Chemical Modification of Graphene Oxide by Copper Compound

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Abstract—Terminal alkyne modified graphene oxide (TAMGO) sheet was prepared first by acylation reaction. After that, pyrazole modified graphene oxide (PMGO) sheet with terminal diazo group was prepared by 1,3-dipolar cycloaddition of bisdiazocompound to TAMGO under solvent-free condition. Then, PMGO reacted with Cu(acac)₂ in chloroform to form terminal copper modified graphene oxide (TCMGO). The presence of copper was proved by the X-ray photoelectron spectroscopy (XPS) spectrum. Thermo gravimetric analysis (TGA) testing indicated that TCMGO presented excellent thermal property comparing with GO.

Keywords — Cycloaddition; Chemical Modification; Copper; Graphene Oxide; Thermal Property.

I. INTRODUCTION

Graphene oxide (GO) is a promising candidate for various materials due to its large theoretical specific surface area (2630 m²g⁻¹), high intrinsic mobility (200,000 cm²V⁻¹s⁻¹),[1, 2] high Young’s modulus (~1.0 TPa),[3] good thermal conductivity (~5000 Wm⁻¹K⁻¹),[4] excellent optical transmittance (~97.7%) and good electrical conductivity.[5, 6] Moreover, GO owns abundant hydrophilic oxygen-containing groups including epoxy, hydroxyl, carboxyl and carbonyl groups, leading to its facile modification and wide application.[7] However, the development of GO is hindered in many fields due to its low solubility in both organic and aqueous solvent.[8] The chemical modification of GO has been proven to be an effective method which renders GO a more versatile precursor for a wide range of applications.[9]

Nowadays, the most well-known structure of GO, which analogous to benzene and polycyclic aromatic hydrocarbons, is the one proposed by Lerf and Klinowski.[10] Chemical modified graphenes (CMGs) are provided by the addition of functional groups to GO platelets using various chemical reactions. A wide range of reactions utilizing carboxylic acids have been developed and applied to modify GO.[11–13] Moreover, the GO platelets contain reactive epoxy groups on their basal planes, which can be easily modified through ring-opening reactions under various conditions.[14, 15]

As far as we know, only few works have been reported on the CMGs by metal compounds. Herein, we reported the first example of CMG by 1,3-dipolar cycloaddition of alkyne with bisdiazocompound under thermal condition. And then copper compound is attached on the surface of GO by the formation of copper-carbennoid, which is generated by the reaction between copper compound and diazo group.

II. METHODS

Preparation of graphene oxide (GO).

GO was prepared through a modified Hummers method using natural graphite powder as the starting material.[16] The synthetic procedure was described as follow: graphite (6 g) and sodium nitrate (3 g) were added into a 1000 mL flask at 0 °C. Then, concentrated H₂SO₄ (150 mL) was added dropwise into the flask under continuously stirring, keeping the reaction temperature at 5 °C for 2 h. Subsequently, 22 g of KMnO₄ was added in batches and the reaction temperature was maintained at about 10 °C. After that, the reaction temperature was elevated to 35 °C and stirred for 2 h. After the reaction is completed, 270 mL of water was poured slowly into the solution under vigorous stirring to obtain dark brown suspension. The suspension was treated further by adding the mixture of H₂O₂ (21 mL, 30%) and water (165 mL) to remove the residual permanganate and MnO₂. The crude product was obtained by vacuum filtration. Then filter residue was washed for four times with warm (40 °C) diluted HCl (3%, 450 mL) solution and dried at 60 °C in oven.

Preparation of terminal alkyne modified graphene oxide (TAMGO).[17]

The GO sheets (200 mg) and 40 mL SOCl₂ were mixed and then refluxed at 70 °C for 36 h. After removing excess SOCl₂ by rotary evaporation, the product was vacuum dried for 24 h. Proprargyl alcohol (4 mL), distilled CHCl₃ (4 mL) and anhydrous triethylamine (2 mL) were mixed and then added dropwise in an ice-water bath under vigorous stirring. The mixture was stirred at 0 °C for another 2 h and then cooled to room temperature for 24 h. The powders were obtained by filtering the mixture through a 220 nm PTFE membrane. The collected powders were dispersed in ethanol (400 mL) and separated by filtration for three times. Then, the collected powders were dispersed in distilled water (400 mL) and

[Image 486x744 to 586x776]
separated by filtration for another three times. TAMGO sheets were obtained by vacuum dried at 35 °C for 24 h.

Preparation of pyrazole modified graphene oxide (PMGO).[18]

Bisdiazo compound (0.12 mol) and TAMGO (150 mg) were mixed in a glass tube at 100 °C under stirring. After 24 h, the reaction mixture was dissolved in 100 mL acetone and centrifuged. The powders were collected and dispersed in acetone (100 mL) and obtained by centrifugation for three times. The precipitate was then washed with excessive distilled H2O (300 mL) for three times and the powders were obtained by centrifuge the mixture. The residue was dried under vacuum at room temperature for 24 hours..

Preparation of terminal copper modified graphene oxide (TCMGO).

A solution of the PMGO (100 mg) in chloroform (20 mL) was slowly added to 20 mL of a chloroform solution of cupric(II) acetylacetonate (Cu(acac)2) (32.0 mg, 32 mmol) at room temperature. The obtained blue suspension was heated at 70 °C for 24 h, and then the precipitate was collected by filtration. The precipitate was washed with abundant distilled H2O (300 mL) for three times. After that, the product was dried under vacuum.

Equipments.

Fourier-transformed infrared (FTIR) spectra were recorded on a Thermo iS10 spectrometer. Thermo gravimetric analysis (TGA) curves were measured with NETZSCH STA 449C thermal analyzer (NETZSCH, Germany). A few milligrams of polymer were heated at a rate of 20 °C min⁻¹ from room temperature to 700 °C under nitrogen atmosphere. X-ray photoelectron spectroscopic (XPS) measurements of polymers were performed on an X-ray photoelectron spectroscopy (XPS) spectrometer (XSAM800, Kratos, UK). Raman spectrum was recorded on a RM-1000 confocal raman microspectroscopy (Renishaw) with excitation wavelength of 514.5 nm using Ar laser. Scanning electron microscopy (SEM) spectra were recorded by JEM-2100 (HR).

III. RESULTS AND DISCUSSION

![Scheme 1. The processes for the chemical modification of GO.](image)

The reaction processes of the chemical modification of GO are shown in Scheme 1. FTIR spectra of GO, TAMGO, PMGO and TCMGO are shown in Fig. 1. The spectrum of GO indicates the presence of O-H stretching at 3430 cm⁻¹, C=C stretching at 1590 cm⁻¹, C-OH stretching at 1220 cm⁻¹, and C–O stretching at 1050 cm⁻¹.[19] In the FTIR spectrum of TAMGO, a weak peak at 3200 cm⁻¹ ascribed to -C≡C- stretching is detected, suggesting the attachment of propargyl alcohol.[20] Moreover, the additional peaks of -CH₂, -CH₃, and -CH₂ groups appear at the range from 2860 to 2965 cm⁻¹.[21] Besides, three peaks at 1080, 790 and 660 cm⁻¹ belong to the stretching of ether group of TAMGO.[22] The formation of pyrazole rings is proven by the -C≡N- stretching at 1630 cm⁻¹, which is shown in the FTIR curve of PMGO.[18] Moreover, the peak referred to -C≡C-stretching disappears and the peak at 2110 cm⁻¹ assigned to diazo group (CHN₂) emerges.[23] The FTIR spectrum of TCMGO describes that the peak at 2110 cm⁻¹ vanishes after PMGO reacts with Cu(acac)₂. Raman spectroscopy is conducted to characterize the chemical structure of GO and TCMGO in Fig. 2. The Raman spectra of GO and TCMGO show two intense peaks at 1330 and 1580 cm⁻¹, which correspond to the D and G band, respectively. After the chemical modification, the I(D)/I(G) ratio increases from 0.79 (GO) to 0.88 (TCMGO) due to an increase in the number of sp² carbons formed on the graphene oxide during chemical functionalization.[24]

![Fig. 1. FTIR spectra of GO, TAMGO, PMGO, and TCMGO.](image)

![Fig. 2. Raman spectra of GO and TCMGO.](image)
(XPS) and the signals of carbonyl, epoxy, and carboxylic acid in the C1s spectra are shown in Fig. 3. The lower binding energy at 284.1 eV belongs to C-C and C=C carbons, and higher binding energy at 286.2 eV corresponds to C-OH from epoxy and hydroxyl groups.\cite{7} Moreover, the peak at 288.4 eV ascribes to the C=O arising from carboxyl group.\cite{25} The intensities of the band corresponding to C-C and C=C (284.1 eV) greatly increase after the chemical modification, which indicates the ratio of sp$^3$ and sp$^2$ carbon increases. On the other hand, the intensity of epoxy and hydroxyl peak decrease sharply, which is induced by the acylation of GO occurred under our experimental conditions. Besides, XPS analysis of Cu 2$p_{3/2}$ (Fig. 4) presents a peak at 933.9 eV, suggesting the existence of Cu(II).\cite{26}

Coating of pyrazole rings and copper compound on the GO sheets can be further proven by TGA results. TGA curve shows that about 50 wt% of pyrazole rings is bound to GO which
degrades between 250-500 °C.[18] And the rest of the material degrades between 500-700°C due to the attachment of Cu(acac)2.[25] Moreover, the rest of the carbon material remains stable up to 700 °C. The morphology of GO and TCMGO has also been characterized using scanning electron microscopy (SEM) (Fig. 6). The multiple sheet structure of GO is shown by the SEM image of the cross-section of fractured GO sheets.[28] On the other hand, TCMGO is shown as a macro-aggregated structure by the chemical modification.

IV. CONCLUSION

In conclusion, we report the chemical functionalization of GO with esterification and cycladdition reactions. FTIR, XPS, Raman, and TGA characterizations prove the successful attachment of pyrazole rings and Cu(acac)2 on the surface of GO. Moreover, the chemical modification greatly enhances the thermal property of GO.

References


