Electroactive Conjugated Polymer / Magnetic Functional Reduced Graphene Oxide for Highly Capacitive Pseudocapacitors: Electrosynthesis, Physioelectrochemical and DFT Investigation

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ABSTRACT

The current study fabricated magnetic functional reduced graphene oxide (MFRGO) by relying on FeCl_4^- magnetic anion confined to cationic 1-methyl imidazolium. Furthermore, for improving the electrochemical performance of conductive polymer, hybrid poly ortho aminophenol (POAP)/ MFRGO films have then been fabricated by POAP electropolymerization in the presence of MFRGO nanorods as active electrodes for electrochemical supercapacitors. Surface and electrochemical analyses have been used for characterization of MFRGO and POAP/ MFRGO composite films. Different electrochemical methods including galvanostatic charge discharge experiments, cyclic voltammetry and electrochemical impedance spectroscopy have been applied to study the system performance. Prepared composite film exhibited a significantly high specific capacity, high rate capability and excellent cycling stability (capacitance retention of ~91% even after 1000 cycles). These results suggest that electrosynthesized composite films are a promising electrode material for energy storage applications in high-performance pseudocapacitors.

Keywords : Capacitor, Nanocomposite, Electrosynthesis

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1. Introduction

The outspreading and development of next generation energy storage devices, supercapacitors (SCs) also called ultracapacitor, for varied applications such as portable electronic devices has received significant attentions in last decades as they are able to deliver high power density and show fast charge/discharge (C/D) capability beside of long life cycle. To improve the performance of supercapacitors and obtain higher electrochemical achievements a long range of materials have been used to consider their potential as electrode. Graphene and reduced graphene oxide (rGO) and carbon nano tubes (CNTs) and derivatives are promising materials to employ in SCs due to high

specific capacitance delivery and surface area based on electrical double layer capacitance (EDLC)[1-5]. 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. Additionally, the functional groups on the FGO structure can enhance the water retention and proton conductivity of the membranes.

Conductive polymers and metal oxide and their composites are other materials with high potential to develop supercapacitors based on pseudocapacitance. Many investigations have substantially carried out to consider the effects of hybrid supercapacitors based on EDLC and pseudocapacitance because this combination showed a synergistic effect and is an appropriate method to enhance electrochemical features [6-15]. Recently ionic liquids (ILs) have been employed

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Fig. 1. Molecular structure of POAP and magnetic functional reduced graphene oxide (MFRGO). (Reprinted from [48] with permission from Elsevier Publications).

increasingly in energy storage devices to improve their performances and great attractions due to the high thermal, chemical and electrochemical stability, low toxicity with good ionic conductivity, introduced them as an ideal material for SC applications. Moreover ionic liquids have been enthusiastically applied as electrolytes because of their wide potential window [16-25]. In addition, ionic liquids have also low viscosities with high conductivities advantages made them to employ in electrochemical devices for fast charge-discharge conditions. Pyrrolidinium and imidazolium are two main applied ionic liquids in electrochemical investigations [26-29]. Pyrrolidinium compared to imidazolium indicated larger electrochemical stability window (ESW) favorable for SCs operating at higher voltage or contributing mainly to the energy density. While Imidazolium actually provides higher ion conductivity with lower viscosity [30-33].

In this study, based on our recent achievements and successful results regarding to synthesis and application of new poly orthoaminophenol (POAP) composite films [34-46], we synthesized new magnetic functionalized reduced graphene oxide (MFRGO) (Scheme 1) and its nanocomposite with a POAP. The synthesized reduced graphene oxide and its nanocomposite were characterized by surface analyses and different electrochemical techniques, respectively. Furthermore, the potential of this novel nanocomposite as an efficient electrode material in electrochemical pseudocapacitors is demonstrated.

The POAP as a conductive polymer when conjugated by functionalized graphene oxide, showed a synergistic effect being responsible for high supercapacitive performance.

2. Experimental

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. All electrochemical experiments were carried out by a Potentiostat/galvanostat (Ivium V21508, Vertex). A conventional three electrode cell with an Ag/AgCl reference electrode (Argent, 3 M KCl) was used in order to carry out the electropolymerization of the POAP. A platinum wire and a carbon paste electrode was used as the counter and working electrodes respectively. Morphological investigations of the polymeric films were carried out by using SEM analysis.

For preparation of MFRGO, firstly, GO was synthesized according to the modified Hummers method from oxidation of natural graphite [47]. Modification of GO and then preparation of MRGO were carried out to as described in our already published paper [35,48]. POAP/MFRGO composites were prepared by electropolymerization in an acidic solution of monomer (ortho aminophenol) on the surface of the MFRGO modified working electrode. Electropolymerizations were conducted by 40 consecutive cycles

Fig. 2. SEM image of FGO, MFRGO(Reprinted from [35 and 38] with permission from Elsevier Publications) and POAP/MFRGO composite film.

Fig. 3. Cyclic voltammograms of POAP and POAP/MFRGO electrodes in 0.1M HClO₄ at the sweep rate of 100 mV·s⁻¹.

Fig. 4. Cyclic voltammograms of POAP/ MFRGO films in different potential sweep rates in the range of 10-400 mV·s⁻¹.

at the sweep rate of 50 mV·s⁻¹ in the potentials between -0.2 to 0.9 V.

3. Results and Discussion

Fig. 2 shows the SEM images used to determine the morphology of the samples. Paper-like structures were the most common observations in all images and can be recognized as MFRGO. SEM image of POAP/MFRGO composite shows porous structure and presence of the MFRGO in the electrosynthesized composite film.

Fig. 3 gives CV curves of polymer and composite electrodes between -0.6V and 0.6V vs. Ag/AgCl in

0.1M HClO₄ aqueous electrolyte solution. It can be seen that the shapes of the CV curves are more or less rectangular within the measured potential window. It is pointed out that the CV curves for the composite not only present a large background current, but also reveal obvious peak currents. The synergistic effect resulting from the interactions of POAP and MFRGO may affect the shape of CV curves. The CV of POAP/ MFRGO electrode shows the incorporation of MFRGO in POAP matrix not only increase the capacitance of composite states, but also save its ideal capacitive behavior. Shape of CV curves represents the pseudocapacitance nature of the electrode.

Fig. 5. (a) Galvanostatic charge and discharge measurements of POAP/MFRGO electrode in 0.1M HClO₄ solution at 0.005mA and (b) during 100 consecutive charge-discharge of composite film at 1mA.

The surface morphology of POAP/ MFRGO film was studied by using the fractal concept. According to obtained results there is a power dependence between the peak current (I_{pc}) in cyclic voltammograms and the corresponding potential sweep rate (v). Thus, the fractal parameter can be obtained easily by plotting the peak current against the sweep rate in log-log scale [35]. Based on this information, Fig. 4 represents cyclic voltammograms of POAP/MFRGO films that were recorded in different potential sweep rates in the range of 10-400 mVs⁻¹. Fractal dimension has been obtained from relationship between the anodic peak current and potential sweep rate in log-log scale. The slope of the line gives the fractal dimensions of 2.60 for electrosynthesized film. The presented values for fractal dimension confirm porous structure of the electrosynthesized composite film.

To further evaluate the potential applications of the electrosynthesized nanocomposite as an electrode material for electrochemical supercapacitors, galvanostatic charging and discharging measurements were carried out between -0.5 and 0.5 V in 0.1 M HClO₄ at 0.005 mA (Fig. 5a). All the charge-discharge curves of the nanocomposite, regardless of the current were symmetrical, indicating excellent electrochemical reversibility. From the discharge curves,

the specific capacitance (C_s) was calculated according to the following equation [35]:

$$C = \frac{I\Delta t}{\Delta V m} \quad (1)$$

Where I is the current loaded, m is reactive material mass, V is the potential change during discharge process and t is the discharge time. By substituting the obtained values in equation 1, the SC of POAP/ MFRGO electrode was found to be 247 F·g⁻¹. Furthermore, stability test results shows, using MFRGO in conductive polymer caused an excellent retention in stability percentage of composite electrode suggesting the good stability toward consecutive cycles (1000 cycles).

Electrochemical impedance spectroscopy (EIS) was carried out to investigate the electrode kinetics and other properties of as-prepared material [49-62]. The EIS data in Fig. 6 can be fitted by a solution resistance R_s , a charge-transfer resistance R_{ct} , a pseudocapacitance (CPE2) from redox process of materials and a constant phase element (CPE1) to simulate the double-layer capacitance. Presented Nyquist plots shows that, the nanocomposites have faster electron transport in the bulk-film and charge transfer in the parallel POAP film/solution interface

Fig. 6. Nyquist plots for POAP/MFRGO electrode.

and MFRGO /solution interface. This fact may suggest that the MFRGO has an obvious improvement effect, which makes the composites have more active sites for faradic reactions and a larger specific capacitance than pure POAP [35].

At the end, electronic properties of the GO and MFRGO are investigated by DFT calculation. Nano-electrochemical science has enabled us to produce new molecular structures, (such as phenylevinylene, thiophene and organic field-effect transistor) with desired properties, and thus can be used to design intelligent nano-electrochemical devices, using quantum mechanical concepts/methodology [63-65]. For example, details of the local charge and energy transfer mechanisms, in these systems/devices should be studied. For example, based on the quantum mechanical Methodology (DFT-method), the local charge and energy transfer in the graphene (G) and graphene oxide (GO) molecular systems are studied. In addition, geometry optimization and calculation of the structural and electronic/vibrational properties (such as energy gap between the frontier orbitals, HOMO and LUMO, electron density, spin density, virial force, local electrostatic force and vibrational frequency) of the G and GO molecular systems have been carried out using B3LYP/6-31G level of theory, using density functional theory (DFT) and within harmonic oscillator (HO) approximation. Sample of results obtained here are shown in Figs. 7-9 (all results

Fig. 7. Energies of the molecular orbitals (a), and the IR spectra (b) of the G molecular system, calculated at DFT-B3LYP/6-31G level of theory.

not reported here for brevity).

Analysis of these results show that the value of the parallel and perpendicular charge/energy transfers in both G and GO molecular systems are considerable, which reflect intra-electrochemical phenomena in these systems. It can thus be predicted that the these intramolecular electrochemical response features depend on the vibrational and electronical structure/properties of these molecule systems and their variation with the external field or external bias voltage intensity. Also, it can be predicted that the reduced GO system device have a higher thermochemical performance than the G system when applied in a real electrochemical circuits. This higher performance can be attributed to the more extended π -conjugated system of the reduced GO system, induced by the applied external bias voltage, and thus the contributions of electrons/phonons (vibrational degrees of freedom) of the metal-

Fig. 8. The contour maps of the local electron density (a), intramolecular virial force (b), and the HOMO (c)/LUMO (d) molecular orbital diagrams of the G molecular system, are calculated at DFT-B3LYP/6-31G level of theory.

Fig. 9. The contour maps of the local spin density (a), intramolecular virial force (b), and the HOMO (c)/LUMO (d) molecular orbital diagrams of the GO molecular system, are calculated at DFT-B3LYP/6-31G level of theory.

lic Fe atoms, and π -conjugated electrons of pyridine groups in the intramolecular charge/energy transfer in this molecular system.

4. Conclusions

In this work, we successfully synthesized MFRGO and POAP/MFRGO composite material through electrochemical method. Multiple measurement methods were employed to study the performances of the material. Importantly, CV, CP and EIS tests show that POAP/ MFRGO composite material has better properties than POAP without MFRGO, suggesting it can be used as supercapacitor electrode material with excellent specific capacitance and ultrahigh specific power, which indicates this material is a promising electrode material used in high power applications.

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