Effect of photocurrent enhancement in porphyrin–graphene covalent hybrids

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ABSTRACT

Graphene oxide (GO) sheets were covalently functionalized with 5-p-aminophenyl-10,15,20-triphenylporphyrin (NH_2TPP) by an amidation reaction between the amino group in NH_2TPP and carboxyl groups in GO. The Fourier transform infrared spectroscopy, nuclear magnetic resonance, scanning and transmission electron microscopies reveal that NH_2TPP covalent bonds form on the double surface of graphene oxide sheets, generating a unique nano-framework, i.e., NH_2TPP-graphene-NH_2TPP. Its UV–visible spectroscopy reveals that the absorption spectrum is not a linear superposition of the spectra of NH_2TPP and graphene oxide, because a 59 nm red shift of the strong graphene oxide absorption is observed from 238 to 297 nm, with significant spectral broadening between 300 and 700 nm. Fluorescence emission spectroscopy indicates efficient quenching of NH_2TPP photoluminescence in this hybrid material, suggesting that photo-induced electron transfer occurs at the interface between NH_2TPP and GO. A reversible on/off photo-current density of 47 mA/cm^2 is observed when NH_2TPP-graphene-NH_2TPP hybrid sandwiches are subjected to pulsed white-light illumination. Covalently-bound porphyrins decrease the optical HOMO/LUMO band gap of graphene oxide by ≈ 1 eV, according to UV–visible spectroscopy. Cyclic voltammetry predicts a small HOMO/LUMO band gap of 0.84 eV for NH_2TPP-graphene-NH_2TPP hybrid sandwiches, which is consistent with efficient electron transfer and fluorescence quenching.

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1. Introduction

Two-dimensional crystalline arrays of carbon atoms arranged in a honeycomb lattice (i.e., graphene), generate small-band-gap semi-metals with unusual electronic and optical properties, including extremely high carrier mobility [1–3]. The linear in-plane dimension of graphene (i.e., ~5 μm), produced from natural graphite, is approximately 4 orders of magnitude larger than its thickness (i.e., 0.34 nm), with the inherent flexibility of macroscopic silk. These characteristics of graphene make it an excellent electron acceptor and ideal charge transport carrier [4–6]. Functionalization of graphene improves its solubility and processability [7–10]. Graphene oxide (GO) sheets can be prepared in solution by oxidizing graphite according to Hummers' method, with the following polar groups on its surface: hydroxyl, epoxyl, and carboxyl [11]. On the other hand, porphyrins exhibit strong absorptions in visible region, and the extensive π-conjugated framework of porphyrins makes them attractive candidates as electron donors and light-harvesting antenna for artificial photosynthetic systems and solar cells.

Several publications discuss photo-induced electron transfer in porphyrin/carbon-nanotube and porphyrin/fullerene hybrid materials [12–16]. To date, the best results have been obtained using donor–acceptor combinations for solar cells that exhibit a type-II hetero-junction band alignment to facilitate exciton dissociation at the interface between donor and acceptor [17–19], with electron transfer to the acceptor and a hole remaining in the donor. These studies suggest that carbon nanotubes are promising candidates for electron acceptors, due to their high mobility and large aspect ratios [20]. In addition, ōcarbon nanotubes can be dispersed effectively in donors such as semiconducting polymers [21,22]. It has been shown that small-diameter single-walled carbon nanotubes (SWCNTs) form type-II heterojunctions with poly-3-hexylthiophene [23,24], and these hybrid materials facilitate ultra-fast charge transfer across the interface generating long-lived charge transfer states in the presence of excess polymer. Recently, porphyrin oligomers have been covalently bound to SWCNT to generate unique electronic and mechanical properties of these hybrid materials [25]. However, the 2-dimensional characteristics of graphene distinguish it from SWCNT in terms of geometry, chemical surface modification, micromorphology, and interfacial electron-transfer properties. Similar to carbon nanotubes and fullerenes, covalent or noncovalent functionalization is attractive to modify graphene. Porphyrin-covalently-functionalized graphene exhibits large nonlinear optical properties [26], and strategies have been devised to modify graphene with porphyrin and its derivatives. Porphyrin-functionalized graphene sheets with good conductivity have been prepared in aqueous suspensions [27]. Graphene functionalization with organic modifiers is attractive for photo-electronic applications, and chemical binding methods provide fabrication

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flexibility. Most recently, Chen reported the graphene oxide covalently functionalized with zinc phthalocyanine for broadband optical limiting, in which nonlinear optical property was investigated [28]. Relationships between the functionalized structure of graphene and photo-induced electron-transfer from donor (i.e., porphyrin) to acceptor (i.e., graphene), as illustrated herein, are beginning to appear in the research literature.

In this research contribution, 5-p-aminophenyl-10,15,20-triphenylporphyrin (NH$_2$TPP) covalently functionalized graphene hybrids have been prepared and their photonic properties were evaluated for opto-electronic applications. The UV–visible absorption and fluorescence emission spectroscopy have been employed to characterize these hybrid materials for efficient photo-induced electron transfer.

2. Experimental

2.1. Materials

All solvents and chemicals are analytical-grade (AG) and were purchased from distributors in Qingdao, China. 5-p-Aminophenyl-10,15,20-triphenylporphyrin (NH$_2$TPP) was synthesized according to procedures described in the literature [29]. GO, produced from natural graphite powder, was provided by Laixi Graphite in Qingdao, China.

2.2. Measurements

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 5700 spectrometer using KBr windows. The UV–visible spectra were measured on a UV755B spectrometer. Fluorescence spectra were recorded on a Shimadzu RF-5310PC spectrometer. Photoelectrochemical measurements were obtained using a three-electrode configuration consisting of an indium tin oxide (ITO) working electrode, a Pt-wire counter electrode, and an Ag/AgCl reference electrode, with 0.5 M Na$_2$SO$_4$ as the electrolyte solution. Samples for photoelectrochemical measurements were coated on the ITO working electrode. Cyclic voltammetry was performed on a CHI760C, with a Pt-dish working electrode, Pt-wire counter electrode, and Ag/AgCl reference electrode, using a solution of 0.1 M tetrabutylammonium (TBAP) in DMF. Scanning electron microscopy (SEM) was performed on Hitachi S-4800. NMR measurement was mainly carried on a ^{1}H nuclear magnetic resonance (^{1}H NMR) spectroscopy, which was recorded on a JNM-ECP600 (600 MHz) spectrometer (JEOL Ltd, Japan) with chloroform-D (CDCl$_3$) as solvent for NH$_2$TPP and NH$_2$TPP-graphene-NH$_2$TPP, and dimethyl sulfoxide (DMSO) as solvent for GO. Tetramethylsilane (TMS) was the internal standard.

2.3. Sample preparation

2.3.1. Synthesis and purification of GO

GO was synthesized from natural graphite powder according to the modified Hummers' method. P$_2$O$_5$ (2.5 g) and K$_2$SO$_4$ (2.5 g) were dissolved in concentrated H$_2$SO$_4$ (12 mL) at 80 °C. Natural graphite powder (3 g) was added to the acidic solution, and the mixture was stirred at 80 °C for 4.5 h. After cooling to ambient temperature, the solution was diluted with deionized water, and allowed to stand overnight. Pretreated graphite was obtained by filtration, washing with deionized water, and drying. Then, pretreated graphite was added to the concentrated H$_2$SO$_4$ (120 mL) and the reaction temperature was maintained at 0 °C, followed by slow addition of KMnO$_4$ (15 g). Next, the solution was stirred at 35 °C for 2.5 h. When the reaction reached completion, the solution was diluted with deionized water (1 L) and 30% H$_2$O$_2$ (20 mL). In order to remove free acid and remaining ions, GO was washed three times with 10% HCl and deionized water. Finally, GO was obtained by vacuum drying at 60 °C 8 h.

2.3.2. Synthesis of NH$_2$TPP-graphene-NH$_2$TPP

Fig. 1 illustrates the reaction scheme to synthesize NH$_2$TPP-graphene-NH$_2$TPP hybrid materials. GO (50 mg) was stirred in SOCl$_2$ (30 mL) at 70 °C for 24 h in a nitrogen atmosphere to activate the carboxylic units by forming acyl chlorides. When this reaction reached completion, excess SOCl$_2$ was removed by distillation and the product was vacuum dried at 20 °C. Then, activated GO was reacted with NH$_2$TPP (50 mg) in N,N-dimethylformamide (DMF, 20 mL) at 120 °C for 50 h under nitrogen. At the completion of this reaction, the DMF solution was cooled to ambient temperature and poured into ether (50 mL) to precipitate the final product, which was recovered by centrifugation. To remove the excess NH$_2$TPP, the samples were ultrasonicated in THF and CHCl$_3$ and centrifugated for 5 cycles. The ultrasonication in each cycle was kept for 2 h. UV–visible spectra were obtained to verify the absence of NH$_2$TPP in the final product after the last washing. Porphyrin-functionalized graphene was dried under vacuum at 60 °C.

3. Results and discussion

As mentioned in the previous section, GO was functionalized with SOCl$_2$ to (i) activate the carboxylic units, and (ii) convert polar hydroxyl, epoxyl, and carboxyl groups on the surface of graphene to acyl chlorides. Then, acyl-chloride-functionalized graphene was reacted with NH$_2$TPP in dimethylformamide (DMF) to form NH$_2$TPP-graphene-NH$_2$TPP sandwiches.

The ^{1}H NMR spectra of GO, NH$_2$TPP and NH$_2$TPP-graphene-NH$_2$TPP (Fig. 2) indicate significant structural change induced by the reaction illustrated in Fig. 1. In the spectrum of NH$_2$TPP, two peaks at 8.88 and 8.97 ppm represent the resonance of H protons at the pyrrole ring in the porphyrin; multiplet peaks near 8.0 ppm are attributed to H proton corresponding to benzene ring of ortho-position; the resonance at 7.0 and 7.2 ppm belongs to the benzene ring of para- and ortho-position of NH$_2$TPP. The peak at 4.0 ppm corresponds to −NH$_2$ group, and the peak at −2.7 ppm corresponds to the proton of N connecting to the pyrrole ring. For the ^{1}H NMR spectra of GO, a broad peak centering at 3.6 ppm presumably arises from proton resonance of −COOH and −OH in GO, another peak at 2.4 ppm was recorded from solvent DMSO. In NH$_2$TPP-graphene-NH$_2$TPP, the broad peak at 9.5 ppm presumably arises from −NH neighboring the carbonyl group. The peak at 2.7 ppm represents the proton resonance of −OH group in graphene. In particular, there is significant shifting of the peak from 4.0 to 9.5 ppm, which is the indication of proton resonance in graphene-CO-NH-phenyl ring segment producing from the reaction between −NH$_2$ group of NH$_2$TPP and −COOH in GO [30]. We conclude that the integral area of the peak is coincident to the ratio of H atomic number compared with other peak areas of proton resonance, based on the calculation of peak area. This large shift is due to the strong influence of π electrons in graphene sheet. As summary, all the information mentioned above indicates that NH$_2$TPP has grafted onto GO surface through covalent bonding.

The UV–visible spectrum of dispersed GO sheets, prior to chemical reaction with NH$_2$TPP, is illustrated in Fig. 3a(1) (black curve), revealing a strong UV absorption at 238 nm and a lower energy shoulder at 299 nm. The characteristic split Soret band for NH$_2$TPP between 390 and 550 nm is illustrated by the blue curve in Fig. 3a(2), with a peak absorption at 419 nm and a series of weak Q-bands at 517, 556, 592, and 651 nm that reflect the highest occupied molecular orbital (HOMO) of the porphyrin [31]. These Q-bands represent an ensemble average of various porphyrin configurations at different torsional angles [31]. The absorption spectrum of NH$_2$TPP-graphene-NH$_2$TPP sandwiches in Fig. 3a(3) (green curve) reveals four important characteristics: (i) the green curve in Fig. 3a is not a linear superposition of the spectra of NH$_2$TPP and GO, (ii) the strong absorption of GO at 238 nm is red-shifted to 297 nm in the sandwich, (iii) the 419 nm absorption due to NH$_2$TPP is very weak, but visible, and (iv) the NH$_2$TPP-graphene-NH$_2$TPP sandwich is responsible for significant spectral broadening (i.e., green curve)