Amphiphilic Graphene

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Amphiphilic Graphene Composites**

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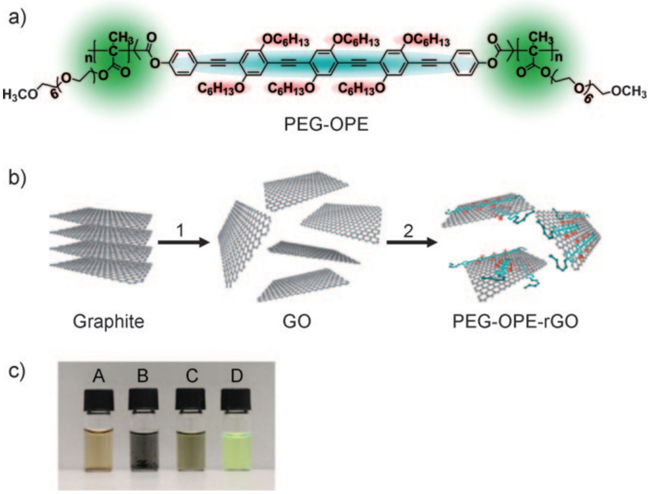
Graphene-based materials are attracting increasing attention because of their excellent and intriguing physical properties.[1] Applications of such materials in micro- and nanoelectronic devices not only require the preserved intrinsic electrical properties of graphene, but also demand that they can be easily incorporated and homogeneously distributed into various matrices.[2] Therefore, sufficient solubility of graphene-based materials in different solvents is a prerequisite for their further practical applications.[3]

Currently, functionalization of graphene is widely used to improve its dispersibility,[4] such as chemical modifications,[5] and covalent[6] or non-covalent functionalizations.[4,7] Among these methods, non-covalent functionalization of graphene with π–π interactions as the binding force between graphene and stabilizers is the most effective and nondestructive method, which enables the modification of material properties without altering the chemical structure of graphene.[8] However, each type of functionalized graphene sheets can only be dispersed in certain solvents, as the physical property of the modified graphene is either lipophilic or hydrophilic, but not both.[9] Until now, amphiphilic graphene sheets that can be dissolved in both organic solvents with low polarity (for example toluene and chloroform) and water-miscible solvents with high polarity (such as ethanol, methanol) have rarely been explored.[2]

Herein, we present the design and synthesis of a novel amphiphilic graphene composite by using an amphiphilic coil-rod-coil conjugated triblock copolymer (PEG-OPE; chemical structure shown in Scheme 1 a) as the stabilizer to modify the reduced graphene oxide (rGO). PEG-OPE is composed of one lipophilic π-conjugated oligomer and two hydrophilic PEG coils, and is synthesized by atom-transfer radical polymerization (ATRP).[10] Details of the synthesis is provided in the Experimental Section. With such a unique molecular architecture, it is anticipated that the conjugated rigid-rod backbone of PEG-OPE would attach to the basal plane of rGO by the strong π–π interaction, whilst the lipophilic side chains and two hydrophilic coils of the backbone would fly away from the surface of rGO to form an amphiphilic outerlayer, consequently facilitating the dis-



Scheme 1. a) Chemical structure of PEG-OPE. b) The synthesis of PEG-OPE-rGO in H_2O. Step 1: Oxidation of graphite yields single-layer GO sheets. Step 2: Chemical reduction of GO with hydrazine in the presence of PEG-OPE produces a stable aqueous suspension of PEG-OPE-rGO. c) Photograph of A) GO and B) rGO in water, C) PEG-OPE-rGO and D) PEG-OPE in methanol.

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persion of modified rGO in both organic low polar and water-miscible high polar solvents.

The PEG-OPE-functionalized rGO was synthesized by a two-step approach (Scheme 1 b). In step 1, graphene oxide (GO) was synthesized from the natural graphite powder by using a modified Hummers method.[11] In step 2, hydrazine was used to reduce GO in the presence of PEG-OPE, which consequently produced a stable suspension of PEG-OPE-functionalized rGO sheets, referred to as PEG-OPE-rGO. The obtained product was purified by washing extensively with methanol followed by centrifugation, ultimately resulting in a brownish-green solution of PEG-OPE-rGO in methanol (see sample C in Scheme 1 c). In comparison, the reduction of GO in the absence of PEG-OPE led to the immediate and irreversible formation of rGO aggregates in aqueous solution (see sample B in Scheme 1 c).

The morphology and structure of PEG-OPE-rGO were studied by tapping-mode atomic force microscopy (AFM) and X-ray diffraction (XRD). Figure 1 shows the AFM images and cross-section analyses of a single-layer GO and PEG-OPE-rGO adsorbed on mica, respectively. The measured thickness of a single-layer GO sheet is about 1.3 nm, which is consistent with the previous reports,[4,6b,11b,c] but larger than the interlayer spacing of GO (0.8 nm) measured by XRD (Supporting Information, Figure S1).[9b,12] The measured thickness of a single layer of PEG-OPE-rGO sheet is 5.8 nm. Thus, the interlayer distance between rGO within PEG-OPE-rGO is about 4.5 nm, which is consistent with the XRD results (Supporting Information, Figure S1). This distance corresponds to the face-on arrangement of the PEG-OPE molecules on both sides of rGO sheets, thus forming a sandwich-like structure.[9b]

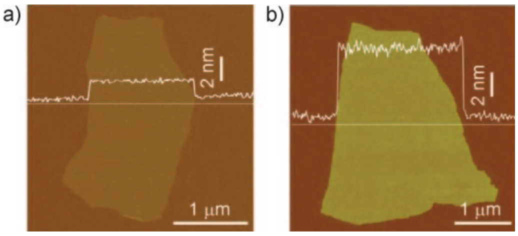

Figure 1. Tapping-mode AFM images and cross-sectional analyses of a) GO and b) PEG-OPE-rGO on mica.

Transmission electron microscopy (TEM), UV/Vis absorption and emission spectra, X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA) were used to further characterize PEG-OPE-rGO. A single-layer PEG-OPE-rGO sheet with perfect reduction was observed by TEM (Supporting Information, Figure S2 a), showing a typical selected area diffraction (SAD) pattern of a single-layer rGO (Supporting Information, Figure S2 c).[13] The reduction of GO to rGO was monitored by the UV/Vis absorption spectra (Supporting Information, Figure S3 a), and the result is consistent with that obtained by XPS (Supporting Information, Figure S4); that is, GO has been deoxygenated and rGO is formed in the presence of PEG-OPE. The emission spectra of PEG-OPE and PEG-OPE-rGO in water (Supporting Information, Figure S3 b) show that the characteristic emission peak of PEG-OPE at 445 nm is completely quenched in PEG-OPE-rGO, indicating an effective electron or energy transfer between these two components owing to the close π–π stacking. These data prove that PEG-OPE can be noncovalently immobilized onto the basal plane of rGO sheets by the strong π–π interaction without affecting the reduction quality of rGO.

Moreover, TGA data (Supporting Information, Figure S5) reveal that PEG-OPE-rGO comprises 31 wt % of rGO. This value is consistent with the estimation based on the molar absorption coefficients of rGO and PEG-OPE.

The solubility of PEG-OPE-rGO was tested in a series of solvents, which include toluene, tetrahydrofuran (THF), chloroform, acetone, dimethyl formamide (DMF), ethanol, methanol, dimethyl sulfoxide (DMSO), and water. As shown in Figure 2, PEG-OPE-rGO is well-dispersed in these solvents, resulting in clear and homogeneous solutions ([PEG-OPE-rGO] = 1.22 mg mL^{-1}). Furthermore, all solutions can last for months, exhibiting excellent stability of PEG-OPE-rGO.

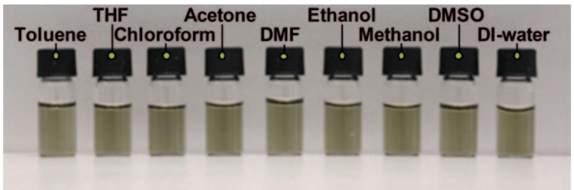

Figure 2. Photographs of PEG-OPE-rGO dispersed in different solvents. [PEG-OPE-rGO] = 1.22 mg mL^{-1}; DI = dionized.

Using the traditional gravimetric method,[8a,14] the solubility limit of PEG-OPE-rGO in toluene, THF, chloroform, acetone, DMF, ethanol, methanol, DMSO, and water was measured to be about 5.1, 5.3, 4.8, 4.6, 5.0, 5.5, 5.7, 5.7, and 5.2 mg mL^{-1} at (24 ± 1) °C, respectively. Figure S6 in the Supporting Information shows PEG-OPE-rGO in methanol and toluene with the concentration of 5.7 and 5.1 mg mL^{-1}, respectively. As PEG-OPE-rGO comprises 31 wt % of rGO, the absolute solubility limit of rGO in toluene, THF, chloroform, acetone, DMF, ethanol, methanol, DMSO, and water is 1.58, 1.64, 1.49, 1.43, 1.55, 1.71, 1.77, 1.77, and 1.61 mg mL^{-1}, respectively. To the best of our knowledge, the solubility limit of PEG-OPE-rGO in these solvents is substantially higher than those reported previously.[3,5a,8b]

It is of importance to evaluate the solubility of PEG-OPE-rGO according to Hansen solubility parameters (HSPs),[3] which are extremely valuable for predicting the solubility of fullerenes,[15] single-walled carbon nanotubes (SWCNTs),[16] and graphene.[3,17] HSPs include three basic parameters, namely δ_D (dispersion cohesion parameter), δ_P (polarity cohesion parameter), and δ_H (hydrogen-bonding cohesion parameter).[18] The values of δ_D, δ_P, and δ_H for the tested solvents are shown in the Supporting Information, Table S1. Recently, Ruoff and co-workers demonstrated that rGO sheets could be well-dispersed in several organic solvents with the value of $\delta_P + \delta_H$ in the range of 13–29.[3] However, their rGO sheets could not be dispersed in solvent with $\delta_P + \delta_H$ less than 10 or higher than 30.[3] Based on our experiments, it clearly shows that PEG-OPE-rGO can be dispersed not only in acetone, THF, DMF, DMSO, and ethanol with the value of $\delta_P + \delta_H$ in the range of 13–29, but also in toluene, chloroform, methanol, and water with the value of $\delta_P + \delta_H$ out the range of 13–29 (Supporting Information, Table S1). Although we have not exhaustively tested all solvents, it is obvious that the solubility of the rGO sheets in the presence of PEG-OPE is greatly improved.

In summary, we have demonstrated an effective method to prepare amphiphilic rGO sheets by using a coil-rod-coil conjugated triblock copolymer (PEG-OPE) as the π–π binding stabilizer. Taking advantage of the amphiphilicity and π-conjugation of PEG-OPE, the functionalized rGO forms a sandwich structure, making it soluble in a variety of solvents, including toluene and water, which are impossible to dissolve the previously reported graphene-based materials. Importantly, our strategy provides new opportunities for molecular engineering of graphene-based materials with perfect solubility/dispersion properties. Moreover, PEG moieties in this novel graphene composite may render the good biocompatibility and high stability in the physiological environment including serum, which allows one to explore graphene in biological systems and discover its potential applications in the attachment and delivery of aromatic, water insoluble drugs into cells.

Experimental Section

The synthesis and NMR spectrum of PEG-OPE are given in the Supporting Information, Scheme S1. The macroinitiator was synthesized according to our previous method.[10a] The block copolymer was synthesized by the atom-transfer radical polymerization (ATRP) in anisole. In a typical experiment, a Schlenk tube was filled with macroinitiator (18.0 μmol), 4,4′-dinonyl-2,2′-dipyridyl (dNBipy) (29.4 mg, 72.0 μmol), poly(ethylene glycol) methacrylate (PEGMA) (100 mL, 716 μmol), and CuBr (5.16 mg, 36.0 μmol) before it was sealed with a rubber septum. After the Schlenk tube was degassed with three vacuum–argon cycles to remove air and moisture, anisole (100 mL) was added to the Schlenk tube, and then the mixture was frozen, evacuated, and thawed three times to further remove air. The Schlenk tube was immersed in an oil bath at 90 °C to carry out the polymerization. After a period of time, the reaction mixture was cooled in liquid N_2 to quench the polymerization, diluted with THF, then passed through a column of neutral alumina to remove the catalysts. The product was redissolved in water and further purified by dialysis against Milli-Q water with a 3.5 kDa molecular weight cutoff dialysis membrane for 3 days. After freeze-drying, PEG-OPE, a grassy green solid, was obtained. $M_n = 12\,000$, $M_n/M_w = 1.31$.

Synthesis of PEG-OPE-rGO: GO was produced from the natural graphite by a modified Hummers method.[11] To prepare the PEG-OPE-rGO dispersion, PEG-OPE (24 mL, 2 mg mL^{-1} in methanol) and hydrazine monohydrate (60 μL, 98 wt % in water) were added to a GO aqueous dispersion (12 mL, 0.07 mg mL^{-1}). After vigorous shaking, the mixture was kept at 85 °C for 48 h. The residual free polymer was removed by washing with methanol and then centrifugation. The obtained PEG-OPE-rGO is stored in methanol as a very stable brownish-green solution, which can last for months without precipitation.

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