Synthesis and characterisations of polydopamine-reduced graphene oxide

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ARTICLE INFO	ABSTRACT
	Graphene has emerged as a promising material due to its exceptional thermal, mechanical and electrical properties. Therefore, it can be considered as a viable candidate for use in electrochemical sensors. However, the van der Waals interactions between the graphene sheets cause the process of agglomeration and limit their applications. In order to improve its stability and dispersibilty, the reduction of graphene oxide (GO) is needed. Herein we report a facile approach to reduce GO using oxidative polymerisation of dopamine. GO was synthesised using modified Hummer method and subsequently immersed in 2 mg/mL stirred dopamine solution at 25 °C for 24h. The resulted GO was dried at 60 °C for 24h and characterised using FTIR-ATR, SEM and EDX. The characterisations confirm the reduction of GO which was then labelled as polydopamine-reduced graphene oxide (P-RGO). Based on FTIR-ATR analysis, P-RGO sample exhibited a lower peak of hydroxyl (-OH) functional group compared to the GO sample. The percentage of oxygen element in P-RGO was also decreased compared to the GO sample.

1. Introduction

Graphene which consists of one-atom-thick planar sheet of carbon atoms has attracted great interest of researchers in both engineering and science fields due to its remarkable electrical, thermal and mechanical properties [1–3]. The reported properties and applications of this honeycomb two-dimensional lattice has provide opportunities for the development of electronic, medical and sensor devices in the future [4,5] One of the methods to produce graphene is by the reduction of graphene oxide [6]. This method offers several advantages: (i) the combination of inexpensive graphite as raw material and cost effective chemical methods yielding high production and (i) the high hydrophilicity of GO forming stable aqueous colloids to assist the assembly of macroscopic structures.

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Graphene oxide (GO) consists of pseudo-2D structure bearing various oxygen functional groups such as carbonyl, epoxide and hydroxyl groups [7]. The aggregation of graphene oxide due to the van der Waals interactions between the graphene sheets limits its applications [7]. In order to overcome this problem, the reduction process of graphene oxide is needed. There are a few methods used to reduce GO such as thermal [8–10], microwave and photo reduction [11–15], and chemical reduction (hydrazine,metal hydrides, ascorbic acid and hydroiodic acid [16–18]. In the absence of dispersant or surfactant, these methods naturally has a tendency to restack into graphite via van der Waals interactions or even agglomerate permanently [19]. Therefore, a mild method to effectively reduce the GO and yet modify the graphene by introducing the functional groups to improve the stability and dispersibility is needed.

Recently, Messersmith and his group introduced a facile and effective method to chemically modify and functionalize material surfaces through oxidative self-polymerization of dopamine in the presence of oxygen under alkaline conditions [20]. The oxidation process of dopamine into polydopamine during polymerization process provides an opportunity for dopamine to act as a reducing agent. In this study, dopamine was used as a reducing agent to reduce the GO and yet introducing the functional groups to improve the stability of reduced GO.

2. Materials and methods
2.1. Synthesis of graphene oxide (GO)

Graphene oxide (GO) was synthesized according to the modified Hummers method [21]. Briefly, 2.0 g of graphite fine powder and 1.0 g of sodium nitrate ($NaNO_3$) were slowly added into the concentrated sulphuric acid (H_2SO_4) at 0 °C under vigorous stirring for 30 min. Then, 6.0 g of potassium permanganate ($KMnO_4$) was gradually added to the mixture and stirred for another 30 min. The temperature of the mixture was raised to 35 °C before 90 mL of distilled water was slowly added to the mixture. The suspension was stirred for 30 min and reacted further by adding hydrogen peroxide (H_2O_2, 30%, 30 mL). The mixture was heated to 98 °C and then stirred for 15 min before adding distilled water (280 mL) and stirred for 7d. In order to wash the obtained graphene oxide, the suspension was centrifuged at 5000 rpm for 10 min. The supernatant was placed inside the cellulose membrane tube surrounded by distilled water. The distilled water was changed every 2 days for a week. After the washing process, the obtained graphene oxide was further centrifuged at 5000 rpm for 10 min. The graphene oxide paste was oven dried at 70 °C for 2 days and grinded into powder.

2.2 Synthesis of polydopamine-reduced graphene oxide (P-RGO)

P-RGO was prepared by oxidative polymerization of dopamine hydrochloride in the presence of GO. The obtained GO (100 mg) was magnetically stirred in dopamine hydrochloride solution (2 mg/mL in 10 mM Tris buffer, pH 8.5) for 24 h followed by centrifugation at 5000 rpm for 15 min and washing using distilled water for three times. The reaction temperature was held at 25 °C. The obtained sample was then dried at 60 °C for 24h.

2.3. Characterisations
2.3.1. FTIR-ATR analysis

The chemical functionality of GO and P-RGO samples was analyzed using Fourier transform-infrared attenuated total reflectance (FTIR-ATR, Thermo-Nicolet iS10) spectrophotometer. The measurement of the infrared spectra was obtained between 4000-400 cm^{-1}.

2.3.2. SEM and EDX analysis

The GO and P-RGO samples were characterized using a SEM (SEM, JEOL, JSM-6390) at an operating voltage of 15 kV and Energy Dispersive X-ray Spectrometer (EDX, Hitachi, SwiftED3000) for chemical analysis.

3. Results and discussion
3.1. FTIR-ATR analysis

The FTIR-ATR spectra of GO and P-RGO samples are shown in Fig. 1. The spectral peaks and their assignments are listed in Table 1. Significant changes in the FTIR-ATR spectra of GO were observed after being reduced by dopamine through oxidative polymerization process. The GO sample showed the broad adsorption band at 3342 cm^{-1}, which was assigned to phenolic hydroxyl group (-OH) [22]. However the intensity of the hydroxyl group decreased in P-RGO sample indicating the reduction process took place during the oxidative polymerisation of dopamine [23]. Moreover, the disappearance of C=O peak (1717 cm^{-1}) in P-RGO sample proved that GO was totally reduced by dopamine. During the polymerization process, dopamine molecules were adsorbed onto GO surface due to electrostatic, hydrogen bonding and π-π interactions which would cause partial reduction of GO to reduced GO [24]. In a weak alkaline solution (pH8.5), dopamine shows fair reducing ability and could be easily oxidized when exposed to other oxidants and dissolved oxygen [25]. Therefore, the presence of abundant oxidative groups in the surface of GO facilitates the oxidation process of dopamine and the reduction process of graphene oxide. Subsequently, polydopamine precursors were formed through the oxidative polymerization process [24].
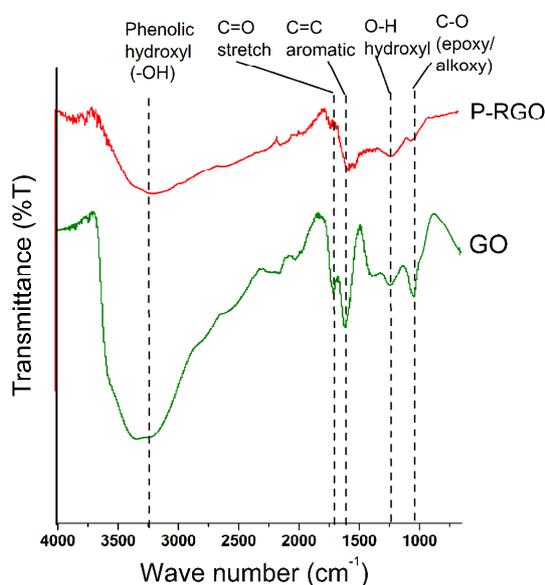

Fig. 1. FTIR-ATR spectra of GO and P-RGO samples

Table 1
Infrared bands of GO and P-RGO samples

Assignment	Wave number (cm^{-1})	
	GO	**P-RGO**
C-O (epoxy/alkoxy)	1246	1048
O-H (hydroxyl)	1391	1210
C=C (aromatic)	1612	1563
C=O (stretch)	1717	-
O-H (Phenolic hydroxyl)	3342	3194

3.2 SEM and EDX analysis

Figure 2 showed the topographies and EDX spectra of the analyzed GO and P-RGO. The surface of GO sample is not homogenous compared to P-RGO which has significantly developed into delaminated layer and forming porous structure. Based on the EDX spectra, the emergence of N element was observed in P-RGO sample due to the presence of dopamine as a reducing agent. Table 2 shows the atomic percentage of carbon (C) and oxygen (O) elements in both GO and P-RGO samples. The obtained results show the atomic percentage of oxygen was significantly reduced from 33.83 ±1.14% in GO sample to 27.72 ±1.02% in P-RGO sample suggesting that the graphene oxide is significantly reduced by dopamine. Moreover, the atomic percentage of carbon in P-RGO increased partly due to the presence of carbon in dopamine structure. It was found that after reduction process the C/O ratio improved from 1.96 (GO sample) to 2.60 in P-RGO sample. Typically, GO will have the C/O ratio ranging from 4.0-2.0 depending on the preparation method and the ratio can be improved after reduction process [9,26].
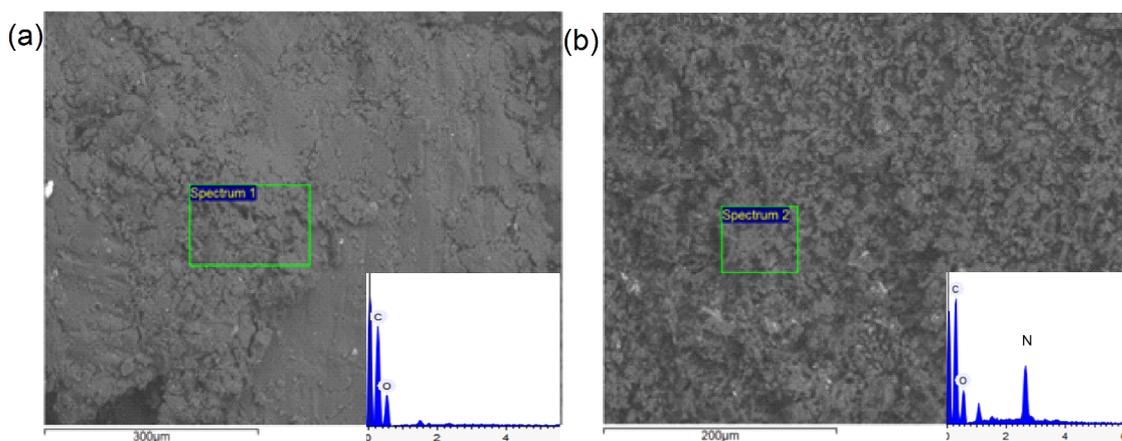

Fig. 2. SEM images and EDX spectra of GO and P-RGO samples

Table 2
The atomic percentage of GO and P-RGO samples

Sample	Atomic percentage (%)	
	Carbon (C)	**Oxygen (O)**
GO	66.16 ±1.14	33.83 ±1.14
P-RGO	72.28 ±1.02	27.72 ±1.02

4. Conclusion

We present an environmentally friendly approach to reduce GO using oxidative polymerization of dopamine. Dopamine not only acts as a reducing reagent to reduce graphene oxide but its functional groups can be further utilized as a platform to attract other compound of interest. It is shown that the peak of hydroxyl group and percentage of oxygen element have been reduced after functionalisation of GO with polydopamine. These results confirm the reduction process of grapheme.

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