Covalent functionalization of reduced graphene oxide using azido-terminated poly(2-isopropyl-2-oxazoline)

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Abstract. Azido-Terminated Poly(2-isopropyl-2-oxazoline)(N₃-PIPOZ) was prepared and it was then functionalized onto reduced graphene oxide (rGO). rGO was prepared from the reduction of graphene oxide (GO) by using hydrazine. The exfoliation of GO was measured using UV-Vis Spectroscopy. As a result, covalent functionalized reduced graphene (rGO-PIPOZ) with good solubility was successfully produced using grafting-on technique. Fourier transform infrared (FTIR) and thermogravimetric analysis(TGA) results proved the attachment of PIPOZ macromolecules onto rGO. rGO-PIPOZ showed best solubility in methanol (MeOH). The production of rGO-PIPOZ can be facilitated to a broad range application of graphene such as in polymer nanocomposites and lithium ion batteries.

1. Introduction

Graphene, a stable 2D single layer of carbon atoms with its fully conjugated, graphene owns thermal, electrical, mechanical and conductivity properties that are greater to carbon nanotubes (CNTs) [1]. Due to its outstanding properties, the superior material has attracted significant attention by worldwide researchers. Various methods can be used to synthesized graphene; for instance chemical vapor deposition, mechanical & chemical exfoliation, annealing a single-crystal SiC under ultrahigh vacuum and epitaxial growth.

However, many drawback of these methods such as high energy requirement, limitation of instrument, low yield and high cost [2]. One of the method to produce bulk quantity of processable graphene through oxidation process of cheap graphite powder to finally produce graphene oxide (GO). As a result, stable GO dispersion in various solvents can produced [3]. GO is an oxidized graphene sheet having its basal planes attached mostly with hydroxyl and epoxide groups, in addition to carboxyl and carbonyl groups located at the GO boundaries [4]. However, the oxidation process of GO interrupted the sp² hybrid carbon network, meaning the failure of the properties of graphene with large pi-conjugated structure. Nevertheless, GO can be reduced to conductive graphene-like sheets by getting rid of the oxygen-containing groups [5] to re-establish pi-conjugated structure of graphene resulting in reduced graphene oxide (rGO) with important properties restored especially for electrical properties [6].

In this research, we studied one-step functionalization of rGO with azido-terminated-Poly(2-isopropyl-2-oxazoline)(N₃-PIPOZ)(Figure 1) to obtain PIPOZ-grafted-rGO (PIPOZ-rGO). Nitrene
chemistry is the key reaction to introduce PIPOZ macromolecules onto rGO. Nitrene radicals are thermally generated from high reactivity of azide groups and can interrupt the double bonds in carbon nanomaterials, such as fullerenes, carbon nanotubes and reduced graphene oxide [7]. PIPOZ is less toxic polymers thus they have been broadly used in biosensors and biomedical. The functionalization of PIPOZ with rGO is likely to improve the usage of nanomaterials in biomedical materials and biomedical engineering.

![Figure 1 Chemical structure of N₃-PIPOZ](image)

2. Methodology

2.1 Preparation of Graphene Oxide

Freeze-thaw method was used to prepare graphene oxide (GO) according to publish article [8]. A mixture of 1.20 g of natural graphite (Ito Graphite Industries) and 0.60 g of NaNO₃ were placed to a 200 mL round bottom flask with a Teflon-coated stir bar prepared with a condenser during heating procedure. 28 mL of H₂SO₄ was added to this mixture and it was cooled to 0 °C using an ice–water bath. 3.6 g of KMnO₄ was slowly added to slurry to maintain the temperature of the mixture below 20 °C. After adding KMnO₄, the temperature of the mixture was raised to 35 °C in an oil bath and held for 30 min while the mixture was strongly stirred. Deionized water (56 mL) was added drop wise to this mixture, and the temperature of the mixture was raised to 98 °C and held for 30 min.

An ice–water bath was used to cool the mixture for 10 min. Then, 1.20 mL of 30% H₂O₂ and 168 mL of deionized water were dropped to the mixture. After cooling at surrounding temperature, the mixture was centrifuged at 3500 rpm for 7 min, and the upper layer of solution (supernatant) was removed. The remaining solid was washed with 340 mL of deionized water a total of four to six times until reached neutral pH. The solid was gathered by centrifugation and dried in vacuum at room temperature 12-20 hours. If not completely dry, the slurry was freeze-dried.

Mortar and pestle were used to ground graphite oxide lightly. 0.01 g of the ground graphite oxide and 5 mL of deionized water was added to propylene tube. The tube was immersed in a liquid nitrogen bath and left there for approximately 30 s until the mixture solution froze. After the mixture was entirely frozen, the tube was soaked in an oil bath set at 60 °C for 10−20 min to thaw the solid and repeat this freeze-thaw process 3 times. Then, the mixture was centrifuged at 3000 rpm for 5 min, and small amount of the upper layer of solution was collected for UV-vis identification. This freeze thaw-centrifugation cycle was duplicated several times. Exfoliated GO was separate by centrifugation (1000 rpm, 10 minutes). Freeze-drying method was used to dry GO or let it be in desiccator until completely dry.

2.2 Preparation of Reduced Graphene Oxide

Into 24 mL of water, dried GO (80 mg) was added to form GO dispersion. Hydrazine hydrate (40 μL) was added into the mixture to complete reduction at 95 ºC for 24 h. Let the mixture cooled before rGO was isolated using centrifugation for 10 min at 2500 rpm, washed few times using water to remove the traces of hydrazine hydrate. The sediment was completely dried under vacuo to give 70 mg of basic reduced graphene oxide (rGO) as a black powder.

2.3 Preparation of PIPOZ grafted reduced graphene oxide (PIPOZ-rGO)

60 mg of rGO was added to 15 mL of N-Methyl-2-pyrrolidone (NMP) in round-bottom flask. The mixture was sonicated for a while to disperse rGO. 30 mg of N₃-PIPOZ was added to this mixture and was stirred completely for 20 min by using nitrogen bubbling and it was then heated at 160 °C under
nitrogen atmosphere for 24 h. It was then cooled to room temperature and centrifuged at 1000 rpm for 30 min to take out unreacted rGO. The supernatant was filtered with TEFLO filter (0.45µm) and isopropyl ether (IPE) was used to precipitate PIPOZ-rGO from black coloured filtrate. The precipitant gave 11.6 mg of crude PIPOZ-rGO. The dark brown sediment was dried under vacuo. The sediment did not contain trace of azide compound as we characterized the dry black powder of final product (PIPOZ-rGO) using FT/IR-4100 infrared spectrophotometer, hence no purification process was needed.

2.4 Characterization method
Dry black powder of PIPOZ-rGO was characterized using Perkin Elmer infrared spectrophotometer. Samples were crushed with KBr and then packed into a thin pellet. TGA was performed with Mettler Toledo model TGA851/SF/1100 model under N$_2$ gas flow. The range of heating was completed from 30 °C to 600 °C, and the heating rate was 10 °C/min.

3.0 Results and Discussion

3.1 Fourier Transform Infrared(FTIR)
The GO IR spectrum (Figure 2a) proves the stretching of C–O epoxide group at 1061 cm$^{-1}$, the C=O carbonyl stretching at 1728 cm$^{-1}$ and O-H hydroxyl group stretching at 3350 cm$^{-1}$ [9]. GO confirms the existence of a great quantity of oxygen functional groups once the GO went through oxidation process due to the high intensity of the main peaks. The peak at 1627 cm$^{-1}$ is related to the vibrations of adsorbed water molecules. Hydroxyl and alkoxy groups were significantly decreased after GO was reduced to rGO. The rGO shows the peaks for hydroxyl and also epoxide group were almost gone (Figure 2b). Wavelength at 2100 cm$^{-1}$ revealed a characteristic absorption peak of N$_3$-PIPOZ due to the azide groups (N$_3$-) (Figure 2d). The absorption peaks due to PIPOZ moiety were obviously discovered after rGO was functionalized with N$_3$-PIPOZ (Figure 2c). Alternatively, the absorption at 2100 cm$^{-1}$ due to azide groups vanished totally, representing PIPOZ was successfully functionalized onto rGO(7).
3.2 Thermogravimetric Analysis (TGA)
Thermal stability of carbonaceous material was determined using TGA. Oxygen functional carbon such as GO tended to oxidize at low temperature whereas graphitized carbon stabilized at high temperature even though at 800 °C (10). TGA is also a valuable instrument to examine the amount of organic matters grafted to carbonaceous materials, because the organic matters covalently hooked up to the plane of graphene-based materials was thermally stripped off in the temperature range from 250 °C to 500 °C. GO was degraded tremendously at around 250 °C and finally at 550 °C, loses up about 90% of its total weight due to breakdown of oxygen-containing functional groups. GO shows low thermal stability due to the attachment of oxygen functional group on its surface. After restoration of pi-conjugated structure of GO during reduction process using hydrazine hydrate, rGO improved its thermal strength. Weight loss of rGO was only 16% at 550 °C.

TGA curves of rGO, PIPOZ-rGO and N$_3$-PIPOZ were compared to find out the amount of PIPOZ attached on rGO. Poor thermal stability of N$_3$-PIPOZ was shown with respect to rGO with total weight loss of 90% at 550 °C (Figure 3c). The polymer parts in PIPOZ-rGO was estimated to be 24%. These results proofed the successful attachment of polymer onto rGO.

![Figure 3 TGA curves of (a) rGO (b) PIPOZ-rGO (c) N$_3$-PIPOZ (d) GO](image)

3.3 Solubility
The dissolvability of PIPOZ-rGO in diverse solvents is shown in Figure 4. N$_3$-PIPOZ micromolecule has good solubility in methanol while weakly distributed in tetrahydrofuran (THF). Dark solution in methanol shows outstanding dispersion of PIPOZ-rGO in this solvent (Figure 4a). This dark brown solution was caused by the presence of rGO. Fairly dispersion was found in chloroform (CHCl$_3$)(Figure 4b) and ether (Figure 4c). However, sedimentation and uncoloured solvent was observed in THF shows poor dispersion of PIPOZ-rGO in THF (Figure 4d). The solubility of PIPOZ-rGO suggested that PIPOZ chains were effectively attached onto rGO.
Conclusion
We established a procedure for functionalization of rGO with azido terminated PIPOZ by using GO that has gone through reduction process by using hydrazine hydrate. We successfully produced soluble rGO with this nitrene chemistry. The successfully introduction of 24% of PIPOZ micromolecule onto the plane of rGO was proved with TGA and FTIR analyses. Solubility test showed high solubility of PIPOZ-rGO in MeOH.

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