Modified Graphene for Supercapacitor Study

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Abstract: By oxidative polymerization method using MnO₂ graphene-polyaniline nanocomposite electrodes have been developed for electrochemical energy storage device applications. The formation of the above nanocomposite indicates that the MnO₂ undergoes oxidative disintegration and results in porous polyaniline (PANI) nanofibers formation on the graphene surface. The electron microscopic (SEM) images clearly showed the presence of porous PANI nanofiber formation on the graphene-PANI nanocomposites. The XRD, SEM and TG analysis confirmed the complete removal/degradation of MnO₂ during the oxidative polymerization of aniline. The electrochemical properties of different graphene-PANI nanocomposites have been investigated using galvanostatic charge-discharge, cyclic voltammetry and electrochemical impedance spectroscopy measurements. Supercapacitive performance has been observed for the graphene-PANI nanocomposite electrode obtained via oxidative polymerization of aniline by MnO₂.

Keywords: Graphene, Nanocomposites, Supercapacitors, Cyclicvoltagrams, Impedance.

I. Introduction

Today, graphene has emerged as a new hope for the entire scientific community due to its unique properties such as large surface area (2630 m² g⁻¹), high strength and stability [1], ultra high carrier mobility [2], excellent thermal conductivity [3,4]. This thin carbon film has become a rapidly rising star on the horizon of material science and condensed matter physics. These fascinating properties of graphene made it to use in the fields of high efficiency sensors [5], fuelcells [6], renewable energy sources [7], electrochemical capacitors [8], electrodes [9] and nanocomposites [10]. But graphene a mono-layered two dimensional sp² hybridized carbon source, because of restacking rate usually failed to attain high surface area with desired electronic properties and electrical double layer capacitance [11]. To exploit graphene based electrode material for supercapacitors many researchers made attempts by incorporating metal oxides such as RuO₂, MnO₂ and Fe₂O₃ in graphene. In addition to this conductive polymers and graphene composites have also been extensively studied and well documented in the literature [12-15]. In the present study an effort has been made to avoid restacking of graphene sheets, nanocomposites of graphene oxide-MnO₂ nanosheets were prepared followed by aniline polymerization in a controlled manner. Aniline polymerizes due to charge transfer interaction [16]. Graphene oxide nanosheets were prepared first from graphite using modified Hummer’s method [17,18]. Graphene oxide –MnO₂ and GO-MnO₂-PANI, reduced GO-MnO₂-PANI were prepared using the method described elsewhere [11]. The prepared samples were characterized by various techniques such as FeSEM, XRD, TGA. Electrochemical studies reveals that specific conductance of GO-MnO₂ is 552 F g⁻¹ at a discharge current density of 0.1 A g⁻¹.

II. Experimental methods

A. Materials:

Graphite flakes are procured from Sigma Aldrich, USA. Sodium Nitrite, Potassium permangnate, Potassium per sulphate, Potassium hydroxide, Aniline, Hydrogen peroxide, Hydrochloric acid, Sulphuric acid etc are procured from sd fine chemicals Mumbai, India.

B. Preparation of graphene oxide: Graphene oxide (GO) from graphite flakes is prepared in the present study by modified Hummer's and Offeman’s method reported elsewhere [17,18]. Graphite of approximately 5 to 20 micrometre size was used as starting materials. During preparation, graphite (0.5g), NaNO₃ (0.5g) and 25 ml of sulphuric acid were mixed thoroughly in an water bath containing ice. Then KMnO₄ (3g) was slowly added by means of separating funnel. After complete mixing, the solution was transferred to another water
Potassium type MnO₂ (birnessite) was synthesized by 200 mL of solution of a mixture of 92.0 mL of ethanol and 33.6 g of potassium hydroxide was added slowly to a beaker containing 150 mL of a solution of 9.48 g of potassium permanganate with vigorous stirring for 1 h. The resultant gel was aged at 80 °C in an oven for 48 h. The product was washed with deionized water to a pH lower than 9 [19,20].

D. MnO₂-GO-PANI nanocomposite preparation

70 mL of GO dispersion and 1.75 g of K-MnO₂ were dispersed into 200 mL distilled water. The resulting mixture was sonicated for 1 h and stirred for 20 h at room temperature. The solution was filtered and dried at 60°C to obtain the GO-MnO₂ nanocomposite. To obtain the M-GO-PANI nanocomposite, the above mixture was transferred to an ice water bath for 30 min and 2.5 mL of aniline (dispersed in 20 mL of 2 M HCl ice cold distilled water) was added to the above mixture, rapidly. The chemical polymerization of aniline was initiated by MnO₂ and formation of polyaniline was observed from the simple color change. After 30 min, 2 g of K₂S₂O₇ was added to the above mixture and stirred for another 1 h to ensure complete polymerization of aniline. The product was washed with ethanol followed by distilled water and dried at 60 °C overnight. The addition of K₂S₂O₇ was not necessary, more than 95% of aniline was polymerized by MnO₂ and addition of K₂S₂O₇ does not have much influence on the M-GO-PANI preparation.

E. M-RGO-PANI nanocomposite preparation

0.5 g of M-GO-PANI nanocomposite dispersed in water was placed into a hot plate at 90°C and stirred. 0.2 mL of hydrazine hydrate was added and stirred for 2 h at 90°C. Then, the resulting sample was filtered, washed with distilled water and dried at 60°C overnight.

G. Characterization Techniques

Field Emission Scanning Electron Microscopy (FESEM):
The morphology of the prepared samples was observed using a Carl-Zeiss SUPRATM 40 field-emission scanning electron microscope. Scanning micrographs were recorded with an accelerating voltage of 5 kV.

WXRD Measurements

Powder X-ray diffraction (XRD) patterns were recorded in a RIGAKU (RINT2000 Tokyo, Japan) diffractometer using Ni-filtered Cu-Kα radiation (λ = 1.5418 Å). Thermogravimetric (TG) experiments (SII, TG/DTA 6300) were carried out using 5–10 mg of the sample in air atmosphere from room temperature to 800 °C at the heating rate of 10 °C min⁻¹. The specific surface area and pore size distribution was calculated using the BET equation.

H. Electrochemical measurement

The mixture containing 85 wt% active material, 10 wt% conducting carbon black, and 5 wt% polytetrafluoroethylene (used as a binder, PTFE, Sigma Aldrich) was well mixed and then pressed onto the Pt mesh. Electrochemical measurements were carried out using a three-electrode cell where platinum and saturated calomel electrode were used as counter and reference electrodes respectively with 1 M H₂SO₄ as the electrolyte. The electrochemical performances of the prepared electrodes were characterized by cyclic voltammetry (CH Instruments, USA), electrochemical impedance measurements and galvanostatic charge-discharge. The specific capacitance of the electrode materials was calculated from the galvanostatic discharge process according to the following equation: \[ C_{\text{single}} = \frac{4 \times I \times \Delta t}{\Delta V \times m} \] Where, \( I \) is the discharge current (A), \( \Delta t \) is the discharge time (s), \( \Delta V \) is the voltage change during the discharge process, and \( m \) is the total mass.
of the active material in both electrodes (g). The impedance spectra were recorded from 10 mHz to 10 KHz with an alternate current amplitude of 10 mV.

III. Results and Discussion
The aniline polymerization process on the graphene surface exhibit a nanocomposite structure also significantly alters the porosity of the nanocomposites. In highly agglomerated graphene-polyaniline nanocomposites the total capacitance will be mainly dominated by the pseudocapacitance from the polyaniline films coated on the graphene surface rather than the electric double layers capacitance (EDLC) from the graphene sheets. Thus, controlling the structure and morphology of the graphene-based electrodes is the key to availing both the pseudocapacitance and EDLC by allowing the effective permeation of the electrolyte.

The aniline polymerization was carried out using the conventional procedure. A layered type MnO₂ (K-OL-1) sheets-GO sheets nanocomposite was prepared [19,20] and chemical oxidation polymerization of aniline was carried out using MnO₂ nanosheets as a sacrificial template and oxidant for chemical polymerization of aniline due to the charge transfer interaction. As shown in Scheme 1, the layered type MnO₂ will form a composite with GO due to the electrostatic force between the Oxygen atoms of the negatively charged oxygen-containing functional groups on GO sheets and Mn[21]. In order to attain graphene oxide (GO) with high edge functional groups, carbon nanofibers (100 nm in diameter and 100 nm in width) were used as the carbon source and the GO was prepared using a modified Hummers method [17,18]. In the first step, the GO/MnO₂ composite was prepared by mixing an appropriate amount of MnO₂ nanosheets and GO nanosheets. Then, an appropriate amount of aniline was added to the above composite and the chemical oxidation polymerization was initiated by reduction of the Mn⁴⁺ ion and the resulting Mn²⁺ ions will go to the solution. This process reveals the formation of slow and uniform polyaniline nanofibers on the graphene surface with significant porosity, which enables better percolation of the electrolyte to access a large surface area. Schematic illustration of the oxidative chemical polymerization of aniline by MnO₂ (M-GO-PANI) is represented in Scheme 1.

A. Scanning Electron Microscopy
The morphology of prepared M-RGO-PANI nanocomposites has been analyzed by FE-SEM at different magnifications (Fig.1). The FE-SEM images of M-RGO-PANI nanocomposites shows agglomerated particle like morphology at lower magnification (Fig. 1a) and the highly ordered surface growth of polyaniline could be seen at the higher magnification (Fig. 1b). And, the growth of PANI on the graphene surface is difficult to observe by FE-SEM images due to the much smaller size of the graphene nanosheets (100 nm to 100 nm). In addition, the fibrous nature of the PANI on the graphene surface offers large porosity to the M-RGO-PANI nanocomposite electrodes that enables the electrolytes to access the large surface of graphene. To validate the porous nature, BET surface area and pore size distribution analyses were carried out for the M-RGO-PANI and RGO-PANI samples. The pore size distribution profile shows the porous nature of the former sample with a pore size distribution from 10 to 30 nm and high surface area of 78 m²/g, whereas the latter sample does not show any porous nature and a low surface area of 15 m²/g. The porous structure of PANI on the graphene surface could be attributed to (i) the chemical oxidative polymerization of aniline by MnO₂ that releases the Mn²⁺ ions slowly into the solution, (ii) the fibrous nature of the PANI formed on the graphene surface.

B. X-ray Diffraction Study
The powder X-ray diffraction (XRD) is shown in Fig. 2. The XRD pattern of GO-MnO₂ shows a sharp peak at 7.13Å corresponding to the OL type layered structure of MnO₂ [19, 20] and the peak broadening observed at higher 2θ range indicates the co-existence of GO in the nanocomposites. However, the line corresponding to the OL-1 type MnO₂ structure (7.13 Å) is completely diminished in M-GO-PANI indicating the complete removal of MnO₂ from the composites. And, a sharp line with high intensity was observed at 2θ = 19.7 owing to the formation of crystalline polyaniline[22] on the graphene surface. The peak broadening at 2θ=25 indicates the presence of graphene in the nanocomposite. Although, there is a possibility that the amorphous MnO₂ that is inactive in XRD might be present in the nanocomposite form.
Graphite $\rightarrow$ GO - chemical $\rightarrow$ GO-$\text{MnO}_2$
C. Thermal Gravimetric Analysis
The TG experiments were carried out to confirm the absence of other MnO₂ nanostructures in the nanocomposites (Fig.3). The TG profile of GO-MnO₂ shows 40% weight loss corresponding to chemically adsorbed water molecules (<200 °C) and the decomposition of GO between 200 to 450 °C and the remaining 60% could be attributed to the presence of MnO₂ in the nanocomposite. Whereas, the TG profile of M-GO-PANI shows 100% weight loss at 400 to 600 °C, this clearly indicates the complete removal of MnO₂ from the above composites during the PANI formation or in another way all the MnO₂ is consumed in the PANI formation.
Fig. 3 TG patterns of (a) GO-MnO₂, and (b) M-GO-PANI nanocomposites.

To explore the potential applications of the synthesized nanocomposite materials, the samples were fabricated into supercapacitor electrodes and characterized with cyclic voltammograms (CV), galvanostatic using charge/discharge measurements and electrochemical impedance analysis. All the experiments were carried out using 1M H₂SO₄ as electrolyte and Pt mesh as current collectors. Fig. 4 shows the charge-discharge profile of the various graphene-PANI nanocomposites prepared via conventional polymerization (GO-PANI and RGO-PANI) and oxidative chemical polymerization by MnO₂ (M-GO-PANI and M-RGO-PANI). It could be clearly seen from the charge-discharge profiles (Fig. 4) that the specific capacitance of GO-PANI (94 F/g) was enhanced almost 4 times when MnO₂ was used for the polymerization (M-GO-PANI, 408 F/g). After the reduction of GO by hydrazine into RGO, all the composite electrodes show significant improvement in the specific capacitance (Table 1). RGO-PANI composite electrodes show great enhancement in the specific capacitance from 94 F/g to 385 F/g, it is nearly equal to the M-GO-PANI electrodes, whereas, the specific capacitance of M-RGO-PANI increases to 522 F/g. This clearly indicates that the conductivity of the electrodes plays a major role on the specific capacitance of the graphene-PANI nanocomposite electrodes. However, samples prepared via oxidative chemical polymerization by MnO₂ show high specific capacitance compared to the (NH₄)₂S₂O₈ initiated polymerization (before and after the GO reduction) owing to their porous nature which ensures the efficient permeation of the electrolyte.

Attempts have been made to confirm the effect of the carbon source, by preparing GO from graphite flakes of 10–20 mm. The GO and RGO prepared from graphite. The specific capacitance of GO-PANI was analyzed. Indeed, the capacitance obtained for M-GO-PANI and M-RGO-PANI nanocomposite electrodes shows 15 to 40% improvement when compared to graphene/polyaniline nanocomposites prepared via the conventional polymerization route in our present study and the literature reported values for it [23,24].

Fig. 4. Galvanostatic charge-discharge profiles.
Table 1. Specific capacitance of various nanocomposite electrode materials in 1 M H₂SO₄ at 0.1 A current density.

<table>
<thead>
<tr>
<th>Electrode materials</th>
<th>Specific Capacitance Fg⁻¹</th>
</tr>
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<tbody>
<tr>
<td>GO Pure</td>
<td>90</td>
</tr>
<tr>
<td>GO-PANI</td>
<td>94</td>
</tr>
<tr>
<td>RGO-PANI</td>
<td>408</td>
</tr>
<tr>
<td>M-GO-PANI</td>
<td>385</td>
</tr>
<tr>
<td>M-RGO-PANI</td>
<td>522</td>
</tr>
</tbody>
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Fig. 5A shows the cyclic voltammograms (CV) of GO, PANI, GO-PANI and M-RGO-PANI nanocomposite electrode in 1 M H₂SO₄ electrolyte at the scan rate of 100 mV s⁻¹. The shapes of the CV curves of M-RGO-PANI is distinct. They shows two characteristic redox peaks at 0.1/0.3 and 0.45/0.6 V vs. Ag/AgCl. The first couple of peaks can be ascribed to the redox transition of PANI between the leuco-emeraldine form (semiconducting state) and polaronic forms (conducting state). The second couple of peaks are attributed to Faradic transitions of emeraldine/pernigraniline or p-benzoquinone/hydroquinone [24,25]. It is in good correspondence with the conclusion arrived at from the above charge-discharge studies. As the high rate performance is one of the basic requirements for an electrode material to be used in supercapacitors, experiments were carried out at different high current densities. Fig. 5B shows the capacitance of GO-PANI, RGO-PANI, M-RGO-PANI nanocomposite electrodes at different current densities. When the current density increased to 1A, 2A and 3Ag⁻¹ the specific capacitance decreased gradually for the electrodes. The electrochemical stability of M-RGO-PANI composite electrode was evaluated at 0.1 A g⁻¹ current density in 1 M H₂SO₄ solution and the resulting stability plot shows the electrode has higher electrochemical stability at the studied current rate (Fig. 5C). After 200 consecutive cycles, high specific capacitance retention of 72% and 98% of the initial specific capacitance was observed for M-RGO-PANI electrode (Fig.6C). The electrochemical impedance (EIS) measurements on the M-RGO-PANI electrode were performed from 10 mHz to 10 kHz with an alternate current amplitude of 10 mV and the resulting Nyquist plots are shown in Fig. 5D. The porous nature of the M-RGO-PANI that facilitates a faster cation insertion/extraction rate. The straight line observed in the lower frequencies represents the diffusive resistance (Warburg impedance,W) of the electrolyte in the electrode materials and the proton diffusion in the host materials.[25, 26] Thus, the observed straight line for the electrodes indicates that the electrodes have low diffusion resistance.

Fig. 5A. shows the cyclic voltammograms (CV) of GO, PANI, GO-PANI and M-RGO-PANI nanocomposite.
Fig. 5B. shows the capacitance of GO-PANI, RGO-PANI, M-RGO-PANI nanocomposites.

Fig. 5C. Electrochemical stability of GO-PANI, RGO-PANI, M-RGO-PANI nanocomposites.

Fig. 5D. Nyquist plots for RGO-PANI, M-RGO-PANI nanocomposites.
IV. Conclusions

Graphene-polyaniline nanocomposite electrodes developed via oxidative polymerization of aniline by MnO₂ on a graphene surface show enhanced specific capacitance for electrochemical supercapacitor applications. The SEM images of the RGO-PANI nanocomposite electrodes clearly show the presence of porous PANI formation. The absence of XRD lines corresponding to MnO₂ OL–1 and 100% weight loss in the TG profile of M-GO-PANI and M-RGO-PANI nanocomposites authenticate the absence/complete removal of MnO₂ from the M-GO-PANI and M-RGO-PANI composites during the oxidative polymerization of aniline. The galvanostatic charge-discharge and cyclic voltammetry of the different nanocomposite electrodes indicate that the oxidative polymerization of aniline by MnO₂ enhances the specific capacitance of M-RGO-PANI greatly due to the formation of porous PANI on the graphene surface.

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VI. References

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