ARTICLE

Spontaneous Cracking of Graphite Oxide Sheet on Oxygen Deficient ZnO Film

Jin-yang Liu[a], Hong-bin Cai[b], Huan-yi Ding[a], Kun Zhang[b], Nan Pan[b], Xiao-ping Wang[a,b*]

a. Department of Physics, University of Science and Technology of China, Hefei 230026, China
b. Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China

(Dated: Received on May 18, 2013; Accepted on May 23, 2013)

Graphite oxide (GO) is an important material of wide applications. Owing to its good mechanical property, the GO sheet is always expected to be stable and remains flat on various substrates. Here we demonstrate for the first time an unexpected behavior of the GO sheet on oxygen deficient ZnO film, namely the spontaneous cracking of the entire GO sheet into many small pieces. This unusual behavior has been carefully investigated by a series of control experiments and SEM, XPS and PL measurements. It is anticipated that the oxygen vacancies in the oxygen deficient ZnO film can annihilate epoxy groups of the GO sheet, resulting in the unzipping of the aligned epoxy groups on GO sheet. A prototype of the white light detector made from the cracked GO sheet is fabricated and the device demonstrates high stability and good reproducibility.

Key words: Graphite oxide, Epoxy group, ZnO film, Oxygen vacancy, Photoresponse

I. INTRODUCTION

The graphite oxide (GO), exfoliated chemically from natural flake graphite, has become a high efficient, low cost, and massive productive material for producing graphene, and has attracted a lot of attentions in chemistry and material science [1−4]. GO is usually synthesized through the oxidation of graphite using oxidants including concentrated sulfuric acid, nitric acid and potassium permanganate with Hummers method, and there are often a variety of oxygen groups (such as epoxide, carbonyl (=CO), hydroxyl (−OH) and phenol groups) on its surface [5]. Due to its unique structure, GO can be either readily dispersed into various solvents or further functionalized [6]. To date, GO has been found potential applications for drug delivery, transparent conductive films [7, 8], polymer composites, lithium ion batteries [9], supercapacitors [10], and photodetectors [11, 12]. Moreover, GO can further be considered as a building block for the electrical nanodevices. For example, Wei *et al.* obtained graphene nanoelectronics by thermochemical nanolithography with a heated atomic force microscope tip to reduce the GO sheets [13]. Recently, Zhang *et al.* achieved the direct writing of electronic devices on graphene oxide by catalytic scanning probe lithography [14].

It is intuitively believed that GO is very stable when it is dispersed on the substrate for the applications such as transparent conductive film and electronic device. To our best knowledge, there has hardly been any report available on the stability of GO on different substrates. In this work, we have systematically examined this important issue. It is found experimentally that GO does remain stable on a variety of substrates, including Si, SiO_2, Au film, ITO, and even LaCaMnO (LCMO) film. However, to our surprise, we have observed that the GO sheets are unstable, even spontaneously cracked into small pieces on the oxygen deficient ZnO films. The unusual phenomenon has been carefully investigated by SEM, PL, and XPS, and a possible interpretation is proposed. A prototype photodetector based on the cracked GO (c-GO) sheet has also been constructed, and its photo-response is demonstrated.

II. EXPERIMENTS

The ZnO films (100 nm thick) were prepared by radical assistance sputtering system (RAS-1100C, Shincron Co., Ltd., Japan) [15, 16]. The annealed ZnO films were obtained through annealing the as-prepared ZnO films at 450 °C for 90 min in the tube furnace. The GO sheets were prepared by chemical exfoliation of the natural flake graphite by a modified Hummers' method [17, 18]. The GO was uniformly dispersed in the deionized water (Milli-Q) with the help of the untrasonic (AS10200A untrasonic cleaner auto science Ltd) and centrifuged (Mikro 200R. Hettich. Germany). Then, 4 μL of 0.1 mg/mL GO solution was drop-coated on different substrates and was dried naturally.

X-ray photoelectron spectroscopy (XPS, ESCALAB

*Author to whom correspondence should be addressed. E-mail: xpwang@ustc.edu.cn

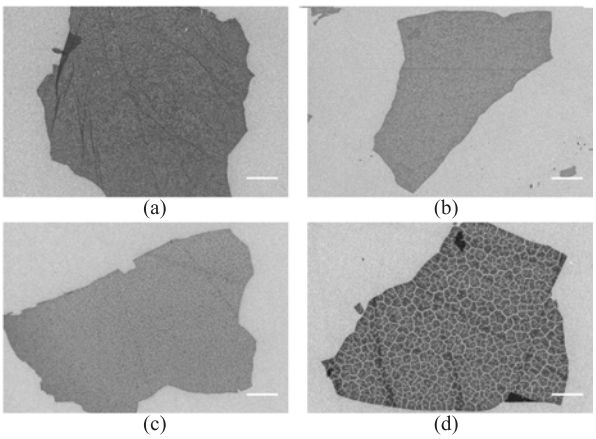

FIG. 1 SEM images of GO coated on the as-prepared (a, b) and annealed (c, d) ZnO film after drying in atmosphere for 3 h (a, c) and 10 h (b, d). The scale bar is 4 μm.

250. Thermo-VG Scientific) was exploited to examine the chemical states of the ZnO film before and after annealing. Photoluminescense of ZnO films was characterized with excitation source of He-Cd pump laser (325 nm, LABRAM-HR) at room temperature. Scanning electron microscope (SEM) (Raith, e-LiNE lithography system, Germany) was used to observe the morphologies of GO sheets. The Keithley-4200 semiconductor characterization system was used to characterize the photoresponse of the device under the white light illumination with the power of 100 mW/cm^2 (Oriel instruments, Newport Corporation. USA).

III. RESULTS AND DISCUSSION

GO sheets are laid on the substrates using drop-coated method. Figure 1 shows the SEM images of the GO sheets on both as-prepared and annealed ZnO films after drying naturally for 3 and 10 h, respectively. As seen from Fig.1 (a) and (b), even after drying for 10 h, single layer GO sheet keeps stable and flat on the as-prepared ZnO film except some wrinkles occurred, which was induced by the deposition process. The results can be well understood because GO possesses a exotic good mechanical property [19]. However, an behavior, the spontaneous cracking of the GO sheet on namely the annealed ZnO film, can be observed. As shown in Fig.1 (c) and (d), a lot of faint gaps in the GO sheets occur after drying 3 h (Fig.1(c)) and the gaps increase with the increasing of drying time. As shown in Fig.1(d), the width of the gaps is about tens of nanometers and their distribution is quite uniform. The average size of the cracked GO (c-GO) pieces is estimated to be about 1−2 μm, while the shape of c-GO is diverse.

It should be pointed out that the spontaneous cracking behavior is unique and reproducible for the annealed ZnO film. Figure 2 (a)−(e) show the SEM images of GO

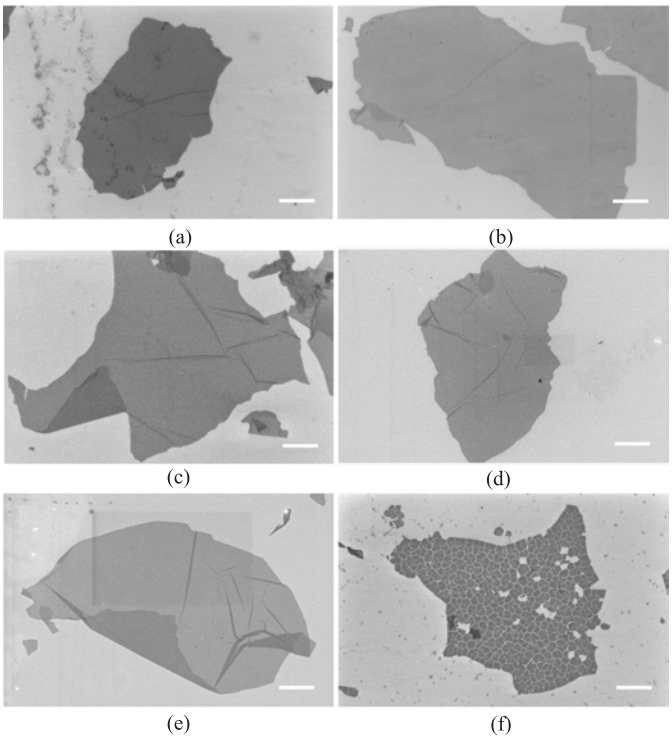

FIG. 2 SEM images of GO sheets on (a) Si, (b) 300 nm SiO_2, (c) 5 nm Au, (d) 100 nm ITO, (e) LCMO film, and (f) the transferred c-GO on SiO_2 substrate. The scale bar is 4 μm.

laid on different substrates including Si, SiO_2, Au, ITO, and LCMO. As seen, the GO demonstrates the similar morphologies to that shown in Fig.1(a), indicating the GO sheet is stable on these substrates. Figure 2(f) shows the result of the c-GO transferred from the annealed ZnO film onto a SiO_2 substrate. Clearly, one can find that some pieces of c-GO have been lost during the transfer process. This further implies that the spontaneous cracking behavior has really taken place in the GO sheet when it is put on the surface of the annealed ZnO film.

In order to understand the reason for the different stability of GO sheets on the as-prepared and annealed ZnO film, we first performed XPS measurements of ZnO films and the results are shown in Fig.3 (a) and (b). It can be found that O1s signals have wide and asymmetric shapes for both ZnO films. According to our previous reports [20, 21], the O1s can be deconvoluted into three Gaussian spectral components, centered at 530.3, 531.6, and 532.5 eV, respectively. Generally, the peak at 530.3 eV is attributed to the Zn−O bonds, and the peak at 532.5 eV is usually attributed to chemisorbed or dissociated oxygen or OH species on the surface of the ZnO thin film, such as $-CO_3$, adsorbed H_2O or adsorbed O_2. The component peaked at 531.6 eV is associated with O_2^- ions, which is correspondent to the oxygen-deficient regions within the ZnO matrix. The intensi-

DOI:10.1063/1674-0068/27/01/87-91

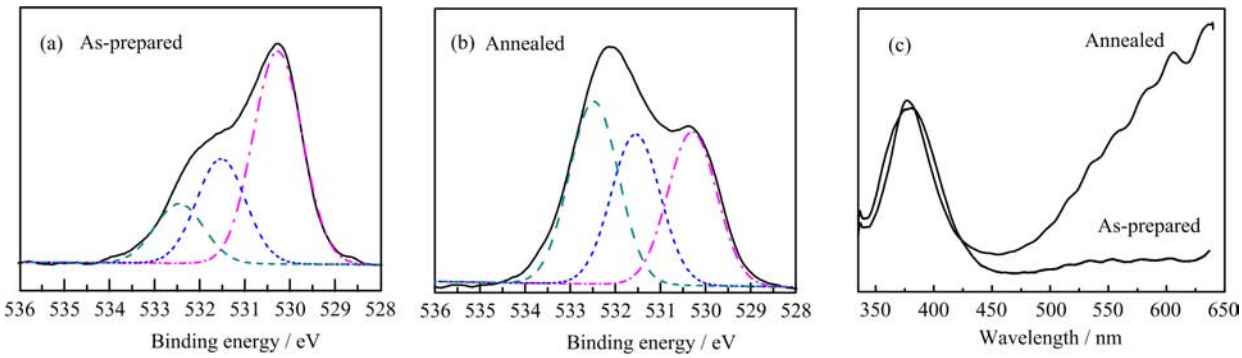

FIG. 3 XPS of O1s (a) the as-prepared and (b) the annealed ZnO films. (c) The corresponding PL results of two ZnO films.

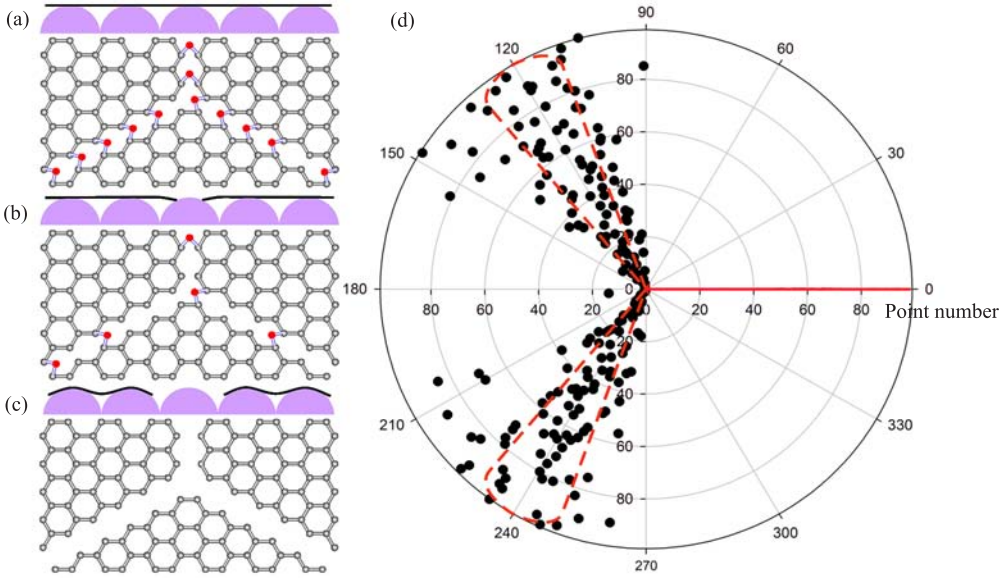

FIG. 4 (a)−(c) The schematic illustration of cracking process of GO sheets through unzipping along the aligned linear epoxy groups and formed three cracking small GO pieces. (d) Statistical results of the angular vertex of adjacent pieces of Fig.1(d).

ties of the peak at 531.6 and 532.5 eV of the annealed ZnO film are much stronger than those of as-prepared ZnO film, implying that the annealed ZnO film contains more oxygen vacancy defects and oxygen-deficient regions. The above conclusion can further be supported by the photoluminescense (PL) measurements of ZnO films. As seen from Fig.3(c), the annealed ZnO film has a strong green and orange light emission compared to as-prepared ZnO film, while both films have similar near band UV emission. Because the green light emission is generally attributed to the oxygen-deficient states, especially oxygen vacancies in ZnO, while the orange luminescence bands result from ioned oxygen vacancies in ZnO [22−25], we can conclude that the annealed sample is an oxygen deficient ZnO film as compared to the as-prepared sample.

On the other hand, it is well known that there are lots of oxygen-based (such as epoxide, carbonyl and hydroxyl) groups on the GO surface [18] and these groups incline to aggregate or be aligned to decrease the surface energy of GO. For example, from the theoretical calculation, Li *et al.* found that once two epoxides were formed on the opposite side of a carbon hexagon, there was a strong tendency for other epoxy groups aligning in a line and then the aligned epoxy groups could induce a rupture of the underlying C−C bonds to form the open epoxide rings [26]. The prediction of aligned linear epoxy groups were directly confirmed by STM observation recently [27].

Based on the facts that the oxygen vacancies existed on the surface of annealed ZnO films and the epoxy groups aligned on the GO sheets, a possible interpretation for the spontaneous cracking of the GO sheet on the annealed ZnO film can thus be proposed. As the GO lying on the oxygen-deficient ZnO film, the epoxy groups on the GO sheet can be annihilated by the surface oxygen vacancy in the annealed ZnO film. Because the aligned epoxy groups are like a zip on the GO, removing one epoxy group from the zip can start up the unzipping process to break GO (Fig.4(a)). As the cracking

DOI:10.1063/1674-0068/27/01/87-91

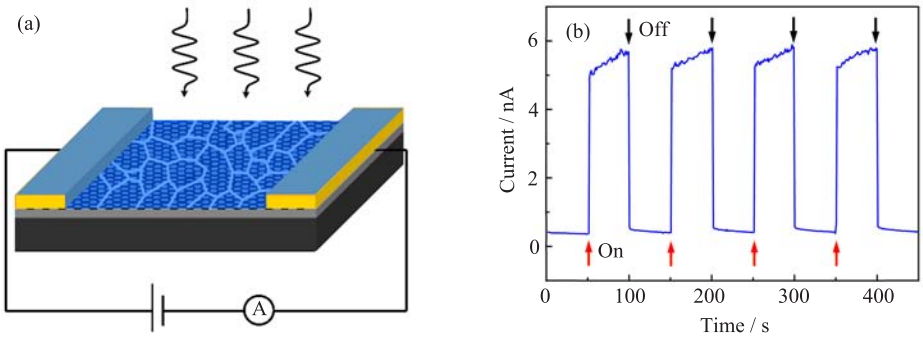

FIG. 5 (a) The schematic diagram of the device. (b) The photoresponse of the devices at 1.0 V bias voltage under the white light with power density of 100 mW/cm^2.

developed, the whole GO will end up into many small pieces (Fig.4(b)). In addition, due to the strong capillary effect between the ZnO films and the flexible GO piece, the small GO piece adheres to the grain surface of ZnO film, resulting in widening the gaps between the pieces (Fig.4(c)). Considering the hexagon structure of GO and mechanical balance, we suggest that the adjacent cracking gaps should present an average angular vertex of 120°. Figure 4(d) plots the statistical results of angular vertex of the c-GO pieces shown in Fig.1(d). As seen, most of the angular vertex is about 120° and the result is well consistent with our above assumption.

The cracks in c-GO pieces may offer an ideal candidate for the nano-electrodes that are useful for a variety of nanodevices such as photodetector, gas sensor, and chemical sensing [28−31]. Herein, we have fabricated a prototype of white light photodetector with c-GO pieces and the schematic drawing is shown in Fig.5(a). The c-GO sheets on the annealed ZnO film are first transferred to the SiO_2/Si and further reduced at high temperature. The contact electrodes are fabricated by EBL with lift-off technology, and CuPc molecules as the photosensitizer are evaporated onto the c-GO pieces. The photoresponse of the device at a bias of 1 V under the white light illumination with power density of 100 mW/cm^2 is given in Fig.5(b). As shown, the photosensitivity of the device (I_{on}/I_{off}) can be as large as ∼10 and the photoresponse is reversible and very stable. Note that there is no any photoresponse for the control devices with the same size based on simple CuPc or reduced c-GO, indicating the nanogap of the cracked GO sheet plays an important role in the photorespense.

IV. CONCLUSION

The spontaneous cracking of the GO sheet on oxygen deficient ZnO film has been observed, which is in stark contrast with the conventional wisdom that the GO should always be stable due to its good mechanical property. Such a unusual phenomenon has been carefully examined by a series of controlling experiments and a possible mechanism is proposed. It can be suggested that the oxygen vacancies in oxygen deficient ZnO film can annihilate the epoxy groups on the surface of GO, leading to the unzipping of the aligned epoxy groups on the GO sheet. A white light detector based on the c-GO pieces has been fabricated, which has achieved high stability and good reproducibility. Our finding may offer new insight on the stability of GO sheet and novel nanogap electrodes for optoelectronic devices.

V. ACKNOWLEDGMENTS

This work was supported by the Ministry of Science and Technology of China (No.2011CB921403), the Chinese Academy of Science (No.XDB01020000), and the National Natural Science Foundation of China.

[1] D. R. Dreyer, S. Park, C. W. Bielawski, and R. S. Ruoff, Chem. Soc. Rev. **39**, 228 (2010).
[2] S. Park and R. S. Ruoff, Nat. Nanotechnol. **4**, 217 (2009).
[3] C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam, and A. Govindaraj, Angew Chem. Int. Edit. **48**, 7752 (2009).
[4] Y. H. Wu, T. Yu, and Z. X. Shen, J. Appl. Phys. **108**, 071301 (2010).
[5] A. Lerf, H. Y. He, M. Forster, and J. Klinowski, J. Phys. Chem. B **102**, 4477 (1998).
[6] J. I. Paredes, S. Villar-Rodil, A. Martinez-Alonso, and J. M. D. Tascon, Langmuir **24**, 10560 (2008).
[7] L. J. Cote, F. Kim, and J. X. Huang, J. Am. Chem. Soc. **131**, 1043 (2009).
[8] Z. G. Geng, G. H. Zhang, Y. Lin, X. X. Yu, W. Z. Ren, Y. K. Wu, N. Pan, and X. P. Wang, Chin. J. Chem. Phys. **25**, 494 (2012).
[9] G. X. Wang, B. Wang, X. L. Wang, J. Park, S. X. Dou, H. Ahn, and K. Kim, J. Mater. Chem. **19**, 8378 (2009).
[10] S. Chen, J. W. Zhu, X. D. Wu, Q. F. Han, and X. Wang, ACS Nano **4**, 2822 (2010).
[11] Y. W. Zhu, S. Murali, W. W. Cai, X. S. Li, J. W. Suk, J. R. Potts, and R. S. Ruoff, Adv. Mater. **22**, 3906 (2010).

DOI:10.1063/1674-0068/27/01/87-91

[12] J. Y. Liu, X. X. Yu, G. H. Zhang, Y. K. Wu, K. Zhang, N. Pan, and X. P. Wang, Chin. J. Chem. Phys. **26**, 225 (2013).
[13] Z. Q. Wei, D. B. Wang, S. Kim, S. Y. Kim, Y. K. Hu, M. K. Yakes, A. R. Laracuente, Z. T. Dai, S. R. Marder, C. Berger, W. P. King, W. A. de Heer, P. E. Sheehan, and E. Riedo, Science **328**, 1373 (2010).
[14] K. Zhang, Q. Fu, N. Pan, X. X. Yu, J. Y. Liu, Y. Luo, X. P. Wang, J. L. Yang, and J. G. Hou, Nature Commun. 3, (2012).
[15] Y. Z. Song and T. Sakurai, Vacuum **74**, 409 (2004).
[16] Q. M. Song, B. J. Wu, B. Xie, F. Huang, M. Li, H. Q. Wang, Y. S. Jiang, and Y. Z. Song, J. Appl. Phys. **105**, 044509 (2009).
[17] G. Williams, B. Seger, and P. V. Kamat, ACS Nano **2**, 1487 (2008).
[18] X. X. Yu, H. B. Cai, W. H. Zhang, X. J. Li, N. Pan, Y. Luo, X. P. Wang, and J. G. Hou, ACS Nano **5**, 952 (2011).
[19] J. W. Suk, R. D. Piner, J. An, and R. S. Ruoff, ACS Nano **4**, 6557 (2010).
[20] H. Y. Ding, Z. Zhao, G. H. Zhang, Y. K. Wu, Z. W. Gao, J. W. Li, K. Zhang, N. Pan, and X. P. Wang, J. Phys. Chem. C **116**, 17294 (2012).
[21] Q. H. Shen, Z. W. Gao, H. Y. Ding, G. H. Zhang, N. Pan, and X. P. Wang, Acta Phys. Sin-Ch. Ed. **61**, (2012).
[22] B. X. Lin, Z. X. Fu, Y. B. Jia, and G. H. Liao, J. Electrochem. Soc. **148**, G110 (2001).
[23] S. A. Studenikin, N. Golego, and M. Cocivera, J. Appl. Phys. **84**, 2287 (1998).
[24] A. B. Djurisic, Y. H. Leung, K. H. Tam, Y. F. Hsu, L. Ding, W. K. Ge, Y. C. Zhong, K. S. Wong, W. K. Chan, H. L. Tam, K. W. Cheah, W. M. Kwok, and D. L. Phillips, Nanotechnology **18**, 095702 (2007).
[25] A. B. Djurisic and Y. H. Leung, Small **2**, 944 (2006).
[26] J. L. Li, K. N. Kudin, M. J. McAllister, R. K. Prud'homme, I. A. Aksay, and R. Car, Phys. Rev. Lett. **96**, 176101 (2006).
[27] D. Pandey, R. Reifenberger, and R. Piner, Surf. Sci. **602**, 1607 (2008).
[28] T. Li, W. P. Hu, and D. B. Zhu, Adv. Mater. **22**, 286 (2010).
[29] W. Chen, H. Ahmed, and K. Nakazoto, Appl. Phys. Lett. **66**, 3383 (1995).
[30] L. D. Qin, S. Park, L. Huang, and C. A. Mirkin, Science **309**, 113 (2005).
[31] Y. D. He, H. L. Dong, T. Li, C. L. Wang, W. Shao, Y. J. Zhang, L. Jiang, and W. P. Hu, Appl. Phys. Lett. **97**, 133301 (2010).

DOI:10.1063/1674-0068/27/01/87-91