

Functionalization of polyallylamine on graphene oxide

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Abstract

This work explains the functionalization of polyallylamine (PAA) on the graphene oxide (GO) sheets following a chemical route. The resulting GO-PAA complex is characterized by using various imaging and analytical tools. In the Raman spectroscopy for both the GO and GO-PAA, the appearance of D and G characteristic bands correspond to the sp^2 and sp^3 contents, respectively, in the carbon sheets. The observation of lowered D/G peak intensity ratio of these peaks from 1.3 for GO to 1.1 for GO-PAA indicates the lowering of the D favored sp^2 content in the GO sheet after PAA functionalization. In the Fourier transform infra-red spectroscopy, the disappearance of the vibrational modes for ketone and carboxyl groups, and appearance of the amine (-NH) group confirms the chemical interaction of GO and PAA triggered with the -NH group of PAA interacting with the oxygen contained hydroxyl, epoxy, and carboxylic groups of the GO sheets to form the GO-PAA complex. Scanning electron microscopy imaging indicates opaque layers with no distinction of flakes after PAA functionalization. Copyright © 2017 VBRI Press.

Keywords: Graphene oxide (GO), Polyallylamine (PAA), GO surface functionalization, GO-PAA complex, functional groups

Introduction

The exceptional physical, electronic, optical and mechanical properties of carbon based nanostructured materials have been demonstrated to be the potential as new materials for possible implementation in nano-electronics and biosensors. Graphene has been considered as an emerging carbon allotrope because of its unique chemical structure consisting of a single-layer sp^2 hybridized carbon atom network [1]. This unique chemical structure gives graphene excellent electrical, mechanical and optical properties, thus attracting much commercial and academic research interest [2]. Research works have been contributed to prepare carbon sheets of graphene, single and multi-wall carbon nanotubes, fullerene, graphene quantum dots for nano-electronics and bio sensing applications [3]. The unique charge transport properties [4] of graphene is exploited for the development of components in the electronic circuiting [5] but for the utilization of this 2D carbon sheet as biosensing test-bed the surface has to be modified for suitable functionalization of molecular and bio-entity detection.

The scientific and industrial research community focuses on preparation of carbon nanomaterials in various forms and study their compatible functionalization with organic and bio-entities. In many cases to achieve stable dispersion of graphene

and proper control of microstructure of nanocomposite, the covalent and non-covalent functionalization of graphene with polymers may be necessary. The non-covalent functionalization relies on the Vander wall forces, electrostatic interaction or π - π stacking. It is easy to carry out without altering the chemical structure of graphene sheets and also provides effective ways to monitor the electronic/optical property and solubility of nano sheets. The covalent functionalization of graphene derivatives is mainly based on the chemical reaction between functional groups of the molecules and oxygen related functional groups on GO and RGO surfaces such as epoxide, hydroxide on the basal planes and carboxyl on the edges. The covalent functionalization holds versatile property due to rich surface chemistry of GO and RGO. It should be noted that covalent and non-covalent functionalization of graphene with polymer chain can improve some properties, but it may be negative for other, especially related to movement of electrons or phonons [6]. The derivatives of graphene, graphene oxides (GO) and reduced graphene oxide have been understood to be the realistic form of graphene with epoxide, hydroxyl and carboxyl functional groups attached to the carbon sheets, and could be easily obtained through oxidizing graphite powders in strong oxidants. Although graphite oxide has been synthesized long ago, its exact molecular structure is

very complex and presence of epoxy and carboxyl groups has been well accepted [7-14]. These functional groups of GO can be chemically modified to produce homogeneous colloidal suspension in various solvents compatible with the organic and biomolecular reactions depending on the required applications. The chemical reaction of isocyanate groups with GO produced isocyanate-modified graphene oxide sheets that are well dispersed in polar aprotic solvent and in the presence of a polymer produced an electrically conductive nanocomposite of polystyrene/graphene. The reaction between carboxylic acid groups of GO and octadecylamine after SOCl_2 activation of COOH groups produced GO modified with aliphatic groups that could be dispersed in organic solvents [11-13]. Presence of epoxy groups is valuable as they facilitate the GO functionalization, compared to other groups such as the carboxyl group which needs activation in the absence of water. Strong nucleophile agents such as amines can readily react with the epoxy group through a ring opening reaction without any external catalytic activation and amines have extensively been employed for the functionalization of GO [7]. The reaction is carried out in aqueous media and ambient atmosphere without catalyst. Many researches have employed multi-step process for amino functionalization of CNT and graphene using large amount of organic solvents. In addition, the presence of some chemical group such as acyl chloride which is sensitive to impurities and moisture makes it difficult to control the reaction [5]. Therefore, effective amino functionalization of GO through one pot reaction with diamines is highly desirable and the reaction is relatively fast, due to the high reactivity of amine and epoxy groups.

In this paper we have explain the functionalization of PAA with GO. PAA consists of long alkyl chain with number of reactive amine group that interact with GO. The Raman, FTIR, and SEM shows the chemical interaction between PAA and GO.

Experimental

Material

Graphite powder for GO synthesis, all the chemicals, and PAA are procured from Sigma Aldrich Co., USA. All the reagents used in the study including sodium nitrate (NaNO_3), potassium permanganate (KMnO_4), sulphuric acid (H_2SO_4), hydrogen peroxide

(H_2O_2), hydrochloric acid (HCl) are used as received without further purification.

Synthesis of GO

GO in powder form is prepared by modified Hummer's method. Graphite powders (2 g, 500 mesh), KMnO_4 (7.3 g), H_2SO_4 (50 mL), and H_2O_2 are used as precursors. Graphite powder (2 g) is added to concentrated H_2SO_4 (50 mL) in a 250 mL flask placed in an ice bath to maintain the temperature at 0°C . Subsequently, NaNO_3 (1g) is added slowly in the flask under stirring and the resulting mixture is stirred continuously for 2 hours while adding 7.3 g of KMnO_4 in small portions to prevent the rapid raise in temperature. Then, the temperature of the reaction mixture is raised to 35°C and stirred for 2 hrs. After completion of the reaction, 90 mL of deionized (DI) water is poured slowly into the solution under vigorous stirring, and dark brown suspension is obtained. H_2O_2 (7 mL, 30%) and DI water (55 mL) are added to the resulting solution to convert the residual permanganate and MnO_2 into soluble MnSO_4 . The resulting suspension is bright yellow in color. The graphite oxide is separated from the reaction mixture by filtration. The yellow-brown graphite oxide powders are washed for three times with warm ($\sim 40^\circ\text{C}$) diluted HCl (3 %, 150 mL), and are dried finally at 40°C for 24 hrs. under vacuum. The graphite oxide is exfoliated to form graphene oxide (GO) sheets by ultra-sonication at room temperature for one hr.

Synthesis of GO-PAA

GO solution is prepared by adding 30 mg of GO is mixed in 10 ml of DI water, ultra-sonicated for 15 mins. to prepare the highly dispersed solution of GO, and 8 mg of PAA is added for each 30 mg of GO maintaining the weight ratio for GO and PAA of 3.75 [7], into the aqueous suspension, followed by ultra-sonication for 6 hrs. to obtain a homogeneous colloidal suspension of the PAA-modified GO sheets that looks darker in color than the original GO solution. The resulting cross-linked GO sheets with the PAA polymer chains were filtered through the wet filter paper, air dried, and washed with DI water for three successive times. Homogeneous colloidal suspension of the chemically modified GO-PAA is prepared by adding the DI water and used in the current study. The schematic of the GO and GO-PAA complex are shown in Fig. 1.

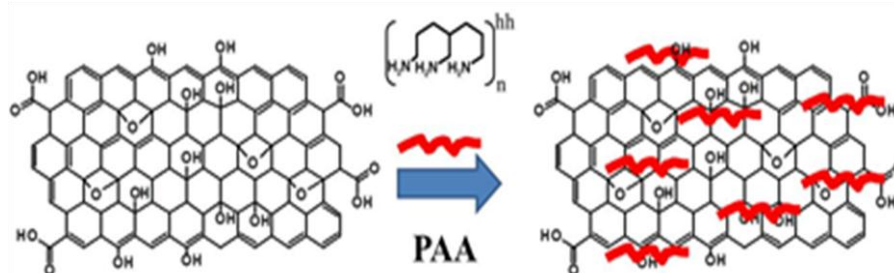


Fig. 1. Schematic for the functionalization of GO with PAA.

Characterizations Techniques

The structural and morphological characterization of GO, PAA, and GO-PAA are pursued through scanning electron microscopy, SEM (ZEISS instrument), Raman (RENISHAW, Invia microscope), and Fourier Transform infra-red, FTIR (Perkin Elmer FTIR spectrometer).

Results and discussion

Raman spectroscopic analysis

Raman spectroscopy is a powerful technique to study the carbon based materials such as graphene and its derivatives especially considering the fact that the conjugated and carbon-carbon double bonds lead to high Raman intensities [15]. Raman spectra for both the GO and GO-PAA are presented in Fig. 2 that show the D band at 1303 cm^{-1} and G band at 1594 cm^{-1} originated from the contents of sp^3 defect sites and sp^2 ordered structures, respectively, present in the GO backbone. The intensity ratio of the D and G band is a measure of the disorder and expressed by the ratio of the sp^3/sp^2 hybridized carbons contents and the additional functional groups attached with the carbon backbone structure. The change of the relative D/G peak intensity ratio from 1.3 for GO to 1.1 for GO-PAA indicates removal of functional groups attached to the carbon with sp^3 hybridization from the GO sheets that lead to the reduction of GO after PAA functionalization.

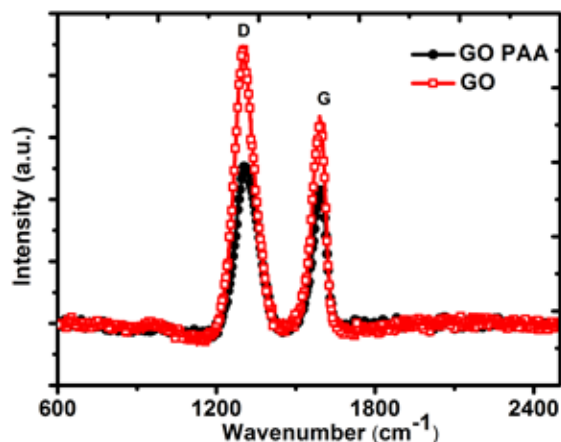


Fig. 2. Raman spectra of GO and GO-PAA in powder form.

Analysis of FTIR spectroscopy

FTIR is used to obtain infrared spectrum of emission and absorption, and utilized to identify the molecular bonding information quantitatively. Here, the FTIR studies are used to investigate the structure and functional groups present in the GO-PAA. FTIR studies of solutions containing GO-PAA complexes with DI-water as solvent is recorded and shown in Fig. 3. An NH_2 group of PAA interacting with the oxygen functional groups hydroxyl, epoxy, and carboxylic groups present in GO sheets. After

interaction of GO sheets with PAA, the disappearance of C-O stretch at 1222 cm^{-1} and C-OH at 1415 cm^{-1} takes place. The exposure of the reactive epoxy groups of GO to the amine groups of PAA lead to ring opening reaction of three-member epoxy groups and create new N-H bond at 1640 cm^{-1} [7]. The appearance of new N-H peak in GO-PAA confirms the chemical interaction of GO and PAA to form GO-PAA complex.

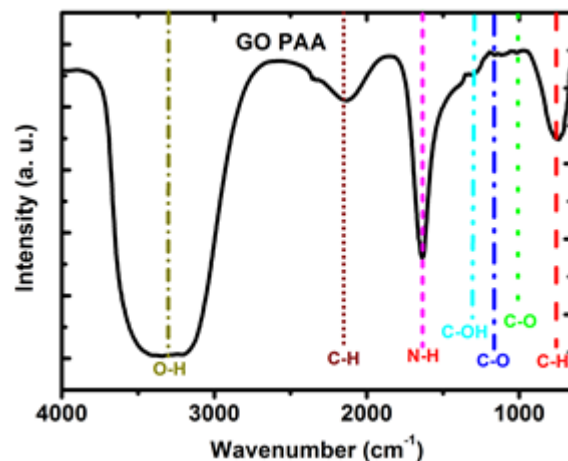


Fig. 3. FTIR spectroscopy of GO-PAA powder dispersed in deionized water.

Morphological study using SEM imaging

GO materials consist of randomly aggregated, thin and crumbled and closely packed sheets with formation of a disordered solid [16]. In addition, the presence of oxygen groups in structure of GO facilitates the intercalation of water molecule into graphite oxide interlayers. Therefore, exfoliation of GO is not due to only hydrophilicity of GO layers, but also due to substantial decrease in the interlayer interaction. The surface morphology of GO-PAA is shown in Fig. 4. SEM of graphene oxide shows transparent, regular, and clear flakes. But after functionalization with PAA, the surface with GO-PAA complexes, become opaque, rough, irregular, and shows the agglomeration of organic contents over the GO flakes.

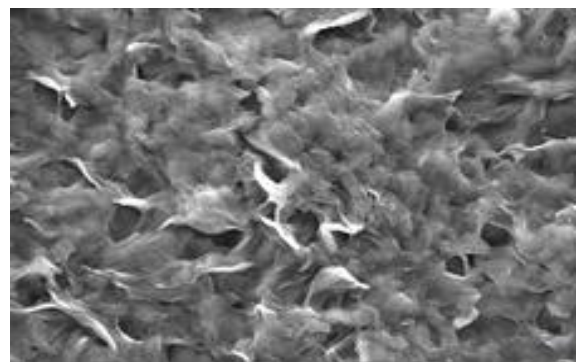


Fig. 4. Surface morphology of GO-PAA in powder forms imaged through SEM.

Conclusion

The current study demonstrates the functionalization of PAA on GO surfaces following chemical route by sonicating the GO with PAA for 6 hours. The newly formed GO-PAA complex is characterized by various imaging and spectroscopic tools. The FTIR, Raman, and SEM suggest the interaction of PAA with GO. PAA is used as an effective linker and stabilizer for the functionalization of graphene oxide. The biocompatibility properties of the currently developed GO-PAA complexes could be further utilized to translate the interesting behaviors in bio sensing applications by fabricating medical devices for detection of bio-entities

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