

Derivatization of Pristine Graphene for Bulk Heterojunction Polymeric Photovoltaic Devices

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Materials and instruments

All chemical materials were analytical grade and commercially available and used without further purification unless otherwise stated. Microcrystalline graphite was purchased from Kermel Chemical Reagent Co. Ltd., Tianjin, China. The others were obtained from Sinopharm Chemical Reagent (Beijing, China). *N,N*-dimethyl formamide (DMF) was dried by distillation over CaH₂ under reduced pressure.

Fourier transform infrared (FTIR) spectra were recorded on a WQF-410 spectrophotometer by using KBr pellets. Raman spectra measurements were carried out with a Raman microspectroscopic setup (RamLab-010) (LabRam, Horiba-Jobin-Yvon, Bensheim, Germany) spectrometer. Thermal properties of the samples were measured using a HCT-1 (HENVEN, Beijing, China) comprehensive thermal analyzer in flowing (50 mL/min) nitrogen atmosphere.

Preparation of Aqueous Dispersed Graphene (PG)

The dispersion was conducted by adding 0.5 g of microcrystalline graphite and 10 mg of polyvinylpyrrolidone (PVP) to the mixture of 90 mL *N*-methyl-2-pyrrolidone (NMP) and 10 mL of toluene, which was sonicated continuous for 7 h.¹ The mixture was centrifuged at 4500 r/min for 20 min to obtain the homogeneously graphene dispersion.

Benzoic Carboxylic acid Functionalized with Graphene (BCFG)

The phenyl carboxylic diazonium salt was prepared by the literature.² 840 mg sodium hydroxide and 2.8 g 4-aminobenzoic acid were added to 240 mL water under stirring. Then 1.5 g sodium nitrite added to the solution slowly at the temperature of 0 °C. The obtained solution was added quickly to 18 mL HCl solution (20%) and stirred for 45 min. The color of solution became pale yellow.

The preparation of BCFG was performed by the addition of diazonium salt to 100 mL of graphene dispersion in an ice bath under stirring and the mixture was maintained in ice bath at 0-5 °C for around 2 days. Next, the reaction solution was stirred at room temperature for 2 days. After reaction, the resulting solution was filtered through 0.2 µm Polytetrafluoroethylene (PTFE) membrane and washed with water, ethanol, acetone, and DMF for several times sequentially, and the final product dispersed in 100 mL DMF.

BCFG covalent bond with 1H, 1H, 2H, 2H-Perfluoro-1-octanol (BCFG-F)

The synthesis of BCFG-F is shown in scheme 1. The surface-bond carboxylic groups in BCFG were used to react with the -OH group of 1H, 1H, 2H, 2H-Perfluoro-1-octanol to the fabrication of BCFG-F nanocomposite material. Typically, *N, N'*-dicyclohexylcarbodiimide (DCC, 15 mg) and *N*-hydroxysuccinimide (NHS, 12 mg) was added to an anhydrous DMF dispersion of purified BCFG 30 mL (0.5 mg/mL) in a 100 mL bottle, and the mixture was cooled to 0 °C in an ice bath and stirred for 4 h. Next, 1H,1H,2H,2H-Perfluoro-1-octanol (30 mg) was added, the reaction mixture was stirred under continuous N₂ flow at room temperature for 4 days and then filtered using a 0.2 µm PTFE membrane. In order to remove free 1H,1H,2H,2H-Perfluoro-1-octanol, the black solid was washed with DMF, methanol, acetone, and toluene for 3 times in sequence. The obtained black BCFG-F was redispersed in 30 mL toluene.

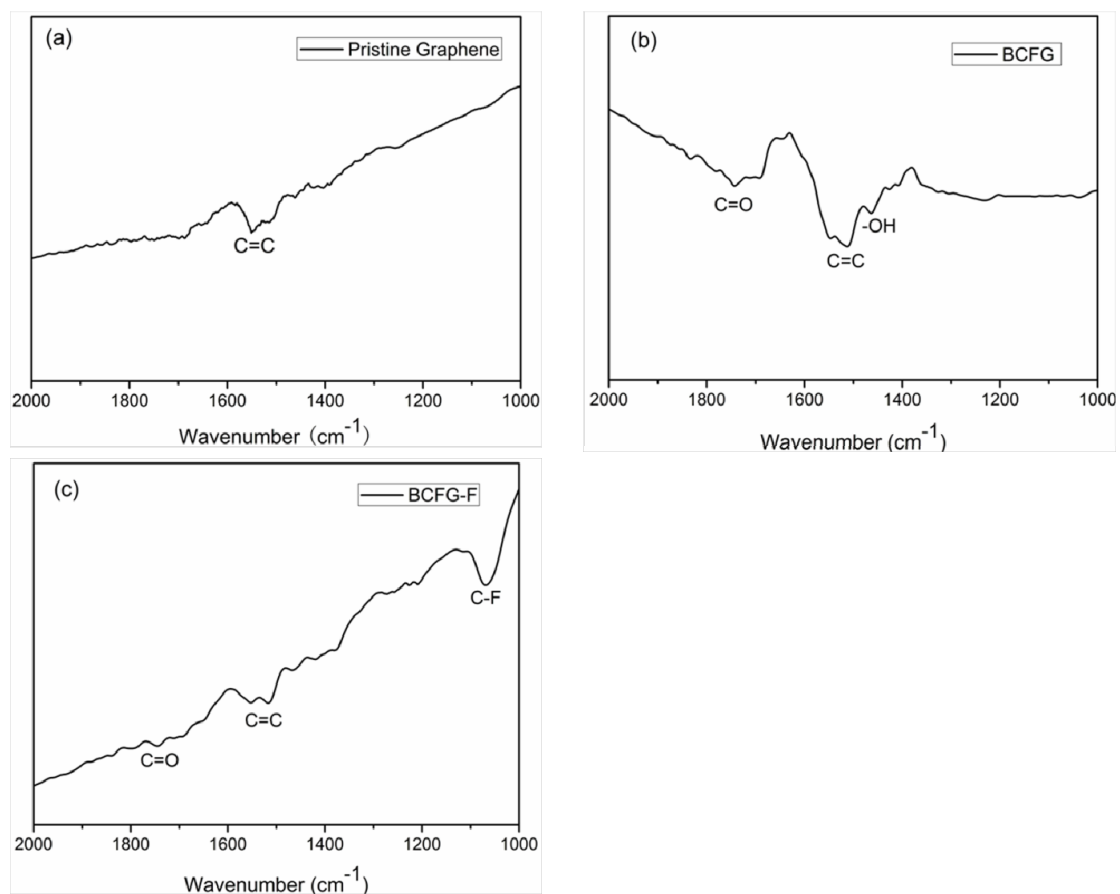


Fig. S1 The FTIR spectrum of the three graphene compounds.

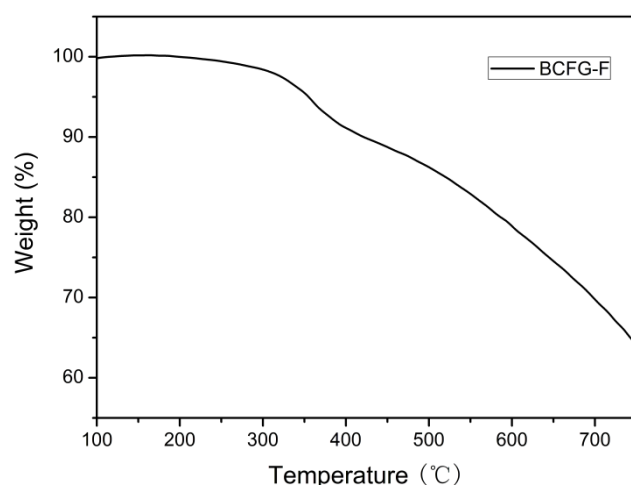


Fig. S2 The TGA curve of BCFG-F in the range from 100 to 750 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ in nitrogen flow.

In order to obtain the uniformly dispersive P3HT/BCFG-F mixed solution, the BCFG-F was firstly dispersed in chlorobenzene by sonicated, maintained half hour. And then, the specific rate of P3HT was added in BCFG-F dispersed solution and also maintained sonicated one hour. The uniform solution was stirred overligh at 40 °C in glove box for fabricating devices.

Solar cells were fabricated in the standard configuration (Fig. 3a). Subsequent layers were deposited on Indium Tin Oxide (ITO) glasses. ITO glass substrates were carefully cleaned with detergent followed by treatment in ultrasonic bath using two different solvents (in acetone and subsequently in isopropanol). Poly (ethylene dioxythiophene) doped with polystyrene sulfonic acid (PEDOT: PSS) conductive polymer was deposited by spin-coating at 4000 rpm using an aqueous solution (film thickness 40nm). The films were thermally annealed for 30 min in an oven at 155 °C. On the top of the film subsequently a layer of P3HT/BCFG-F was spin coated at 1000 rpm from a chlorobenzene solution. The concentration of P3HT was 18mg/ml with BCFG-F content of 5wt%, 7.5wt%, 10wt% and 12.5wt% (ratio to P3HT). The films were also annealed at 160 °C for 30 min. LiF (5 nm) and Al (100 nm) were then vacuum-deposited as the top contact.

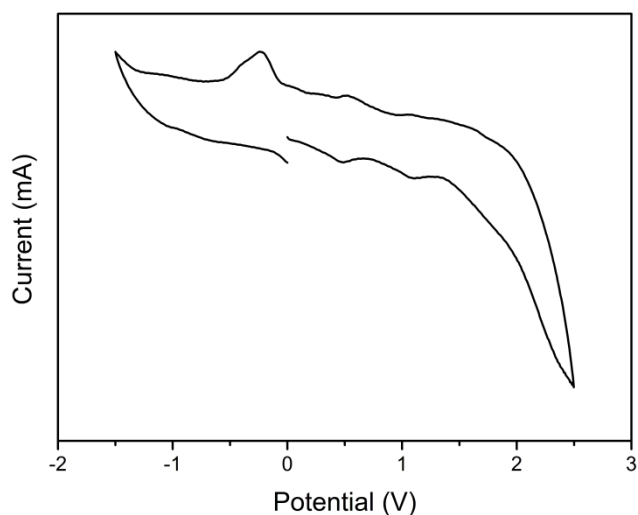


Fig. 3 The CV curve of BCFG-F.

To estimate their HOMO and LUMO energy levels, cyclic voltammetry (CV) was carried out by using a standard three-electrode system, which consists of platinum sheet coated with BCFG-F as the working electrode prepared by drop-casting of BCFG-F/DCB

solution onto its surface, a platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. CV was recorded in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) as the supporting electrolyte. The HOMO and LUMO energy levels in eV as well as the electrochemical energy gap (Eg in eV) of the samples were calculated according to the following equations:

$$E_{\text{HOMO}} - e (E_{\text{ox}} + 4.8) \quad (1)$$

$$E_{\text{LUMO}} - e (E_{\text{red}} + 4.8) \quad (2)$$

Where Eox and Ered are the onset of oxidation and reduction potential, respectively.

The corresponding LUMO and HOMO levels were -4.0 and -5.4, respectively.

Reference:

1. C. E. Hamilton, J. R. Lomeda, Z. Z. Sun, J. M. Tour and A. R. Barron. High-Yield Organic Dispersions of Unfunctionalized Graphene. *Nano Lett.*, 2009, 9, 3460.
2. M. Jahan, Q. Bao, J.X. Yang, K.P. Loh. Structure-directing role of graphene in the synthesis of metal organic framework nanowire. *J. Am. Chem. Soc.*, 2010, 132, 14487.