

Synthesis of Aqueous Dispersion of Graphenes via Reduction of Graphite Oxide in the Solution of Conductive Polymer

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1. Introduction

Graphene is a quasi-two-dimensional material. Two-dimensional conductor graphene has recently attracted attention due to in-plane mechanical, thermal, and electronic properties as well as its applications in future optoelectronic devices. These excellent properties may be relevant at the nanoscale if graphite can be exfoliated into thin nanoplatelets, and even down to the single graphene sheet level. Recently, the size of graphene films produced is limited to small sizes because the films are produced mostly by exfoliating graphite, which is not a scalable technique. Graphene sheets were produced by chemical reduction of exfoliated graphite oxides [1-5]. Hydrophilic graphite oxide was prepared by oxidation of pristine graphite [6,7] and it has functional groups such as epoxide, diol, ether, ketone, and hydroxyl groups. These functional groups in graphite oxide impart water solubility to the individual sheets. Solution processable graphite oxide has been used to fabricate paper like films with excellent mechanical properties, as well as electrically conductive polymeric composites [8]. But because of these functional groups, graphite oxide is electrically insulating. High conductivity graphene nanosheets were prepared via chemical reduction process of graphite oxide to graphite. But in the process of reduction, reduced graphite flakes agglomerate and eventually precipitate. This precipitated graphite flakes could not be re-dispersed by sonication in water containing surfactants. To avoid agglomeration of graphene, other host polymers such as poly(4-styrenesulfonic acid) must be used, which hamper the electron-transfer property of the graphenes [9,10].

The solution processing compatibility of graphenes make the material attractive for large area applications. But chemically reduced GO films showed low conductivities as high as 0.5 S/cm. However such level of conductivity is not sufficient for transparent electrode applications. So, we explore the direct preparation method of graphene solution by the reduction of graphite oxide in the solution ionic conductive polymer. As a result, we obtained a stable aqueous dispersion of graphene. The obtained graphene, coated with conductive polymer, can be re-dispersed in water. The structural and electrical properties of graphene were also examined with FT-IR, SEM, XPS, and 4-point probe conductivity method.

2. Experimental

2.1 Materials and methods

Graphite oxide was synthesized from natural graphite, obtained from Sigma-Aldrich Company. Hydrazine hydrate was used for the reduction of graphite oxide. Deionized water was used as solvent. Poly(4-styrenesulfonic acid) (PSS) and Nafion were used as surfactants. These materials were obtained from Sigma-Aldrich Company. PEDOT:PSS (Baytron P), was purchased as an aqueous dispersion from H.C.Starck, Germany. The actual solid content in Baytron P is 1.5-2% according to the manufacturer. All of the reagents were used as received without further treatment.

Fourier transform infrared (FT-IR) spectra were recorded in the range 400–4000 cm^{-1} with a 4 cm^{-1} resolution from KBr pellets on a Perkin-Elmer Spectrum. UV/Vis spectra of aqueous graphene dispersion were collected using a Shimadzu UV-2550 UV/Vis spectrophotometer. The chemical state and composition of the graphene thin films were examined by a Perkin Elmer XPS (model PHI 5500) apparatus at a base pressure in the vacuum chamber lower than 107 Pa. The mixture of PEDOT/PSS and polymer-coated graphene was prepared by the solution of polymer-coated graphene adding into PEDOT/PPS solution and stirred for 1hr. The mixture was filtered with 0.45 μm Teflon filter before being used for spin coating. The spin-coated film was dried at 120 $^{\circ}\text{C}$. Before spin coating, substrates were cleaned using TCE, water, and ethanol. The film thickness was determined using Alpha-step. The sheet resistance of films was measured by four-point probe method at room temperature.

2.2 Preparation of water-soluble graphene oxide (GO)

Graphene oxide was prepared using modified Hummers method from graphite [11]. The graphite was chemically oxidized by treatment with NaNO_3 , KMnO_4 , H_2SO_4 , and H_2O_2 , and washed with mixed aqueous solution of 3wt% H_2SO_4 and 0.5wt% H_2O_2 .

Impurities were removed by centrifugation. The final resultant water solution was passed through a weak basic ion-exchange resin to remove the remaining HCl acid. Then water was removed through a drying process. Finally, the brown powder was obtained.

2.3 Chemical reduction of graphite oxide

GO (100 mg) was dispersed in 100 ml of water. This dispersion was sonicated until it became clear with no visible particulate matter. Hydrazine hydrate was added and the solution was heated in an oil bath at 100 $^{\circ}\text{C}$ for 24 h. Reduced GO gradually precipitated out as a black solid. This product was isolated by filtration and washing copiously with water. The obtained reduced graphite oxide powder was dried on the vacuum oven at 150 $^{\circ}\text{C}$ for 24 h. This material could not be re-suspended even after prolonged ultrasonic treatment in water.

2.4 Nafion-coated graphite sheets via reduction of graphite oxide

GO (100 mg) was dispersed in 100 ml of water and the resulting suspension was sonicated for 1 h. After adding Nafion to the aforesaid suspension and stirring for 4 h, hydrazine hydrate was added to the above mixture. The mixture was continuously stirred at 100 $^{\circ}\text{C}$ for 24 h. As the reduction proceeds, color of polymer-coated graphite oxide change from brown to black. The polymer-coated graphene was isolated via filtration with PVDF membrane (0.45 μm pore size) and washed with water. Nafion-coated graphene can be re-dispersed in water upon sonication, forming black suspensions.

2.5 PSS-coated graphite sheets via reduction of graphite oxide

GO (100 mg) was dispersed in 100 ml of water and the resulting suspension was sonicated for 1 h. After adding poly(4-styrenesulfonic acid) to the aforesaid suspension and stirring for 4 h, hydrazine hydrate was added to the above mixture. The mixture was continuously stirred at 100 °C for 24 h. As the reduction proceeds, color of polymer-coated graphite oxide change from brown to black. The polymer-coated graphene was isolated via filtration with PVDF membrane (0.45 μm pore size) and washed with water. PSS-coated graphene can be re-dispersed in water upon sonication, forming black suspensions.

3. Results and discussion

The graphite oxide is electrically insulating. The conductivity of graphene can be obtained by removal of the oxidized moieties in the graphite oxide by chemical reduction. But in the process of reduction, reduced graphite flakes agglomerate and eventually precipitate. We prepared the stable aqueous dispersions of graphite nanoplatelets by chemical reduction in the aqueous polymer, Nafion or PSS. Figure 1 shows pictures of the water dispersion of reduced graphite and PSS- and Nafion-coated graphene. Reduced graphite was not dispersed in water but PSS-coated graphene (RGO-PSS) and Nafion-coated graphene (RGO-Nafion) were dispersed readily in water. During reduction, Nafion (or PSS) interact with platelets to compete with hydrophobic interaction between the graphite platelets. But once Nafion (or PSS) is attached to the graphite platelet surface, agglomeration of the graphite platelet is stopped [9].

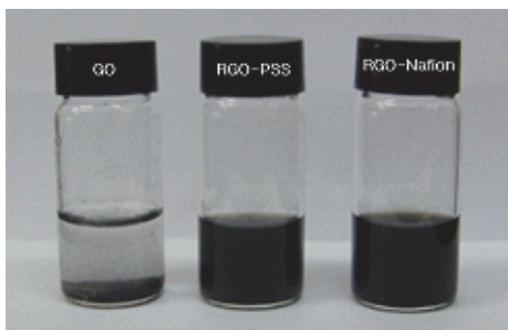


Fig. 1. Water dispersions of reduced graphite oxide (a), reduced graphite oxide with PSS (b) and Nafion (c)

Figure 2 shows the FT-IR spectra of GO before reduction, and after reduction without and with PSS or Nafion. In figure 2a, a FT-IR spectrum of GO shows a broad absorption band at 3390 cm⁻¹, which is related to the OH groups, and absorption bands at 1629 cm⁻¹ and 1720 cm⁻¹, which are typical of carbonyl and carboxyl groups. Figure 2c and 2d show the characteristic bands, corresponding to PSS and Nafion.

In figure 2, we know that there are considerable changes in FT-IR spectra of GO after treatment with hydrazine hydrate. The hydrazine hydrate treatment eliminated all of GO bands, giving evidence for the almost removal of the oxygen-containing groups (figure 2b, 2c, 2d). As a result of this, the graphene was prepared by chemical reduction in aqueous polymer solution, PSS or Nafion.

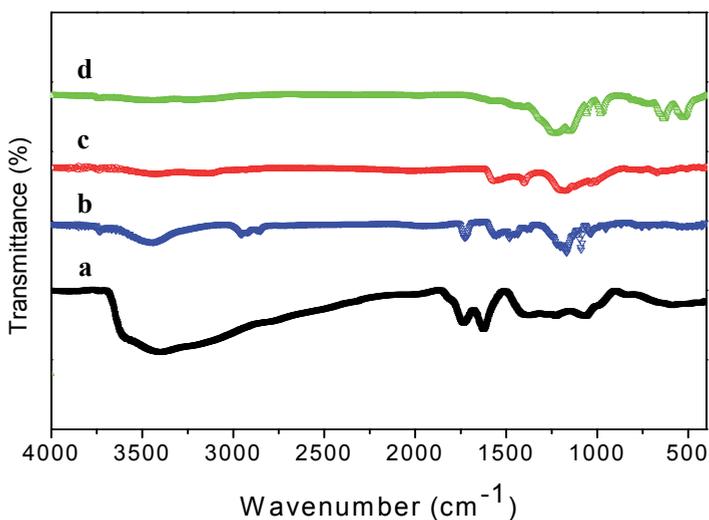


Fig. 2. FT-IR spectra in KBr of the samples GO (a), RGO (b), RGO-PSS (c), RGO-Nafion (d)

Figure 3 shows the UV/Vis spectra of polymer-coated RGO in water. RGO-PSS has two absorption peaks in the UV/Vis spectrum. The absorption at 230 nm ascribed to the PSS and that at 280 nm to reduced graphite oxide. It is known that the peak at 280 nm is the characteristic peak of graphite in solution. The intensities of the signal of the polymers (PSS and Nafion) are also small, indicating the polymer is strongly attached to the graphene surface [8]. In figure 3(b), Nafion-coated graphene show only the peak of the RGO. Due to the higher absorbance of RGO, Nafion peak may be getting masked in the spectrum, because there is not the absorption peak in UV/Vis spectrum of nafion. In figure 3, RGO-PSS and RGO-Nafion have all the characteristic peak of RGO. This shows that polymer-coated graphene have the stable state in the water solution. The chemical composition of both PSS- and Nafion-coated graphene was monitored by X-Ray photoelectron spectroscopy (XPS). Figure 4 shows XPS analysis of graphite oxide and polymer-coated graphenes. The C 1s XPS spectrum of GO indicates a considerable degree of oxidation with four major signatures corresponding to carbon atoms in different functional groups. They are non-oxygenated ring C at 284.8 eV, C of C-O bonds at 286.1 eV, C of C=O at 287.3 eV, and that of carboxylate carbon (O-C=O) at 289.0 eV [12]. Oxygen functionalities of the graphite oxide were decreased during the reduction progressed. C 1s XPS of RGO-PSS and RGO-Nafion also showed similar to spectra of GO. However the intensities of oxygenated carbon peaks are considerably decreased, implying reduction. In addition, there is an additional component at 285.8 eV corresponding to C bound to nitrogen of hydrazones. The C 1s XPS spectrum of the Nafion-coated reduced graphite oxide sample also contains a component peak at 292.7 eV corresponding to the fluorine-bonded carbon atoms from Nafion.

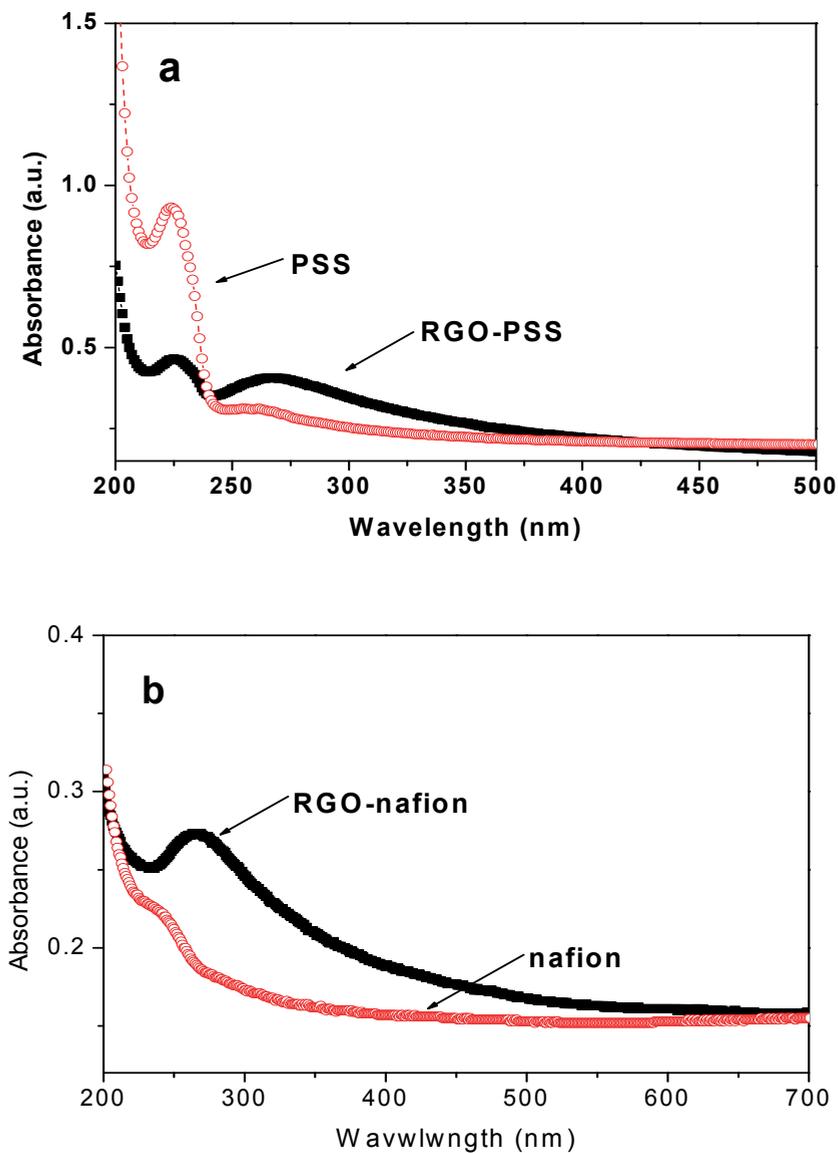


Fig. 3. UV-Vis spectra of the polymer-coated graphene. PSS-RGO (a), Nafion-RGO (b).

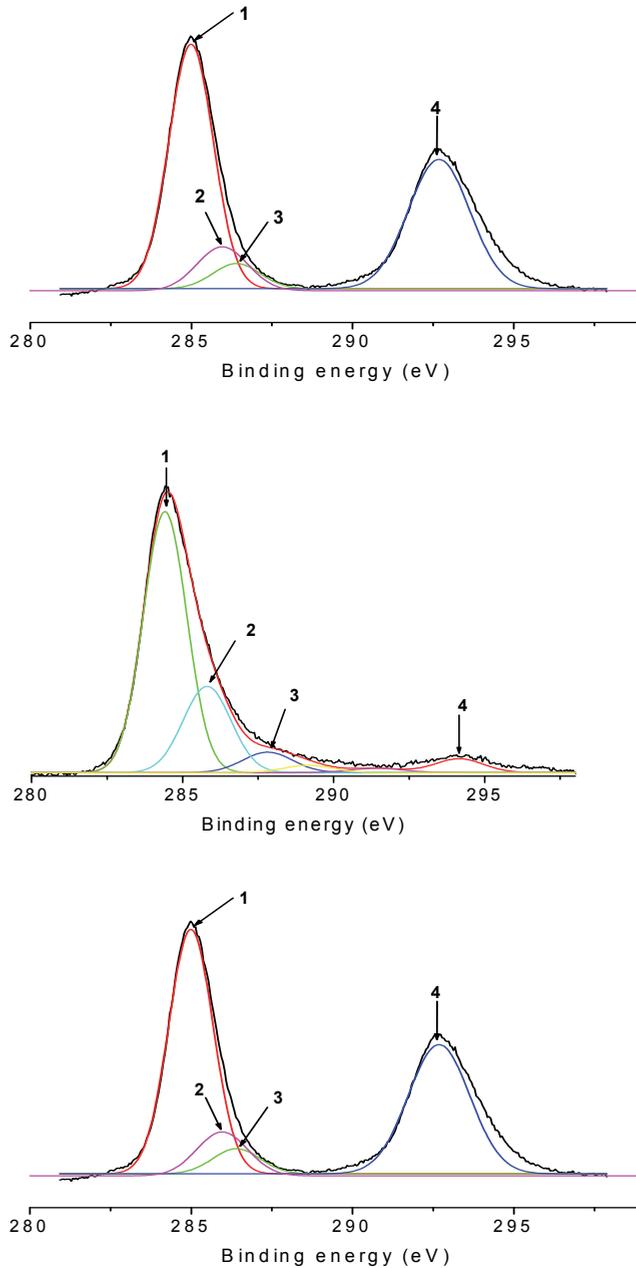


Fig. 4. XPS analysis of graphite oxide (a), PSS-coated graphene (b), Nafion-coated graphene (c).

The conductivities of PEDOT films as a function of the graphene content were shown in figure 5. The thickness of the films range 0.1 μm to 0.3 μm . As the polymer-coated graphene content in PEDOT/PSS solution increase from 0 to 1.2wt%, the conductivity of graphenedoped PEDOT film increases. The PEDOT/PSS film with RGO-Nafion increased significantly from 0.25 S/cm for pure PEDOT film and reached 12 S/cm, and the film with RGO-PSS showed 3.2 S/cm when graphene was doped to $1.2 \times 10^{-3}\text{wt}\%$ in PEOT solution. The conductivity of PEDOT doped Nafion-coated graphene were increased approximately 60-fold than the origin PEDOT film. This indicates that the doped graphene strongly influences the conductivity of PEDOT film. The film of PEDOT doped with RGO-Nafion had also higher conductivities than films doped with RGO-PSS. It is known that Nafion has ionic conductive property and PSS is the insulating material. As a result, it implies that the graphene coated with ionic conductive material contributes to enhancement of conductivity than that coated insulating material.

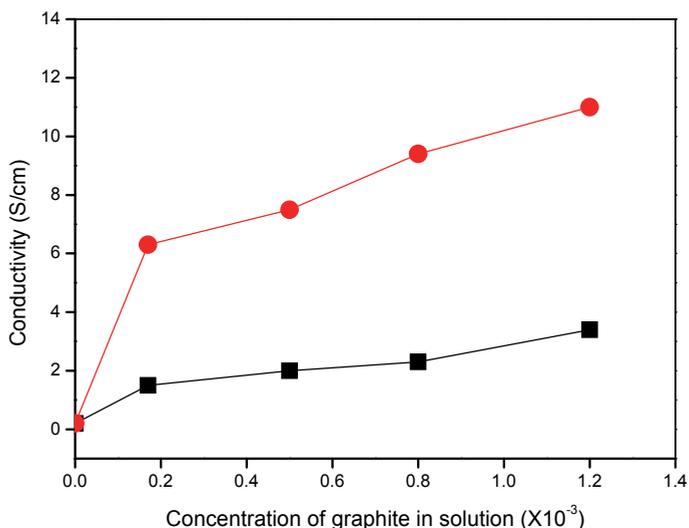


Fig. 5. Conductivity of PEDOT films with varying doping content

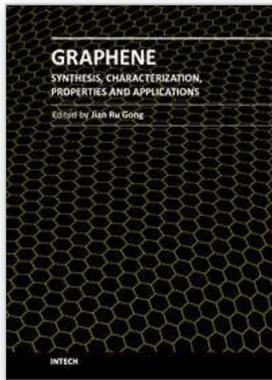
4. Conclusion

In this study, we carried to the reduction of graphite oxide in the soluble Nafion, ionic conductive polymer. Reduced graphite was not dispersed in water but polymer-coated graphenes (RGO-PSS and RGO-Nafion) were dispersed readily in water, and readily forms stable dispersed state. There are considerable changes in FT-IR spectra of GO after treatment with hydrazine hydrate, implying successful reduction of graphite oxide in aqueous solution of Nafion. UV/Vis spectrum of RGO-Nafion is similar to the characteristic peak of RGO. It indicated that Nafion-coated graphene have the stable state in the water solution.

The PEDOT film with Nafion-coated graphene increased significantly from 0.25 S/cm for pure PEDOT film and reached 12 S/cm. The film of PEDOT doped Nafion-coated graphene had also higher conductivities than films doped PSS-coated graphene.

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