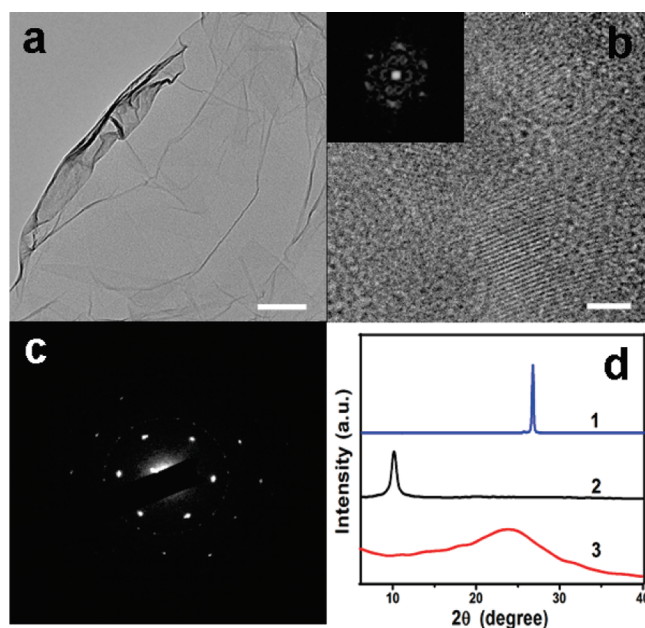

Figure 5. (a) TEM and (b) HRTEM images of CRG sheets. The insert in (b) is a FFT pattern of HRTEM image. (c) SAED, and (d) XRD patterns of the pristine graphite (1), GO (2), and CRG sheets (3). The scale bars in (a) and (b) equal 100 and 2 nm, respectively.

and hydroxyl functional groups were removed. Comparably, the intensities of the C 1s XPS peaks of the CRG reduced with hydroxylamine for 1 and 12 h are almost the same (parts c and d of Figure 3). This result illustrates that the reducing reaction might reach the equilibrium state within 1 h revealing the hydroxylamine has strong reduction capability to GO. The carbon to oxygen (C:O) ratios deduced from XPS data of the GO and CRG prepared with different reduction times, were compared with those of the CRGs produced with L-ascorbic acid and hydrazine in Table 1. It shows clearly that, in the case of hydroxylamine, the C:O ratio of the CRG increased from 1.7:1 to 6.1:1 after only half an hour, and reached to 9.8:1 after one hour. In contrast, the C:O ratios of the CRG reduced using L-ascorbic acid and hydrazine increased from 2.0:1 to 5.7:1, and from 2.7:1 to 10.3:1,[24] need 48 and 24 h, respectively. These results demonstrate unambiguously that the hydroxylamine can reduce the GO efficiently.

The detailed morphology and crystalline structure of as-generated single-layered CRG sheets were studied by AFM, TEM, SAED, and XRD. Figure 4 depicts a typical tapping mode

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Scheme 1. Schematic Representation of the Proposed Mechanism for the Reduction of GO with Hydroxylamine
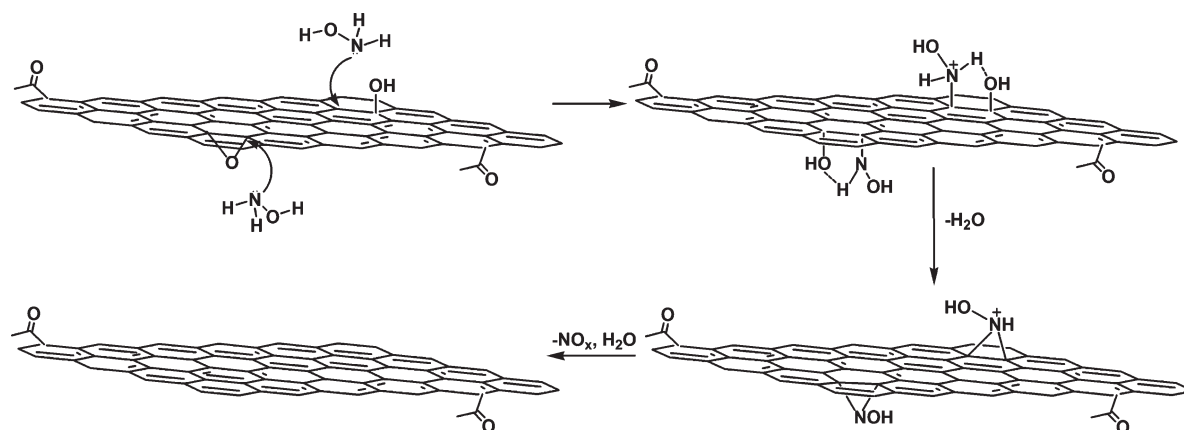

Table 2. Electrical Conductances of the CRG Generated Using L-Ascorbic Acid, Hydrazine, and Hydroxylamine As Reductants

reductant	reduction time/h	reaction temp /°C	electrical conductance/Sm^{-1}
L-ascorbic acid	48	23^a	800
NH$_2$NH$_2$	24	90	1187
NH$_2$OH	1	90	1122

^{a} The reduction was performed at relatively lower temperature, because L-ascorbic acid reacts with water severely at 90 °C.

AFM image and the crossing section profile of as-generated CRG sheets deposited on freshly cleaved mica surface. The uniform contrast of the AFM images of CRG sheets implies that all of them possess the same thickness. The thickness is about 0.7 nm measured from the crossing section profile curve (part b of Figure 4) revealing the single layered motif. The morphology of the CRG was further confirmed using TEM imaging. Figure 5 shows a TEM image of CRG sheet deposited on Cu grid (without the carbon film). Except for a few wrinkles, the uniformity and relatively low contrast of the TEM image demonstrate that the CRG have uniformed layer motif. To get insight into the crystalline structure of the CRG sheets, high-resolution transmission electron microscopy (HRTEM) image and the SAED patterns were recorded. The HRTEM image, as seen in part b of Figure 5, shows the hexagonal patterns that are verified by the fast Fourier transform (FFT) result (insert in part b of Figure 5). The corresponding SAED pattern, part c of Figure 5, shows hexagonal symmetry diffraction spots revealing that the CRG sheets have crystalline state. The bulk crystalline structure of the CRG powders was characterized using XRD. It was found that, instead of the XRD peak of GO (d-spacing 8.77 Å, 2θ = 10.07°), a new broaden diffraction peak (d-spacing 3.72 Å, 2θ = 23.88°) appeared that closes to the (002) XRD peak (d-spacing 3.35 Å, 2θ = 26.56°) of the pristine graphite. The overall results demonstrate that the GO is readily reduced by hydroxylamine.

The mechanism that hydroxylamine reduces metal ions has been proposed.[37,38] However, the GO has several different oxygen-containing groups, such as epoxide, hydroxyl, and carboxylic groups, the detailed mechanisms for reducing these groups by hydroxylamine are not clear to us at moment. However, as shown in Scheme 1, for the reduction of epoxide groups on the GO, we speculate that the hydroxylamine molecules might attack the carbon atom of the epoxide to turn it as a hydroxyl group accompanying with one proton transfer. After releasing one H$_2$O molecule, an N-hydroxylaziridine intermediate was formed. The hydroxylamine molecules may also attack the β carbon of the hydroxyl group in the GO and transfer a proton to the hydroxyl group to release it as H$_2$O coming with the formation of a similar N-hydroxylaziridine intermediate, too. The N-hydroxylaziridine intermediate will quickly convert into a conjugated vinyl (ethenyl) group and release unstable specie of nitrogen oxide (NO$_X$) and H$_2$O. As evidenced by IR spectra, the carboxyl groups were reduced; however, the reducing mechanism is not fully understood yet.

The high electrical conductance is a distinctive character for the CRG in comparison with the GO, which reflects also the reduction extent of the GO. To evaluate the electrical conductance of the CRG, the circle pallets with thickness of ~0.25 mm and the diameter of 10 mm of CRG powders, reduced by hydroxylamine for 1 h at 90 °C, by hydrazine for 24 h at 90 °C, and by L-ascorbic acid for 48 h at 23 °C (L-ascorbic acid reacts with water severely at 90 °C, therefore, the reduction was performed at relatively lower temperature) were prepared using a tablet compression machine. The electrical conductivity of CRG was measured using a digital four-point probe system.[28] To get a reliable electrical conductance data, the probes were carefully placed on the CRG, and five different sites of each sample were chosen to measure. The results were summarized in Table 2. The electrical conductance data of the CRGs prepared by using hydroxylamine, hydrazine, and L-ascorbic are 1122, 1187, and 800 S/m, respectively. This result is fully in agreement with the C to O ratios shown in the Table 1 and demonstrates unambiguously that hydroxylamine is an efficient reductant for GO reduction. It is worth pointing out that the as-prepared CRG sheets could be suspended stably at ambient conditions in the reaction mixture (aqueous) for at least several days. The reason might be that the pH of the reaction mixture was kept above 10, at which the CRG surface should be negatively charged, which repulses each other electrostatically and prevents the aggregation.[17]

CONCLUSIONS

In summary, we have demonstrated that the GO sheets could be reduced efficiently by hydroxylamine in an aqueous system under moderate conditions. The as-generated CRG sheets can be suspended stably in the aqueous solution without using any stabilizers, which should be a benefit to the further processing and also the practical applications of the CRG. The mechanism for removal of epoxide and hydroxyl groups from GO has been proposed and will be helpful for exploitation of the novel strategies for graphene preparation. Given the low price of hydroxylamine in comparison with L-ascorbic acid, less poisonous properties than those of hydrazine and its derivates, and pronounced reduction capability under mild conditions, the reduction of the GO with hydroxylamine could be used as a simple and efficient route to the bulk preparation of graphene.

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REFERENCES

(1) Lee, C.; Wei, X.; Kysar, J. W.; Hone, J. *Science* **2008**, *321*, 385.

(2) Balandin, A. A.; Ghosh, S.; Bao, W.; Calizo, I.; Teweldebrhan, D.; Miao, F.; Lau, C. N. *Nano Lett.* **2008**, *8*, 902.

(3) Novoselov, K. S.; Morozov, S. V.; Mohinddin, T. M. G.; Ponomarenko, L. A.; Elias, D. C.; Yang, R.; Barbolina, I. I.; Blake, P.; Booth, T. J.; Jiang, D.; Giesbers, J.; Hill, E. W.; Geim, A. K. *Phys. Status Solidi B* **2007**, *244*, 4106.

(4) Geim, A. K.; Novoselov, K. S. *Nat. Mater.* **2007**, *6*, 183.

(5) Geim, A. K. *Science* **2009**, *324*, 1530.

(6) Rao, C. N. R.; Sood, A. K.; Subrahmanyam, K. S.; Govindaraj, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 7752.

(7) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Crigorieva, I. V.; Firsov, A. A. *Science* **2004**, *306*, 666.

(8) Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. V.; Morozov, S. V.; Geim, A. K. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 10451.

(9) Hernandez, Y.; Nicolosi, V.; Lotya, M.; Blighe, F. M.; Sun, Z.; De, S.; McGovern, I. T.; Holland, B.; Byrne, M.; Gun'Ko, Y. K.; Boland, J. J.; Niraj, P.; Duesberg, G.; Krishnamurthy, S.; Goodhue, R.; Hutchison, J.; Scardaci, V.; Ferrari, A. C.; Coleman, J. N. *Nat. Nanotechnol.* **2008**, *3*, 563.

(10) Kim, K. S.; Zhao, Y.; Jang, H.; Lee, S. Y.; Kim, J. M.; Kim, K. S.; Ahn, J.-H.; Kim, P.; Choi, J.-Y.; Hong, B. H. *Nature* **2009**, *457*, 706.

(11) Sutter, P. W.; Flege, J.-I.; Sutter, E. A. *Nat. Mater.* **2008**, *7*, 406.

(12) Berger, C.; Song, Z.; Li, X.; Wu, X.; Brown, N.; Naud, C.; Mayou, D.; Li, T.; Hass, J.; Marchenkov, A. N.; Conrad, E. H.; First, P. N.; Heer, W. A. d. *Science* **2006**, *312*, 1191.

(13) Berger, C.; Song, Z.; Li, T.; Li, X.; Ogbazghi, A. Y.; Feng, R.; Dai, Z.; Marchenkov, A. N.; Conrad, E. H.; First, P. N.; Heer, W. A. d. *J. Phys. Chem. B* **2004**, *108*, 19912.

(14) Wang, H.; Robinson, J. T.; Li, X.; Dai, H. *J. Am. Chem. Soc.* **2009**, *131*, 9910.

(15) Li, H.; Pang, S.; Feng, X.; Mullen, K.; Bubeck, C. *Chem. Commun.* **2010**, *46*, 6243.

(16) Park, S.; Ruoff, R. S. *Nat. Nanotechnol.* **2009**, *4*, 217.

(17) Li, D.; Muller, M. B.; Gilje, S.; Kaner, R. B.; Wallace, G. G. *Nat. Nanotechnol.* **2008**, *3*, 101.

(18) Stankovich, S.; Dikin, D. A.; Piner, R. D.; Kohlhaas, K. A.; Kleinhammes, A.; Jia, Y.; Wu, Y.; Nguyen, S. T.; Ruoff, R. S. *Carbon* **2007**, *45*, 1558.

(19) Li, X.; Zhang, G.; Bai, X.; Sun, X.; Wang, X.; Wang, E.; Dai, H. *Nat. Nanotechnol.* **2008**, *2008*, 538.

(20) Zhu, C.; Guo, S.; Fang, Y.; Dong, S. *ACS Nano* **2010**, *4*, 2429.

(21) Wang, Z.; Zhou, X.; Zhang, J.; Boey, F.; Zhang, H. *J. Phys. Chem. C* **2009**, *113*, 14071.

(22) Lomeda, J. R.; Doyle, C. D.; Kosynkin, D. V.; Hwang, W.-F.; Tour, J. M. *J. Am. Chem. Soc.* **2008**, *130*, 16201.

(23) Tung, V. C.; Allen, M. J.; Yang, Y.; Kaner, R. B. *Nat. Nanotechnol.* **2009**, *4*, 25.

(24) Stankovich, S.; Piner, R. D.; Chen, X.; Wu, N.; Nguyen, S. T.; Ruoff, R. S. *J. Mater. Chem.* **2006**, *16*, 155.

(25) Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. *Nature* **2006**, *442*, 282.

(26) Dubin, S.; Gilje, S.; Wang, K.; Tung, V. C.; Cha, K.; Hall, A. S.; Farrar, J.; Varshneya, R.; Yang, Y.; Kaner, R. B. *ACS Nano* **2010**, *4*, 3845.

(27) Furst, A.; Berlo, R. C.; Hooton, S. *Chem. Rev.* **1965**, *65*, 51.

(28) Zhang, J.; Yang, H.; Shen, G.; Cheng, P.; Zhang, J.; Guo, S. *Chem. Commun.* **2010**, *46*, 1112.

(29) Si, Y.; Samulski, E. T. *Nano Lett.* **2008**, *8*, 1679.

(30) Wang, G.; Yang, J.; Park, J.; Gou, X.; Wang, B.; Liu, H.; Yao, J. *J. Phys. Chem. C* **2008**, *112*, 8192.

(31) Chen, W.; Yan, L.; Bangal, P. R. *J. Phys. Chem. C* **2010**, *114*, 19885.

(32) Pei, S.; Zhao, J.; Du, J.; Ren, W.; Cheng, H. M. *Carbon* **2010**, *48*, 4466.

(33) Salas, E. C.; Sun, Z.; Luttge, A.; Tour, J. M. *ACS Nano* **2010**, *4*, 4852.

(34) Compton, O. C.; Nguyen, S. T. *Small* **2010**, *6*, 711.

(35) Allen, M. J.; Tung, V. C.; Kaner, R. B. *Chem. Rev.* **2010**, *110*, 132.

(36) Zhu, Y.; Murali, S.; Cai, W.; Li, X.; Suk, J. W.; Potts, J. R.; Ruoff, R. S. *Adv. Mater.* **2010**, *22*, 3906.

(37) Nichols, M. L. *J. Am. Chem. Soc.* **1934**, *56*, 841.

(38) James, T. H. *J. Am. Chem. Soc.* **1939**, *61*, 2379.

(39) Leopold, N.; Lendl, B. *J. Phys. Chem. B* **2003**, *107*, 5723.

(40) Robinson, D. M.; Hoppe, T. J.; J; Paslay, T.; Purser, G. H. *Int. J. Chem. Kinet.* **2004**, *38*, 124.

(41) Choudhary, V. R.; Jana, P.; Bhargava, S. K. *Catal. Commun.* **2007**, *8*, 811.

(42) Titelman, G. I.; Gelman, V.; Bron, S.; Khalfin, R. L.; Cohen, Y.; Bianco-Peled, H. *Carbon* **2005**, *43*, 641.

(43) Hummers, W. S.; Offeman, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 1339.

(44) Reich, S.; Thomsen, C. *Philos. Trans. R. Soc. London, Ser. A* **2004**, *362*, 2271.

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