



One-step fabrication of heterogeneous conducting polymers-coated graphene oxide/carbon nanotubes composite films for high-performance supercapacitors



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ABSTRACT

Composite films of heterogeneous conducting polymers-coated graphene oxide/carbon nanotubes (CPs-GO/CNTs; CPs, PPy and PEDOT) have been fabricated via one-step electrochemical co-deposition. Scanning electron microscope and transmission electron microscopy characterizations indicate that the as-prepared CPs-GO/CNTs composites show a GO supported CPs-coated CNTs ternary hybrid microstructure. The electrochemical measurements including cyclic voltammetry, galvanostatic charge/discharge measurements, and electrochemical impedance spectroscopy tests manifest that the capacitive performances of CPs-GO electrodes are obviously promoted as the introduction of CNTs, and the PEDOT-GO/CNTs electrodes exhibit the more significantly improved electrochemical performances as the more CNTs introduced. Furthermore, the as-prepared PPy-GO/CNTs and PEDOT-GO/CNTs ternary composites achieve a high areal specific capacitance (142.2 mF cm^{-2} and 99.0 mF cm^{-2} at 1.0 mA cm^{-2} , respectively), together with superior rate capability, and excellent cycle stability (maintain 97.3% and 99.2% of initial capacitance for 5000 cycles, respectively), which are essential for their applications in high-performance supercapacitor electrodes.

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1. Introduction

The environmental friendly and high-efficiency energy storage systems have drawn tremendous attention as the urgent demand for the sustainable and renewable energy and resources in recent years. Supercapacitors, as one kind of devices for energy-storage and power supply, have been investigated extensively to meet the increasing demand for applications such as portable electronic, digital communications, and powering vehicles due to their superior rate capability, high power density, and long cycle-life compared to secondary batteries [1–4]. However, supercapacitors only store approximately 10% of energy per volume or gravimetric unit (i.e., low energy density) compared to batteries [5]. As the core component of such an energy storage system, electrodes directly determine the capability, charge delivery rates and efficiency of supercapacitors. So currently a large number of studies have been carried out to develop the new electrode materials to improve the

energy density of supercapacitors retaining high power density simultaneously [6–8].

The energy storage in supercapacitors is based on two mechanisms: electrical double-layer capacitance (EDLC) and pseudocapacitance. EDLC stores charge by adsorption of electrolyte ions onto the surface of electrodes, commonly use carbonaceous materials like active carbon, carbon nanotubes, and graphene et al. The response to potential changes is rapid for EDLC, but the ion adsorption is restricted on their surface, therefore EDLC show high power density but low energy density [9,10]. Pseudocapacitance derives from reversible redox reactions at or near the surface of electrodes, usually used materials such as conducting polymers (CPs), transition metal oxides and hydroxides, carbides, and nitrides. The pseudocapacitors shows high energy density, can reach as large as ten times that of double-layer capacitors. However, the increase in energy density for pseudocapacitors often leads to lower power density and poorer cycle stability [11,12]. This can be attributed to the sluggish reaction kinetics and low coulombic efficiency because redox reactions in bulk of pseudocapacitive materials are diffusion-controlled. Thus with the aim of constructing supercapacitors with high energy density while maintain high power density, some hybrid electrode

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materials have been synthesized to combine unique properties of various materials with synergistic effects [13,14].

CPs have been investigated widely as electrode active materials for supercapacitors due to their low cost, easy synthesis, and high pseudocapacitance [15]. Graphene oxides (GO), have a large specific surface area, can be easily fabricated from natural graphite and stably disperse in water as the oxygen containing functional groups resulting in negative charge surface. Some studies have been made to prepare the hybrids consisting of CPs and GO for high-performance supercapacitors. For instance, Zhang et al. synthesized PANI-GO composites through one-pot electrochemical polymerization [16], Wu et al. prepared CPs-GO (CPs, PANI and PPy) composites with an in-situ oxidative polymerization [17], Cao et al. investigated 3D PPy-GO composite electrodes through electrochemical deposition [18], moreover, PPy-GO composites have also been fabricated by electrochemical deposition in our previous study [19]. Although these CPs-GO composites exhibited relatively good capacitive performances, the GO with insulated nature (conductivity of $1.28 \times 10^{-9} \text{ S cm}^{-1}$) within the composites still hindered their electrochemical performances [18]. Hence, to further promote the electrochemical performances of CPs-GO composites, some researches were performed to synthesis the CPs-rGO composites by the further reduction of GO [20–24]. However, the further reduction of GO resulted in the relatively complicated procedures for electrode preparation and some studies indicated that the capacitive performances of CPs-rGO electrodes obtained were less improved. Carbon nanotubes (CNTs), possess high conductivity, ideal surface area, low specific weight, and high chemical stability, have been widely used as the electrode materials of supercapacitors [25]. Especially the carboxylated CNTs with anionic nature can act as the counter-ions introduced into the composites during the polymerization of CPs. So it is expected that the electrochemical performances of CPs-GO can be improved significantly by introducing CNTs with high conductivity via simple one-step electrochemical co-deposition. In the electro-deposition to form ternary composites of CPs-GO/CNTs, the oxidative polymerization of CPs monomer takes place, during which the anionic GO and carboxylated CNTs simultaneously acts as both the charge carriers in deposition solution and also the counter ions for charge balancing of CPs. For the ternary composites of CPs-GO/CNTs, the CPs can contribute high Faradaic pseudocapacitance, GO sheets and CNTs with large surface area provide the large electric double layer capacitance, meanwhile the introduced CNTs with high conductivity can makes up the disadvantage of insulating GO for high-efficiency charge transfer.

As two types of commonly used CPs, polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT) were employed in this study. CPs-GO/CNTs ternary composite films electrodes were fabricated via a facile one-step electrochemical co-deposition method. As the comparison, CPs-GO electrodes were prepared with the same electrochemical method. Their compositions and morphologies were characterized with Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), and transmission electron microscopy (TEM). The electrochemical

behaviors of electrodes prepared were studied with cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) measurements, and electrochemical impedance spectroscopy (EIS) tests. The ternary CPs-GO/CNTs composites prepared by a simple one-step electrochemical co-deposition are expected to significantly promote the electrochemical performances of CPs-GO electrodes by introducing CNTs with high conductivity.

2. Experimental

2.1. Materials

Pyrrrole (99%) and 3,4-ethylenedioxythiophene (EDOT, Ourchem[®], 99%) were purchased from Aladdin and Sinopharm (Shanghai, China), respectively. 325 mesh of natural graphite powder was supplied by Tianjin Guangfu Research Institute. Multi-wall carbon nanotubes (CNTs) were obtained from Chengdu Organic Chemicals Co. Ltd, their length and outer diameter were 0.5–2 μm and <8 nm, respectively. Fluorine-doped tin oxide conducting glasses (FTO, $8 \Omega \text{ sq}^{-1}$) were purchased from Heptachroma SolarTech (Dalian, China).

2.2. Fabrication of electrodes

Graphene oxide (GO) was made from natural graphite powder using the modified Hummers method and subsequent ultrasonication-assisted exfoliation [26,27]. The carboxylated CNTs (CNTs-COOH) were prepared by acid treatment. In brief, as-received MWCNTs were pretreated in 3 M HNO_3 at 140°C under stirring for 72 h to remove the metal catalysts, followed by the pretreated CNTs were shortened and functionalized with carboxyl group by ultrasonication in a mixture of concentrated H_2SO_4 and HNO_3 (volume ratio of 3:1) at 40°C for 2 h, subsequently rinsed with deionized water until the pH reached around 6.0, then the CNTs-COOH were collected and dried. As shown in Fig. 1a, the CPs-GO/CNTs composite films electrodes were fabricated by a facile one-step electrochemical co-deposition, in which the FTO conducting glasses ($1 \text{ cm} \times 1 \text{ cm}$ conductive areas marked with dotted portion) were used as the substrate of electrodeposition due to their high conductivity and usually employed as the conductive substrate for dye-sensitised solar cells (DSSCs). The glasses were cleaned ultrasonically with acetone and deionized water successively before use. The mixed solution for electrodeposition was composed of CPs monomer (0.2 M pyrrole or 0.01 M EDOT), 1 mg mL^{-1} GO, and 1 mg mL^{-1} CNTs-COOH without any supporting electrolyte. Prior to use, the mixed solution was adequately dispersed through ultrasonication. The electrochemical co-deposition was conducted with a constant current density of 1 mA cm^{-2} for 30 min, the large-area Pt foil and saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. After that, the composite films coated conducting glasses electrodes were rinsed with deionized water to remove unreacted monomer and oligomer residues and dried at ambient temperature. The mass of films was measured by weighing

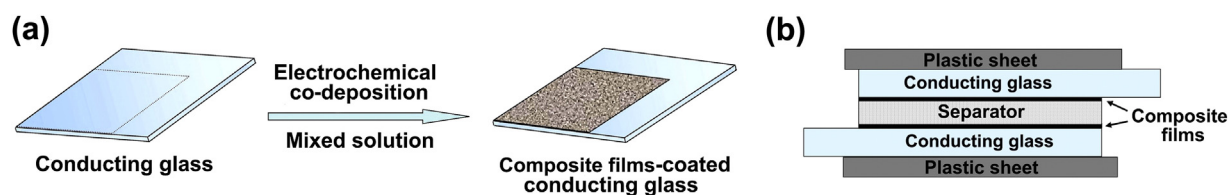


Fig. 1. Schematic diagrams of the electrochemical co-deposition for CPs-GO/CNTs ternary composites (a) and the two-electrode configuration for electrochemical measurements (b).

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