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Preparation of water soluble graphene using polyethylene glycol: Comparison of covalent approach and noncovalent approach

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ABSTRACT

Formulation of stable aqueous graphene solution is attempted either through esterification of GO with PEG and subsequent reduction in covalent approach or in situ chemical reduction of aqueous GO solution in the presence of NH_2–PEG–NH_2 in noncovalent approach. While covalent approach produces insoluble graphite-like precipitation, noncovalent approach produces practically homogeneous reduced graphene solution for several months without any precipitate. Noncovalent interaction between NH_2–PEG–NH_2 and graphene is crucial for formulating fully reduced graphene solution with high stability. Various wet process such as spin-coating, ink-jet printing, and spraying can be directly utilized to formulate graphene-based electronic devices such as transparent electrode or anti-static coating without any additional reduction process which is necessary when insulating GO solution is used instead. Non-conducting NH_2–PEG–NH_2 can be simply removed from conducting graphene film by simple filtration and washing process to formulate pure graphene film because interaction between graphene and NH_2–PEG–NH_2 is not covalent. The initial surface resistance of graphene thin film with NH_2–PEG–NH_2 is in the range of $10^6\ \Omega/\square$ but it decreases to $10^4\ \Omega/\square$ after removing NH_2–PEG–NH_2.

1. Introduction

Recently, graphene has received great interests due to its fascinating electrical and mechanical properties in various applications [1]. Graphene is a 2D analog of single-walled carbon nanotube (SWNT) and can show enhanced hole-electron mobility in its ideal 2D planer structure due to perfect overlap of neighboring π orbitals in its conjugation structure [2]. Therefore, graphene-based electrodes or semi-conductors have been extensively considered as next generation transparent electrodes or semiconductors, which replace indium tin oxide (ITO) or Silicon in current industry [3].

The major obstacle for utilizing graphene in electronic applications is its insolubility in fully reduced state owing to strong dispersion forces between graphene plates. Therefore, graphene oxide (GO), which is prepared from strong oxidation reaction of natural graphite utilized in wet process instead of insoluble graphene [4]. While GO is soluble in aqueous media, it is insulating due to partial breakage of sp_2–sp_2 bonds into sp_3–sp_3 bonds for introducing some pendent groups such as hydroxy, carboxylic acid, and epoxy [5]. Transformation of insulating GO into conducting graphene requires strong reducing agents such as hydrazine monohydrate, which is detrimental in display or semiconductor industry due to its strong toxicity and reactivity to other parts of devices.

Therefore, extensive synthetic efforts have been focused on preparing soluble graphene in various solvents. Two approaches have been revealed to produce homogeneous and stable graphene dispersion in solution. In the first approach, covalent bonds are formed between pendent groups of GO and some small molecules or polymers through the formation of ester [6], amide [7], amine [8], or urethane linkages [9]. Attached small molecules or polymers are known to survive during reduction process in the surface of reduced graphene and can minimize interplate adhesion of graphene sheets after reduction, which renders enough solubility in various solvents. But the presence of substituents in reduced graphene plate might deteriorate electrical performance of parent graphene plate because the presence of substituents requires sp_3 orbitals, which can be introduced with a sacrifice of sp_2-conjugation structures of graphene plates. In the second approach, few researches report utilization of noncovalent chemistry to prepare soluble graphene. High molecular weight surfactant such as Pluronic has been known to form stable graphene dispersion in water through micellar encapsulation [10]. Also, sodium salt of pyrene butyric acid has been reported to form stable graphene dispersion in water through π–π interaction between pyrene

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moieties and π orbitals of graphene surface [11]. Noncovalent chemistry has clear advantages compared with covalent chemistry because it is quite simple and facile removing of interacting molecule is possible. In addition, the parent electrical properties of ideal graphene structure, which does not possess any sp_3 orbitals can be preserved through this noncovalent approach.

Here, we report facile preparation of aqueous reduced graphene solution using amine-terminated polyethylene glycol (NH_2–PEG–NH_2) through noncovalent interaction with graphene. Simple mixing and subsequent reduction of aqueous GO solution with NH_2–PEG–NH_2 produces homogeneous and stable aqueous solution of reduced graphene. This noncovalent chemistry for soluble graphene will open up further applications of graphene materials, which necessitate wet process.

2. Experimental

2.1. Materials and instruments

Dimethyl sulfoxide (DMSO), sulfuric acid, concentrated hydrochloric acid, $KMnO_4$, P_2O_5, $K_2S_2O_8$, H_2O_2 (30 wt.% in water), *N-N*-dicyclohexylcarbodiimide (DCC), 4-methylaminopyridien (DMAP), hydrazine monohydrate (30% aqueous solution), polyethylene glycol (molecular weights of 300 Da, 4×10^3 Da, and 2×10^4 Da, respectively), and NH_2–PEG–NH_2 (amino-terminated polyethylene glycol having both terminal amine groups with molecular weight of 600 Da) were purchased from Sigma–Aldrich Corporation and used as received. Natural graphite (average particle size of 4 μm) was purchased from Qingdao Tianhe Graphite Co. Ltd. Anodized aluminum oxide (AAO) membrane (Anodisc 47, pore size of 0.2 μm) was purchased from Whatman International Ltd. Molecular weight cut-off membrane (Spectra/Por biotech cellulose ester dialysis membrane, MWCO: 100,000 Da) was purchased from Spectrum Laboratories, Inc. UV–vis spectra were obtained from UV–vis spectrometer of Hewlett Packard. Photoluminescence spectra were obtained from L550B luminescence spectrometer of PerkinElmer. FT-IR spectra were obtained from IR100/IR200 spectrometer of Thermoelectron Corporation. DLS data were obtained from particle size analyzer (ELS-Z) of Otsuka Electronics Corporation. SEM images were obtained from JSM-6700 field emission scanning electron microscope of GELO Corporation. AFM images were obtained from XE-100 atomic force microscope of PSIA. All photo images were taken by α350 DSLR camera of Sony Corp.

2.2. Synthesis of graphene oxide

Graphene oxide was prepared from natural graphite by a modified Hummers method [12]. In the first step, pre-oxidized graphite powder was synthesized through a reaction of natural graphite (3 g), sulfuric acid (12 mL), $K_2S_2O_8$ (2.5 g), and P_2O_5 (2.5 g). All the reaction mixture was heated at 80 °C for 5 h. After cooling to room temperature, 500 mL of deionized water was added to the mixture and kept overnight while stirring. After filtration using AAO membrane, pre-oxidized GO was obtained and briefly dried in air. This pre-oxidized GO (2 g) was further oxidized by addition of sulfuric acid (120 mL), $KMnO_4$ (15 g), and water (250 mL) in ice–water bath. After dilution with water (700 mL), excess $KMnO_4$ was decomposed by addition of H_2O_2 (30 wt.% in water, 20 mL) and then HCl (10 wt.% in water, 1 L) was added to remove any remaining metal ions. The resulting yellow brown GO solution was filtered again using AAO membrane and then washed with deionized water several times. The resulting brown GO powder was shortly dried in air and then transferred into 1 L of deionized water to make bright brown GO solution. This GO solution was dialyzed using molecular weight cut-off membrane (MWCO: 100,000 Da) with deionized water more than 1-week and finally brown fibrous GO powder was obtained after freeze-drying of GO solution under reduced pressure. For experiments, fresh GO solution (1 mg of GO in 10 mL of deionized water) was prepared and sonicated more than 1 h just before use.

2.3. Synthesis of soluble graphene using PEG (covalent approach)

GO (4 mg) and PEG (0.5 g for PEG (MW 300 Da)) were suspended in anhydrous DMSO for 70 °C for 3 days while stirring under nitrogen. After cooling to room temperature, a solution of DCC (0.185 g) and DMAP (0.0135 g) in anhydrous DMSO (4 mL) was added and the reaction mixture was stirred at room temperature for 3 days. To reduce GO into graphene, hydrazine monohydrate (0.1 mL) was added and the mixture was heated at 80 °C for 24 h. Then, the reaction mixture was filtered using AAO membrane (pore size of 0.2 μm and diameter of 47 mm) and dark black solid was obtained after several washes with deionized water. After complete drying under vacuum, 5 mg of insoluble black powder was obtained. FT-IR spectra of this powder were obtained using KBr pellet.

2.4. Synthesis of soluble graphene using NH_2–PEG–NH_2 (noncovalent approach)

8 mg of NH_2–PEG–NH_2 was simply mixed with aqueous 10 mL of GO solution (1 mg of GO) at room temperature. Because both GO and NH_2–PEG–NH_2 are soluble in water, the mixture are also transparent. To prepare homogeneous graphene solution, hydrazine monohydrate (0.1 mL) was added and all the reaction mixture was maintained at 80 °C for 24 h in nitrogen. The GO solution with initially bright brown color is getting darker in the progress of reduction to graphene solution. Prepared graphene solution was practically homogeneous and stable for more than 6 months without any aggregate or precipitation. DLS, UV–vis, and PL spectra were obtained before and after reduction, respectively.

2.5. Preparation of graphene film

Aqueous graphene solution was transferred on AAO membrane (pore size of 0.2 μm and diameter of 47 mm), which is inserted into vacuum-attached membrane filtration glassware. After complete filtration and successive washing with deionized water, black-colored graphene films were obtained and dried under vacuum for 12 h just before characterization. Some of graphene film was introduced into liquid nitrogen and cleaved to produce specimens for FE-SEM analysis. SEM images of this graphene film were obtained either in top-view or side-view.

3. Results and discussion

3.1. Preparation of GO

Graphene is a singly layered sp_2-conjugated carbon material, which resembles the composition and structure of single-walled carbon nanotube. Better overlap between sp_2 orbitals makes graphene one of the candidates for next generation electrode or semiconductor materials. While ideal graphene film can be produced using CVD process in large area, graphene has not been utilized in various wet processes because it is completely insoluble in any solvent. Instead, insulating GO can be utilized for wet processes because GO is soluble in aqueous media with the help of short sonication. For our study, GO was synthesized by modified Hummus method in two steps. We found freeze-drying is one of efficient ways to storage of GO as solid material. Actually, filtration of GO requires extensive filtration time (generally 1 day to filter