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Nanocomposite of p-type conductive polymer/functionalized graphene oxide nanosheets as novel and hybrid electrodes for highly capacitive pseudocapacitors

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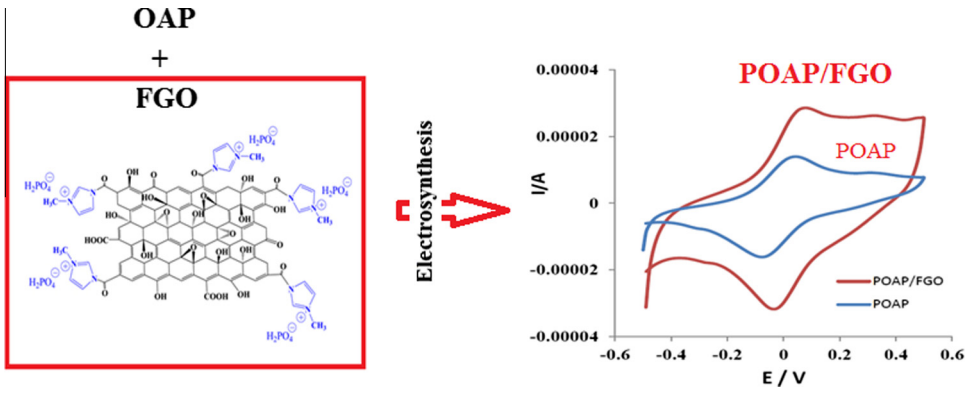
GRAPHICAL ABSTRACT



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ABSTRACT

An effective approach for increasing the life cycle of poly ortho aminophenol (POAP) as a p-type conductive polymers is combining conventional conductive polymers and nanomaterials to fabricate hybrid electrodes. In this paper, functionalized graphene oxide (FGO) has first been synthesized using a chemical approach. Hybrid POAP/FGO films have then been fabricated by POAP electropolymerization in the presence of FGO nanoparticles as active electrodes for electrochemical supercapacitors. Based on the atomic scale study results, it seems that $H_3PO_4^-$ oxygen atoms and terminal pyridine ring nitrogen atoms play a crucial role in the intramolecular charge and energy transfer in the FGO molecular systems. Theoretical studies, surface and electrochemical analyses have been used for characterization of POAP/FGO composite films. Different electrochemical methods including galvanostatic charge discharge experiments, cyclic voltammetry and electrochemical impedance spectroscopy have been applied to study the system performance. This work introduces new nanocomposite materials for electrochemical redox capacitors with such advantages as the ease of synthesis, high active surface area and stability in an aqueous electrolyte.

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1. Introduction

Polyaniline (PANI) is one of the most important conducting polymers because of its unique electrical, optical, and optoelectrical properties, as well as ease of preparation and excellent environmental stability. Aminophenols are interesting substituted anilines. POAP gives a surface film of interesting electrochemical and electrochromic properties when electropolymerized in acidic media. This film is electroactive in aqueous and non-aqueous solutions containing protons, but no response is observed at pH values of over 7. A variety of results for conductivity of the POAP film reported in the literature [1–3] show that the electrochemical response of POAP is strongly influenced by the experimental procedure used to produce the polymer film, dopant anions and the purity of the starting monomer [1–3]. Carbon based nanomaterials having a high surface area and good electrical conductivity have attracted the attention of scientific community for different applications. These carbon based nanomaterials (activated carbon, carbon nanotubes, and graphene) have been used as substrates for metal oxide nanoparticles and conductive polymers for supercapacitor applications [4–8]. These conducting carbon materials provide a fast electron transfer rate during Faradaic charge transfer reactions and hence enhance the capacitance [9–14]. Additionally, these carbon nanomaterials provide the platform for the decoration of metal oxide nanoparticles to avoid their agglomeration, hence more utilization of nanoparticles. Polymer carbon nanocomposites provide the solution for the insulating nature of conducting polymers at dedoped states by using carbon nanomaterials as substrates to grow nanostructured polymers [4–8]. The functionalization of graphene enhances the capacitance and provides anchoring sites for decoration of metal oxide nanoparticles and conductive polymers. Metal oxide (RuO_2, TiO_2, and Fe_3O_4) nanoparticles decorated over functionalized graphene nanocomposites and conductive polymer coated functionalized graphene have also been tested for supercapacitor applications. The use of graphene as a support for metal oxide nanoparticles and conductive polymers avoids the agglomeration of nanoparticles to achieve more utilization of metal oxide characteristics and growth of nanostructured conductive polymers. This helps in achieving a high value of capacitance [15–17].

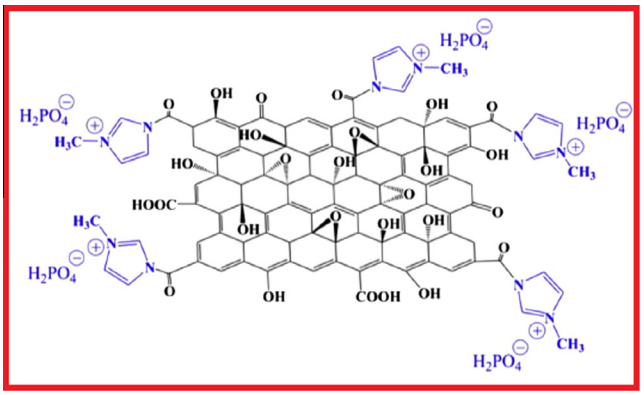

Fig. 1. Molecular structure of functionalized graphene oxide.

Functionalized GO (FGO) nanosheets have recently been developed as attractive fillers for electrode and membrane modifications. The functional groups of FGO could ease the dispersion of FGO in organic solvents. Therefore, composite membranes with improved distribution of nanofillers in polymer matrix could be expected [18], while the GO particles can hardly be dispersed in some organic solvents and aggregation problems may occur [19]. Additionally, the functional groups on the FGO structure can enhance the water retention and proton conductivity of the membranes [19].

In the present work, room temperature, electrochemically synthesized POAP/FGO electrodes have been presented as efficient potential candidates in supercapacitor application. The objectives if this work were increasing the capacitance of POAP electrodes by using FGO (Fig. 1) to form a composite electrode and moreover increase the cycle ability of the electrode. The capacitive behavior of nanocomposite has been tested by cyclic voltammetry, galvanostatic charge discharge and impedance spectroscopy techniques.

2. Experimental

2.1. Reagent and materials

All the chemical materials used in this work, obtained from Merck Chemical Co., were of analytical grade and used without further purification. Double distilled water was used throughout the experiments.

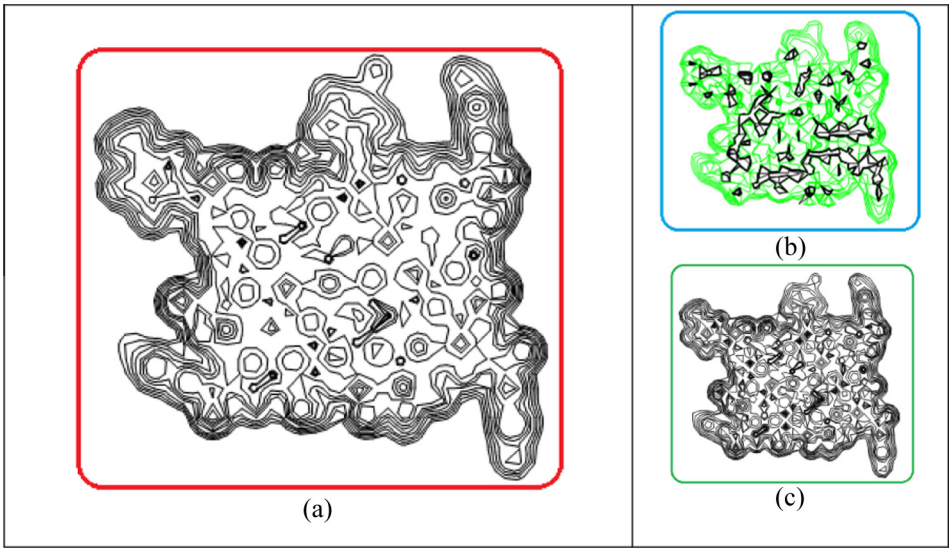

Fig. 2. The contour maps (topology of the electronic properties) of the local electron density (a), Laplacian of electron density (b), and virial force (c) of the molecular system graphene oxide (GO), are calculated using AIM theory.