Carbon 115 (2017) 285–292

Contents lists available at ScienceDirect

Carbon

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

Less defective fluorine-containing graphene with good dispersity: Preparation, characterization, and application in transparent conductive thin film

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ARTICLE INFO

Article history:
Received 27 September 2016
Received in revised form
3 January 2017
Accepted 8 January 2017
Available online 9 January 2017

Keywords:
Graphene
Pentafluorophenyl
Less-defect
Transparent conductive thin film

ABSTRACT

With the rapid development of science and technology on graphene, the demand for graphene grows significantly so that it is necessary to develop convenient, scalable, and low-cost methods to prepare graphene or its derivatives with high quality. Herein, a novel approach is reported for the preparation of pentafluorophenyl-functionalized graphene (PFP-*f*-graphene) on a considerable scale of hundreds of milligram using commercially available graphite as starting material. In this process, pentafluorophenyl-functionalized graphene was obtained via the *in situ* diazonium formation procedure and mild sonication treatment. The pentafluorophenyl- functionalized graphene was characterized by Raman spectroscopy, SEM, TEM, AFM, TGA, and XPS, and it was proved to be less defective. This functionalized graphene possesses good dispersity (up to 0.4 mg/mL in *N*,*N*-dimethylformamide after one week) in common organic solvents. Transparent conductive thin films with the sheet resistance as low as 47 Ω/sq were fabricated by filtering the PFP-*f*-graphene dispersion in DMF followed by annealing. Moreover, PFP-*f*-graphene can be easily modified with either hydrophilic or hydrophobic polymers.

1. Introduction

Graphene is a novel 2D one-atom-thick carbon material with a hexagonal crystal structure. Since it was first prepared from highly oriented pyrolytic graphite (HOPG) [1], this 2D material has drawn enormous interests in material science due to its excellent properties [2–4]. In recent years, numerous researches on graphene have been performed in diverse fields such as nanoelectronic devices [5–7], sensors [8,9], catalysts [10], drug delivery [11,12], and energy storage materials [13,14]. As the graphene-related science and technology is developing rapidly, the demanding for more high-quality graphene and therefore, new approaches to obtain high-quality graphene are still very necessary for a long time in the future.

To date, many approaches of preparing graphene have been developed and can be mainly outlined as following five categories: (1) Mechanical exfoliation of graphite. Graphite layers were peeled off using Scotch tape for affording monolayer or few-layer graphene sheets [1]. (2) Liquid phase exfoliation. Exfoliation of graphite occurred in solvents via a sonication process [15–17]. (3) Chemical vapor deposition (CVD). This is another promising approach to produce graphene by depositing hydrocarbon gas onto suitable metal substrates at high temperature [18–21]. (4) Thermal decomposition of SiC. SiC surface was located in an ultrahigh vacuum condition and graphene was coated on it after annealing [22,23]. (5) Exfoliation of graphite oxide following chemical reduction. Graphite oxide was prepared by oxidizing graphite with strong chemical oxidants and then graphene was produced from graphite oxide through reduction process [24–26]. Although we have already owned various ways of preparing graphene, all existing methods have their respective inadequacies such as high cost, low scalability, and unavoidable defects on graphene sheets. A perfect method to produce graphene with low cost, large scale and less or no defects is still a great challenge. Thus, developing convenient and efficient approaches for affording high- quality graphene is still a significant target for researchers.

In recent years, on the basis of previous work focusing on fullerene and carbon nanotubes chemistry, several strategies to

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http://dx.doi.org/10.1016/j.carbon.2017.01.021

functionalize graphene sheets have been developed including diazotization reaction [27–29], free radical addition [30], and 1,3-dipolar cycloaddition [31–33]. Exfoliated graphene sheets were usually adopted as the substrates in these works for introducing functionalities on the sheets as more as possible. Inspired by the aforementioned works about covalent functionalization of graphene sheets, we tried to develop a more efficient method for the preparation of functionalized graphene with less defects and good dispersity. It is well-known that graphene is the basic structure of graphite and from the viewpoint of chemistry, graphene and graphite should have the same or similar chemical reactivity, and the only difference is that the specific surface area of graphene is much larger than that of graphite. So we think that if the substrate is changed from graphene into graphite, the functional groups should be mainly connected onto the brim of the sheets and the sp^2 carbon hexagonal lattice should remain as far as possible. After exfoliation of the functionalized graphite, graphene with less defects and good dispersity will be obtained.

Herein, we exhibit a facile method for preparing pentafluorophenyl-functionalized graphene (PFP-*f*-graphene) sheets with less defects and good dispersity as shown in Fig. 1. In this method, graphite was first intercalated via H_2SO_4 to give acid-intercalated graphite (AIG). Next, AIG was functionalized via diazotization reaction and then underwent a sonication period in organic solvent to afford the desired PFP-*f*-graphene sheets. Because the functional groups were introduced onto the surface of graphite before exfoliation, the sp^2 carbon hexagonal lattice structure was nearly not damaged. Therefore, PFP-*f*-graphene sheets are less defective graphene sheets and have good dispersity in several organic solvents. Moreover, transparent thin films were produced by filtering the PFP-*f*-graphene dispersion in DMF followed by annealing and these films showed good conductivity. PFP-*f*-graphene was also further modified with either hydrophilic or hydrophobic polymers via nucleophilic substitution reaction between the *para*-F and $-NH_2$ group.

2. Experimental section

2.1. Materials and reagents

Flake graphite (Shanghai Yifan Graphite Co. Ltd., 1000 mesh), sulphuric acid (H_2SO_4, Aldrich, 95.0%–98.0%), phosphorus pentoxide (P_2O_5, Aldrich, 98%), potassium persulfate ($K_2S_2O_8$, Aldrich, 99.0%), pentafluoroaniline (PFA, Alfa Aesar, 98%), octadecylamine (ODA, Aldrich, 97%), sodium nitrite ($NaNO_2$, Alfa Aesar, 98%), 2,2'-azobis(isobutyronitrile) (AIBN, Aldrich, 98%), *N*,*N*-dimethylformamide (DMF, Aldrich, 99.8%), and ethanol (Aldrich, anhydrous, 99.5%) were used as received.

2.2. Preparation of PFP-f-graphene

15 g of $K_2S_2O_8$ and 15 g of P_2O_5 were added into 50 mL of H_2SO_4 with stirring. The mixture was then heated to 80 °C followed adding 30 g of flake graphite slowly. The reaction lasted 6 h at 80 °C for giving black slurry and excess deionized water was added. After staying overnight, the supernatant was removed and deionized water was added again. This procedure was repeated several times until pH of supernatant reached the range between 6.0 and 7.0. Finally, the mixture was dried at 105 °C to provide AIG.

200 mg of AIG was dispersed in 100 mL of H_2SO_4 by sonication at 53 Hz for 1 h. Then, 200 mL of deionized water was added and the solution was heated to 80 °C under N_2. 254 mg of PFA, 12 mg of AIBN, and 96 mg of $NaNO_2$ were added subsequently. After 2 h, the reaction mixture was diluted with large amounts of deionized water and then filtered through a 0.45 μm PTFE membrane followed by washing repeatedly with deionized water, acetone, and DMF. The obtained black solid, pentafluorophenyl-functionalized graphite (PFP-*f*-graphite), was dried *in vacuo* at 40 °C overnight.

Finally, PFP-*f*-graphene suspension was obtained after PFP-*f*-graphite was exfoliated in DMF by sonicating at 53 Hz for 30 min followed by centrifugation at 4000 rpm/min for 30 min.

2.3. Preparation of transparent conductive thin film from PFP-f-graphene

PFP-*f*-graphene dispersion in DMF (1 mg/mL) was filtered through a 0.02 μm anodic aluminum oxide (AAO) membrane and then washed with ethanol. AAO membrane was then etched in alkaline aqueous solution (0.5 g of NaOH/20 mL of deionized water) until AAO membrane disappeared. Deionized water was added into the solution and washed the PFP-*f*-graphene membrane until the solution turned neutral. The membrane was then transferred onto a PET film. Finally, the film was annealed at 150 °C for 1 h to afford the transparent conductive thin film (Fig. 2).

2.4. Further modification of PFP-f-graphene

20 mg of PFP-*f*-graphene was dispersed in 30 mL of DMF via sonicating at 53 Hz for 30 min. Next, 0.47 g of PEG-NH_2 ($M_n = 750$ g/mol) or 0.17 g of ODA was added into the dispersion. The reaction was performed at 160 °C for 1 day under Ar. The reaction mixture was then filtered through a 0.45 μm PTFE membrane followed by washing repeatedly with deionized water, acetone, and DMF. The obtained filter cake was dried *in vacuo* at 40 °C overnight for affording PEG-functionalized graphene (PEG-*f*-graphene) or ODA-functionalized graphene (ODA-*f*-graphene).

2.5. Characterization

Field emission transmission electron microscope (FE-TEM) images were taken by a JEOL JEM-2100F instrument operating at an accelerating voltage of 200 kV. AFM images were taken by a Veeco Nanoscope IVa MultiMode SPM in the tapping mode. UV/vis spectra and transmittance analysis were measured by a Hitachi U-2910 spectrophotometer (scan number: 2, scan speed: 400 nm/min, resolution: 0.5 nm). For Raman (Thermo Scientific DXR, semiconductor laser, wavelength: 532 nm, scan number: 3, power at the sample: ~6.8 mW), XPS (PHI 5000c ESCA photoelectron spectrometer), and thermogravimetric (TGA, TA Q500) analysis (heating rate: 10 °C/min in N_2), powder samples were directly used without any further treatment.

3. Results and discussion

3.1. Characterization of PFP-f-graphene

In our initial research, we tried to use pristine graphite powder directly as starting material for the diazotization reaction to obtain PFP-*f*-graphene. However, the product was not exfoliated adequately according to TEM observation and it could not disperse well in organic solvents. After careful analysis, we thought that the efficiency of diazotization reaction was not high enough to afford adequate pentafluorophenyls onto the brim of graphite sheets because the layer distance of graphite was too small, which was not favorable for the approach between the reagents and the brim of the sheets. Therefore, we prepared AIG at 80 °C using H_2SO_4 as intercalation molecules and then AIG was used as starting material for the diazotization reaction. Compared to that of pristine graphite powder, AIG possessed a larger layer distance [34], which made it favorable for the approach between the reagents and the brim of