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

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**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 4000Ω/square and transmittance of about 78% at 550 nm.

**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 solution-phase 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 "hydroxylamine 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...
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 × 10.5 × 5 or 20.5 × 20.5 × 5 cm³ (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 μg/cm². After the mixture was placed overnight, the temperature of the oven was increased to 40°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 monochromatic 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 μg/cm²) deposited on the glass substrates (17 × 16 cm²) and on the PET substrate (10 × 9 cm²). 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/cm² 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/cm², which
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 C 1s XPS peaks (Fig. 3(a)) show that the NG-TF contains the C–C, C–N, C–O and O–C–O–R groups [2]. The fitted N 1s 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 C 1s and N 1s 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 I 3d 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 cm\(^{-1}\) and D band at 1352 cm\(^{-1}\), the NG-TF prepared by using hydroxylamine as reductant shows D and G band at 1356 and 1602 cm\(^{-1}\) 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\(^{-1}\) (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 Ω/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 Ω/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.

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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