Materials Letters 116 (2014) 23-26

Contents lists available at ScienceDirect



Materials Letters

journal homepage: www.elsevier.com/locate/matlet

# Transparent N-doped graphene films on substrates fabricated by hydroxylamine diffusion induced assembly



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materials letters

Yunzhen Chang, Gaoyi Han<sup>\*</sup>, Dongying Fu, Feifei Liu

Institute of Molecular Science, Shanxi University, Taiyuan 030006, China

#### ARTICLE INFO

Article history: Received 13 September 2013 Accepted 23 October 2013 Available online 29 October 2013

Keywords: Transparent film N-doped Graphene Assembly Carbon materials Thin films

## ABSTRACT

Transparent N-doped graphene films (NG-TF) on substrates have been fabricated by using approach of "hydroxylamine diffusion induced assembly". The films have been characterized by X-ray photoelectron spectroscopy, scanning electron microscopy, UV–visible and Raman spectroscopy. The results indicate that the N atom has doped into graphene sheets and the transmittance of the films at 550 nm has linear relationship versus the films' thickness, and that the surface resistance of the films decreases with the increase of graphene thickness deposited on the substrates. The optimum NG-TF exhibits a surface resistance of about 4000  $\Omega$ /square and transmittance of about 78% at 550 nm.

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#### 1. Introduction

Graphene has attracted much attention in various fields of science and technology such as electronics, composite materials, catalysis, biomedicine, energy generation and storage [1–4] since it has been reported by Novoselov et al. [4] owing to its excellent mechanical strength, high electrical, thermal conductivities and optical transmittance (97.7% for single layer) [5–7]. The graphene-based materials produced through chemically reducing graphene oxide (rGO) has been considered to be the more efficient, inexpensive and simple approach to large-scale use although methods of mechanic exfoliation, epitaxial growth and chemical vapor deposition (CVD) [8,9] have developed to prepare high-quality graphene. Besides the graphene-based paper-like films, powder, hydrogels and aerogels prepared from GO, the transparent films of graphene are the other interesting materials due to their potential use in transparent electrodes.

Up to date, in addition to using CVD, graphene-based transparent films have also been prepared through filtration-transfer, spin coating, dip-coating, spraying, Langmuir–Blodgett assembly, liquid–liquid or liquid–air interfaces self-assembly by using the GO as the sources [10–12]. On the other hand, N doping is another effective approach to tailor the properties of graphene and expand their applications [13]. Compared with the N-doping approaches performed under harsh conditions such as CVD and plasma treatment [14] etc, N-doped graphene synthesized by solutionphase has been considered to be a feasible approach due to its simple, low-cost and larger-scale production.

Considering that the GO has hydroxyl and epoxide functional groups on the basal plane and carbonyl and carboxyl groups at the edges [15] and that the oxygen-containing groups will interact with reagents containing amine or hydroxyl groups to form precipitate or gel, we develop a facile approach named as "hydro-xylamine diffusion induced assembly (DIA)" to prepare N-doped graphene transparent film (NG-TF) on substrates in large scale (Fig. 1). Firstly, the dilute GO suspension is injected into the bottom of ethanol solution of hydroxylamine which acts as chemical reductant and dopant, the GO solution will spread out on the bottom because of the different density between the water and ethanol. Then the GO sheets coagulate slowly to form thin film on the substrate at room temperature with the help of hydroxylamine flocculants, finally the desired NG-TF on substrates was obtained after the evaporation of the solvent under heating.

#### 2. Experiment

*Materials*: Natural graphite powder (325 mesh) was purchased from Tianjin Guangfu Research Institute. Hydroxylamine hydrochloride was obtained from Tianjin North Fine Chemical Co., Ltd., and all other chemicals were of analytical grade. GO was prepared by oxidation of natural graphite powder according to the method reported previously [2,3], the GO dispersion was diluted to about 5.0 mg/mL, and treated under the ultrasonication for 10 min before use. Hydroxylamine was generally prepared through the

<sup>\*</sup> Corresponding author. Tel.: +86 3517 010 699; fax: +86 351 7016358. *E-mail address*: han\_gaoyis@sxu.edu.cn (G. Han).



Fig. 1. Schematic diagram of "hydroxylamine diffusion induced assembly" for preparing NG-TF.



Fig. 2. Photographs of NG-TF deposited on glass (A), PET (B), the SEM image of the NG-TF with 90 (C) and 70% transmittance (D).

reaction of equal molar hydroxylamine hydrochloride with potassium hydroxide in ethanol solution and used instantly.

Fabrication of NG-TF: The container with the size of  $10.5 \times$  $10.5 \times 5$  or  $20.5 \times 20.5 \times 5$  cm<sup>3</sup> (length × width × height) containing appropriate substrate (glass plate with a thickness 1.1 mm or polyethylene terephthalate (PET)) at the bottom were adjusted to leveling in an oven, and then was filled with 45 or 200 mL ethanol solution of hydroxylamine (0.2 mg/mL). Subsequently, 4.0 or 16.0 mL GO dilute dispersions with different concentrations were carefully injected into the bottom of the container to make the amount of GO on the substrates ranged from 0.55 to 5.1  $\mu$ g/cm<sup>2</sup>. After the mixture was placed overnight, the temperature of the oven was increased to 40  $^\circ\text{C}$  and kept this temperature for 2.0 h, and the temperature was then increased to 100 °C slowly. Successively the temperature was increased to about 150 °C and kept this temperature for 4.0 h after the solvent has been evaporated and dried. Finally, the NG-TF deposited on the glass or PET was taken out carefully and washed by water thoroughly.

*Characterization*: The morphologies of the samples were observed by using a JEOL-JSM-6701 field-emission microscope (SEM). X-ray photoelectron spectroscopy (XPS) was performed with an ESCAL-ab 220i-XL spectrometer (VG Scientific, England) using monochromic Al Ka source at 1486.6 eV. Raman spectra were recorded on a JobinYvon Lab RAMHR800 microscopic confocal Raman spectrometer by using laser of 514 nm as incident light. The transmittance of the films was determined by using a HP-8453 UV-visible spectrometer.

#### 3. Results and discussion

By using dilute dispersion of GO and controlling the mass on unit area, the NG-TF with different thicknesses can be easily deposited on the glass and PET. Fig. 2(A) and (b) shows the photographs of the obtained transparent films (the mass of GO on unit area about 2.52 ug/cm<sup>2</sup>) deposited on the glass substrates  $(17 \times 16 \text{ cm}^2)$  and on the PET substrate  $(10 \times 9 \text{ cm}^2)$ . Compared with the blank area of the upper left corner shown in Fig. 2(A), the NG-TF deposited on the substrates is relatively uniform except some dark edges. The SEM image shown in Fig. 2(C) indicates that the discontinuous NG-TF has formed on the substrates when used GO is only about 1.03 µg/cm<sup>2</sup> because of the formed conglomeration of GO. While the continuous NG-TF (Fig. 2(D)) with some wrinkles is formed when used GO is about 3.83 µg/cm<sup>2</sup>, which



Fig. 3. XPS of C1s (A), N1s (B) of the NG-TF reduced by hydroxylamine (a) and treated by HI vapor later (b).



Fig. 4. UV-vis spectra of NG-TF with different GO amounts (A) and the plots of the transmittance (B-a), surface resistance of NG-TF before (B-b) and after (B-c) treated by HI vapor versus the mass of GO on unit area.

indicates that the continuous films can be fabricated when the films are not too thin.

Compared with the XPS of GO, it is found that the N-doped graphene have been synthesized through this process (Fig. S1 and S2). The fitted C1s XPS peaks (Fig. 3(a)) show that the NG-TF contains the C–C, C–N, C–O and O=C–OR groups [2]. The fitted N1s XPS peaks (Fig. 3(B)) at 398.6, 399.8 and 402.1 eV are assigned to pyridinic, pyrrolic and quaternary type of N, respectively [16]. After the NG-TF being treated by the vapor of HI at 150 °C, the similar C1s and N1s XPS spectra are found except the relative content of the different atomic type for C and N has some changes (Table S1 and S2). Furthermore, the presence of I3d XPS peaks (Fig.S3(A)) at 620.3 and 631.8 eV indicates that the iodine has doped in the NG-TF [17]. The Raman spectra of GO show the G band at 1592  $\text{cm}^{-1}$  and D band at 1352 cm<sup>-1</sup>, the NG-TF prepared by using hydroxylamine as reductant shows D and G band at 1356 and 1602 cm<sup>-1</sup> respectively, while the NG-TF treated by HI vapor shows a broad G band which can be divided into two peaks [18,19] located at 1622 and 1592 cm<sup>-1</sup> (Fig. S3B), which reveals that the doping-I makes the G band shift and show two G bands.

The NG-TF shows an absorption peak at the UV range, and the light transmittance decreases with the increase of the film's thickness in the whole range of the spectra (Fig. 4(A)). It is interesting to find that the absorption peak located at UV range has shifted to long wavelength, which indicates that the size of the conjugation of the graphene sheets became larger with the increment of the thickness. The light transmittance of NG-TF at 550 nm exhibits a linear relationship with the mass of GO in unit area (Fig. 4B-a), and the surface resistance of the NG-TF decreases with the increment of the films' thickness (Fig. 4B-b). Furthermore, the surface resistances of the NG-TF deposited on substrates have decreased after being treated by HI vapor at 150 °C (Fig. 4B-c). For example, the surface resistance of the NG-TF films decreases

from 12,000 to 3000  $\Omega$ /square after treated by HI vapor at 60% light transmittance, which is better than that reported in literature [12]. It is well known that the conductivities of NG-TF are strongly influenced by the quality of GO, it is found that the surface resistance can decrease to 4000  $\Omega$ /square at 78% transmittance (550 nm) when the GO prepared by the method of literature [20] is used as precursor.

The composite transparent films of NG-TF can also be fabricated by using this process. For example, the composite films containing  $TiO_2$  and porphyrine have also fabricated on glass substrate by using the mixture of the components and show the combining characteristics of the components (Fig. S5–S8).

#### 4. Conclusion

Different from the preparation of the transparent graphene films such as filtration and spinning coat, we have prepared the NG-TF deposited on substrates in large-scale by using DIA process, during which the molding of GO is carried out at room temperature, the reduction of GO and the N-doping are achieved simultaneously under atmospheric pressure and at low temperature. The obtained NG-TF deposited on the substrates may be used as transparent electrodes in some electronic devices. This method provides a facile approach to prepare NG-TF and its composites in large scale.

#### Acknowledgments

We appreciate funding from NSFC (21274082 and 21073115) and Shanxi province (2012021021–3), and the Program of NCET (NCET-10–0926).

### Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2013.10.096.

#### References

- Stoller MD, Park SJ, Zhu YW, An JH, Ruoff RS. Nano Lett 2008;8:3498–502.
   Fu DY, Han. GY, Chang YZ, Dong JH. Mater Chem Phys 2012;132:673–81.
   Chang YZ, Han GY, Li MY, Gao F. Carbon 2011;49:5158–65.

- [4] Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, et al. Science 2004;306:666-9.
- [5] Lee C, Wei XD, Kysar JW, Hone J. Science 2008;321:385-8.
- [6] Balandin AA. Nat Mater 2011;10:569–81.
  [7] Cai W, Zhu Y, Li X, Piner RD, Ruoff RS. Appl Phys Lett 2009;95:123115–7.
  [8] Bai H, Shi GQ. Adv Mater 2011;23:1089–115.

- [9] Zhang YH, Chen ZY, Wang B, Wu YW, Jin Z, Liu XY, et al. Mater Lett 2013;96:149-51.
- [10] Wang X, Zhi L, Mullen K. Nano Lett 2007;8:323-7.
- [11] Kim F, Cote LJ, Huang J. Adv Mater 2010;22:1954–8.
  [12] Chen FM, Liu SB, Shen JM, Wei L, Liu AD, Chan-Park MB, et al. Langmuir
- 2011;27:9174-81.
- [13] Wang H, Maiyalagan T, Wang X. ACS Catal 2012;2:781-94.
- [14] Zhang CH, Fu L, Liu N, Liu MH, Wang YY, Liu ZF. Adv Mater 2011;23:1020-4. [15] Li D, Muller MB, Gilje S, Kaner RB, Wallace GG. Nat Nanotechnol 2008;3:101-5.
- [16] Chang YZ, Han GY, Yuan JP, Fu DY, Liu FF, Li SD. J Power Sources
- 2013;238:492-500.
- [17] Cai W, Lin Z, Strither T, Smith LM, Hamers RJ. J Phys Chem B 2002;106:2656-64.
- [18] Kudin KN, Ozbas B, Schniepp HC, Prudhomme RK, Aksay IA, Car Roberto. Nano lett 2008;8:36-41.
- [19] Sadezky A, Muckenhuber H, Grothe H, Niessner R, Poschl U. Carbon 2005;43:1731–42.
- [20] Xu YX, Sheng KX, Shi GQ. J. Mater. Chem 2011;21:7376–80.