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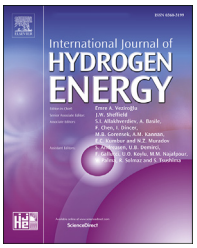

Reduced graphene oxide decorated with thionine, excellent nanocomposite material for a powerful electrochemical supercapacitor

Hossein A. Alinajafi, Ali A. Ensafi, B. Rezaei*

Department of Chemistry, Isfahan University of Technology, Isfahan 84156–83111, Iran

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ABSTRACT

In this paper, reduced graphene was decorated with thionine to synthesize Th/rGO nanocomposite via diazonium reaction. The nanocomposite was identified using several techniques including SEM, EDX, XRD, XPS, and IR techniques. The behavior of the nanocomposite, as a supercapacitor electrode, was examined using cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy. The results obtained demonstrated that the nanocomposite has an excellent specific capacitance of 1255 F/g at a current density of 0.5 A/g. Furthermore, the stability of the electrode was examined after 5000 cycles. The results showed that 93% of the initial capacity appears after 5000 cycles.

Introduction

Because of climate change and fast progress of the global economy, energy has attracted scientists' attention. Environmental pollution, huge mining costs and fossil fuel consumption highlighted the need for an efficient, clean and renewable energy source, and energy storage techniques [1].

Electrochemical capacitors (ECs) are among important kinds of energy storage in that they provide higher energy densities compared to traditional electrostatic capacitors and higher power densities compared to battery systems. They are characterized by the following two primary charge storage mechanisms. The first, the electrochemical double layer capacitor (EDLC) is closely related to traditional capacitors because the charge is stored electrostatically in the double layer that forms at the electrode/electrolyte interface and ideally no Faradaic charge transfer occurs in the interface, unlike the second type of device, the pseudocapacitor. Its energy storage mechanism is characterized by highly reversible redox reactions on the surface, and in the bulk of the compound, i.e., the transition between the various oxidation states in transition metal oxides is followed by the intercalation and de-intercalation of electrolyte ions. The advantages of ECs are the following: high specific capacitance, high specific power, and energy density, low material cost and toxicity and long cycle life (because of their high reversibility) [2–5].

In the studies conducted in this connection, various materials have been deployed to increase supercapacitors' specific capacitance. For instance, some studies deploy

* *Corresponding author.*
E-mail addresses: Ensafi@cc.iut.ac.ir, aaensafi@gmail.com, ensafi@yahoo.com (A.A. Ensafi).
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conducting polymers, whereas another researches deploy metal oxides. Finally, some other researches used carbon nanomaterials [6,7].

Nanocomposite based carbon materials are highly used for supercapacitor applications, which are due to their high specific capacitance (Cs) and high stability [8]. Porous compounds and carbon-based materials increase EDLC. The pseudocapacitors' capacity is approximately ten to one hundred times higher than carbon-based compounds [9,10]. Accordingly, building a composite, which has these features has attracted researchers' attention.

In this paper, reduced graphene oxide/thionine nanocomposite (Th/rGO nanocomposite) was synthesized using diazonium reaction. Reduced graphene oxide (rGO) with a high surface area and thionine with pseudocapacitor property are used. The combined effect of these parameters results in a significant enhancement of the nanocomposite capacity. One of the methods for improving the specific capacity of graphene is doping heteroatoms on the structure of graphene. In this study, instead of doping the heteroatoms on the structure of graphene, thionine, which contains heteroatoms of nitrogen and sulfur was used and the surface of graphene was modified by thionine. Thus, both the specific capacity of graphene and the pseudocapacity of thionine were combined, and this leads to an increase in the specific capacity.

Th/rGO nanocomposite was identified by scanning electron microscopy (SEM), energy dispersive X-ray method (EDX), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Brunauer–Emmet–Teller, and infrared spectroscopic techniques (IR).

To study the potential applicability of the nanocomposite in supercapacitor application, the behavior of the nanocomposite was studied using several electrochemical methods such as cyclic voltammetry (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS). The findings of our research revealed that Th/rGO nanocomposite is an appropriate and excellent material for supercapacitor fabrication with large amounts of Cs *vs.* other related materials.

Experimental

Reagents

Double distilled water was used to prepare all of the solutions for this research. All materials used in this work, such as thionine, HCl, H_2SO_4, $NaNO_2$, $KMnO_4$, and graphite were provided by Merck Company.

Apparatus

The characterization of the synthesized materials was done by several techniques such as SEM, EDX (SEM and EDX, Model XL30, Philips), XRD (Model D8-Advance Bruner), FT-IR (Model JASCO FT-IR, 680 plus) and XPS (ultra-high vacuum (UHV) set-up equipped with a concentric hemispherical analyzer and VG Microtech twin anode XR3E2 X-ray).

Electrochemical tests were conducted using an Autolab device (Model PGSTAT 30 potentiostat/galvanostat), which was controlled by a microcomputer. The electrochemical measurements were conducted in a cell with the following three-electrodes: an auxiliary electrode (platinum wire), a reference electrode (Ag/AgCl saturated by KCl) and a working electrode (glassy carbon electrode (GCE) modified with Th/rGO nanocomposite). Brunauer–Emmet–Teller (BET) method was performed on a Nova Station A, Quantachrome surface analyzer.

Preparation of graphene oxide and reduced graphene oxide

In the first step, GO was synthesized using modified Hummer method [11]. For the preparation of rGO, 0.10 g of GO was added to 100 mL of H_2O. The combination of water and GO was sonicated for 15 min to prepare a suspension of GO. The suspension temperature was stored at 0 °C. Afterwards, $NaBH_4$, 5 times more than GO, was added to the suspension of GO and, then, it was rotated for 24 h. The obtained compound was rGO. Finally, the rGO was filtered, cleaned with deionized water and left at room temperature so that it was dried.

Preparation of Th/rGO nanocomposite

The Th/rGO nanocomposite was synthesized by diazonium reaction. For this purpose, a solution of 0.5 M HCl, 0.05 M of $NaNO_2$ and 0.05 M thionine was prepared at 0 °C. 0.50 g Fe powder was added to the solution. Then, 150 mg of rGO was prepared as the suspension and was added to the above solution and it was rotated for 24 h. Finally, the obtained product was filtered, cleaned with deionized water and left at room temperature so that it was dried [12,13]. Scheme 1 shows the process of the preparation of the Th/rGO nanocomposite.

Modified electrode fabrication

For the modification of the GCE surface by the Th/rGO nanocomposite, a 2.0 mg/mL suspension of Th/rGO nanocomposite in water was prepared. Before modifying the surface of the GCE by the Th/rGO nanocomposite, the surface of the GCE was varnished with 0.05 mm Al_2O_3 powder for 3 min and it was then sonicated in C_2H_5OH/H_2O (1:1 v/v) bath for 5 min. Finally, 10 μL (0.020 mg) of the Th/rGO nanocomposite suspension were dropped at the surface of the GCE and was dried at 25 °C.

Results and discussion

Identification of GO, rGO, and Th/rGO nanocomposite

The morphology of the synthesized GO was studied by SEM method. SEM images of GO (Fig. 1A) confirms the synthesis of the GO with very thin layers. As the figure shows, the thickness of the GO sheets is under 50 nm. EDS technique was deployed to analyze the components in the GO structure and to guarantee that no impurity was present in the synthesized GO structure. As shows in Fig. 1B, appearance of carbon and oxygen peaks and non-existence of another elements' peaks confirm the purity of the synthesized GO. The obtained information about the prepared GO from FT-IR and Raman spectroscopy and XRD technique are presented in supplementary information and Fig. 1.

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