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Electrochemically reduced graphene oxide/carbon nanotubes composites as binder-free supercapacitor electrodes

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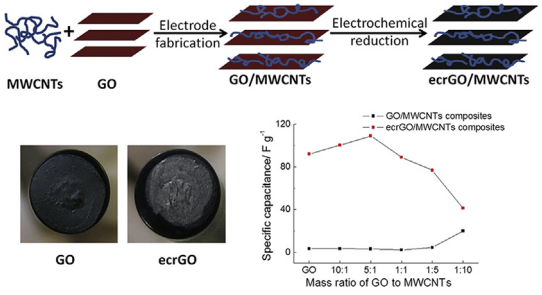
HIGHLIGHTS

- Binder-free electrodes were fabricated with MWCNTs and ecrGO for supercapacitors.
- MWCNTs as "spacers" insert between the graphene sheets to enlarge surface areas.
- GO can be reduced to ecrGO by a facile and controllable electrochemical method.
- The ecrGO/MWCNTs composite (GO:MWCNTs = 5:1) showed the highest C_{sp}.
- The composite (5:1) have high retention of 93% after 4000 charge/discharge cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

Binder-free composites of electrochemically reduced graphene oxide (ecrGO) and multiwalled carbon nanotubes (MWCNTs) were fabricated as supercapacitors electrodes operating in aqueous systems. GO was found to be electrochemically reduced according to the XRD and Raman data. Therefore, this facile and controllable method was applied to reduce GO in the GO/MWCNTs composites, generating ecrGO/MWCNTs composites. The ecrGO/MWCNTs composites exhibit higher specific capacitance (C_{sp}) than ecrGO because the intercalation of MWCNTs into ecrGO sheets increases the surface areas, according to the TEM, XRD and N_2 adsorption-desorption results. The composites with different mass ratios of GO to MWCNTs (10:1, 5:1, 1:1, 1:5, 1:10) were investigated. The ecrGO/MWCNTs composite (GO: MWCNTs = 5:1) showed the highest C_{sp} from the cyclic voltammetry results at a scan rate of 10 mV s^{-1}, and it expressed C_{sp} of 165 F g^{-1} at a current density of 1 A g^{-1} and 93% retention after 4000 cycles of charge/discharge. When the mass ratio of GO to MWCNTs further decreases to 1:10, the C_{sp} of the composites declines, and the ecrGO/MWCNTs composite (GO: MWCNTs = 1:10) performs a nearly pure double-layer capacitor. However, the composites containing more MWCNTs can maintain better capacitive behavior at higher rates of charge/discharge.

1. Introduction

Supercapacitors, as energy storage devices, involve two energy storage mechanisms: electric double layer capacitors (EDLCs) by

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storing energy through the simple physical adsorption of ions, and pseudocapacitors by producing energy from redox reactions during charge/discharge [1,2]. Carbonaceous materials, such as carbon nanotubes, carbon fibers, graphene and activated carbon, have been widely investigated for the electrodes of supercapacitors [2–5], because they exhibit good conductivity, chemical stability and mechanical strength.

Multiwalled carbon nanotubes (MWCNTs) are considered as a promising electrode material for supercapacitors, due to the large surface area, good conductivity and high mechanical strength [4]. However, pristine MWCNTs have low capacitance (~38 F g^{-1} [6–8], varying with scan rates and types of electrolytes [8]), because only the electrostatic adsorption of ions contributes to the energy storage mechanism, and the hydrophobicity of MWCNTs also limits ions to accessing the electrode surfaces [9]. In order to overcome these limitations, functionalization of MWCNTs with strong thermal acids is widely used to improve their capacitance [10,11]. The capacitance of MWCNTs can also be improved by decorating with conducting polymers [12] or transition metals [13,14] which produce the pseudo-capacitance. In addition, some CNT based materials with 3D network structure have been developed [15,16] to improve the efficiency of ions accessing to the electrode surfaces, but these methods are time consuming and cumbersome to operate.

Theoretically, graphene can possess high double-layer capacitance due to its exceptional surface area (~2630 m^2 g^{-1}) [17]. However, the capacitance of graphene reported in experimental measurements is much lower than expected. This is because graphene sheets easily stack together, resulting in difficulty for the ions in permeating to the surface of graphene [18]. Therefore, some 3D structural materials have been developed using graphene or its composites with other carbon materials to facilitate the ion permeability to electrode surfaces [19–21].

In this study, GO as a graphene precursor and MWCNTs as "spacers" were used to fabricate binder-free electrodes, wherein the MWCNTs intercalate between the graphene sheets to avoid the graphene sheets stacking together. The reasons of the use of GO as a graphene precursor are as follows: First, GO can disperse homogeneously in water due to the hydrophilic groups, such as carboxyl and carbonyl groups on the surface of GO [22]. On the other hand, the basal plane of GO is hydrophobic [23], and contains π carbon bonds which can attract the π carbon bonds of MWCNTs through the π-π interaction [24]. GO, therefore, can serve as a surfactant to disperse MWCNTs in water to form GO/MWCNTs suspension in fabrication of electrodes. Second, GO can form a membrane after drying, thus no binder is necessary to fabricate electrodes.

GO has extremely poor conductivity (typical insulator, 10^{12} Ω sq^{-1} or higher [23]) because of the disruption of the sp^2-bonded carbon matrix by polar functional groups. To achieve better conductivity and higher capacitance, it is usually reduced to graphene. Therefore, electrochemical reduction [25,26] was used to reduce the GO in the GO/MWCNTs composites to form the electrochemically reduced GO (ecrGO) in the present study, producing the ecrGO/MWCNTs composites as binder-free electrodes. Compared with other reduction approaches such as chemical reduction [20,27] and thermal processing [19,21,28], the electrochemical reduction is more facile, low-cost and environmentally friendly. The schematic of the fabrication of the binder-free ecrGO/MWCNTs electrodes is shown in Fig. 1.

In this work, the capacitive and electrochemical performance of the composites was investigated in acids. Additionally, Raman spectroscopy, X-ray diffraction (XRD), Transmission electron microscopy (TEM) and the BET surface area analysis were used to characterize the composites of ecrGO/MWCNTs.

2. Experimental

2.1. GO/MWCNTs electrode fabrication

Multiwalled carbon nanotubes (length: 1–12 μm, outside diameter: 13–18 nm, purity: > 99 wt%) and graphene oxide (5 g L^{-1}, 79% carbon and 20% oxygen) were obtained from Cheap Tubes Inc., USA and Graphene-supermarket Inc., USA respectively. 5 g L^{-1} GO was diluted to 1 g L^{-1} with DI water and subjected to a 5-min ultrasonic process. The stable suspension of GO/MWCNTs were obtained by mixing 1 g L^{-1} GO and MWCNTs with different mass ratios (GO: MWCNTs = 1:0, 10:1, 5:1, 1:1, 1:5, 1:10) with 2-h ultrasonic treatment. A platinum plate, used as a current collector, was covered by suspension of GO/MWCNTs, and dried in an oven for 8 min at 150 °C to form the GO/MWCNTs binder-free electrodes. The mass loading of GO/MWCNTs composites on working electrode is around 1.8 mg cm^{-2}.

2.2. ecrGO/MWCNTs electrode preparation

The electrochemical reduction of GO/MWCNTs on electrodes was carried out with cyclic voltammetry (−1.2 V − 0 V) in a 0.5 M NaCl solution at a scan rate of 50 mV s^{-1}. A three-electrode system (platinum wire as a counter electrode and Ag/AgCl as a reference electrode), and a VersaSTAT potentiostat/galvanostat (Princeton Applied Research, USA) were employed.

2.3. Materials characterization

The morphology of the ecrGO/MWCNT composites was characterized by transmission electron microscopy (TEM, JEOL JEM-2010). The samples were dispersed in ethanol with 10 min of ultrasonic vibration. The dispersion was placed on a holey-carbon coated copper grid, and dried in an oven at 60 °C for 5 min. Raman spectra of the GO/MWCNTs composites and ecrGO/MWCNTs were recorded on a MicroRaman/Photoluminescence spectrometer (Renishaw InVia) equipped with a 633 nm Ar ion laser. The phase structures of the composites and their constituents were characterized by an X-ray diffraction (XRD) system (PANalytical), ranging from 5° to 50° at a scan rate of 5° min^{-1}. The nitrogen adsorption/desorption isothermal curves of the composites were obtained using an Autosorb instrument (Quantachrome Instruments) at 77 K, and the surface areas were calculated based on the Brunauer-Emmett-Teller (BET) method.

2.4. Electrochemical measurements

The electrochemical performance of the electrodes was measured in 1 M HCl by a VersaSTAT potentiostat/galvanostat (Princeton Applied Research, USA), using a pure Pt wire and Ag/AgCl as a counter electrode and a reference electrode respectively. The electrochemical techniques employed in this study included cyclic voltammetry (CV), chronopotentiometry (charge and discharge at constant currents) and electrochemical impedance spectroscopy (EIS). The EIS was applied in a frequency range from 100 kHz to 0.1 Hz using a dc voltage of 0.4 V (the middle voltage of the operating potential window 0 V − 0.8 V), superimposed with an ac amplitude of 5 mV.

3. Results and discussion

3.1. Formation of ecrGO by electrochemical reduction of GO

GO films were immersed in 0.5 M NaCl and electrochemically reduced to ecrGO films by cycling between −1.2 V and 0 V at a scan