Amino-functionalization of graphene nanosheets by electrochemical exfoliation technique

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ABSTRACT

An electrochemical exfoliation route to functionalize graphene nanosheets (GNs) directly from a graphite electrode exposed to N-containing electrolyte is explored under constant-voltage (5–12 V) model. The selection of electrolytes (i.e., $(NH_4)_2HPO_4$, $(NH_4)_2SO_4$, and NH_4NO_3) used herein turns out to be a crucial factor in affecting the amidation level and amino group distribution on as-prepared GNs. The low-potential exfoliation assists an in-situ amino-functionalization reaction, imparting high N-surface coverage on GNs. The electrochemical exfoliation in $(NH_4)_2HPO_4$ is prone to the chemical doping of N element into sp^2 domain, whereas using $(NH_4)_2SO_4$ and NH_4NO_3 electrolyte takes parallel pathway: chemical N doping and decoration of amino and amide–carbonyl groups at edges of GNs. The N/C ratio on the GN sample can reach as high as 8.4 at%, confirmed by X-ray photon spectroscopy. The tunable photoluminescence response of GN dots due to the amino functionalization is investigated, using a band-gap structure model. Accordingly, the efficient approach exhibits a controllable processing method for producing GN product because of its well-defined amidation extent and one-step process without any surface modification treatment.

1. Introduction

Graphene nanosheets (GNs), a two-dimensional network of sp^2-hybridized carbon atoms into hexagonal structure [1], have displayed many charming properties that are useful for practical applications such as transparent conducting film [2], catalyst support [3], lithium-ion battery [4,5], detectable molecule separation [6], semiconductor [7], and electrochemical capacitor [8]. However, the suitability of GNs for these applications is generally restricted by the zero band gap of pristine GNs, resembling the electrochemical behavior of original graphite precursor. Doping of GNs with different atoms including sulfur, boron, and nitrogen is capable of altering electronic and optical properties of GNs [9]. The dopant atoms can tune the electronic band structure of GNs with a desired energy gap between valence and conduction bands [1]. Accordingly, the doping of GNs would be a practical route to tailor available charge density by an incorporation of non-carbon atoms with excess electrons (e.g., nitrogen: n-type doping) or electron deficiency (e.g., boron: n-type doping) [10].

It is generally recognized that nitrogen-doped carbon offers unique properties that can benefit several applications such as quantum graphene dots and other optical characters [11,12]. Several methods have

been successfully developed to prepare N-doped graphene samples, using NH_3 annealing followed by N^+-ion irradiation [1], hydrothermal reaction with ammonia [11,13], ammonia-ultrasonic bathing method [12], chemical doping of epitaxial graphene by 4-amino-2,2,6,6-tetramethyl-1-piperridinyloxy [14], and chemical doping of trans- and cis-azobenzene [15]. Usually, some carbon atoms at core/edges of graphene honeycomb matrix could be replaced by nitrogen, or N-containing groups reside at edges or defects, e.g., amino group [16]. Thus, the N dopants prefer to bind at defects, such as point defects or the interface layer below the graphene layer [14,17]. As a result, the relative abundance of different N dopant types depends on the starting materials used to prepare GNs, the method of preparation, and the experimental conditions [16].

Based on the above deduction, one strategy combining the exfoliation of GNs from graphite and the chemical doping can be devised. The commonly-used techniques that are being developed for producing GN samples include chemical oxidation of graphite powders (e.g., Hummers' method) [18], solid-phase synthesis from citric acid [19], solvent extraction [20], chemical vapor deposition [21], solution-phase exfoliation of graphite [22], and mechanical cleavage from graphite paper [23]. Recently, an electrochemical exfoliation method has

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emerged due to its simplicity, efficient synthesis, and environmental friendliness [24–29]. The electrochemical exfoliation of GNs from graphite electrodes in various solutions (e.g., LiOH, H_2SO_4, $(NH_4)_2SO_4$ and $NH_3 \cdot H_2O$) can achieve high-quality GN products. More recently, oxone as a novel electrolyte and the electrochemically enhanced oxidation were responsible for the excellent aqueous dispersibility, effective exfoliation and the reasonably high yield (up to 60.1%) [30]. In this work, we report an exfoliation route incorporated with in-situ chemical doping of nitrogen, capable of electrochemically exfoliating GNs with different amidation extents from graphite plates, using one-step electrochemical exfoliation approach in N-containing electrolyte. The working potential serves as a crucial factor in determining the N atomic ratio and the functional group on the GN samples. The present work develops one efficient protocol that adopts one-step electro-chemical exfoliation technique to synthesize the GNs with different amidation levels, using three types of N-containing electrolytes, e.g., $(NH_4)_2HPO_4$, $(NH_4)_2SO_4$ and NH_4NO_3.

2. Experimental

2.1. Electrochemical exfoliation of amino-functionalized graphene

The procedure for electrochemically exfoliate functionalized GN from graphite electrodes was reported in our previous study [31]. First, highly-oriented pyrolytic graphite (HOPG) with a dimension of $2 \times 2 \times 1.5\ cm^3$ served as an electrode and source of GNs. One home-made cell two-electrode configuration was used for the fabrication of GN products, in which stainless steel foil and Teflon tank were used as counter electrode and reactor, respectively. Three types of electrolyte were prepared using 10 wt% $(NH_4)_2HPO_4$, $(NH_4)_2SO_4$ and NH_4NO_3. The graphite electrodes were slowly immersed in 200 mL electrolyte, and the distance between the graphite electrode and counter electrode was set at 5 cm. The electrochemical exfoliation process was performed by applying two-step DC bias on the graphite electrode: 1 V for 20 min and then different potentials (i.e., 5, 7, 9, and 12 V) for 30 min. Afterward, the as-prepared GNs were collected and dried at 105 °C in an oven overnight. The exfoliation experiments for each electrolyte were repeated three times. Prior to materials characterization, all samples have been rinsed by distilled water in a home-made sediment tower, allowing them for particle classification. The rinsing process ensured almost no contamination of electrolyte species onto the graphene surface. To estimate the yield of GNs, the graphite electrodes were carefully weighted before and after the exfoliation process. The GN samples, prepared by the electrochemical exfoliation incorporated with chemical amidation, were designated to GN-P, GN-S, and GN-N series, according to the electrolyte type: $(NH_4)_2HPO_4$, $(NH_4)_2SO_4$ and NH_4NO_3, respectively. The sequent number represented the operating voltage. For instance, GN-P5 indicates that the GN sample was obtained by electro-chemically exfoliating the GN product from the graphite electrode in the presence of $(NH_4)_2HPO_4$ at 5 V.

2.2. Characterization of amino-functionalized graphene

The micro-structural morphology of N-modified GN samples was inspected by using high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2100). Fourier transformed infrared (FTIR, Nicolet Avatar 360 FTIR) spectroscopy was employed to identify surface functional groups on GN samples. For each sample, 32 scans in the spectral ranges (i.e., 500–4000 cm^{-1}) were recorded with a resolution of 4 cm^{-1}. The chemical composition of N-modified GN samples was characterized by using X-ray photoelectron spectroscopy (XPS). The XP spectra were recorded by a Fison VG ESCA210 spectrometer with Mg-Kα radiation. Both the C 1s and N 1s spectra were deconvoluted by using a non-linear least squares fitting program with a symmetric Gaussian function. The surface composition of as-prepared GN samples was calculated with an appropriate sensitivity factor. To feature their

optical properties, one centrifugal stratification process was adopted to sieve N-modified GNs, using polymeric filters with different nominal pore sizes. This sieving technique was capable of obtaining GN samples with uniform particle size distribution, ranged from 2 to 3.5 nm. The particle size distributions of each GN sample were analyzed by atomic force microscopy (AFM, Ardic P100). The ultraviolet-visible (UV–vis) absorbance spectra of N-modified GN suspensions were characterized by using an UV–vis spectrometer (Agilent Technology Cary 60). The wavelength scan rate was set at 60 nm/min, each GN suspensions were prepared with a solid content of 0.05 mg GN/1 mL distilled water in quartz cells. For comparison, the distilled water was used as a blank. An optic spectrometer (FLS920P Edinburgh Analytical Instrument) was adopted to analyze the photoluminescence (PL) emission and excitation spectra of N-modified GN suspensions. The PL measurements were carried out at ambient temperature.

3. Results and discussion

HR-TEM and selected-area diffraction (SAD) were employed to shed some lights on the morphology and crystalline structure of as-prepared GN samples. The HR-TEM micrographs of different GNs (i.e., GN-P5, GN-S5, and GN-N5), as illustrated in Fig. 1a–c, reveals wrinkled or folded morphologies with a few stacked layers. The GNs look like a transparent silk with several micrometers in the length. The SAD patterns for each GN sample display several rings (see the inset of Fig. 1a–c), indicating the presence of polycrystalline structures. This finding reflects that the influence of N-containing electrolyte type on the morphology and crystallinity of GNs seems to be minor. Fig. 1d represents FTIR spectra of different samples, where the broad band at 3300–3500 cm^{-1} is assigned to O—H (hydroxyl) groups [24] from the adsorption of moisture. The bands at 1082, 1445, and 1640 cm^{-1} are ascribed to C—O, C—O—C (epoxy), C=O (carbonyl) groups attached to the surface of GN samples. It is worth noting that the N-containing groups show up in all GN samples at 1159, 1525, and 2900–3200 cm^{-1}, attributed from the existence of C—N (nitryl), N—H (amino), N—H in plane stretching of amine groups, respectively [12,32]. The other group, amide–carbonyl (NH—CO) stretching vibration, appears at 1652 cm^{-1} on all GN samples. It is generally recognized that the OH (hydroxyl) groups (i.e., at 3300–3500 cm^{-1}) tend to be physically adsorbed onto the GN sample, whereas the N—H in plane group takes place at 2900–3200 cm^{-1} [33]. As observed from Fig. 1d, the GN-P5 sample shows the highest transmittance band, as compared to the others. This can be inferred from one explanation that the occupancy of amine occurs at the edges in place of oxygenated moieties via the pathway of nucleophlic substitution reaction with N-containing electrolyte by ring opening reaction [12]. The result is presumably due to the electrochemical exfoliation in the presence of $(NH_4)_2HPO_4$, inducing faster chemical kinetics of ring opening than that in other two electrolytes, i.e., $(NH_4)_2SO_4$ and NH_4NO_3.

To inspect the observation, XPS was employed to characterize atomic composition on as-prepared GN samples. The XPS demonstrates that all GN samples prepared in different N-containing electrolytes show similar features and chemical environments, i.e., N 1s (~399 eV), C 1s (~284 eV), and O 1 s (~532 eV). The survey-scan XPS spectra for all samples operated at different electrolyte have been provided in ***Electronic Supporting Information*** (see Fig. S1). However, the variations of N/C and O/C atomic ratios with the exfoliation potential display different trends (see Fig. 2), as to the GN samples electrochemically exfoliated in $(NH_4)_2HPO_4$, $(NH_4)_2SO_4$ and NH_4NO_3. The oxidation level (i.e., O/C atomic ratio) on the as-prepared GN samples shows an order as $(NH_4)_2HPO_4 > NH_4NO_3 > (NH_4)_2SO_4$, whereas the amidation level (i.e., N/C atomic ratio) has a sequence as $(NH_4)_2HPO_4 > (NH_4)_2SO_4 > NH_4NO_3$. It is of interest that the GN-P series sample exhibits higher O/C and N/C ratio, as compared to the other two serial samples. The O/C and N/C ratios on GN-P5 sample can reach as high as 28.0 and 8.4 at%, respectively. The N/C atomic ratio as