



Facile preparation of polypyrrole/graphene oxide nanocomposites with large areal capacitance using electrochemical codeposition for supercapacitors



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HIGHLIGHTS

- PPy/GO nanocomposites were fabricated by facile electrochemical codeposition.
- The areal capacitance of conducting polymer/GO composites is firstly reported.
- The composites reveal large areal capacitance and superior cycle stability.
- The deposition time affects the capacitive behavior of the composites obviously.

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ABSTRACT

A simple and low-cost electrochemical codeposition method has been introduced to fabricate polypyrrole/graphene oxide (PPy/GO) nanocomposites and the areal capacitance of conducting polymer/GO composites is reported for the first time. Fourier transform infrared spectroscopy (FTIR), Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD) are implemented to determine the PPy/GO nanocomposites are successfully prepared and the interaction between PPy and GO. The as-prepared PPy/GO nanocomposites show the curly sheet-like morphology, superior capacitive behaviors and cyclic stability. Furthermore, the varying deposition time is implemented to investigate the impact of the loading amount on electrochemical behavior of the composites, and a high areal capacitance of 152 mF cm^{-2} is achieved at 10 mV s^{-1} CV scan. However, the thicker films caused by the long deposition time would result in larger diffusion resistance of electrolyte ions, consequently exhibit the relatively lower capacitance value at the high current density. The GCD tests indicate moderate deposition time is more suitable for the fast charge/discharge. Considering the very simple and effective synthetic process, the PPy/GO nanocomposites with relatively high areal capacitance are competitive candidate for supercapacitor application, and its capacitive performances can be easily tuned by varying the deposition time.

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1. Introduction

As a type of electrochemical energy storage device, supercapacitors have attracted considerable attention over the past decades. Owing to the higher power density and longer cycle life than secondary batteries and higher energy density compared to conventional capacitors, they are applicable in some systems such as hybrid electric vehicles, portable electronics, mobile

communications, etc., and are believed to have potential to fill the power/energy gap between traditional dielectric capacitors and batteries/fuel cells [1–5].

Currently, a major limitation of state-of-art supercapacitors lies in their relatively low energy density compared with batteries/fuel cells [6]. It is well known that the electrode material is a key component that determines supercapacitor's capacity, so a large number of researches have been made to develop new high-performance electrode materials [7–10]. Generally, the charge storage mechanism of supercapacitors could be classified into two types: electrochemical double layer capacitors (EDLCs) and faradaic pseudocapacitors (also referred to as redox supercapacitors). The

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former capacitance comes from the pure electrostatic charge accumulated at the electrode/electrolyte interface, and the electrodes were mainly based on carbon materials including activated carbon, carbon nanotubes, and graphene etc., while the latter energy is stored by a fast and reversible faradaic redox reaction on the electrode surface formed with electroactive materials, such as transition metal oxides and conducting polymers [11–13]. Researches show that each electrode materials has its advantage and disadvantage. Commonly, carbon materials show high power density and long cycle life but low capacitance [14]. While transition metal oxides have higher energy density than carbon materials and better cycling stability than conducting polymer materials, but exhibit a drawback of poor conductivity [15]. Conducting polymers possess high energy density, but they exhibit the disadvantage of a low cycle life because swelling and shrinkage may occur during doping/dedoping processes [16]. Based on the mentioned characteristic of different electrode materials above, considerable attention has been devoted to exploring hybrid of different materials to obtain high-performance capacitive electrode materials. Yang et al. [17] reported cobalt monoxide (CoO)-doped graphitic porous carbon microspheres effectively combined the electric double-layer capacitance and pseudo-capacitance when used as the electrode in supercapacitor, which led to a higher operation voltage and gave rise to a significantly higher energy density. Wei et al. [18] prepared polyaniline (PANI)/graphite oxide nanocomposite films by electropolymerization of aniline monomers onto graphite oxide-coated conducting glass slides with spin coating technique, which demonstrated a much more enhanced durability than the pure PANI films. So this study would be devoted to developing the composite electrode materials combining advantages of double-layer capacitance and pseudocapacitance, which contribute indivisible to the total electrochemical capacitance value of a supercapacitor.

PPy is the important material for electrodes of supercapacitors due to its high specific capacitance and electrical conductivity, low cost and chemical stability, however, it exhibits poor stabilities during the charge/discharge process [19,20]. Graphene, a single atomic plane of graphite, is regarded as an excellent electrode material for supercapacitors due to its high specific surface area, superior electrical conductivity, and chemical stability, but the capacitance values are limited by the microstructures in the materials [21,22]. Therefore, based on the complementary properties of PPy and graphene, considerable efforts have been made to incorporate graphene or its derivatives into PPy-based composite materials. The study by Biswas [23] showed the composite electrode of graphene nanosheets and polypyrrole nanowires has a high specific capacitance of $\sim 165 \text{ F g}^{-1}$ with a nearly ideal rectangular cyclic voltammogram at increasing voltage scan rates and high electrochemical cyclic stability. Mini et al. [24] prepared the high-performance supercapacitor electrodes with electrophoretic deposition of graphene, upon which the PPy layer was electropolymerized. Lim et al. [25,26] reported the electrochemical polymerization of polypyrrole/graphene (PPy/GR) using sodium *p*-toluenesulfonate (NapTS) as a supporting electrolyte, which indicated the presence of graphene enhanced the electrochemical performances of PPy tremendously. Some efforts have been made on the composites of graphene with conducting polymer, it is still a challenge to synthesize conducting polymer/graphene composites as electrode materials with the high capacitance, good rate performance, and cycle stability for supercapacitors, and what's more, almost all the related researches focus on the mass specific capacitance of electrode materials. Up to date, no work has been reported on the investigation of areal capacitance of conducting polymers/GO nanocomposites. For applications such as small scale electronics and

stationary energy storage devices where areal capacitance is a better indicator of the supercapacitor performance than mass specific capacitance although the mass specific capacitance has always been used in the literature for comparison of the supercapacitor performance [27,28].

In this research, PPy/GO nanocomposites electrodes were fabricated using a facile one-step electrochemical co-electrodeposition method. The influence of deposition time (i.e. deposition amount) on the capacitive performances including areal capacitance of the PPy/GO nanocomposites electrodes was investigated, and the performance of three type of representative nanocomposites electrodes with varying deposition time were compared detailedly. The compositions and morphology as well as the structures of the composite films were studied using Fourier transform infrared spectroscopy (FT-IR), Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and scan electron microscope (SEM), electrochemical behaviors of composite films were investigated using cyclic voltammetry (CV) and galvanostatic charge/discharge measurements (GCD) and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Reagents and materials

Natural graphite powder (325 mesh) was purchased from Tianjin Guangfu Research Institute. Pyrrole (A.R., Shanghai Chemical Reagent) was purified through distillation under reduced pressure and stored at a temperature less than 5°C . FTO conducting glasses were obtained from Dalian Heptachroma SolarTech (DHS-FTO22-8-02, $8 \Omega \square^{-1}$), $10 \text{ mm} \times 10 \text{ mm}$ conductive areas were exposed as the electrochemical codeposited substrate. Prior to use, the glasses were ultrasonically cleaned in acetone and deionized water successively.

2.2. Electrochemical codeposition of PPy/GO nanocomposites

GO was prepared by oxidizing the natural graphite powder and subsequent exfoliation by ultrasonication according to the method reported in literature [29,30]. The obtained GO aqueous dispersion was treated with freeze drying and preserved at the room temperature. During the procedure of deposition, an aqueous solution containing 0.25 M pyrrole monomer and 2 mg mL^{-1} GO was dispersed under ultrasonication for about 15 min to form a metastable homogenous colloidal solution, which could last for more than 24 h at room temperature. After that, PPy/GO nanocomposites were electrodeposited onto the FTO conducting glasses in a galvanostatic mode (Fig. 1a), which a current of 1.0 mA cm^{-2} was applied for varying time ranging from 200 to 2700 s. After the electrodeposition, the composites-coated glasses were washed with adequate deionized water to remove the unreacted substance, followed by drying at room temperature under ambient air environment, which is exhibited in Fig. 1b. During the deposition, the cleaned FTO conducting glasses were fixed in a two-electrode cell with a large-area Pt sheet acting as the counter electrode and pseudo-reference electrode. For FT-IR test, pure PPy was deposited from solutions containing 0.25 M pyrrole monomer and 1 M KCl with the same procedure.

2.3. Characterization

2.3.1. Components and structures analysis

PPy and PPy/GO films were scraped from the surface of films deposited onto FTO conducting glasses for the FT-IR, TEM, XPS, and

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