



Electrochemical functionalization of graphene nanosheets with catechol derivatives as an effective method for preparation of highly performance supercapacitors



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ABSTRACT

Performance enhancement of supercapacitors has been recently discussed. In this paper a novel and facile procedure for functionalization of graphene with some electroactive molecules is presented. The graphene has been functionalized by catechol-based molecules, which are electroactive molecules with electrochemically reversible properties. The functionalized graphene exhibits very effective pseudocapacitor behavior for charge storage. For the first time, with the aim of an electrosynthesis procedure, catechol is covalently attached on graphene sheets. This attachment has been investigated by electrochemical, X-ray photoelectron spectroscopy and attenuated total reflectance methods. Catechol molecules have been attached via formation of etheric and ester bonds on the surface of graphene. As a result, the functionalized graphene sheets show a reversible electrochemical behavior and can be used as pseudocapacitor electrodes with an excellent stability. The electrochemical results of the prepared electrodes reveal rather high specific capacity of 288 F g^{-1} at a high current density of 28 A g^{-1} , which shows remarkably enhanced performance for supercapacitor applications.

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1. Introduction

According to growth of renewable energy sources, demands for advanced energy storage devices, with high efficiency are increasing [1]. Supercapacitors (SCs) are one of the most important energy storage devices with high power density as well as cyclic stability [2]. Nowadays, based on the applications of SCs, fabrication of them with high energy density and retention of high power density and good life time are challenging issues. To improve the energy density, different methods have been discussed [3]. Based on the charge storage mechanism, they are classified as electrochemical double layer capacitors (EDLCs, carbon based electrodes) and reversible Faradaic redox reactions, which is called pseudocapacitors [2]. Carbon based SCs are based on the physical adsorption of ions at the interface of electrode surface and electrolyte. Therefore, SCs with this mechanism can profit from the stability and conductivity of carbon materials [4,5]. So far, different carbon nanostructures have been applied for SC electrodes

assembling; for instance carbon nanotube (CNT) [6], graphene [7–9] carbon spheres [10], carbon nanofibers [11] and activated carbon [12]. Despite the advantages of carbon materials, increase of energy density is a challenging issue and different structures have been designed to enhance the charge storage capacity [4]. One solution to enhance the energy density of EDLCs is combining physical adsorption charge storage with electrochemical charge storage mechanism that occurs at pseudocapacitors. This combination can be done by synthesis of different composites of carbon materials with conducting polymers or metal oxides [13–15]. The other way for this combination can be achieved by attachment of electroactive organic molecules to carbon structures [16–18].

Synthesis of carbon nanocomposites with conductive polymers [19,20] or metal oxides [21,22], as efficient approaches, can improve the energy density in SC applications. Furthermore, it can improve low cycle stability and power density problems of metal oxides and conducting polymers. Different composite structures heretofore have been developed, but rapid fading of capacitance due to the volume change during charge–discharge cycles has not been resolved completely.

In order to increase the energy density, third approach with desirable life time has been proposed. In this notable method, electroactive organic molecules attached covalently to carbon

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materials. Some organic molecules such as 1,2-dihydroxybenzene (catechol) and its derivatives [17], o-phenylenediamine, o-aminophenol [18] and 2-Aminoanthraquinone [16] show redox behaviors. When they covalently attached on carbon substrates, they can represent reversible reactions; therefore, electrodes can have both pseudocapacitance and EDLC mechanism simultaneously. Thus, the energy density of the electrode enhances and results to a stable behavior without any structural disturbance. In addition, there is another approach in this field, which dissolves these electroactive molecules in the electrolyte of SCs [23,24]. Here, various carbon materials were used for electrode assembling and catechol or hydroquinone was added to acidic electrolyte [25–27]. Although the obtained capacitances were increased significantly, the cycle stabilities was not improved, which may be due to instability of catechol or hydroquinone in solution.

Graphene as an interested carbon structure, have been used extensively for fabrication of batteries and SC electrodes. In comparison with other carbon structures, it shows better electrochemical activities. Moreover, as a suitable substrate, it has been used to synthesize composite structures with metal oxides [28–31] and conducting polymers [32,33]. Also, graphene can be covalently functionalized with small and electroactive organic molecules. So far, various procedures have been reported to immobilize these molecules on the structure of graphene. Most of the introduced methods use time-consuming multi-step processes and organic solvents, which operate in high temperatures [16,34–37]. Xie et al. using 24 hours reflux procedure at 80 °C, attached benzoxazole and benzimidazole covalently on the graphene sheets and in the next step, the obtained product was reduced by hydrazine. As a result, the functionalized graphene sheets with these molecules, presented capacitances of 296 F g⁻¹ and 367 F g⁻¹, respectively, at a current density of 0.8 A g⁻¹ and proper cycling stability [18]. In another report, Shi et al. [16] covalently attached 2-Aminoanthraquinone on the surface of graphene sheets by reflux at 80 °C for 36 hours. In the next step, the functionalized sheets were self-assembled into macroporous hydrogels with sodium ascorbate at 80 °C for 3 hours. The functionalized graphene aerogel showed higher capacity (258 F g⁻¹ at 0.3 A g⁻¹) in comparison with graphene aerogel (193 F g⁻¹) with a desirable cycle stability. Accordingly, application of a rapid and simple method can be efficient for graphene functionalization. Among the most interesting and innovative chemical technologies, the electrochemical methods provide a desirable and powerful means for highly pure production. In fact, the electrochemical procedures, especially electrosynthesis methods, will induce some electrochemical advantages such as energy specificity, absence of toxic reagents and solvents and chemical selectivity [38].

Based on these considerations, we are reporting an efficient and simple method for covalent immobilization of an electroactive molecule, catechol, on graphene nanosheets. Electrosynthesis is used as a novel and effective approach to attach the catechol molecule on the structure of graphene sheets, which is an electroactive species with a reversible behavior. Based on this approach, the amount of charge storage of graphene based electrodes can be increased.

2. Experimental

2.1. Chemicals and synthesis procedure

All chemicals were of synthetic grade and used as received without further purification. Catechol, 4-methylcatechol and 4-nitrocatechol were purchased from Merck. Aqueous solutions for cyclic voltammetric and galvanostatic studies were prepared

with de-ionized water (18 MΩ). Graphene oxide nanosheets (Fig. S5, AFM and SEM) was synthesized by Hummers' method [39] and purified by dialysis and centrifugation. The graphene oxide (GO) was partially reduced (PrGO) by using small amounts of hydrazine (GO: hydrazine with 1:14 weight ratio) at 80 °C for 45 min. Then, 2 mL PrGO aqueous dispersion (1.4 mg mL⁻¹) mixed with 20 μL of Nafion solution (5 wt% in ethanol) and stirred for 5 hours to form PrGO ink. A portion of 25 μL of this ink was cast on the pyrolytic graphite surface (4 mm diameter) and baked at 70–75 °C for 20 min, before the electrochemical tests. The electrode was immersed in a 10 mM of catechol in an acidic electrolyte solution (2 M H₂SO₄) and cyclic voltammetric method was used for the immobilization of catechol molecules at the electrode surface. Around one hundred consecutive cycles were done at this electrode with a scan rate of 10 mVs⁻¹. To purify the electrode from the physically adsorbed catechol molecules, the electrode was immersed in 2 M H₂SO₄ and 50 CV cycles was applied to it.

2.2. Instruments and Characterizations

Cyclic voltammetry (CV) and chronopotentiometry (CP) measurements were carried out by using a conventional three-electrode configuration cell on a Potentiostat/Galvanostat (AUTOLAB 302) consisting of Pt rod as counter electrode and Ag/AgCl as the reference electrodes. The specific capacitance values have been calculated from the applied discharge current (*I*), mass of the graphene sheets (*m*=0.035 mg on 0.1256 cm²), discharge time (Δt), and operating potential (ΔV) using the following equation: $C_s = \frac{I \Delta t}{m \Delta V}$

Coated Pyrolytic graphite with PrGO or catechol functionalized PrGO (CPrGO) were cut (0.5 cm thickness) and analyzed by X-ray photoelectron spectroscopy (XPS), attenuated total reflectance (ATR) and Raman analysis. XPS data acquisition was performed by means of a hemispherical analyzer with an Al K α x-ray source (1486.6 eV) operating at a vacuum pressure lower than 7–10 Pa. ATR spectroscopy was done by a Bruker, Equinox 55 instrument (370–4500 cm⁻¹, resolution 0.5 cm⁻¹). Raman spectroscopy was carried out by a Bruker instrument (Germany) with a spectral resolution less than 3 cm⁻¹ and Laser wavelength of 785 nm.

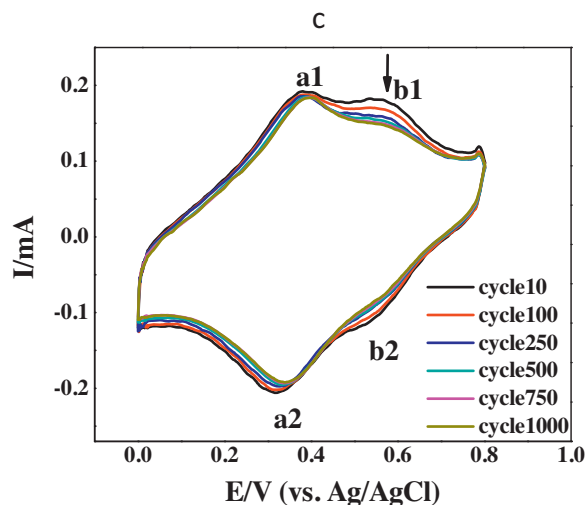


Fig. 1. a) Cyclic voltammetry of PrGO on the electrode in the presence of catechol in 2 M H₂SO₄ at scan rate of 10 mVs⁻¹ b) successive cyclic voltammetry of CPrGO in 2 M H₂SO₄ after the electrosynthesis, c) stability of attached catechol molecules on PrGO at consecutive scans (1000 scans).

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