

Graphene/Cobalt Oxide/Polyaniline composites for super-capacitor application

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Abstract: Graphene/Cobalt oxide/polyaniline (G/Co₃O₄/PANI) composite is synthesized by polymerization. In this paper we observed that, G/Co₃O₄/PANI composites exhibit high specific capacitance than pure PANI. With Graphene oxide (GO) as support material, Cobalt oxide can be nucleated and high transfer of electron is provided by PANI. The samples were examined by Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) and Raman Spectroscopy. Electrochemical properties of these samples were measured by cyclic voltammetry (CV) and galvanostatic charge/discharge.

Keywords: Graphene, Composite material, Scanning Electron Microscopy, X-Ray Diffraction, Cyclic Voltammetry.

1. Introduction

Graphene oxide (GO) is of great interest due to its low cost, easy access, and widespread ability to convert to graphene [1-5]. At present, a conventionally-modified Hummers method is the primary method for preparing GO. Graphite is commonly chosen as the starting material due to its availability and low cost. The graphite was oxidized to GO and then exfoliated which forms 2-D nanosheets [6]. Exfoliated graphene sheets possess large surface areas. Graphene can be coupled with the conducting polymers [7, 8] or with the metal oxides [9-14] shows promising application in the field of super capacitors. The transition metal oxide like MnO₂, RuO₂ exhibits high specific capacitance and also provides excellent reversibility [15]. Conducting Polymers are preferred as they exhibit high flexibility and specific capacitance. Among the polymers, the promising electrode material preferred are polyaniline (PANI) as they are very cheap, can be synthesized easily and exhibit high conductivity [16]. The super capacitor can store and convert energy. Compared to batteries and conventional capacitors, super capacitors exhibits higher power density and longer life cycle. Super capacitors finds its applications in the field of electrical, electronics, memory based systems and defense systems [17]. Nowadays graphene sheets are synthesized on a large scale [18, 19]. This leads to the synthesis of graphene composites for the application of super capacitors. In this paper, we report a process for synthesizing G/Co₃O₄/PANI composite.

2. Experiment

2.1 Synthesis of Graphene oxide

GO was synthesized from graphite powder by a modified Hummers method [20, 21], in which pre-oxidation of graphite was followed by oxidation with Hummers' method. In the pre-oxidation, the graphite powder (4.0 g) was added with stirring into the concentrated H₂SO₄ (40 mL) solution in which K₂S₂O₈ (2.0 g) and P₂O₅ (2.0 g) were completely dissolved at 80°C. The mixture, in a beaker, was kept at 80°C for 4.5 h using an oil bath after that the mixture was cooled down and was diluted with 1 L of distilled deionized (DDI) water. The pre-treated product was filtered and washed until the pH of filtrate water became neutral. The shiny, dark-

gray, pre-oxidized graphite was dried in air overnight. Then, it was dispersed by stirring into chilled H₂SO₄ (92 mL) in a flask in an ice bath. KMnO₄ (12 g) was added slowly with stirring to keep the temperature of reaction mixture below 20 °C. The resulting thick, dark green paste was allowed to react at 35 °C for 3 h followed by addition of H₂O (184 mL) to give a dark brown solution. After additional stirring for 2 h, the dark brownish solution was further diluted with distilled water (560 mL) and then H₂O₂ (30%, 40 mL) was added slowly and the colour of the mixture turned into brilliant yellow. The mixture was allowed to settle overnight and the supernatant was decanted. The remaining product was washed with 10% HCl solution with stirring and the brownish solution was allowed to settle overnight. The supernatant was decanted and the remaining product was centrifuged and washed with deionized (DI) water. The washing process was repeated until the pH of the solution became neutral. After filtration and dried under vacuum, GO was obtained as a grey powder.

2.2 Synthesis of G/ Co₃O₄ composites

The G/ Co₃O₄ composites were synthesized according to the literature [22]. 200 mg of G and dispersing it to 400 mL of distilled water and the mixture was ultrasonicated for 2 h. cobalt (II) nitrate hexahydrate (2.56 g) and urea (2.64 g) were added into the GO suspension. Vigorous stirring is done for 10 min. Then the solution is heated in microwave oven for 10 min. The solution is then cooled at room temperature and centrifuged. The powder was dried at 70 °C for 12 h. Finally the resulted powder is heated in a muffle furnace at 320 °C for 1 h for calcinations.

2.3 Synthesis of G/Co₃O₄/PANI composites

Typically 0.125 M aniline monomer is mixed with 1 M HCl and 15 mg G/cobalt oxide composite is added to it under stirring. Then an equal volume of 0.125 M ammonium per sulfate (APS) solution was added with 1M HCL and mixed into the above mixture and kept in an ice bath at 0–4 °C for 3 h. Finally, Graphene/cobalt oxide /PANI composite is centrifuged and dried at 80 °C for 12 h.

2.4 Characterization methods

The obtained sample is characterized X-ray Diffraction (XRD) by using the system (D8 bruker), UV visible spectroscopy (V-670) has used to found the electronic structure of the samples via absorbance spectrum. Field Emission Scanning Electron Microscopy (Hitachi SU 6600) was used to find the structure of the composite materials. And electrochemical measurements were done by using the system CHI 660C for both cyclic voltammetry and galvanostatic charge/discharge.

2.5 Electrochemical measurements

The Cyclic voltammetry (CV) and galvanostatic charge/discharge were measured by the three electrode system. The working electrode is prepared by coating 1mg of active material (G, G/Co₃O₄/PANI and G/Co₃O₄) on the glassy carbon electrode and 2μL of nafion is added for binding. The counter and the reference electrode used as carbon foil and Ag/AgCl. The electrolyte used is 6M KOH electrolyte solution. The electrochemical measurements are performed using CHI 660C electrochemical workstation.

3. Results and Discussion

The Fig 1 shows XRD pattern of G/Co₃O₄/PANI composite. We confirm the PANI at diffraction peak at 23.09° [18]. The interlayer distance of graphene layer is 3.4 Å calculated from the diffraction peak of graphene (2 theta value 26.09°). Other peaks like 2θ=18.5° and 20.7° corresponding to the Co₃O₄ nanoparticles.

Scanning Electron microscope reveals the structure of Co₃O₄ /Graphene composite. It can be seen from the image (Fig 2(a)). The graphene consists of few layer graphene sheets and the agglomeration Co₃O₄ nanoparticles were inserted between the layers of the graphene. Due to the covalently bonded Co₃O₄ with graphene, it has high charge storage behavior than graphene investigated by cyclic voltammetry. Energy dispersive spectroscopy (EDS) analysis of this region, given in the fig 2(b) confirms the existence of Co and O in the ratio of 3:4. However, the shape of the Co₃O₄ nanoparticles is not observed due to low magnification.

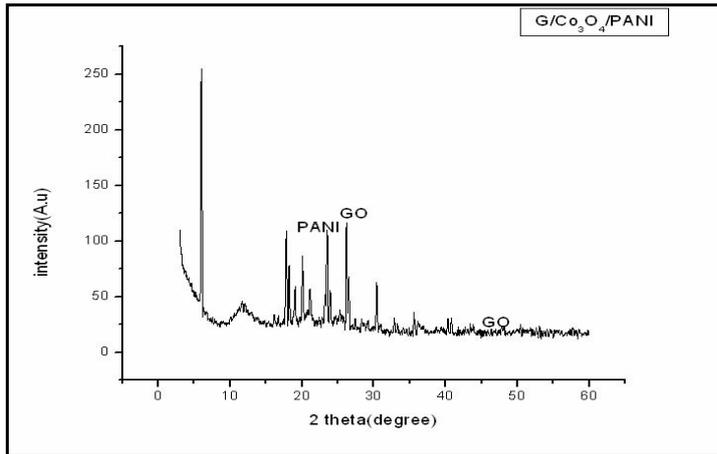


Figure 1: XRD pattern of Graphene/Cobalt oxide/PANI composite.

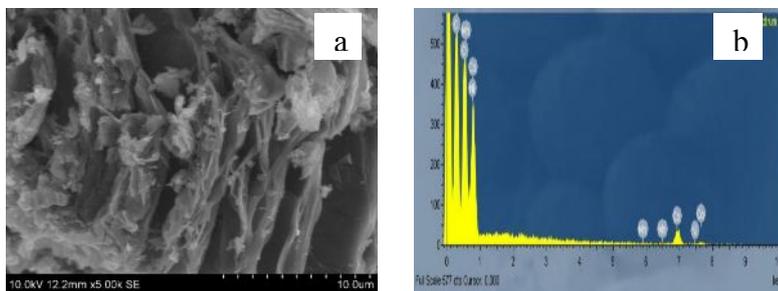


Figure 2: (a) SEM image of Graphene/ Co_3O_4 and (b) EDS spectrum of Graphene/ Co_3O_4

UV spectroscopy measurements show the optical properties of cobalt oxide as well as the electronic conjugation of the composites. The absorption peak at 230 nm for G has well agreement with the previous reports [19]. Two strong peaks at 218 and 275 nm were obtained from G/ Co_3O_4 composites indicating that the electron transition from $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ for graphene, cobalt oxide respectively. Apart from these peaks one weak peak observed at 775 nm indicates the charge transfer from ligand to metal of cobalt oxide[20]. UV spectrum for G/ Co_3O_4 /PANI composites is shown in Fig 3. The peak at 225 nm corresponding to $n \rightarrow \sigma^*$ transition of graphene. The major absorption peak obtained at 349 nm indicates the $\pi \rightarrow \pi^*$ transition of benzene rings in PANI. The UV absorption spectrum of PANI agreement with the earlier reports.

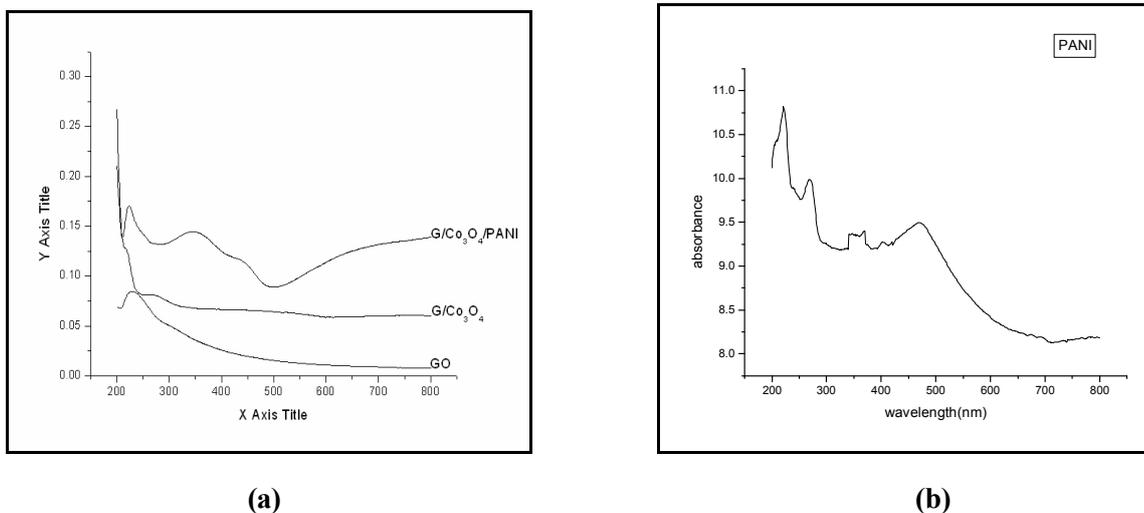


Figure 3: UV Vis spectrum of (a) GO, G/ Co_3O_4 and G/ Co_3O_4 /PANI and (b) pure PANI

Fig4 shows the cyclic voltammetry results of the composites. The CV experiments were done in the potential range from 0 to -0.8 v at different scan rates like 5, 20,100 mv/s. The shapes of the CV loop in our experiment are close to rectangle, indicating the ideal capacitive behavior. The specific capacitance is calculated from the obtained data.

The high specific capacitance is obtained in the case of G/Co₃O₄ composite for all the scan rates rather than G and G/Co₃O₄/PANI composite. In the case of G/Co₃O₄/PANI composite, PANI is dominated the surface area of Graphene as well as cobalt oxide. Due to this problem, it shows low value of specific capacitance than other. The values of the specific capacitance of the samples are tabulated in table 1.

Table 1: Specific capacitance values (F/g) of the samples calculated from Cyclic Voltammetry at different scan rate:

Sample	5 mv	20mv	100 mv
GO	1.22	0.82	0.4105
G/Co ₃ O ₄	1.93	0.88	0.345
G/Co ₃ O ₄ /PANI	0.391	0.1842	0.0715
PANI	0.1928	0.0989	1.147

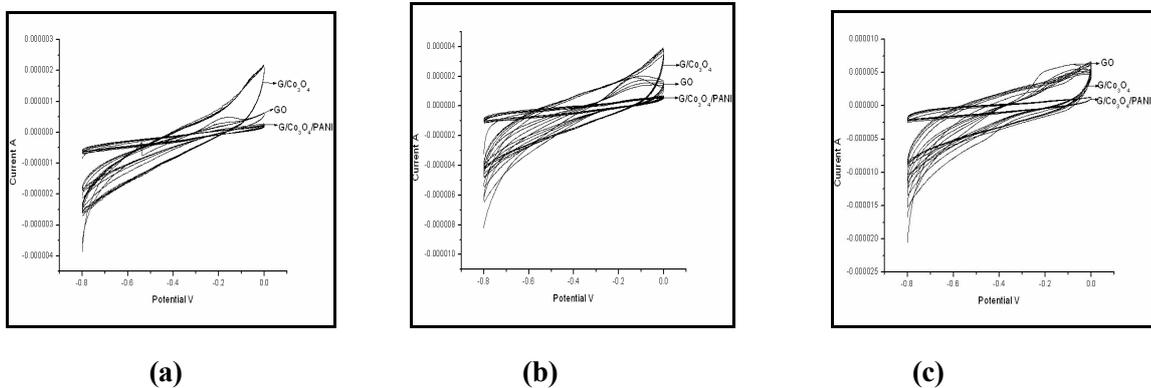


Figure 4: CV results for different scan rates. (a) 5 mv, (b) 20 mv, (c) 100 mv

The charge and discharge behavior of the composite was measured by chrono-potentiometry from 0 to -0.8V at a constant current of 2 μA, as shown in Fig 5. The specific capacitance of charging and discharging are obtained from the chrono-potentiometry data shown in table 2.

Table 2: Specific capacitance values (F/g) from chrono-potentiometry

Sample	Charging	Discharging
GO	17.5	38.75
G/Co ₃ O ₄	125	287.5
G/Co ₃ O ₄ /PANI	3.125	9
PANI	6.475	7.837

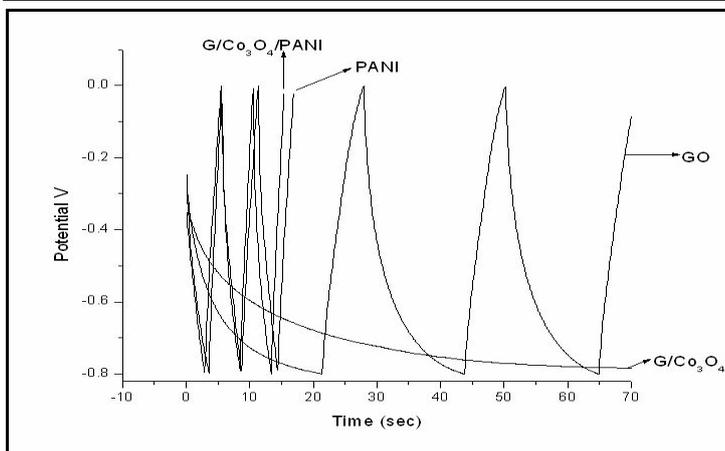


Figure 5: Galvanostatic charge/discharge current density at 2μA

4. Conclusion

G/Co₃O₄/PANI composite has been synthesized successfully. We confirmed the composite through XRD and UV characterizations. Electrochemical measurements were used for finding the specific capacitance of the composites. The maximum specific capacitance was obtained for G/Co₃O₄ composite. In the case of G/Co₃O₄/PANI, the PANI blocks the surface area of the graphene composite. It has confirmed from the CV and CP results.

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