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Improved dispersibility of graphene oxide in o-dichlorobenzene by adding a poly(3-alkylthiophene)

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ABSTRACT

The dispersibility of graphene oxide (GO) in *o*-dichlorobenzene was improved by adding poly(3-hexylthiophene) (P3HT). The resulting GO dispersion was stable for up to one week. Transmission electron microscopy, UV–Vis spectroscopy, Raman spectroscopy and photoluminescence spectroscopy indicated that the crystallization of P3HT molecules on the GO surface prevented GO sheets from strong π–π interactions, and thus greatly increased the dispersibility of GO in organic solvent. The crystallization of P3HT molecules is a physical and reversible process, and it is time and temperature dependent. The crystallization process becomes remarkable with prolonged aging time and decreasing temperature. Other conjugated polymers, including poly(3-butylthiophene) and poly(3-hexylthiophene)-*b*-poly(ε-caprolactone), were further examined by the same method, and similar phenomena were also observed, indicating that the simple method of using a poly(3-alkylthiophene) to improve GO dispersibility in organic solvent is universal.

1. Introduction

Graphene is a monolayer material, consisting of 2D structure sp^2-hybridized carbon, in addition to 0-D fullerenes, 1–D nanotubes and 3-D graphite. Graphene has been regarded as the "next generation material" due to its unique chemical and morphological structure, unusual electronic property and large surface area, which endows it with numerous applications in various fields, such as sensors [1–3], field-effect transistors [4], composites [5–10], supercapacitors [11] and organic photovoltaic devices [12,13].

Despite a lot of attentions have been paid to the investigations on graphene and graphene oxide (GO), the scalable dispersion and the long-term stability of graphene sheets still remain as challenges for graphene based materials due to the strong π-π interactions between graphene sheets, which limits its applications [14,15]. Therefore, various methods have been developed by researchers to improve the dispersibility of GO. Among them, chemical method, which functionalizes GO by reacting with oxidative groups, carboxyl, carbonyl and epoxy groups, is promising and widely used [16–18]. For example, after reacting with phenyl isocyanate, GO surface was decorated with isocynante and it was easily dispersed in *o*-dichlorobenzene (ODCB), this GO dispersion could be used as an electron acceptor when mixed with conjugated polymer in organic solar cells [13]. Similar approaches have been used to prepare stable graphene dispersions in organic solvents by functionalization with alkylamines [19].

Although chemical method shows a remarkable effect on improving the GO dispersibility, this method involves

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chemical reaction between GO and chemicals, which increases the risk of the destruction of bulk GO structure and properties [20]. Therefore, physical method with no destruction risk, which is based on the noncovalent molecular interaction such as π–π stacking and ionic interaction, was introduced to improve GO dispersibility. For example, Xu et al. used a water soluble pyrene derivative, 1-pyrenebutyrate, as a stabilizer since the two components have strong affinity through π-stacking [21]. Liang et al. developed a novel approach towards large-scale processable graphene sheets in organic solution based on a transfer process assisted by ionic interactions [22]. Further, after doping the surface of conjugated polymer by deposition of thin layer GO, the conductivity of poly(3-hexylthiophene) (P3HT) films increased by six orders of magnitude [23].

As mentioned above, graphene and GO are widely used in photo-electronic devices as an electron acceptor. In such devices, a proper electron donor is needed to match graphene to achieve better photo-electronic conversion efficiency. Until now, functional polymers, poly(3-alkylthiophene)s (P3ATs) and their derivatives with conjugation structure, are the better candidates [24]. One can imagine that if we could find a method to tune the GO dispersibility by using P3ATs, it will make valuable contribution to scientific and industrial communities of P3ATs and GO. Actually, similar researches have previously been reported on improving the dispersibility of carbon nanotubes (CNTs). For example, P3HT hybrids with CNTs by exploiting the π–π interaction resulted in efficient dispersion of CNTs in the P3HT solution [25]. And modified with linear conjugated poly(arylene ethynylene)s, CNTs could be dispersed in organic solvent due to a surface coating mechanism [26].

We developed a method to increase GO dispersibility in organic solvent using P3ATs. This method is simple, easy operating, and universal, proved by loading P3HT, poly (3-butylthiophene) (P3BT) and poly(3-hexylthiophene)-*b*-poly(ε-caprolactone) (P3HT-*b*-PCL) copolymer into ODCB containing GO powders. The resulting GO dispersion is stable for up to one week, and the mechanisms of P3ATs increasing GO dispersibility were elucidated from the point of that the P3ATs crystallize on the GO surface through intermolecular π–π stacking interactions. This approach shows a potential for thin film device fabrication and makes a valuable contribution to the scientific and industrial communities.

2. Experimental section

2.1. Materials

P3HT (M_w = 63,000 g/mol, regioregularity ca. 95%) and P3BT (M_w = 56,000 g/mol, regioregularity ca. 93%) were purchased from Rieke Metals Inc. and used without further purification. P3HT-*b*-PCL copolymer (M_w = 43,000 g/mol), containing P3HT block component with M_w = 19,000 g/mol and regioregularity ca. 96%, was synthesized according to [27]. Graphite powders (spectral purity) and ODCB (anhydrous, 99%) solvent were obtained from Sinopharm Chemical Reagent Co. Ltd. and Sigma–Aldrich Co. Ltd., respectively. H_2SO_4 (A.R.), HCl (37.5 wt.% aqueous solution), $K_2S_2O_8$ (A.R.), P_2O_5 (A.R.), $KMnO_4$ (A.R.), and H_2O_2 (30 wt.% aqueous solution) were obtained from Beijing Chemical Works.

2.2. Sample preparation

Graphite powder (5 g) was put into an 80 °C solution of concentrated H_2SO_4 (7.5 ml), $K_2S_2O_8$ (2.5 g), and P_2O_5 (2.5 g). The dark blue mixture was allowed to cool to room temperature and slowly stirred over a period of 6 h. After carefully diluted, filtered and washed with distilled water, the product was dried in air at ambient temperature overnight. This preoxidized graphite was then subjected to oxidation using a Hummers' method [17,28]. Briefly, the oxidized graphite powder (5 g), and H_2SO_4 (115 ml) were placed in a flask in an ice-water bath. $KMnO_4$ (15 g) was added slowly with stirring over 1 h. After 2 h stirring, the distilled water (230 ml) was added to the mixture. In 15 min, the reaction was terminated by the addition of a large amount of distilled water (700 ml) and 30% H_2O_2 solution (12.5 ml). The oxidation product was purified by rinsing with 1:10 HCl solution (1250 ml), followed by repeatedly washing with copious amount of distilled water until the pH of the filtrate was neutral, and then filtered through standard filter paper with a Bushner funnel. The filtered material was dialyzed against deionized water for 1 week followed by ultrasonic for 1 h by a probe sonicator with sonication (950 w, 40% amplitude). Then the final product of GO was freeze-dried in a freeze dryer.

The freshly prepared GO powders were added into ODCB (0.2–1 mg/ml), and then sonicated for one hour. The pure P3HT solution with a concentration of 1 mg/ml was prepared in ODCB. The GO/P3HT suspensions with different concentrations were obtained by mixing the above prepared GO dispersion and P3HT solution, and then followed by immediate sonication for 2 min. GO/P3BT and GO/P3HT-*b*-PCL suspensions were prepared using the same method. For Raman spectra, P3HT film was prepared by drop coating 10 mg/ml of P3HT solution on a Si substrate, and the P3HT/GO suspension concentration was 10:10 mg/ml. The GO samples for AFM and TEM analyses were prepared from the GO dispersion in water, which is sonicated for 1 h, and then transferred to Si substrate or copper grid covered with carbon film, followed by evaporation of water. The P3HT and GO/P3HT samples for TEM analysis were prepared from the P3HT solution and GO/P3HT suspension in ODCB as described above.

2.3. Instruments

Sonication was performed on a Scientz-II D ultrasonic cell crusher (Ningbo Scientz Biotechnology, Co. Ltd., China). AFM analysis was carried out in tapping mode on Veeco Multimode equipped with NanoScope V Controller under ambient conditions. Transmission electron microscopy (TEM) was performed on a JEOL JEM-1011 transmission electron microscope operated at 100 kV. UV–Vis absorption spectra were acquired on a Lambda 750 spectrometer (Perkin–Elmer, Wellesley, MA). For temperature-dependent UV–Vis absorption, a silver hot stage (Linkam THMS 600, England) was installed on the Lambda 750 spectrometer. The temperature of the hot stage was controlled through a Linkam TMS 94 controller. The samples were heated at a rate of 10 °C/min and stabilized