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Influence of pH condition on colloidal suspension of exfoliated graphene oxide by electrostatic repulsion

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ABSTRACT

A facile chemical process is described to produce graphene oxide utilizing a zwitterions amino acid intermediate from graphite oxide sheets. 11-aminoundecanoic acid molecules were protonated to intercalate molecules into the graphite oxide sheets to achieve ion exchange, and the carboxyl groups were then ionized in a NaOH solution to exfoliate the graphite oxide sheets. In this way, the produced graphene oxide nanosheets were stably dispersed in water. The delaminated graphene nanosheets were confirmed by XRD, AFM, and TEM. XRD patterns indicated the d_{002}-spacing of the graphite greatly increased from 0.380 nm and 0.870 nm. AFM and TEM images showed that the ordered graphite crystal structure of graphene nanosheets was effectively exfoliated by this method. The prepared graphene nanosheets films showed 87.1% transmittance and a sheet resistance of 2.1×10^3 Ω/square.

1. Introduction

Recently, the isolation a single layer of graphene from graphite has attracted increasing attention because the resulting graphene exhibits novel physicochemical properties such as high values of its Young's modulus, fracture strength, thermal conductivity, specific surface area, electrical conductivity, etc. [1–10]. Graphene was initially isolated by mechanical exfoliation, peeling off the top surface of small mesas of pyrolytic graphite, but this method is not suitable for large-scale production [9,10].

Gaphene can be prepared by chemical processing, involving graphite oxidation, exfoliation, and reduction. This method is the most suitable for producing large-scale production of single graphene nanosheets at low cost [11]. Graphite oxide has been mainly produced by the Brodie [12], Staudenmaier [13], and Hummers methods [14]. These methods involve the entire oxidation of graphite in the presence of strong acid and oxidizing agents. The level of the oxidation can be varied on the basis of the method, the reaction conditions, and the precursor graphite used.

More recently, extensive research has been attempted to prepare graphene from graphite oxide. However, the obtained graphene tends to form irreversible agglomerates or even restack to form graphite through van der Waals interactions in solvents due to its high specific surface area [8]. There have been different methods reported to prepare graphene oxide from exfoliated graphite oxide such as rapid thermal expansion, chemical exfoliation, and ultrasonic dispersion [9]. Chemical exfoliation proceeds by weakening the van der Waals cohesive force upon insertion of reactants in the interlayer space. Subsequently the loosened layer stacking is disrupted when the intercalant decomposition produces a high gas pressure. As a consequence, the sp^2 lattice is partially degraded into a sp^2–sp^3 sheet that possesses less π–π stacking stability. Chemical exfoliation can be performed in suspension and hence up-scalability is straightforward and could offer a route to large scale graphene production [11].

The exfoliation to achieve graphene oxide nanosheets can be prepared by the chemical modification of graphite oxide by organic molecules, for example, the reaction of graphite oxide with octadecylamine, isocyanates, reducing agents, etc. Si and Samulski reported a water soluble sulfonated graphene [8]. In recent work by Fan et al., graphite oxide was exfoliated under alkaline conditions [15]. In Liu et al., graphene, functionalized with oleylamine and soluble in non-polar organic solvents, was produced on a large scale with a high yield by combining the Hummers process for graphite oxidation, an amine-coupling process to make oleylamine-functionalized graphite oxide, and a novel reduction process using trioctylphosphine [16].

However, as-prepared graphene itself is not soluble and cannot be dispersed in water or in any organic solvent. Therefore, among processes to make graphene through chemical fictionalization, it is still a challenge to make suitably exfoliated graphene from graphite oxide. The surface charge (zetapotential) of graphene oxide nanosheets shows that those sheets have negative charges when dispersed in water. This suggests that electrostatic repulsion between negatively charged graphene oxide nanosheets could generate such sheets in a stable aqueous suspension [17].

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The use of aminoundecanoic acid exfoliated graphene oxide nanosheets for transparent and conductive films has not been studied previously.

Therefore, we described a facile chemical process of making graphite oxide, in which the electrostatic repulsion between guest species and inorganic host layers resulted in the delamination of the layered graphene oxide nanosheets. 11-aminoundecanoic acid was first intercalated into the interlayer of the graphite oxide by ion exchange in acidic conditions. Then, the delamination of 11-aminoundecanoic acid intercalated graphite oxide into the elementary layers was carried out in a basic condition.

2. Material and methods

2.1. Preparation of graphite oxide

The pristine graphite flake was made based on the Hummer's method [14]. 11-aminoundecanoic acid was dissolved in deionized water, and the pH value was adjusted to 2 using HCl solution to protonize 11-aminoundecanoic acid. Then, a mixed solution of graphite oxide was added dropwise to the 11-aminoundecanoic acid aqueous solution at room temperature and stirring. The ion-exchanged graphite oxide was filtered, thoroughly washed with acidified water (pH=3), and dried at 50 °C in a vacuum oven. The particles were dispersed in deionzed water; the pH value was adjusted to a certain pH (10, 12, and 14) using NaOH solution. The reaction mixture was treated at room temperature for two days, and the resulting slurry was washed several times by repeated centrifuging and replacement of the washing water. Finally, the obtained samples were dried at 40 °C for one day and were denoted as GA-10, GA-12, and GA-14, respectively. Fig. 1 illustrates this process. These solutions were dip-coated on glass substrates, which were pre-cleaned by the RCA (Radio Corporation of America) method. The substrate was withdrawn upward at a continuous speed of 3 mm/s. Finally, the prepared GA-12 films were immersed in $NaBH_4$ for reduce the graphene oxide nanosheets to graphene nanosheets at 80 °C and denoted as GN-A.

3. Characterization

The structural properties of the samples were also evaluated with an X-ray diffractometer (XRD, DMAX 2500/Rigaku) with Cu$K\alpha$ radiation. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB220i-XL (VG Scientific) spectrometer with monochromatized Mg$K\alpha$ X-ray radiation as the X-ray source for excitation in order to confirm the surface chemistry of graphite flake, graphene oxide, and graphene. Corresponding images of the graphene nanosheets were obtained by atomic force microscopy (AFM, Nanoscope Multimode IVa / Digital Instrument) and transmission electron microscopy (TEM, JEM2100F / JEOL). The sheet resistance was measured by a four-probe tester (Mitsubishi, MCP-T610). The optical transmittance of the film was characterized using a UV–vis spectrophotometer (Shimadzu, UV-2501PC) from 300 to 800 nm wavelengths. The sheet resistance was measured by a four-probe tester (Mitsubishi, MCP-T610).

4. Results and discussion

The structural properties of pristine graphite flake, graphite oxide, and graphene nanosheets were characterized using the XRD analysis, as shown in Fig. 2. For the pristine graphite flake, the sharp and intensive peak at $2\theta=26.6^\circ$ indicated the highly organized layered structure with an interlayer spacing of 0.330 nm (Fig. 2a). After the graphite chemical oxidizes with strong acids, its XRD peaks correspond to a layered structure with a basal spacing of 0.820 nm. According to previous research, the inter-layers of graphite can be intercalated by various molecules or ions such as oxygen functional groups, NO_3^-, and SO_4^{2-} [7,18]. Generally, 11-aminoundecanoic acid is used as a modifier for clay or layered double hydroxides to exfoliate them [17,19]. The zwitterion has an amino group ($-NH_2$) and a carboxylic group (–COOH) in the molecule. It is protonized to form cationic $-NH_3^+$ in acidic media. Thus, the 11-aminoundecanoic acid molecules in the acidic conditions can easily enter into the graphite oxide to accomplish ion exchange with interlayer cations. In this study, exfoliation of the graphite oxide after it is modified with 11-aminoundecanoic acid was greatly facilitated by alkaline media. After graphite oxide exfoliated with 11-aminoundecanoic acid at pH=12, no apparent peaks were detected in the patterns for GA-12, which may be attributed to very thin graphene layers due to the high degree of exfoliation, as shown in Fig. 2a.

When we change the pH values of NaOH, the XRD patterns of the obtained graphene nanosheets show a typical broad peak with an obvious disappearance of the characteristic peaks, which

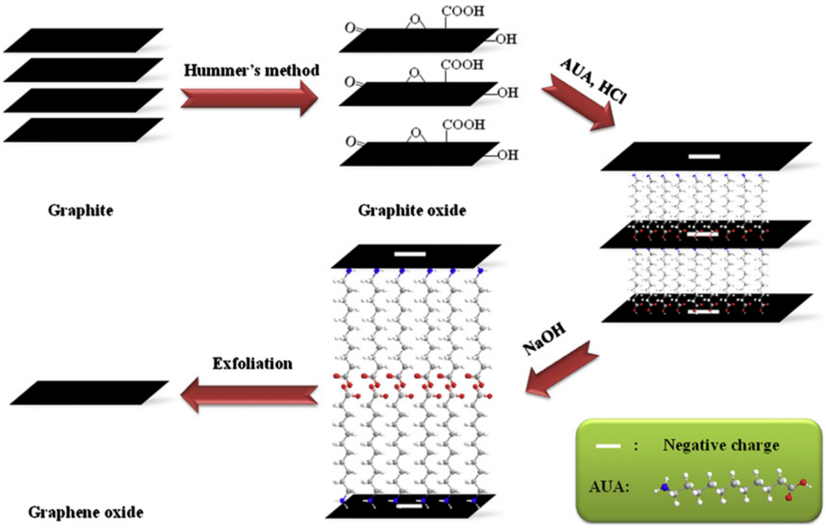

Fig. 1. Preparation procedure of graphene nanosheets.

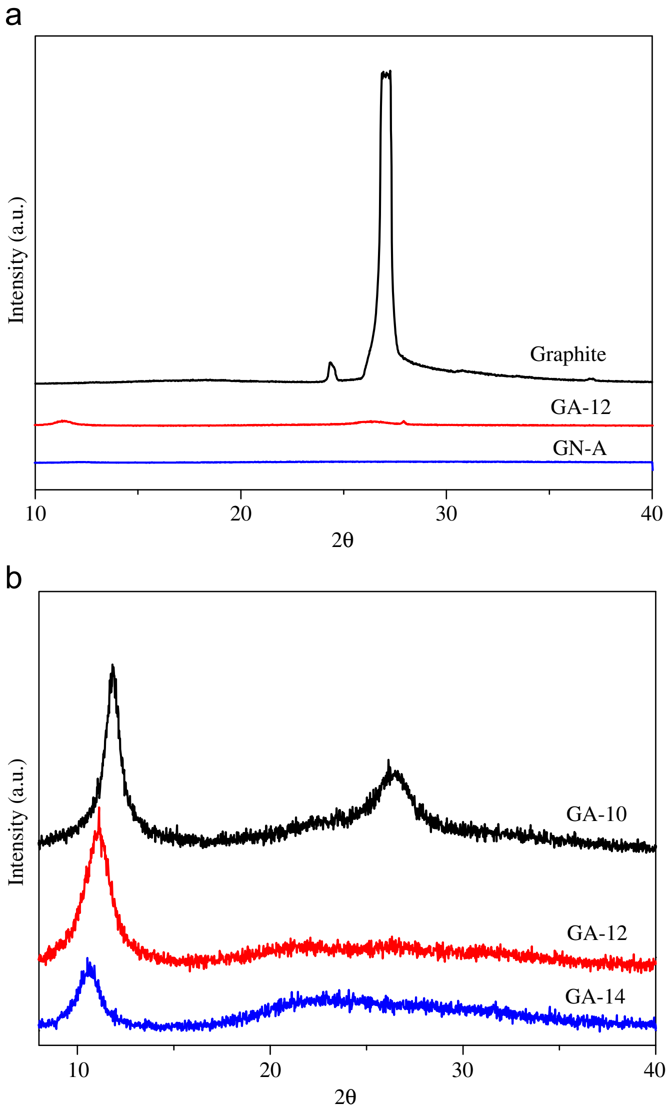

Fig. 2. XRD patterns of graphite flake (a), prepared graphene oxide nanosheets (b), and graphene nanosheets (after reduction GN-A, a).

might be attributed to very thin graphene layers due to the high degree of exfoliation. This result indicates that the graphene nanosheets are exfoliated into a monolayer or few-layers, resulting in a new lattice structure that is significantly different from the pristine graphite flake and graphite oxide. The interlayer spacing of the graphene nanosheets (23.7°, 0.335 nm) is smaller than that of other prepared graphene nanosheets (GA-10: 0.376 nm, GA-12: 0.415 nm, and GA-14: 0.400 nm). The higher basal spacing of GA-12 may be due to the presence of residual oxygen, indicating incomplete reduction of graphene oxide to graphene nanosheets. The absence of sharp basal peak (the 2θ range of 10–13°) suggests that each host sheet is in irregular orientation in the graphene oxide slurry and the disappearance of long-range graphite oxide due to the delamination of graphene oxide layers into individual nanosheets.

XPS was used to investigate the introduction of atomic concentrations on the natural graphite, GA-12, and GN-12, as shown in Table 1. The oxygen concentration of natural graphite was only a small proportion of 0.47%, but after thermal expansion and chemical oxidation treatments, it drastically increased to 28.55%. This result is attributable to an increase in the amount of surface oxygen groups, such as epoxide, hydroxyl, carbonyl, and carboxyl groups [30]. The chemical reduction process decreased much of oxygen content on the surfaces of GA-12, reducing the O/C ratio from 0.400 to 0.201. It is known that graphene oxide is chemically reduced, which is probably due to the reduction of oxygen functional groups of graphene oxide by $NaBH_4$.

Table 1
Atomic concentrations of graphite, GA-12, and GN-12 [%].

Samples	Elements		
	C 1*s*	O 1*s*	O/C ratio
Graphite	99.53	0.47	0.005
GA-12	71.45	28.55	0.400
GN-12	83.27	16.73	0.201

AFM is used to determine the thickness of the graphene-based sheets, and shown in Fig. 3a and b. Apparently, the fully exfoliated graphenes are observed with an average nanosheet size of 250 nm. By line scanning across the plain area of the nanosheets, the thickness of the graphene nanosheets obtained by acetate acid solution pre-treatment is found to be about 2.5 nm (Fig. 3b). This value is still somewhat larger than the theoretical thickness for a perfectly flat sp^2-carbon-atom network [20,21]. We observed that a stable graphene nanosheet suspension could be quickly prepared by exfoliating a graphite oxide suspension by a host–guest electrostatic repulsion in aqueous solution; this can be seen in Fig. 3c. TEM is also used to characterize the degree of exfoliation of graphite oxide (GA-12), and shown in Fig. 4. This figure shows the transparency and how the graphene consists of 1–7 layers [22]. The interlayer spacing was measured to be 0.410 nm, which is consistent with the experimental value of 0.415 nm obtained from the above XRD results.

Recently, carbon-based carbon materials were used as transparent conductive materials [23–30]. Up to now, few layer or one layer graphene-based films with sheet resistance of $\sim 4\times10^6$ Ω/square have been reported [28]. Here we explore the direct use of the exfoliated graphene for fabricating solution-processed, all thin films with high electrical conductivity and varying degrees of transparency. We compare the efficiency of chemical exfoliation method for preparing graphene films. Fig. 5 shows the sheet resistances of graphene films transferred on cover glass measured by the van der Pauw method [29]. The wavelength 550 nm is known as typical of indicating the transparency of transparent conductor. Further analysis was made to establish the correlation between the electrical resistivity and optical transparency measured at a wavelength of 550 nm, as shown in Fig. 5.

It shows the sheet resistance of the graphene films as a function of pH conditions. We found that the pristine graphene oxide shows a higher electrical resistance of 1.1×10^{11} Ω/square. However, the exfoliated graphene exhibited a low sheet resistance from 3.0×10^3 Ω/square to 1.8×10^3 Ω/square. As the pH values increase, the transmittance is observed to increase. The sheet resistance of GA-14 is 2.1×10^3 Ω/square whereas that of few layers of graphene at a transmittance of 87.1% (at 550 nm). Theoretically, the sheet resistance of a graphene film should be constant and related to that of a multilayer film. As Ruoff et al. reported that the sheet resistance of spray-coated graphene films show highest sheet resistance ($\sim 7.5\times10^3$ Ω/square) as a function of transmittance at $\lambda = 550$ nm ($\sim$88%). In general, the sheet resistance decreased with decreasing the thickness of films, which was attributed to improved orientation and structure of the film [31]. This result clearly indicates that the chemical exfoliation process is efficient in increasing the number of graphene layer from graphite oxide, and this method is potential for improving quality and large scale of graphene for use in transparent conductive electrode applications.

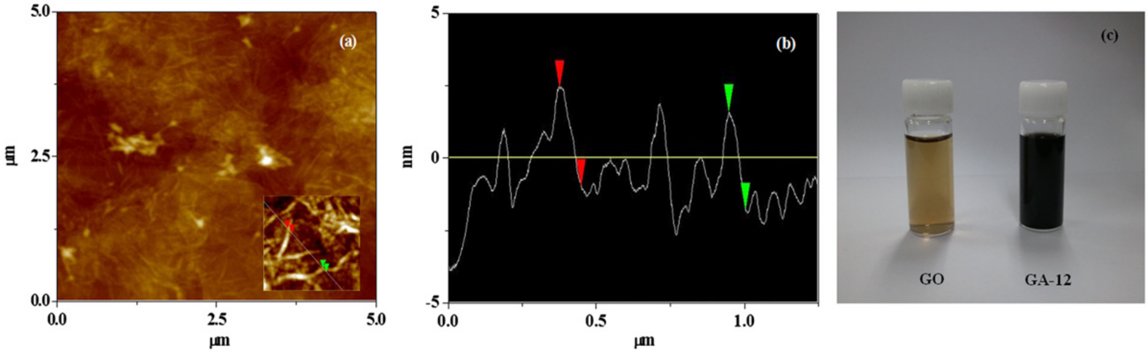

Fig. 3. AFM topography image (a) and photographys (b) of graphene nanosheets (GA-12).

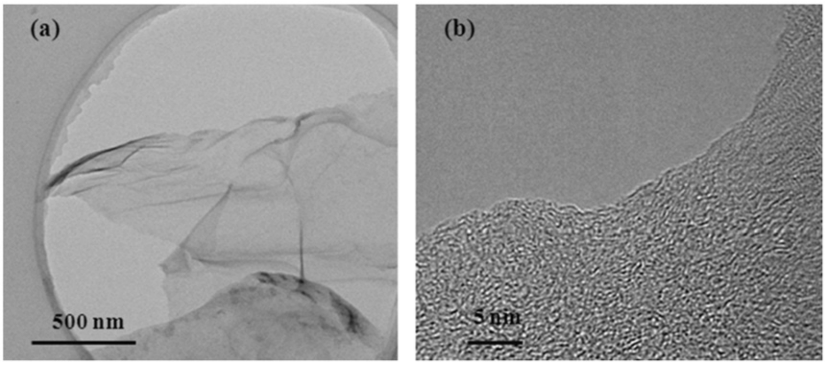

Fig. 4. TEM image of graphene nanosheets: (a) a disordered multilayer; (b) a monolayer.

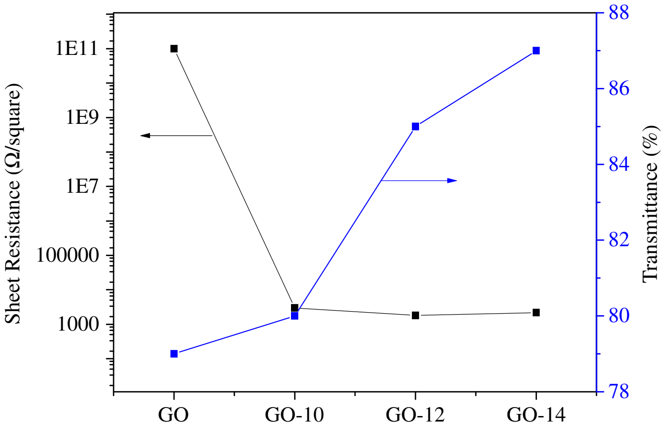

Fig. 5. Sheet resistance and transmittance of the graphene films as a function of pH conditions.

5. Conclusions

In conclusion, a facile chemical method was described to prepare transparent and conductive graphene-based films utilizing a zwitterions amino acid intermediate from graphite oxide sheets. 11-aminoundecanoic acid molecules were protonated to intercalate molecules into the graphite oxide sheets to achieve ion exchange, and the carboxyl groups were then ionized in a NaOH solution to exfoliate the graphite oxide sheets. XRD patterns indicated the d_{002}-spacing of the graphite greatly increased from 0.330 nm to 0.415 nm. AFM and TEM images showed that the ordered graphite crystal structure of graphene and the graphene oxide nanosheets were effectively exfoliated by this method. The prepared graphene nanosheets films showed 87.1% transmittance and a sheet resistance of 2.1×10^3 Ω/square.

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