Experimental and theoretical studies on the composite composed of graphene oxide and polyaniline

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ABSTRACT

The formation of graphene oxide–polyaniline was studied experimentally and theoretically. Both methods reveal that there is an existence of graphene oxide–polyaniline due to the interaction between oxygen functional groups of graphene oxide and polyaniline. The intercalation of polyaniline into layers of graphene oxide expands the space distance of layers in graphene oxide. The presence of polyaniline in composites can be proved by scanning electron microscope (SEM) and cyclic voltammograms of obtained composites. The formation of graphene oxide – polyaniline was also proved by theoretical calculation of adsorption energy when polyaniline interacts with graphene oxide

Introduction

Graphene, has been the major focus of recent research to exploit an sp^2 hybrid carbon network in applications such as capacitors, cell images, sensors, devices, drug delivery, and solar cell due to its unique electronic, mechanical and thermal properties. In addition, graphene is an ideal material for electrochemistry because of its very large 2-D electrical conductivity (550 S cm^{-1}), surface area (2630 m^2 g^{-1}) and a large number of electrochemical favorable edge carbons per mass of graphene which facilitate electron transfer between molecules to an electrode substrate with a low overpotential [1,2,3,4,5]. However, dispersibility in water of graphene is very low. This results in flocculation and precipitation when graphene is dispersed in water [6,7]. Therefore, it is difficult to compatibilize the graphene with other components.

Graphene oxide is a single sheet of graphite oxide with oxygen functional groups on basal planes and edges, a water-soluble nano-martial prepared through extensive chemical oxidation of graphite (GR) crystals to introduce oxygen containing defects in the GR stack, followed by complete exfoliation of the solid into sheets of atomic thickness by either thermal or mechanical treatments. The tunable oxygen functional groups of GO facilitate surface modifications and make it a promising material for preparation of composites. Nevertheless, the poor electrical conductivity of GO always prevents it from experiencing high electrochemical activity performance. Therefore, the incorporation of an electrically conductive and electrochemically active second phase in free-standing GO material is very necessary to enhance its pristine electrochemical properties [8].

Polyaniline (PANI) has been considered as the most promising conducting polymers because of its low cost and ease of synthesis [9], controllable conductivity, highly electrochemical activity and good biocompatibility. Therefore, PANI materials have been widely and intensively studied as electrical, electrochemical, and biomaterials [10,11]. Recently, extensive efforts have been made to prepare chemically GO-PANI composite powder, which is expected to exhibit various functional properties [12]. Especially, PANI has been considered to reinforce the electrochemical capacitance of GO material. However, electrochemical polymerization of monomers on an electrode surface offers many advantages over chemical methods. The obtained product is a solid, does not need to be extracted from the initial monomer/oxidant/solvent mixture, and is easily amenable to numerous techniques of characterization such as *in situ* UV-visible, infrared, and Raman spectroscopies and *in situ* conductometry [**Error! Bookmark not defined.**].

Accompany with development of technologies, the development of computational calculation reduces cost and time consuming of experimental study. Theoretical calculation orients experimental studies and help to explain experimental results more clearly. Therefore, the combination of theoretical and experimental studies is a new trend in study of chemistry.

In this paper, we report theoretical and experimental results on graphene oxide – polyaniline composites. Experimental results in this study were obtained by using different techniques: X-ray diffraction (XRD), Scanning electron microscope (SEM) and from cyclic voltammetry. The theoretical results were acquired using method of density functional theory (DFT).

Experimental Part:

Aniline (Merck) was distilled under reduced pressure and stored under nitrogen prior to use. The GR flake has been purchased from Sigma Aldrich. Distilled water (18 MΩ) was used, and all other chemicals were analytical grade reagents and used as received. All solutions were purged with nitrogen before electro-chemical measurements.

Preparation of Graphene oxide (GO)

GO was synthesized from flake graphite by a modified Hummer's method [13]. Detail procedures were reported in previous work [14].

Preparation of Graphene Oxide - Polyaniline (GO-PANI)

GO-Anilinium required for electropolymerization was prepared in the following way. A total of 0.5 g of GO was dispersed in 100 mL of 0.5 M sulfuric acid containing 0.1 M aniline, purged with nitrogen for a few minutes, and stirred for 2 hours at room temperature. The dispersion was washed and

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centrifuged with excess of distilled water. The resulting wet solid GO-anilinium was re-dispersed in 50 mL of 0.5 M sulfuric acid solution. Electrochemical polymerization was carried out on a platinum sheet electrode at a constant electrode potential of $E_{SCE} = 750$ mV at room temperature. Another platinum cylinder electrode and a saturated calomel electrode (SCE) were used as auxiliary and reference electrodes, respectively. The electrolyte near the working electrode area was kept under slow magnetic stirring (rpm = 80) to maintain the homogeneity of the dispersion. GO-PANI deposited on the working electrode was washed with distilled water and dried at room temperature. Samples are used in IR, TGA, SEM, and XRD measurements were dried at 60°C for 24 hours to remove water content in these sample.

Characterization:

Autolab PGSTAT302N potentiostat connected to a computer was used to record cyclic voltammograms (CVs). Electrochemical polymerization and measurements were carried out in a three-electrode cell under a nitrogen atmosphere. The platinum sheet electrode was used as working electrode. Another platinum sheet electrode and a SCE were used as counter, and reference electrodes, respectively. Scanning electron microscope (SEM) was performed by a Hitachi S-4800 field emission scanning electron microscope at 5 kV. Thermogravimetric analysis (TGA) was carried out on a Shimazu DTG-60H instrument at a heating rate of 10°C/min under air flow of 50 mL/min.

Theoretical Methods:

In this study, graphene oxides (GOs) were employed with different functional groups epoxy (C-O-C), hydroxyl (C-OH) and carbonyl (-COOH) groups, and polyaniline was also used for modeling with its three main forms: leucoemeradine (LE), emeraldine (EM) and pernigranilin (PE). All calculations were performed using of density functional theory (DFT) method with generalized gradient approximation (GGA) and basis sets of DZP. All these procedures were attached with SIESTA software [15]. Adsorption energy was calculated as following expression: $E_{ad} = E_F - E_I$, where E_{ad} is adsorption energy, E_I and E_F are energy of system before and after adsorption, respectively
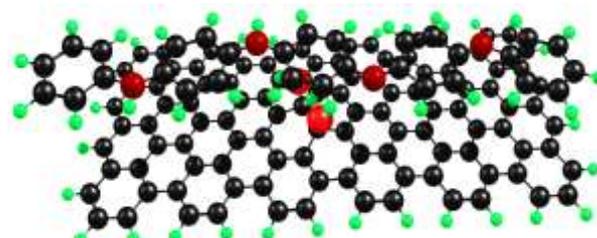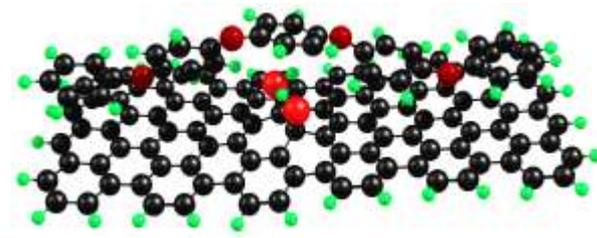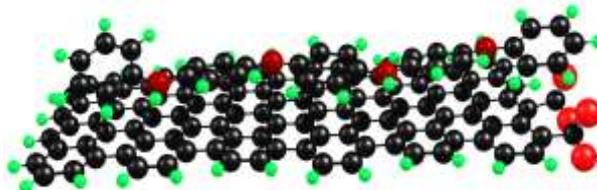
Results and Discussion:

COC-LE

COC-EM
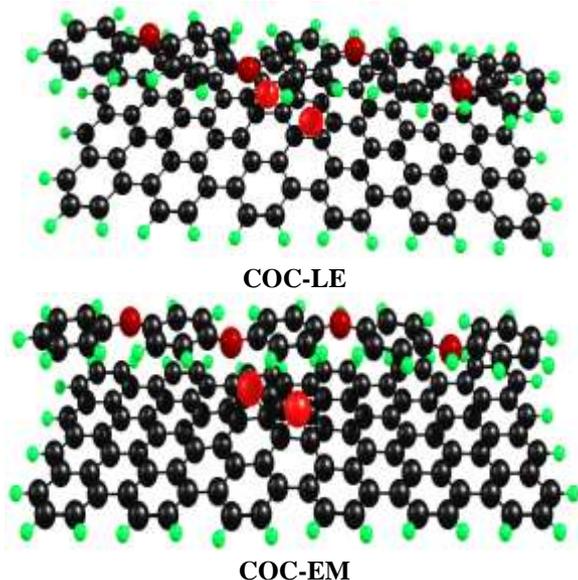
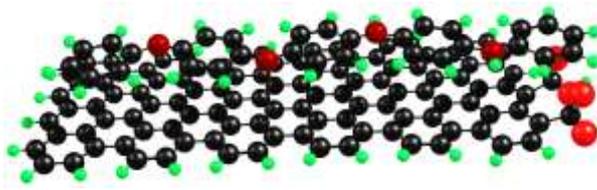**COC-PE**
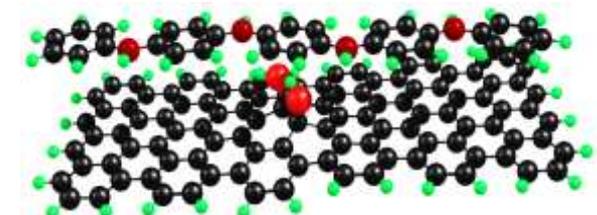
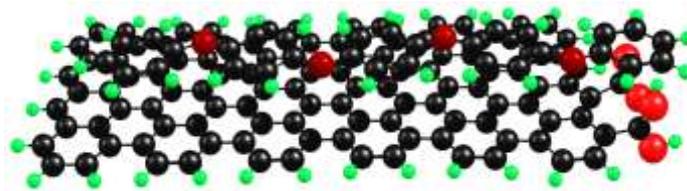**OH-LE**

OH-EM

OH-PE

COOH-LE

COOH-EM

COOH-PE

Figure 1: Adsorption modeling of PANIs on GOs

As shown in the Table 1 and Fig. 1, theoretical results show that all forms of polyaniline can be adsorbed on surface of graphene oxide easily with negative value of adsorption energy. Results also reveal that there is no hybridization between PANI and GO, therefore the adsorption of PANI on GO can be classified as physical adsorption though value of adsorption

energy is negatively large. According to the results obtained from theoretical calculations we can conclude that he adsorption of PANIs on GO is exothermic process ($\Delta H < 0$) and occurs relatively vigorously. When composites of graphene oxide-polyaniline are formed, energies of band gap are decreased. This leads to a better conductivity these composite in comparison to pure graphene.

Table 1: Adsorption energy (kJ mol^{-1}) and bandgap (eV) of GO-PANIs

Functional Group-PANI	Adsorption energy	Bandgap (*Eg*)
COC	-	0.42
COC-LE	-315.505	0.20
COC-EM	-286.270	0.33
COC-PE	-303.927	0.37
OH	-	0.92
OH-LE	-263.211	0.55
OH-EM	-178.304	0.92
OH-PE	-292.156	0.52
COOH	-	0.93
COOH-LE	-305.857	0.53
COOH-EM	-312.900	0.85
COOH-PE	-321.198	0.55

Cyclic Voltammetric Measurements

CVs of pure PANI and GO-PANI nanocomposite deposited on a platinum electrode were recorded in an aqueous solution of 0.5 M H_2SO_4 and are shown in Figure 2. It can be found that there are two pairs of redox peaks in CV curves of pure PANI and the composite with the first one observed at $E_{SCE} = 200mV$, attributed to the transformation of a semiconducting state (leucoemeraldine form) and a conducting sate (polaronic emeraldine form) [16], and the second one at $E_{SCE} = 750$ mV, which is due to conversion of emeraldine into pernigraniline form. A pair of humps in the region of $E_{SCE} = 0.30$-0.50 V has been assigned to over-oxidation products [**Error! Bookmark not defined.**,17]. The shape of the CVs of GO-PANI is similar to those of PANI. This indicates that GO layers do not influence the electrochemical properties of PANI nor does the intercalation favor a polymer with different properties (such as, e.g., molecular weight) as far as could be evidenced with this electrochemical technique. There is only a minor shift of the reduction peaks associated with the pernigraniline-emeraldine transition which might indicate some not yet understood interaction between GO and PANI, and the emeraldine-leucoemeraldine transition which can be explained by the partial deprotonation of emeraldine salt in the GO-PANI composite in aqueous media [18].
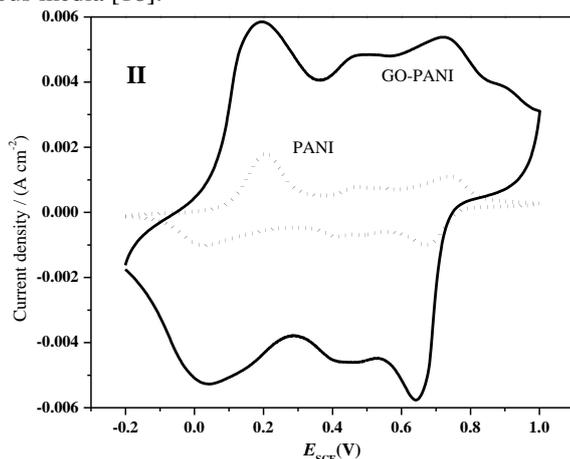

Figure 2: CVs of PANI and GO-PANI composite in 0.5 M H_2SO_4 solution

From CV curves of GO-PANI film, it is obvious that GO-PANI film was relatively stable as it was not damaged or peeled off from the electrode surface after continuous potential cycling for up to 20 cycles. As shown in Fig. 2, intensity in CVs of GO-PANI is much higher than that of in CVs of PANI. This means that, according to the calculation reported elsewhere [19], the capacitance GO-PANI composite is much higher than that of PANI film. This is one of properties needed for being a good candidate material in electronic applications.

Thermogravimetric analysis (TGA)

The composition and structure of the GR, GO, PANI, and GO-PANI composites were further studied by thermogravimetric analysis. As shown in Fig. 3, all the materials show a small amount of mass loss at the temperature less than 170°C (0.2; 14.2; 10.1, and 9.5% for GR, GO, GO-PANI, and PANI, respectively) due to the deintercalation of H_2O [20].
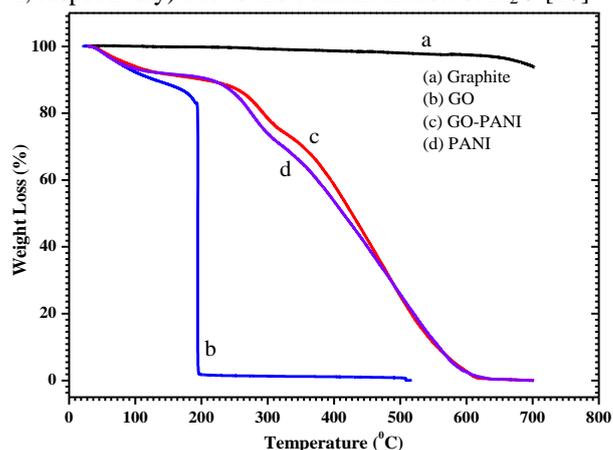
Figure 3: Thermogravimetric analysis of GR, GO, PANI and GO-PANI composites

For GO, after exfoliation of graphite, the obtained GO exists in a form of single or several layers, and therefore it is easy to be oxidized at low temperature. The oxidation of GO occurs vigorously at the temperature raging from 180°C to 200°C. Most of the GO mass (84.5%) is lost in this range of temperature. The low thermal-stability might be due to the absence of Van der Waals forces between layer in GO. Compared with GO, a mass loss of only 0.2% can be observed for GR from room temperature to 200°C. It is clear that there is no significant weight loss in the temperature range from 25-700°C. For PANI and GO-PANI, the trend of TGA curves is similar. A mass loss of around 10% can be observed from ambient temperature to 200°C. Most of the mass of PANI and GO-PANI lost in the range between 200 and 600°C. However, the oxidation of GO-PANI composite with less steep slope is relatively slower than that of PANI, showing the better thermal stability of GO-PANI in comparison to PANI. This might be explained due to the interaction between GO and PANI.

Table 2: TGA data of Graphite, GO, GO-PANI and PANI

Sample	Weight loss % at temperature [°C]			Major degradation temperature [°C]	Weight retention [%] at 500°C
	190	250	500		
Graphite	0.2	0.4	2.0	-	98
GO	17	98.6	99.2	194.4	0.8
GO-ANI	9.5	12.5	74.6	450	25.4
PANI	9.0	14.2	74.2	450	25.8

Morphology analysis

The morphology of GR, GO, PANI, and GO-PANI was characterized using scanning electronic microscope (SEM). As shown in Fig. 4, GO–PANI exists in a layered and wrinkled form with PANI fibers distributed between and on the surface of graphene oxide sheets. In the contrary, surface of GR and GO is clear with edges of layers and without fibers of PANI. The change in structure of GR, GO and GO-PANI was also proved by the change of interlayer space in these materials. This change was determined by their X-ray diffraction patterns which was reported in previous paper [**Error! Bookmark not defined.**] .

(a)

(b)

(c)
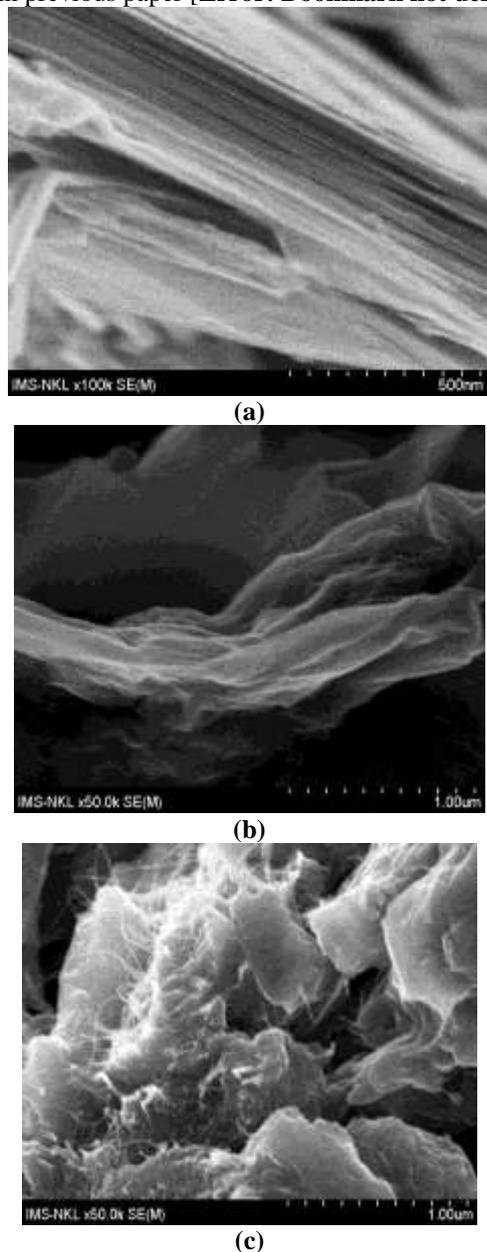
Figure 4: SEM images of GR (a), GO (b) and GO-PANI composite (c)

Conclusion:

GO-PANI nanocomposite was studied theoretically and experimentally. The obtained composites synthesized electrochemically were characterized with different advanced techniques. The analyzed results reveal that there is an intercalation of PANI into sheets of GO which changes the space distance between layers of GO. Theoretical results reinforce the experimental results by giving evidences to prove the existence of GO-PANI composites at different form of PANI. The intercalation of PANI does not influence the electrochemical properties of PANI in the composites.

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