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Liquid-phase exfoliation of expanded graphites into graphene nanoplatelets using amphiphilic organic molecules

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ABSTRACT

Graphenes with a two-dimensional lattice of carbons have been widely employed in diverse applications owing to their excellent electrical, thermal, mechanical, and gas-barrier properties. However, the frequently-used reduced graphene oxide (rGO), which is synthesized from natural graphites by strong oxidation and subsequent reduction via highly toxic components, exhibits imperfect characteristics because of remaining defect sites on its basal planes. Therefore, in this work, we present a convenient way to prepare graphene nanoplatelets (GNPs) with minimized defect sites on their basal planes employing liquid-phase exfoliation of edge-functionalized expanded graphites (EGs) with amphiphilic organic molecules. Exfoliated GNPs revealed approximately sub-7-nm-thickness and showed stable dispersibility in an organic media during 9 months. Furthermore, spray-coated GNP films presented homogeneously stacked morphologies without noticeable agglomerations.

1. Introduction

Graphitic carbon nanomaterials (CNMs), including graphenes, carbon nanotubes, and carbon blacks have been extensively investigated as electrically/thermally conductive nanomaterials in the fields of transparent electrodes [1,2], electromagnetic interference (EMI) shielding [3,4], thermal interface materials (TIMs) [5,6], and planar heaters [7,8]. Among various CNMs, graphenes with two-dimensional laminar structure have emerged as promising component materials possessing exceptional thermal (3000–6000 W/mK) and electrical ($\sim 10^6$ S/cm) conductivities as well as outstanding mechanical robustness (Young's modulus: $\sim$1 TPa) [9–15]. Moreover, since well-dispersed graphenes have structurally larger *xy*-planar dimension and surface area than those of other CNMs, they can used in numerous area contacts between neighboring graphenes, resulting in similar performance with smaller quantities than other CNMs [5,16,17].

Few- or single-layer graphenes can be synthesized by three main methods, namely, mechanical exfoliation ("Scotch-tape" method) [18], chemical vapor deposition (CVD) [19], and chemical exfoliation (oxidation/reduction) [20]. To employ graphenes in many applications including electrically/thermally conductive coating/filler materials and reinforced materials, chemical exfoliation is the most realistic and beneficial approach in terms of mass production and convenient solution-based processability. The most common method of chemical exfoliation is the oxidation of graphite into graphite/graphene oxide (GO) by strong oxidizing agents and the subsequent reduction of GO into reduced graphene oxide (rGO) by chemical/thermal treatments [21]. However, despite partial restoration of graphitic structure on the surface of rGO by reduction, the graphitic structure is not fully recovered and includes significant defects on its basal planes. Thus, the desired properties of the graphene cannot be revealed in the rGO, and furthermore, they can be easily aggregated without stabilizers after the reduction process [20,22]. Hence, development of graphenes with minimized defects and stable dispersibility in an organic media is important for diverse applications [23–25].

In this study, we present a straightforward strategy to prepare the dispersible graphene nanoplatelets (GNPs) with minimized defects on their basal planes employing the liquid-phase exfoliation of end-functionalized expanded graphites (*f*-EGs) using amphiphilic organic molecules. Amphiphilic organic molecules with a polar amine group and non-polar pyrene group underwent non-covalent grafting and π–π stacking at the *f*-EG's edges and basal planes under sonication, respectively, and simultaneously, *f*-EGs were readily exfoliated into approximately sub-7-nm-thick GNPs. Furthermore, this GNP solution showed the stable dispersibility during 9 months without a large quantity of surfactants and became a homogenous film on a quartz substrate without noticeable agglomerations via simple spray-coating. This approach is an effective and simple method to fabricate the dispersible GNPs with low defect sites on their basal planes.

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2. Experimental

2.1. Materials and methods

Expandable graphite was purchased from GK (grade: ES 350 F5, Germany). The sulfuric acid (H_2SO_4, 95–98%) and the nitric acid (HNO_3, 37–38%) were purchased from J.T. Baker (USA). The 1-aminopyrene (Py-NH_2, 97%) and n-methyl-2-pyrrolidone (NMP, 99%) were purchased from Sigma–Aldrich (USA).

As-received expandable graphites were thermally expanded in a high-temperature furnace at 1000 °C for 20 s, and worm-like EGs were fabricated. EG powders were treated with a mixture of H_2SO_4 and HNO_3 (3:1, v/v) under stirring at 90 °C for 1–48 h. The *f*-EG powders were repeatedly washed with deionized water until a pH of 7 was achieved, and the powders were dried overnight in an oven at 65 °C. Py-NH_2 molecules were dissolved in NMP solvents, and *f*-EGs were subsequently added to the Py-NH_2 solution mixing with a bath-type sonicator (concentration of *f*-EGs: 1 mg mL^{-1}) for 90 min. The mass ratio of Py-NH_2 and *f*-EG is 1:6. After the sonication process of the mixture, residual Py-NH_2 moieties were removed by several iterations of the following washing process: centrifugation at 15,000 rpm for 30 min, the removal of supernatant solution, and the addition of pure NMP. After that, non-exfoliated EGs were removed by re-centrifugation of washed GNP solution at 3000 rpm for 30 min.

The conductive transparent films were fabricated employing the spray-coating method on quartz substrates heated above 180 °C by a hot-plate using an exfoliated GNP dispersion (C: 87%, O: 13%). According to the number of spray coatings, the transmittance of the GNP films was homogeneously changed.

2.2. Characterization

The morphologies of EGs and GNPs were investigated by means of a field emission scanning electron microscope (FE-SEM, Hitachi S-4800, accelerating voltage: 15 kV), atomic force microscope (AFM, SPI3800N/SPA400, Seiko Instruments Inc.), and field emission transmission electron microscope (FE-TEM, JEM-2100F, JEOL). The oxygen contents and chemical functional groups in *f*-EGs were investigated by Raman spectroscopy (514.5 nm laser, LabRam HR, Horiba Jobin–Yvon), Fourier transform infrared spectroscopy (FT-IR, IFS-66/S, Bruker), and X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Electron). The transmittance and electrical sheet resistance of the films were measured using a UV–VIS spectroscope (Jasco, V530) and a 4-point probe system (MCP-T360, Mitsubishi Chemical), respectively.

3. Results and discussion

Fig. 1 shows the experimental procedure for preparing the dispersible GNPs in an organic media using a liquid-phase exfoliation process. Commercially-available expandable graphite was thermally expanded by thermal shock in a preheated furnace at 1000 °C for 20 s, resulting in the worm-like EGs. To attach the functional groups on the edges of the EG, EGs were refluxed with a H_2SO_4:HNO_3 (3:1, v/v) mixture at 90 °C for 1–48 h. After repeated washing of *f*-EGs until a neutral pH was achieved, *f*-EGs were mixed with Py-NH_2 molecules, which were homogeneously predissolved in NMP solvents. Subsequently, *f*-EG/Py-NH_2 solution was sonicated for 90 min and readily exfoliated into individual GNPs. We note that NMP is a well-known solvent for exfoliating the pristine graphite because its surface tension (40.1 mJ/m^2) matches well with the range of 40–50 mJ/m^2, as suggested by Coleman et al. [26] Residual Py-NH_2 molecules, which did not participate in the exfoliation of *f*-EG, were removed by several repeated centrifugations and solvent-exchange with a pure NMP. At the final solvent-exchange step, GNP dispersion was re-centrifuged to remove the non-exfoliated *f*-EGs. The concentration of the finally-prepared GNP dispersion was 0.5 mg mL^{-1}.

To analyze the degree of functionalization of *f*-EG according to the acid-treatment time, XPS analysis was performed in Table 1. The functional groups on the *f*-EG were formed by acid treatment at 90 °C for 1–48 h. The pure EG with no acid-treatment showed a composition of 96.8% carbon (C), 3.2% oxygen (O), and 30.3 C/O ratio. As the acid-treatment time increased up to 48 h, the composition of *f*-EG revealed 82.3% C, 17.7% O, and 4.6 C/O ratio. This composition value was saturated from 15 h of acid-treatment time. We note that the time for functionalizing the EGs can be shortened by controlling the temperature of acid treatment. According to the experimental results, *f*-EGs with 82.3% C, 17.7% O, and 4.6 C/O ratio also could be obtained by the acid treatment at 130 °C for only 2 h. Fig. 2(a)–(c) exhibits the C 1s peak of the high resolution XPS spectra including EG (96.8% C, 3.2% O), *f*-EG (87.3% C, 12.7% O), and GO (63.7% C, 36.3% O). As shown in Fig. 2(a), pure EG mainly showed peaks of graphitic C—C (285 eV) with low C—OH (hydroxyl) (286.3 eV), whereas GO showed peaks with many oxygenated groups such as C—OH, C—O—C (epoxy) (287.1 eV), and O═C—OH (carboxyl) (289.4 eV) (Fig. 2(c)). We note that the low C—OH peak

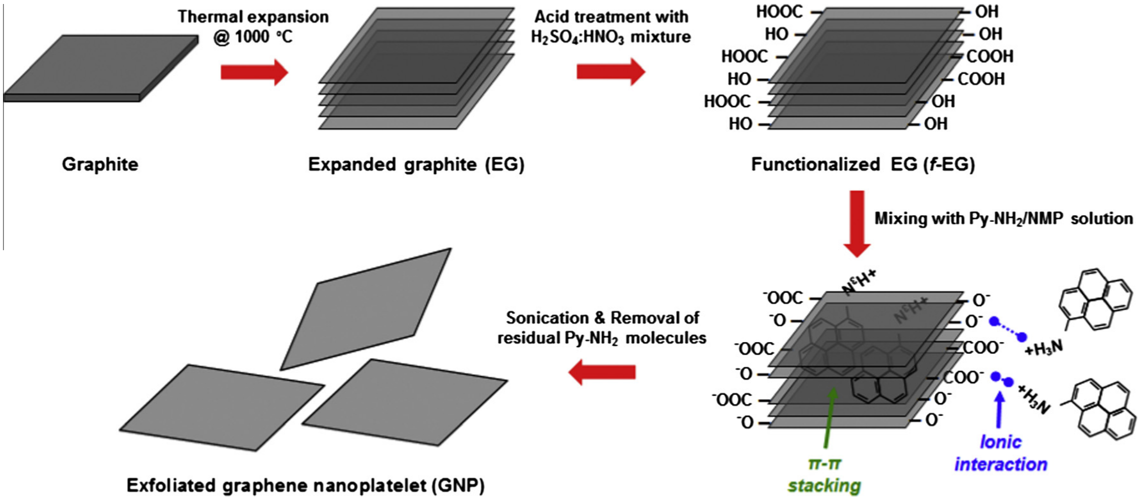

Fig. 1. Experimental procedures for preparing dispersible GNPs using a liquid-phase exfoliation process.