NANO-MICRO LETTERS ARTICLE
www.nmletters.org

A Facile Route for the Large Scale Fabrication of Graphene Oxide Papers and Their Mechanical Enhancement by Cross-linking with Glutaraldehyde

Nantao Hu, Lei Meng, Rungang Gao, Yanyan Wang, Jing Chai, Zhi Yang*, Eric Siu-Wai Kong, Yafei Zhang*

(Received 10 October 2011; accepted 18 November; publication online 24 November 2011.)

Abstract: A facile route for the large scale production of graphene oxide (GO) papers and their mechanical enhancement has been presented in this work. The novel paper-like GO made from individual GO sheets in aqueous suspension can be achieved in large scale by a simple drop casting method on hydrophobic substrates. Significant enhancement in mechanical stiffness (341%) and fracture strength (234%) of GO paper have been achieved upon modification with a small amount (less than 10 wt%) of glutaraldehyde (GA). The cross-linking reaction takes place between hydroxyl groups on the surface of GO and aldehyde groups of GA, through forming hemiacetal structure, which can result in distinct mechanical enhancement of the GO papers.

Keywords: Graphene oxide paper; Glutaraldehyde; Cross-linking; Mechanical enhancement

Citation: Nantao Hu, Lei Meng, Rungang Gao, Yanyan Wang, Jing Chai, Zhi Yang, Eric Siu-Wai Kong and Yafei Zhang, "A Facile Route for the Large Scale Fabrication of Graphene Oxide Papers and Their Mechanical Enhancement by Cross-linking with Glutaraldehyde", Nano-Micro Lett. 3 (4), 215-222 (2011). http://dx.doi.org/10.3786/nml.v3i4.p215-222

Introduction

As a nanometer-thick two-dimensional analog of carbon nanotubes, graphene has aroused much attention owing to its unique combination of electronic, mechanical, chemical, and thermal properties [1-6]. Lots of potential applications have been proposed in various fields, including filler materials [7], field-emission devices [8], nanoscale electronic devices [9], sensors [10,11], paper-like materials [12-16] and among others. Many approaches, including micromechanical exfoliation of graphite [17], chemical vapor deposition [18-22], and solution-based chemical reduction of graphite oxide (GO) [23-26], have been developed to prepare graphene materials. Since sonication treatment can result in a colloid suspension of GO in water, preparation of graphene through reduction of GO can be considered as a fascinating method due to its cost-effective and easily scalable operation.

As we know, GO consists of a hexagonal carbon network having both sp^2- and sp^3-hybridized carbons bearing hydroxyl and epoxide functional groups on its "basal" plane, together with carboxyl and carbonyl groups distributed on the edges [27]. It can be considered as an excellent intermediate for the large scale preparation of graphene materials, as well as a promising candidate for various applications, especially for the preparation of paper-like materials [28]. Many paper-like ordered macrostructures have been assembled by using GO as building blocks through several methods, such as flow-directed assembly by filtration [12,29-31], Langmuir-Blodgett assembly [32,33] and self-assembly

---

Key Laboratory for Thin Film and Microfabrication of the Ministry of Education, Research Institute of Micro/Nano Science & Technology, Shanghai Jiao Tong University, Shanghai, 200240, P. R. China
*Corresponding authors. E-mail: zhiyang@sjtu.edu.cn, yfzhang@sjtu.edu.cn

by evaporating the hydrosol of GO [28], etc.

In this article, we propose a general drop casting method to prepare macroscopic GO papers by using a hydrophobic substrate. Although a similar solvent-casting method [34] has been reported for the preparation of GO-based thin films, the morphology and mechanical properties of the resulting thin-film materials have not been elucidated in detail, and the integration of the freestanding films with a large area have not been declared, as well. Therefore, we exploit drop casting method to prepare GO papers on hydrophobic substrates, and the resulting GO papers with large areas and acceptable mechanical properties can be easily peeled off the substrates. Further mechanical enhancement has been achieved by the addition of a small amount (less than 10 wt%) of glutaraldehyde (GA) during the process of membrane fabrication. This method is very easy to operate and suitable for the scalable production of the GO papers with the thickness ranging from several micrometers to hundreds of micrometers.

Experimental details

Materials

The natural graphite (200 meshes) used in this study was obtained from Shandong Tianyuan Co. Ltd in China. Glutaraldehyde (GA) were analytical grade and used as received.

Preparation of the graphene oxide (GO)

The GO was prepared by a modified Hummers method which has been illustrated by previous work [35]. The typical procedure was as follows, graphite (2 g) and concentrated sulfuric acid (50 ml) were mixed in a 250 ml of flask while keeping vigorous stirring. After adding 5 g of $NaNO_3$, the mixture was allowed to be stirred for 1 hour, and followed by cooling to 0℃ using an ice-water bath. 7.3 g of $KMnO_4$ was added in small portions during 2 hours. Subsequently, the reaction temperature was increased to 35℃. After 2 hours of further stirring, the reaction was quenched by adding 0.2 l of ice water and 7 ml of H_2O_2 (30%). The resultant GO was filtered, washing with plenty of aqueous HCl (3%) until no precipitation of $BaSO_4$ occurred in the presence of aqueous $BaCl_2$ solution. Further washing with water was carried out until the chloride test with $AgNO_3$ was negative, and the resultant products were dried at 40℃ for 24 hours in the vacuum oven.

Preparation of GO papers and cross-linked GO papers

The GO paper can be obtained by a simple drop casting method, just similar with the general route for the fabrication of polymer films [36,37]. The typical procedure was as follows, 240 mg of GO powder was dispersed in 80 ml of water, and the suspension was allowed to be ultrasonicated for 1 h, in order to disperse GO sheets in the water efficiently. The resultant suspension was poured onto a PTFE plate in the oven with the temperature at 80℃. After drying for 12 h, the GO paper with the thickness of 30 μm was easily peeled off the plate, and as a result, the freestanding paper was obtained. The GO papers with other thicknesses can be obtained by changing the concentration of GO aqueous solution.

In order to prepare GO papers cross-linked with GA, different concentration of GA was added in the suspension after the GO sheets dispersed in the water efficiently, and the film fabrication process was the same as mentioned above. Three different concentration of GA (1 wt%, 5 wt%, and 10 wt%) were used here, and the obtained cross-linked GO papers were designed as GO-1, GO-5, and GO-10, respectively.

Characterization

Atomic force microscope (AFM) images were acquired by using a Multimode Nanoscope V scanning probe microscopy (SPM) system (Veeco, USA) with Picoscan v5.3.3 software. A tapping mode was carried out to obtain the images under ambient conditions. The morphology of the graphite and GO were also observed by FE-SEM using a Carl Zeiss SUPRA SMT AG scanning electron microscope (LEO1525, Carl Zeiss, Oberkochen, Germany) with the accelerating voltage at 5kV. The thermogravimetric analysis (TGA) of natural graphite was performed under an argon atmosphere using a heating rate of 10℃/min from 50℃ up to 600℃. To avoid thermal expansion of the GO due to rapid heating, GO samples were also heated from 50℃ to 500℃ at 1℃/min. FTIR spectra were recorded on a Bruker (Germany) VERTEX 80v vacuum FTIR spectrometer over a range from 400 to 4500 cm^{-1} with DTGS or MCT as detector. The mechanical properties of GO papers were obtained via tensile testing on a Q800 dynamic mechanical analyzer (DMA, TA instruments). The samples were mounted using film tension clamps with a clamp compliance of ca. 0.2 μm/N. A preload of 0.1 N was executed, and force was loaded with a force ramp rate of 0.2 N/min under ambient condition.

Results and Discussion

Modified Hummers method [35] was applied here to oxidize and split graphite sheets, and as a result, GO was formed. During the process of chemically oxidization of graphite, the strong oxidant reagents in the reaction systems split the graphite sheets, as well as decrease the size of GO sheets, resulting in unpredictable edges of GO monolayer sheets. This can be effectively proved by AFM and SEM (see Fig. 1 and Fig. 2). Plate like sheets of GO can be directly observed with irregular edges. In order to form the separated GO sheets, the resultant GO needs to be undergone sonication treatment. And the GO can be easily dispersed in water as soon as the sonication treatment was executed. Consequently, a colloid aqueous solution of GO (0.5 mg/ml) was successfully achieved. The height profile of the AFM image (see Fig. 1(b)) indicates that the thickness of the obtained GO sheet is about 0.97 nm, suggesting the successful achievement of the single layer GO sheets [7].

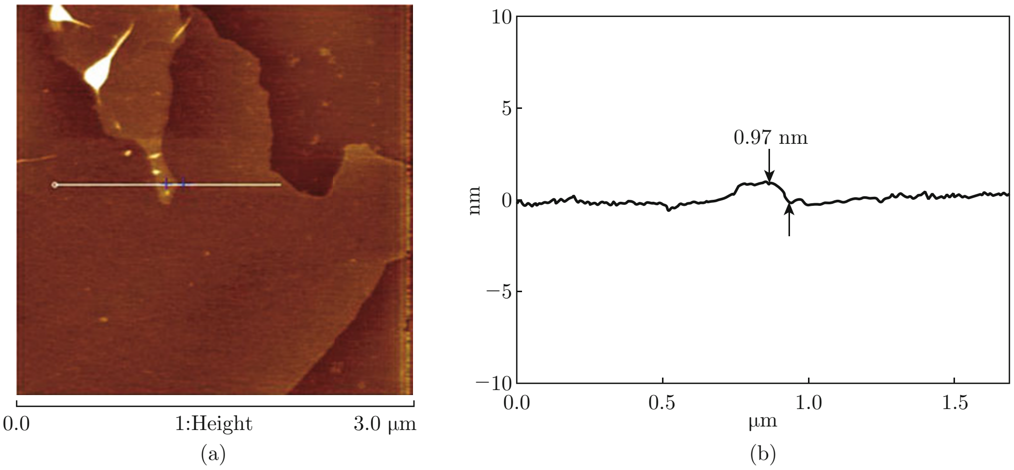

Fig. 1 AFM image of (a) graphene oxide and (b) the height profile of the AFM image.

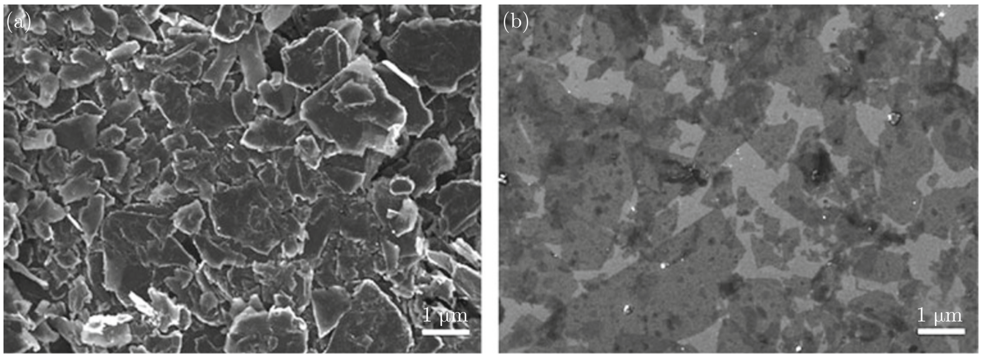

Fig. 2 SEM images of (a) natural graphite and (b) GO.

After GO aqueous solution has been formed, drop casting method was carried out in order to form GO papers. The hydrophobic substrate (PTFE) was used here, in order to make sure the achievement of the freestanding GO papers. Since GO sheets contains lots of -COOH groups (ca. 41 wt% as shown in Fig. 3), the obtained GO papers exhibit hydrophilic behavior. Therefore, the hydrophobic substrate plays a very important role in the formation of the freestanding GO papers, especially when the thickness of the GO paper is lower than 10 μm. The large scale production of GO papers with different thicknesses (ranging from several micrometers to several hundreds of micrometers) can be achieved by peeling the dried GO papers off PTFE plate easily. Furthermore, the thickness of the GO paper can be adjusted by changing the concentration of GO aqueous solution. As shown in Fig. 4(b) and 4(c),

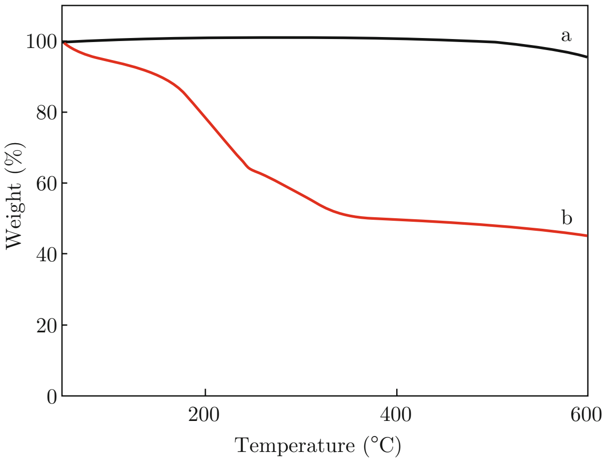

Fig. 3 Thermogravimetric analysis results of a) natural graphite and b) GO at an argon atmosphere.

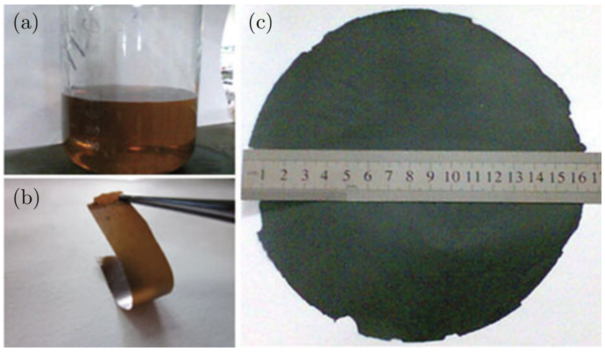

Fig. 4 Photographs of (a) GO dispersions (0.5 mg/mL), (b) GO paper strip (5 micrometers, and (c) GO paper with thickness at 30 micrometers.

we can see that the thickness of GO papers is 5 μm and 30 μm, when the concentration of GO suspension is 0.5 mg/ml and 3 mg/ml, respectively.

The proposed schematic process for the formation of GO papers (as illustrated in Fig. 5) is similar with the result reported by Chen C [28]. It's suggested that the temperature plays a key role in the formation of GO papers. The relatively higher temperature (below 100℃) can lead to the rapid evaporation of water, which can result in the self-assembly of GO sheets in aqueous solution. Accompany with the evaporation of water, the GO sheets self-assembled on the surface of water, and as the evaporation of water is ongoing, the GO papers become thicker and thicker. The hydrophobic substrate can make sure the complete self-assembly of GO sheets in aqueous solution. And finally, the GO paper can be formed after all of water has been removed.

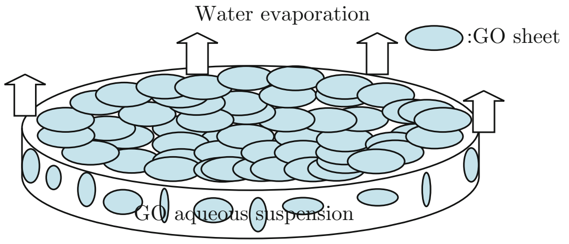

Fig. 5 The proposed schematic process for the formation of GO paper on the PTFE substrate.

The resultant GO paper strips with the thickness of 30 μm were employed for mechanical measurements. The preliminary results as shown in Table 1 indicate that the obtained GO paper exhibits lower modulus (1.7±0.2 GPa) and strength (20.2±1.0 MPa) compared with the GO membranes prepared by filtration method [12]. However, the drop casting method is fascinating and can be considered as a more suitable route for the large scale production of GO papers. Comparing with the general polymer film systems, such as PVA [38], PU [39], etc., the mechanical properties of GO papers are encouraging, and show potential applications in many fields.

Table 1 The mechanical properties of GO papers crosslinked with different concentration of GA.

Sample	Modulus (GPa)	Strength (MPa)	Strain (%)
GO	1.7±0.2	20.2±1.0	1.6±0.1
GO-1	1.7±0.1	38.2±1.6	2.8±0.2
GO-5	6.1±0.2	45.1±2.3	2.3±0.1
GO-10	7.5±0.3	67.5±3.3	2.2±0.1

In order to enhance the mechanical properties of the obtained GO papers, GA has been added in the GO aqueous suspension with different concentrations during the process of GO papers fabrication. It was suggested that the cross-linking reaction took place after the temperature at 80℃ was applied. The obtained cross-linked GO papers were characterized by DMA, and the mechanical properties have been listed in Table 1. We can see that GA plays a very important role in the increase of the mechanical properties of GO papers. When the concentration of GA is as low as 1 wt%, there are little changes on the modulus, while an increase of strength (89.1%) and strain (75.0%) of the paper can be achieved. When the concentration of GA is increased to 10 wt%, the modulus, strength and strain were increased to 7.5±0.3 GPa, 67.5±3.3 MPa, and 2.2±0.1%, respectively. These results are encouraging, since the strength is similar with that of the membranes prepared by filtration method [12], although the modulus is still a little lower.

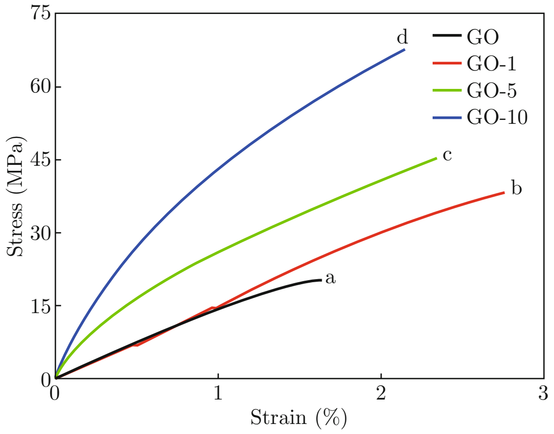

Fig. 6 Mechanical properties of (a) pure GO paper and GO papers crosslinked with (b) 1 wt%, (c) 5 wt%, and (d) 10 wt% of glutaraldehyde.

The effects of the variation of the addition of GA on the mechanical properties of GO paper have also been concluded as shown in Fig. 6 and Fig. 7. We can see that the modulus has little changes when the concentration of GA is very low. And further increase of the concentration of GA results in the increase of the modulus. Differently, the strength of the paper is increased as the increase of the concentration of GA. The variation of the strain of the GO paper exhibits a distinct different character, the strain increases when the concentration of GA is fixed at 1 wt%, and further increase of the concentration leads to decrease of the strain. The variation behaviors of GO papers cross-linked by GA with the concentration higher than 10 wt% haven't been studied, since the obtained films are very brittle and easy to be cracked.

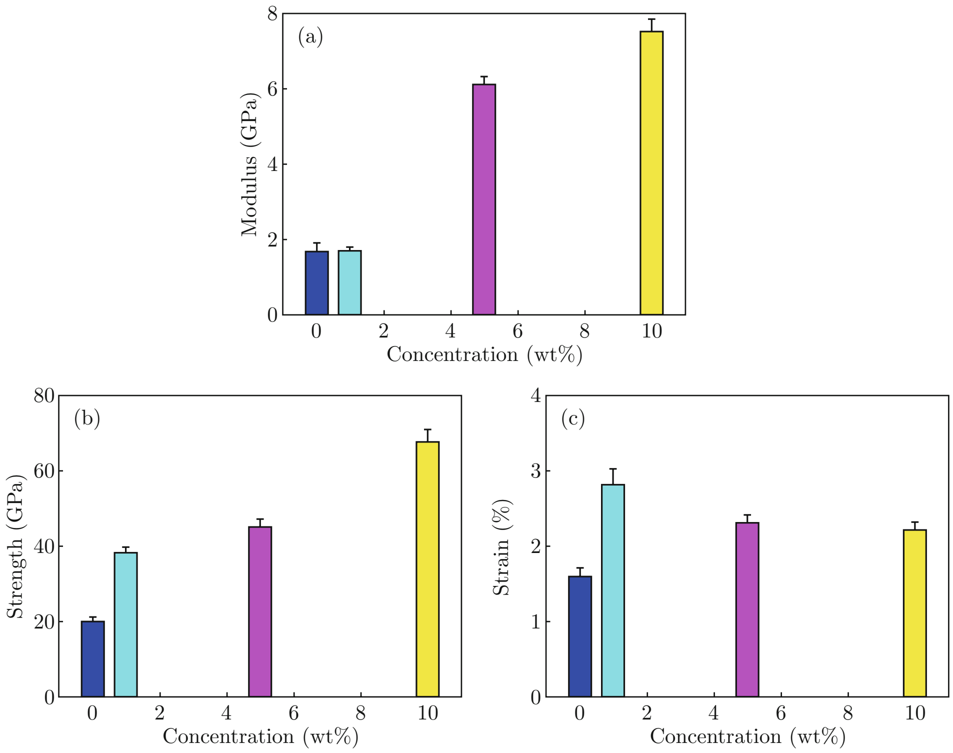

Fig. 7 The variation of (a) modulus, (b) strength, and (c) strain of GO papers crosslinked with different concentration of glutaraldehyde.

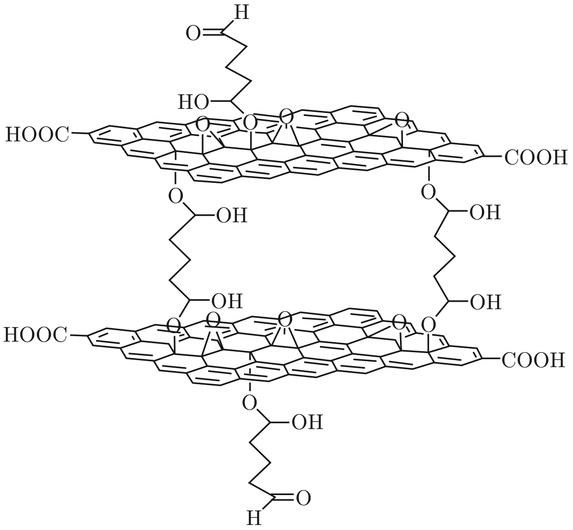

Fig. 8 The proposed schematic model of the crosslinking reaction between graphene oxide paper and glutaraldehyde.

As we know, GO contains functional groups (e.g. hydroxyl, epoxide, and carboxyl groups), which benefits for its further functionalization [40-42]. Especially hydroxyl groups, they can react with aldehyde through forming hemiacetal structure [43]. GA, which contains two aldehyde functional groups in the molecules, can react with GO sheets as a cross-linker and result in the mechanical enhancement of the obtained GO papers (The proposed schematic structure of the cross-linked GO sheets is illustrated in Fig. 8).

The FT-IR spectroscopy was used to track the variation of the functional groups associated with GO. Figure 9 shows the FT-IR spectra of natural graphite

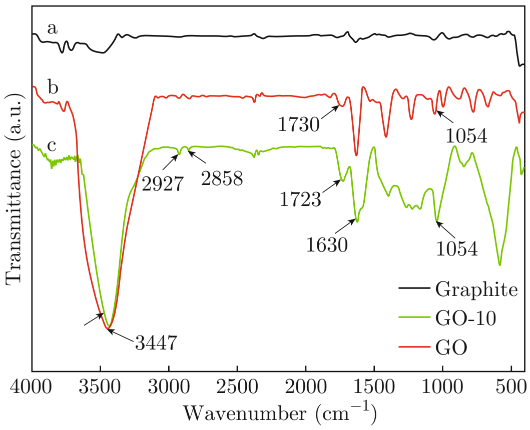

Fig. 9 FT-IR spectra of a) natural graphite, b) GO, and c) crosslinked GO film with 10 wt% of glutaraldehyde.

(Fig. 9a), GO (Fig. 9b), and cross-linked GO with 10 wt% of GA. As for the natural graphite, the characteristic peak located at ~1625 cm^{-1} (C=C band) assigned to skeletal vibrations of graphitic domains, and the band at ca. 3500 cm^{-1} was due to the O-H stretching mode of the absorbed water. After the oxidation was executed, the appearance of the peak located at 1740 cm^{-1}, correspondence to the characteristic of -COOH (C=O in carboxylic acid), proved the successful achievement of GO preparation. Other strong evidences for the successful preparation of GO can be also observed in Fig. 9b. The peak of O-H at ~1400 cm^{-1}, together with the band at ca. 3450 cm^{-1}, was due to the O-H stretching mode of -COOH groups and -OH groups attached on the surface of GO. Furthermore, the peak located at ~1054 cm^{-1} appeared as well, which was due to the vibration of C-O in carboxylic acid groups or epoxy groups on the surface of GO. The cross-linked GO has also been characterized by FTIR, the spectra are shown in Fig. 9c. The peaks located at 2927 and 2858 cm^{-1}, correspond to the C-H stretch modes of the crosslink molecules. The relative intensity between 1054 cm^{-1} and 1630 cm^{-1} (I_{1054}/I_{1630}) increases, i.e., the increase of the intensity of C-O stretch mode happens, which suggests that the cross-linking reaction has taken place.

The covalent linkages of GA between the adjacent GO sheets result in a great enhancement of the mechanical properties of GO papers. Actually, GA plays a very important role in the self-assembly of GO nanosheets in the aqueous solution, as well. With little amount of GA, GO sheets can self-assemble more orderly, which can be proved by the SEM images as shown in Fig. 10. The cross-section morphologies of GO paper (Fig. 10(a)) and cross-linked GO paper with 10 wt% of GA (Fig. 10(b)) are distinctly different. We can see that the GO paper prepared by drop casting method is less compact than the membranes prepared by filtration method. Unlike the filtration method, the driving force for the self-assembly of GO nanosheets can not be controlled very well during the process of water evaporation. And fortunately, this can be improved by the addition of a little amount of GA. As shown in Fig. 10(b), the cross-section of cross-linked GO papers exhibit more compact morphology, which suggests that the addition of GA leads to the orderly stacking of GO nanosheets during the process of water evaporation. And as a result, much more compact GO paper can be obtained. This is very exciting, since the addition of a little amount of GA can result in the formation of covalent linkages between the adjacent GO sheets as well as the orderly stacked GO nanosheets, and consequently significant enhancement of the mechanical properties of GO papers can be achieved.

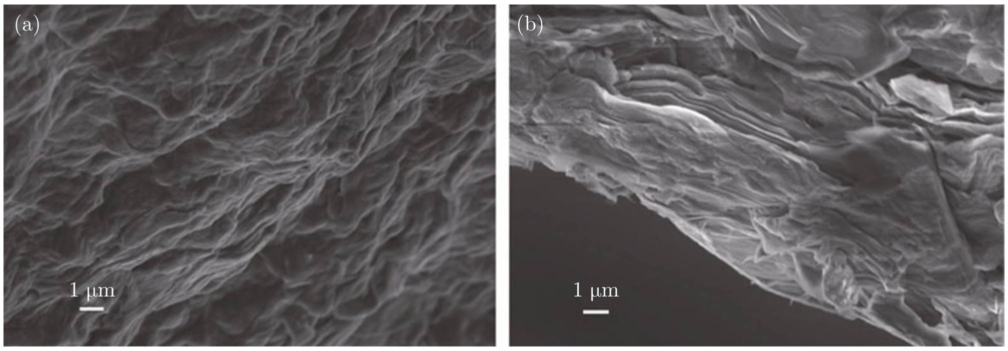

Fig. 10 SEM images of the cross-section of (a) GO film and (b) crosslinked GO film with 10 wt% of glutaradehyde.

Conclusions

In summary, the graphene oxide (GO) paper can be prepared by a simple drop casting method by drying GO aqueous solution on a hydrophobic substrate. The resultant GO paper can be peeled off the substrates easily and the freestanding GO papers can be fabricated in large scales. Significant enhancement in mechanical stiffness (341%) and fracture strength (234%) of GO paper can be achieved upon modification of GO papers with a small amount (less than 10 wt%) of glutaraldehyde. This fascinating method is very easy and paves the way for the industry preparation of GO papers, which have a bright future for many potential applications.

Acknowledgements

The authors gratefully acknowledge financial supports by the National Natural Science Foundation of China (No. 51102164 and 50902092), Science and Technology Commission of Shanghai Municipality (No. 1052nm06800 and 1052nm02000), Shanghai Pujiang Program (No. 11PJD011), and the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning.

References

[1] A. K. Geim and K.S. Novoselov, Nat. Mater. 6, 183

(2007). http://dx.doi.org/10.1038/nmat1849

[2] C. Lee, X. Wei, J.W. Kysar and J. Hone, Science 321, 385 (2008). http://dx.doi.org/10.1126/science.1157996

[3] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao and C. N. Lau, Nano Lett. 8, 902 (2008). http://dx.doi.org/10.1021/nl0731872

[4] K. I. Bolotin, K. J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim and H. L. Stormer, Solid State Commun. 146, 351 (2008). http://dx.doi.org/10.1016/j.ssc.2008.02.024

[5] M. D. Stoller, S. Park, Y. Zhu, J. An and R. S. Ruoff, Nano Lett. 8, 3498 (2008). http://dx.doi.org/10.1021/nl802558y

[6] Y. Zhang, Y. W. Tan, H. L. Stormer and P. Kim, Nature 438, 201 (2005). http://dx.doi.org/10.1038/nature04235

[7] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen and R. S. Ruoff, Nature 442, 282 (2006). http://dx.doi.org/10.1038/nature04969

[8] X. Li, X. Wang, L. Zhang, S. Lee and H. Dai, Science 319, 1229 (2008). http://dx.doi.org/10.1126/science.1150878

[9] P. Avouris, Z. Chen and V. Perebeinos, Nat. Nanotechnol. 2, 605 (2007). http://dx.doi.org/10.1038/nnano.2007.300

[10] V. Dua, S. P. Surwade, S. Ammu, S. R. Agnihotra, S. Jain, K. E. Roberts, S. Park, R. S. Ruoff and S. K. Manohar, Angew. Chem. Int. Ed. 49, 2154 (2010). http://dx.doi.org/10.1002/anie.200905089

[11] J. T. Robinson, F. K. Perkins, E. S. Snow, Z. Wei and P. E. Sheehan, Nano Lett. 8, 3137 (2008). http://dx.doi.org/10.1021/nl8013007

[12] D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. B. Dommett, G. Evmenenko, S. T. Nguyen and R. S. Ruoff, Nature 448, 457 (2007). http://dx.doi.org/10.1038/nature06016

[13] S. Park, K. S. Lee, G. Bozoklu, W. Cai, S. T. Nguyen and R. S. Ruoff, ACS Nano 2, 572 (2008). http://dx.doi.org/10.1021/nn700349a

[14] S. Park, N. Mohanty, J.W Suk., A. Nagaraja, J. An, R.D. Piner, W. Cai, D. R. Dreyer, V. Berry and R. S. Ruoff, Adv. Mater. 22, 1736 (2010). http://dx.doi.org/10.1002/adma.200903611

[15] X. Wang, H. Bai, Z. Yao, A. Liu and G. Shi, J. Mater. Chem. 20, 9032 (2010). http://dx.doi.org/10.1039/c0jm01852j

[16] J. Oh, J. H. Lee, J. C. Koo, H. R. Choi, Y. Lee, T. Kim, N. D. Luong and J. D. Nam, J. Mater. Chem. 20, 9200 (2010). http://dx.doi.org/10.1039/c0jm00107d

[17] K. S. Novoselov, A. K. Geim, S. V Morozov., D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Crigorieva and A. A. Firsov, Science 306, 666 (2004). http://dx.doi.org/10.1126/science.1102896

[18] C. Berger, Z. Song, T. Li, X. Li, A. Y. Ogbazghi, R. Feng, Z. Dai, A. N. Marchenkov, E. H. Conrad, P. N. First and W. A. D. Heer, J. Phys. Chem. B 108, 19912 (2004). http://dx.doi.org/10.1021/jp040650f

[19] A. Dato, V. Radmilovic, Z. Lee, J. Phillips and M. Frenklach, Nano Lett. 8, 2012 (2008). http://dx.doi.org/10.1021/nl8011566

[20] 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 457, 706 (2009). http://dx.doi.org/10.1038/nature07719

[21] A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. S. Dresselhaus and J. Kong, Nano Lett. 9, 30 (2009). http://dx.doi.org/10.1021/nl801827v

[22] P. W. Sutter, J. I. Flege and E. A. Sutter, Nat. Mater. 7, 406 (2008). http://dx.doi.org/10.1038/nmat2166

[23] D. Li, M. B. Muller, S. Gilje, R. B. Kaner and G. G. Wallace, Nat. Nanotechnol. 3, 101 (2008). http://dx.doi.org/10.1038/nnano.2007.451

[24] S. Park and R. S. Ruoff, Nat. Nanotechnol. 4, 217 (2009). http://dx.doi.org/10.1038/nnano.2009.58

[25] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammers, Y. Jia, Y. Wu, S. T. Nguyen and R. S. Ruoff, Carbon 45, 1558 (2007). http://dx.doi.org/10.1016/j.carbon.2007.02.034

[26] V. C. Tung, M. J. Allen, Y. Yang and R. B. Kaner, Nat. Nanotechnol. 4, 25 (2009). http://dx.doi.org/10.1038/nnano.2008.329

[27] J. W. Suk, R. D. Piner, J. An and R. S. Ruoff, ACS Nano 4, 6557 (2010). http://dx.doi.org/10.1021/nn101781v

[28] C. Chen, Q. H. Yang, Y. Yang, W. Lv, Y. Wen, P. X. Hou, M. Wang and H. M. Cheng, Adv. Mater. 21, 3007 (2009). http://dx.doi.org/10.1002/adma.200803726

[29] Y. Xu, H. Bai, G. Lu, C. Li and G. Shi, J. Am. Chem. Soc. 130, 5856 (2008). http://dx.doi.org/10.1021/ja800745y

[30] D. Li, M. B. Muller, S. Gilje, R. B. Kaner and G. G. Wallace, Nat. Nanotechnol. 3, 101 (2008). http://dx.doi.org/10.1038/nnano.2007.451

[31] H. Q. Chen, M. B. Muller, K. J. Gilmore, G. G. Wallace and D. Li, Adv. Mater. 20, 3557 (2008). http://dx.doi.org/10.1002/adma.200800757

[32] X. Li, G. Zhang, X. Bai, X. Sun, X. Wang, E. Wang and H. Dai, Nat. Nanotechnol. 3, 538 (2008). http://dx.doi.org/10.1038/nnano.2008.210

[33] L. J. Cote, F. Kim and J. X. Huang, J. Am. Chem. Soc. 131, 1043 (2009). http://dx.doi.org/10.1021/ja806262m

[34] G. I. Titelman, V. Gelmana, S. Brona, R. L. Khalfinb, Y. Cohenb and H. Bianco-Peled, Carbon 43, 641 (2005). http://dx.doi.org/10.1016/j.carbon.2004.10.035

[35] J. Zhang, H. Yang, G. Shen, P. Cheng, J. Zhang and S. Guo, Chem. Commun. 46, 1112 (2010). http://dx.doi.org/10.1039/b917705a

[36] N. Hu, H. Zhou, G. Dang, X. Rao, C. Chen and W. Zhang, Polym. Int. 56, 655 (2007). http://dx.doi.org/10.1002/pi.2187

[37] N. Hu, H. Zhou, G. Dang, C. Chen, J. Jing and W. Zhang, Polym. Int. 57, 927 (2008). http://dx.doi.org/10.1002/pi.2429

[38] S. W. Chang, V. P. Chuang, S. T. Boles, C. A. Ross and C. V. Thompson, Adv. Funct. Mater. 19, 1 (2009). http://dx.doi.org/10.1002/adfm.200900181

[39] Y. Kurimoto, M. Takeda, A. Koizumi, S. Yamauchi, S. Doi and Y. Tamura, Bioresour. Technol. 74, 151 (2000). http://dx.doi.org/10.1016/S0960-8524(00)00009-2

[40] S. Niyog, E. Bekyarova, M. E. Itkis, J. L. McWilliams, M. A. Hamon and R. C. Haddon, J. Am. Chem. Soc. 128, 7720 (2006). http://dx.doi.org/10.1021/ja060680r

[41] Y. C. Si and E. T. Samulski, Nano Lett. 8, 1679 (2008). http://dx.doi.org/10.1021/nl080604h

[42] J. I. Paredes, S. Villar-Rodil, A. Martinez-Alonso and J. M. D. Tascon, Langmuir 24, 10560 (2008). http://dx.doi.org/10.1021/la801744a

[43] P. Podsiadlo, A. K. Kaushik, E. M. Arruda, A. M. Waas, B. S. Shim, J. D. Xu, H. Nandivada, B. G. Pumplin, J. Lahann, A. Ramamoorthy and N. A. Kotov, Science 318, 80 (2007). http://dx.doi.org/10.1126/science.1143176