

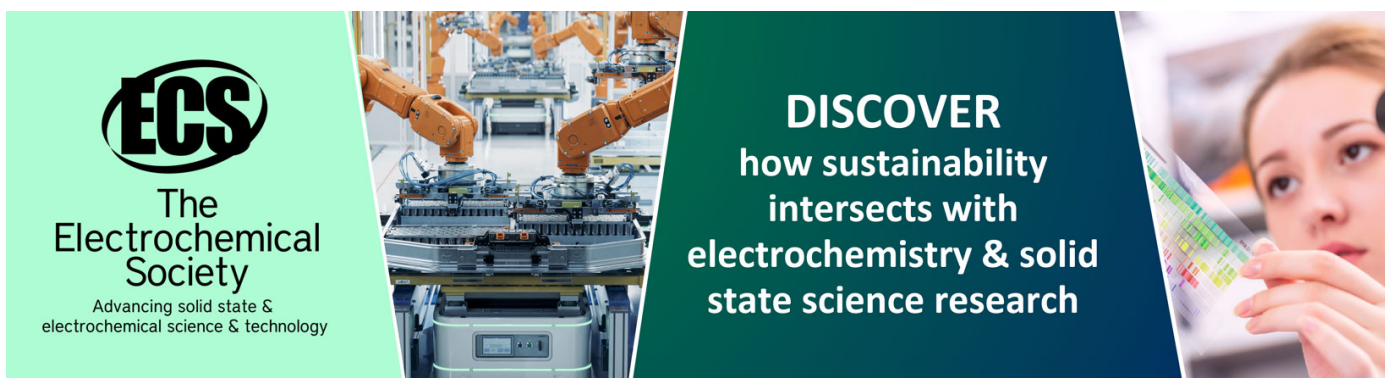
A simple and efficient method to prepare graphene by reduction of graphite oxide with sodium hydrosulfite

To cite this article: Tiannan Zhou *et al* 2011 *Nanotechnology* **22** 045704

View the [article online](#) for updates and enhancements.

You may also like

- [Quantification of the atomic surfaces and volumes of a metal cluster based on the molecular surface model](#)
Yifan Yu and Junzhi Cui
- [Muonic atom formation using the two-state approximation in different energy regions](#)
B Rezaei and S Jesri
- [A high-accuracy phase shifting retrieval approach based on phase shifts search](#)
Jiaosheng Li, Qinnan Zhang, Hanlin Wang et al.



ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

A simple and efficient method to prepare graphene by reduction of graphite oxide with sodium hydrosulfite

Tiannan Zhou¹, Feng Chen^{1,3}, Kai Liu¹, Hua Deng¹, Qin Zhang¹,
Jiwen Feng² and Qiang Fu^{1,3}

¹ College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, People's Republic of China

² State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Science, Wuhan 430071, People's Republic of China

E-mail: fengchen@scu.edu.cn and qiangfu@scu.edu.cn

Received 27 September 2010, in final form 25 November 2010

Published 20 December 2010

Online at stacks.iop.org/Nano/22/045704

Abstract

Inspired by an ancient reducing method used in textile production, sodium hydrosulfite was used to reduce graphite oxide as an efficient reducing agent in our work. The reduced materials were characterized by x-ray photoelectron spectroscopy, thermogravimetric analysis, wide-angle x-ray scattering, Raman spectroscopy, solid state ¹³C NMR spectroscopy and electrical conductivity measurements, respectively. The results showed that graphite oxide can be reduced with sodium hydrosulfite in a few minutes, with a degree of reduction comparable to those achieved with hydrazine. It provides an efficient method to reduce graphite oxide and could be used as a method to prepare novel composites.

 Online supplementary data available from stacks.iop.org/Nano/22/045704/mmedia

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since the first report of graphene in 2004 [1], it has attracted great interest due to the unique electronic [2, 3], thermal [4], and mechanical properties [5, 6] that arise from its flat monolayer of carbon atoms packed in a two-dimensional honeycomb lattice.

Graphene can be produced by four different methods [7], including chemical vapor deposition, micromechanical exfoliation of graphite, epitaxial growth on electrically insulating surface, and creation of colloidal suspensions by chemical reduction. So far, the chemical reduction method has received the most attention as it is considered as the possible route for industrial production thanks to its simple procedure and low cost. Industrially produced graphene could be used for a wide range of applications, such as solar cells and hydrogen storage [8], paper-like materials [5], multifunctional coatings,

sensors [9], nanoelectromechanical devices [10], and polymer composites [11], etc.

The production of graphene from graphite oxide (GO) includes two steps: exfoliating graphite in solvent with three classical methods [7], and reducing dispersed single-layer GO sheets with reducing agents (where hydrazine [12, 13] or dimethylhydrazine [14] are often used). To improve the reduction efficiency, a thermal reduction process is usually used after the chemical reduction process [13, 15]. However, the production of graphene or graphene composites has been largely limited in many research fields due to the toxicity of hydrazine-based reducing agents. Therefore, it is extremely important to find a new reducing agent to replace those toxic agents. Recently, sodium borohydride (NaBH₄) and strong alkalis were reported to reduce GO in order to replace toxic hydrazine [16, 17]. Gao *et al* reported L-ascorbic acid could reduce GO under mild conditions. This supplies an environmentally friendly approach to produce water-soluble graphene. However, the practical application is constrained by

³ Authors to whom any correspondence should be addressed.

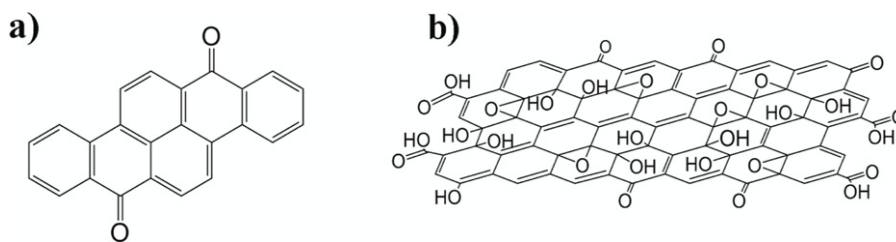


Figure 1. (a) The scheme of the vat dye from the textile industry (vat yellow 4) which inspired the idea of reducing GO by $\text{Na}_2\text{S}_2\text{O}_4$. (b) The typical structure of GO prepared by Hummer's method.

its lengthy experimental time (48 h) [18]. Therefore, finding an efficient route to prepare reduced graphite oxide (rGO) still remains a great challenge.

By carefully analyzing the chemical structure of GO, it is noted that GO has a similar structure to the vat dye used in the textile industry (figures 1(a) and (b)), as their aromatic benzene rings are covalently attached with oxygen functional groups. Inspired by an ancient reducing method used in the textile industry, a mixture of sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$) and sodium hydroxide (NaOH) is used to reduce GO in the current study, where the NaOH acts as a catalyst and stabilizer. With the additional mixture of NaOH and $\text{Na}_2\text{S}_2\text{O}_4$ into the GO suspension at 60°C , the color of the solvent was changed from yellow-brown to black in 15 min. The obtained black material was then characterized by solid state ^{13}C NMR spectroscopy, x-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), wide-angle x-ray scattering (XRD), Raman spectroscopy, and electrical conductivity measurements, respectively. It is demonstrated that GO has been successfully reduced to graphene. Since the dye reduction using $\text{Na}_2\text{S}_2\text{O}_4$ in the dye industry is a simple and natural method, which has been commercialized for many years, it is believed that the reduction of GO using $\text{Na}_2\text{S}_2\text{O}_4$ is so far a better method with great potential for commercial production of graphene and its composites.

2. Experimental details

2.1. Materials

Graphite powder was purchased from Qingdao Black Dragon Graphite Co., Ltd. Potassium permanganate (KMnO_4), sulfuric acid (H_2SO_4 98%), hydrogen peroxide (H_2O_2), sodium nitrate (NaNO_3), NaOH and $\text{Na}_2\text{S}_2\text{O}_4$ were purchased from Kermel Chemical reagent plant (Tianjin, China). They were used as received.

2.2. Methods

The preparation of water-soluble, single-layered GO was achieved using Hummer's method [19]. Briefly, graphite (2 g) was mixed with NaNO_3 (1 g) and H_2SO_4 (50 ml) at 0°C , then KMnO_4 (6 g) was slowly added into the system. Then, the mixture was stirred at room temperature for 30 min after being kept at 0°C for 2 h. Distilled water (100 ml) was slowly added into the system, the temperature was kept well below 98°C for 3 h. The mixture was further treated with 5%

H_2O_2 (50 ml), filtered and washed with distilled water. As-purified GO suspensions were then dispersed in distilled water and ultrasonicated for 15 min. The obtained brown dispersion was then subjected to centrifugation, and the stable supernatant solutions were carefully extracted to cast film.

To prepare the substrate for film casting, glass slides were immersed in piranha solution (7:3, H_2SO_4 : H_2O_2 mixture) for 1 h followed by washing with distilled water. The aqueous solutions of GO prepared above were dropped onto the substrates, and dried at 80°C in vacuum. The GO films were immersed in reducing agent aqueous solution (12.5 mg ml^{-1} of $\text{Na}_2\text{S}_2\text{O}_4$ and 50 mg ml^{-1} of NaOH) at 60°C for 15 min. The color of the GO films was changed from yellow-brown to metallic gray. After that, rGO films were washed in distilled water to remove the by-product (Na_2SO_3) and residual reducing agents, and then dried at 80°C in vacuum.

Polyvinyl alcohol (PVA)/rGO composites were prepared as follows: GO was dissolved in 20 ml of water and treated with ultrasound for 15 min at room temperature to yield a clear solution. PVA (1 g) was dissolved in distilled water (10 ml) at 98°C . The GO aqueous dispersion was gradually dropped into the PVA solution, and stirred at 98°C for 30 min. The homogeneous PVA/GO solution was poured into an aluminum dish and kept at 60°C for 18 h to cast the film. The PVA/GO film was immersed in reducing agent solution (12.5 mg ml^{-1} of $\text{Na}_2\text{S}_2\text{O}_4$ and 50 mg ml^{-1} of NaOH) at 60°C for 1 h, and the prepared PVA/rGO film was washed in distilled water until the by-product and residual reducing agents were removed. After that, the film was dried at 60°C for 5 h.

2.3. Characterization

The ^{13}C solid state NMR spectra were produced on a Varian Infinity-Plus300 NMR spectrometer at room temperature, with a 4 mm double resonance magic angle spinning (MAS) probe at Larmor frequencies of 299.9 MHz for ^1H and 75.5 MHz for ^{13}C . The XRD patterns of the samples were obtained by X'Pert Pro x-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418\text{ nm}$). Samples were scanned at a scan speed of $0.5^\circ\text{ min}^{-1}$. A micro-Raman spectrophotometer (Renishaw) was used to characterize the GO and rGO. The laser was excited by the 136M Het resource with a wavelength of 514.5 nm. The XPS (Axis Ultra DLD, Kratos Co., UK) was performed using focused monochromatized $\text{Al K}\alpha$ radiation (15 kV) in order to demonstrate any variation in the ratios between carbon and oxygen, and the existence of functional

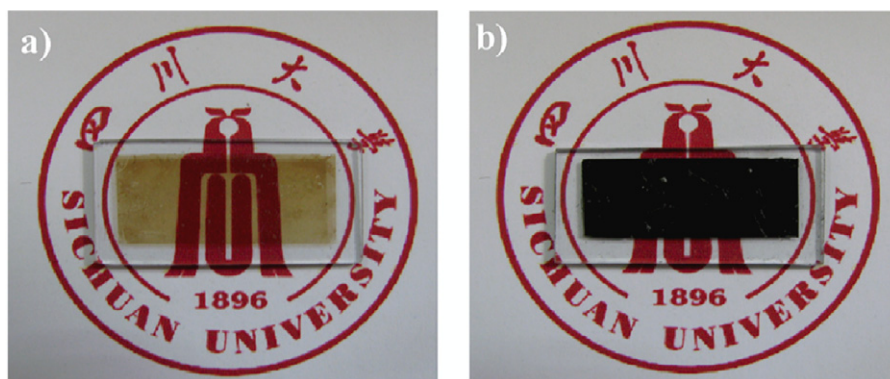


Figure 2. (a) The picture of yellow-brown GO before reduction. (b) The color changed to black after being reduced by $\text{Na}_2\text{S}_2\text{O}_4$.

groups. Combustion analysis was performed on EURO EA300 (Euro vectro S.P.A; USA). TGA (TGA Q500, TA Instruments) was performed under N_2 flow, and the sample was heated from room temperature to 650°C at a rate of $10^\circ\text{C min}^{-1}$. The resistance of the sample was measured with a Keithley 6487 electrometer. The two-point method was used. The structures of the rGO were investigated with an atomic force microscope (AFM, SPA400/SPI4000, Seiko Instruments Inc). The multimode AFM instrument was operated in tapping mode. Olympus tapping mode cantilevers with the spring constants ranging from 51.2 to 87.8 N m^{-1} (as specified by the manufacturer) were used. The thickness of the rGO film was measured by an Inspect F (FEI) scanning electron microscope (SEM) operated at an acceleration voltage of 5 kV .

3. Results and discussion

In our work, the GO sheet was exfoliated using Hummer's method. The thickness of these well-exfoliated GO sheets is around 1 nm , thicker than single graphene sheet. It implies that the GO sheets are covalently bounded with oxygen and the displacement of the sp^3 -hybridized carbon atoms (figure S1 in the supplementary material available at stacks.iop.org/Nano/22/045704/mmedia). The GO suspension was dipped onto hydrophilic glass substrates and dried at 60°C for 1 h , and then the sample was immersed in the reduction solution containing $\text{Na}_2\text{S}_2\text{O}_4$ and NaOH at 60°C for 15 min . During the reducing process, the GO film turns black. Figure 2 shows the color change of GO from yellow-brown to black after reduction. In addition, it is noted that the rGO film can be easily peeled off from the hydrophilic glass substrate and floats on the surface of the reduction solution. Due to the hydrophilic nature of GO, this phenomenon indicates an obvious change of wetting property from hydrophilic to hydrophobic after reduction.

The interlayer distance was determined with XRD measurement. As shown in figure 3, the interlayer distance of graphite is increased to $8.86 \text{ \AA}$, while it was exfoliated and decreased to $3.77 \text{ \AA}$ after reduction. The distance of graphite plates is $3.37 \text{ \AA}$ ($2\theta = 26.48^\circ$) due to the tightly packed monolayer of carbon atoms. It is expanded to $8.86 \text{ \AA}$ ($2\theta = 9.98^\circ$) by grafting with functional groups, such as hydroxyl, epoxy, and carboxyl during oxidation. However, the interlayer

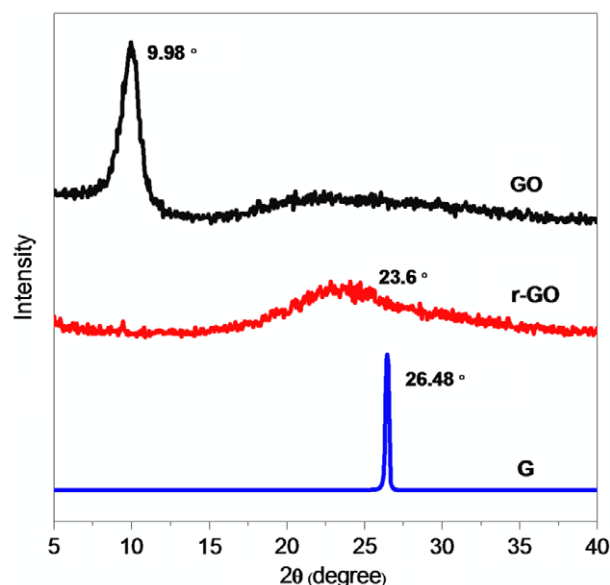


Figure 3. The XRD of graphite, GO and rGO.

distance returns back to $3.77 \text{ \AA}$ ($2\theta = 23.6^\circ$) after reduction, indicating most of the oxygen functional groups have been removed. The broadened peak and reduced peak intensity indicate that graphene was exfoliated into single-layered or few-layered sheets and with the formation of a new lattice structure which is significantly different from the graphite.

To confirm the reduction effect, TGA was used to study the thermal stability of GO and rGO, as shown in figure 4. In agreement with previous reports, GO is thermally unstable and starts to lose mass (10%) upon heating, even below 100°C , the main mass loss (20%) takes place at around 200°C , due to the decomposition of the labile oxygen functional groups, yielding CO , CO_2 , and steam. The mass loss is over 30% above 500°C due to the removal of more stable oxygen functionalities. However, no significant mass loss is observed even at 750°C for rGO, which indicates that most of the oxygen functional groups have been removed during reduction. In addition, the combustion analysis (figure S2 in supplementary material available at stacks.iop.org/Nano/22/045704/mmedia) reveals that the content of carbon is increased from 46.8 to $69.8 \text{ wt\%}$

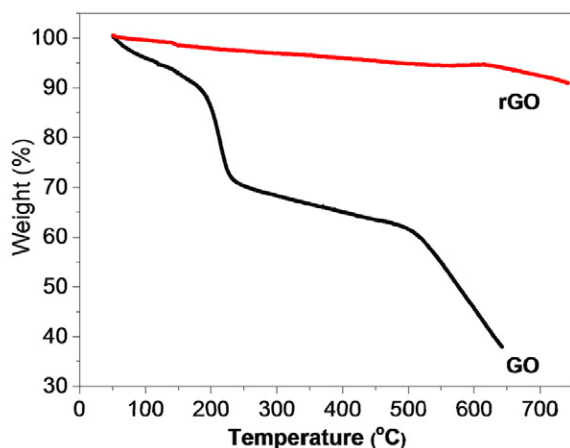


Figure 4. The TGA plots of GO and rGO.

after reduction, and that of hydrogen is decreased from 4.1 to 2.7 wt% after the same process. This result also indicates that the oxygen has been mostly removed during the reducing progress. Nevertheless, there still are some residual oxygen functional groups, such as carboxylic groups, which are hardly reduced. It should be noted that the reduction method used here is somewhat inferior to some existing reduction methods, which shows carbon content in the reduced material is more than 70%. There are several factors which may affect the reduction efficiency, such as the proportioning of reducing agents and the reduction temperature. So in our future work, we will study how the reduction degree of GO could be further improved.

Raman spectroscopy was employed to evaluate the transformation from graphite to GO and then to rGO. As shown in figure 5, pristine graphite demonstrates a strong band at 1597.7 cm^{-1} (G band) and a weak band at 1348.9 cm^{-1} (D band). The G band and D band are attributed to the first-order scattering of the E_{2g} vibrational mode in the graphite sheet and structure defects, respectively. For the Raman spectrum of GO, the D band becomes prominent and the G band is broadened and shifts to 1572 cm^{-1} , indicating the formation of sp^3 carbon by functionalization. After being reduced, the ratio of the intensities (I_D/I_G) is markedly increased from 0.73 for GO to 1 for rGO. This phenomenon could be explained by the formation of some new and small sp^2 domains during reduction [13].

To illustrate the formation of graphene, XPS was used to characterize the removal of oxygen groups. Figure 6(a) shows two main oxygen peaks arising from C–O (hydroxyl and epoxy, $\sim 286.7\text{ eV}$) and C=O (carbonyl, $\sim 288\text{ eV}$) groups for GO. After reduction, the main peak related to C–C/C–H remains unchanged for rGO, but the two main peaks related to the oxygen group are significantly weakened and the C/O ratio increases from 67% for GO to 79% for rGO (figure 6(b)). This indicates that most of the oxygen functional groups were removed after reduction. The solid state ^{13}C NMR spectra was also carried out to characterize the reduction of GO with $\text{Na}_2\text{S}_2\text{O}_4$ (figures 6(c) and (d)). For GO, peaks of the epoxide and hydroxyl groups are obvious at 56 and 80 ppm, and the

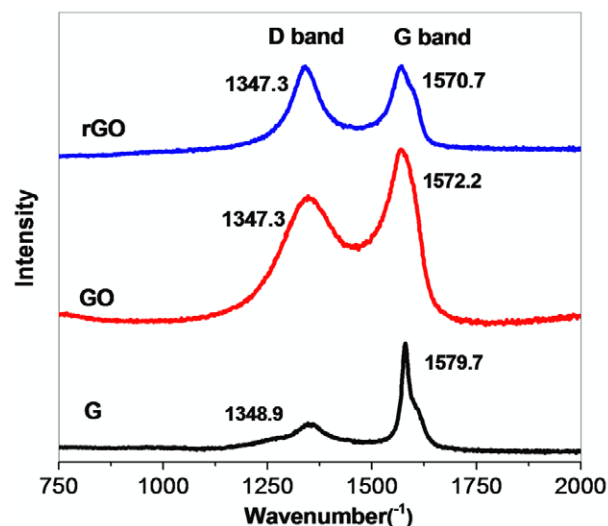


Figure 5. The Raman spectra of graphite, GO and rGO.

peak of un-oxidized sp^2 carbons is observed at 130 ppm. After reduction, those peaks of oxygen functional groups become smaller and weaker; meanwhile, the peak of the sp^2 carbon atoms becomes sharper, suggesting the formation of graphene-based materials. Once again, this provides evidence that most of the epoxy and hydroxyl functional groups have been removed by using $\text{Na}_2\text{S}_2\text{O}_4$ as the reducing agent. These results, combined with XRD, TGA and Raman spectroscopy, indicate the formation of graphene.

The electrical conductivity is perhaps the best indicator of the extent to which the graphite oxide has been reduced. Therefore, the electrical conductivity measurement of rGO and GO films was carried out ($\sim 1.5\text{ }\mu\text{m}$ thick measured by SEM). The conductivity of GO is measured to be $3 \times 10^{-4}\text{ S m}^{-1}$ in our work, it is much lower than pristine graphite ($2500 \pm 15\text{ S m}^{-1}$) [13] due to the fact that the extended π -conjugated structure has been destroyed during oxidation. After reduction, the conductivity of rGO is increased to 1377 S m^{-1} , which is about seven orders of magnitude higher than that of GO and comparable to that of pristine graphite. The obtained degree of reduction is comparable to those provided by hydrazine ($2420 \pm 200\text{ S m}^{-1}$) [13]. Therefore, the recovered electrical conductivity of rGO film indicates that the extensive conjugated sp^2 -carbon network has been rebuilt in the reducing process. In addition, the fact that the conductivity of rGO was slightly lower than that of pristine graphite can be attributed to the remaining peripheral carboxyl groups, the residual epoxide and hydroxyl groups.

Presently, the reduction mechanism of GO using $\text{Na}_2\text{S}_2\text{O}_4$ is still an open question. Gao *et al* [18] revealed that the GO was reduced using vitamin C due to its nucleophilic nature. In our case, the $\text{Na}_2\text{S}_2\text{O}_4$ is an efficient reducing agent with a low electrode potential ($E^\theta\text{ SO}_3^{2-}/\text{S}_2\text{O}_4^{2-} = -1.12\text{ V}$) in alkaline solution, easily dissociates two protons and becomes a nucleophile. When epoxide and hydroxyl groups of the GO are attacked by a nucleophile with a back-side $\text{S}_\text{N}2$ nucleophilic reaction, H_2O is released and results in the formation of an intermediate. Finally, a thermal elimination leads to

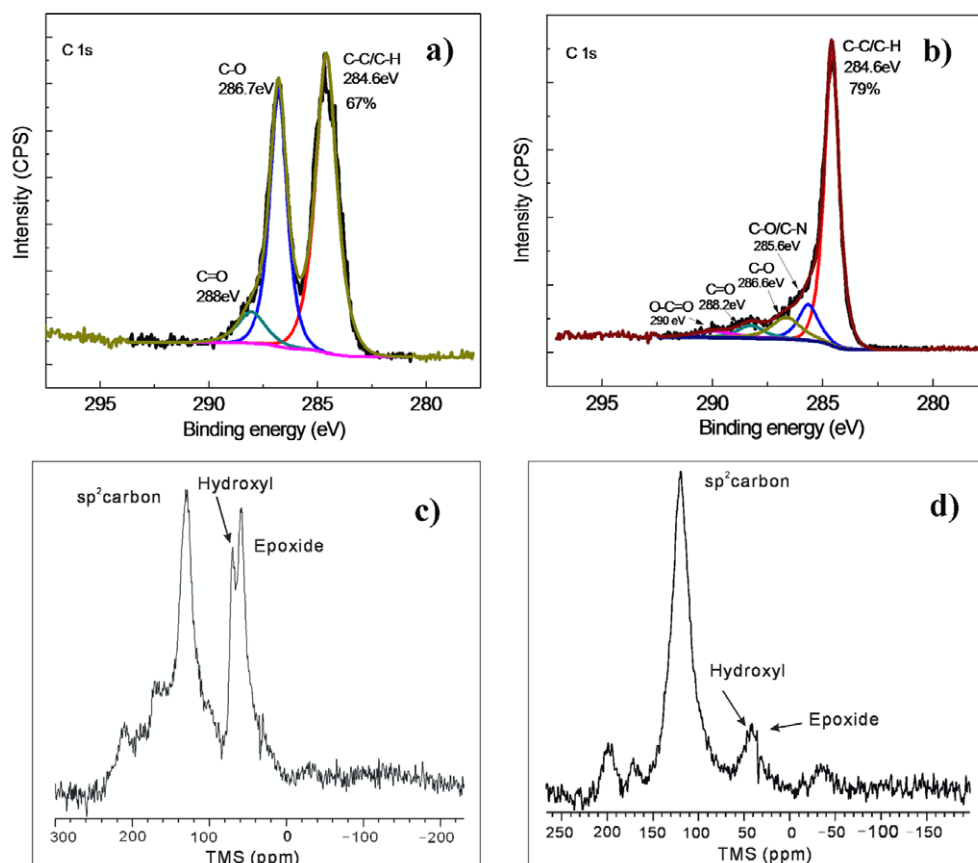


Figure 6. (a) and (b) The XPS of GO and rGO, (c) and (d) the solid state ^{13}C NMR spectra of GO and rGO.

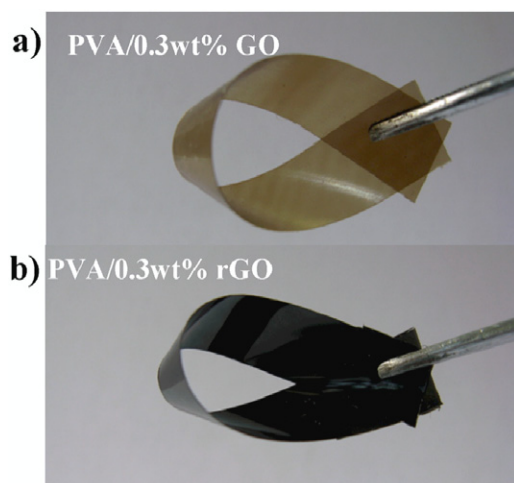


Figure 7. (a) and (b) The color of the PVA/0.3 wt% GO film was changed from yellow-brown to black after being reduced.

the formation of reduced graphene, and the reducing agent ($\text{S}_2\text{O}_4^{2-}$) is oxidized to sulfite (SO_3^{2-}).

This method provides a novel way to prepare graphene and its composites. Fabricating PVA/rGO composites undergoes two steps: the first step is preparing PVA/GO composites by casting PVA/GO aqueous solution; then it is followed by immersing the PVA/GO composites into reducing agent solution for 1 h at 60°C . As shown in figures 7(a) and (b), the

color of the film composites was changed from yellow-brown to black after reduction of the PVA/0.3 wt% GO film. Those composites containing GO are changed from non-conductive to conductive after reduction, and the conductivity of composites containing 0.3 and 3 wt% rGO are 1.3×10^{-8} and $8.9 \times 10^{-3} \text{ S m}^{-1}$, respectively. It is comparable to those results obtained using hydrazine as reducing agent [20].

So far, several reducing agents have been reported for the reduction of GO, including hydrazine, ascorbic acid, and glucose. Here we demonstrate that sodium hydrosulfite can be used to efficiently reduce GO. This method has several advantages compared with previous reported reducing agents. Firstly, it has been used for many years in the dye industry and it is a simple and efficient method. Secondly, the by-product (Na_2SO_3) can be easily removed by water, with no accompanying side-effect on the resultant graphene and its composites. Thirdly, the reducing process is also a fast method (takes only few minutes), which could be the best advantage of such a reducing agent. Therefore, we believe that the reduction of GO using sodium hydrosulfite is so far the best method, with great potential for commercial production of graphene and its composites.

4. Conclusions

We have discovered an efficient route for the reduction of exfoliated GO. Efficient reduction of GO is achieved in

Na₂S₂O₄ solutions at moderate temperatures. It is also demonstrated that GO can be reduced within the polymer matrix by this method. The reduction mechanism still needs further investigation. Nevertheless, it is believed that this method provides a novel way for large-scale production of graphene by reducing GO.

Acknowledgments

We express our sincere thanks to the National Natural Science Foundation of China for financial support (50973065, 50873063, and 20874064).

References

- [1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 *Science* **306** 666
- [2] Gómez-Navarro C, Weitz R T, Bittner A M, Scolari M, Mews A, Burghard M and Kern K 2007 *Nano Lett.* **7** 3499
- [3] Novoselov K S, Geim A K, Morozov S V, Jiang D, Katsnelson M I, Grigorieva I V, Dubonos S V and Firsov A A 2005 *Nature* **438** 197
- [4] Prasher R 2010 *Science* **328** 185
- [5] Dikin D A, Stankovich S, Zimney E J, Piner R D, Dommett G H B, Evmenenko G, Nguyen S T and Ruoff R S 2007 *Nature* **448** 457
- [6] Stankovich S, Dikin D A, Dommett G H B, Kohlhaas K M, Zimney E J, Stach E A, Piner R D, Nguyen S T and Ruoff R S 2006 *Nature* **442** 282
- [7] Park S and Ruoff R S 2009 *Nat. Nanotechnol.* **4** 217
- [8] Wang X, Zhi L and Mullen K 2007 *Nano Lett.* **8** 323
- [9] Fowler J D, Allen M J, Tung V C, Yang Y, Kaner R B and Weiller B H 2009 *ACS Nano* **3** 301
- [10] Bunch J S, van der Zande A M, Verbridge S S, Frank I W, Tanenbaum D M, Parpia J M, Craighead H G and McEuen P L 2007 *Science* **315** 490
- [11] Eda G and Chhowalla M 2009 *Nano Lett.* **9** 814
- [12] Lomeda J R, Doyle C D, Kosynkin D V, Hwang W F and Tour J M 2008 *J. Am. Chem. Soc.* **130** 16201
- [13] 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
- [14] Wang G, Yang J, Park J, Gou X, Wang B, Liu H and Yao J 2008 *J. Phys. Chem. C* **112** 8192
- [15] Becerril H A, Mao J, Liu Z, Stoltenberg R M, Bao Z and Chen Y 2008 *ACS Nano* **2** 463
- [16] Shin H J et al 2009 *Adv. Funct. Mater.* **19** 1987
- [17] Fan X, Peng W, Li Y, Li X, Wang S, Zhang G and Zhang F 2008 *Adv. Mater.* **20** 4490
- [18] Gao J, Liu F, Liu Y, Ma N, Wang Z and Zhang X 2010 *Chem. Mater.* **22** 2213
- [19] Hummers W S and Offeman R E 1958 *J. Am. Chem. Soc.* **80** 1339
- [20] Salavagione H J, Martinez G and Gomez M A 2009 *J. Mater. Chem.* **19** 5027