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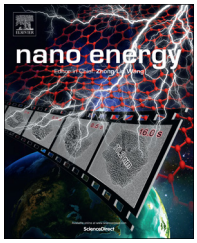

RAPID COMMUNICATION

In situ synthesis of SWNTs@MnO_2/polypyrrole hybrid film as binder-free supercapacitor electrode

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Abstract
In this study, a flexible hybrid film based on single-wall carbon nanotubes (SWNTs) was fabricated. The SWNTs@MnO_2/Polypyrrole (PPy) film was used as a supercapacitor electrode without binders to achieve high capacitance. The binder-free electrode with SWNT and PPy layers improved the conductivity of the electrode materials, as well as the ion diffusion rate and charge-transfer resistance, thus achieving excellent electrochemical performance compared with SWNTs@MnO_2 electrodes. The specific capacity was 351 F g^{-1} based on the total weight of the electrodes with energy density of 39.7 Wh kg^{-1} and power density of 10 kW kg^{-1}. Our study could provide a novel and facile strategy for the development of high-performance energy storage devices.

Introduction

The rapid development of electronic devices and equipment has resulted in the growing for high-power density devices in the modern electronic industry, especially for application in electric and hybrid electric vehicles. Thus, supercapacitors have attracted considerable attention in recent years. Supercapacitors have higher power density than lithium-ion batteries and conventional dielectric capacitors. In addition, supercapacitors have other advantages, such as low cost, short charging time, and long life cycle, compared with secondary batteries. For these reasons, supercapacitors have become the most promising candidate for next-generation power devices from backup power for memory and portable electronics to electric vehicles [1-4].

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Although the energy density of supercapacitors is lower than that of secondary batteries, more applications can be developed if such energy density is improved while maintaining power density. Supercapacitors can achieve higher energy density in an organic electrolyte than in an aqueous electrolyte. However, the power density of organic electrolyte-based supercapacitors is usually lower than that based on aqueous electrolytes because of poor electronic conductivity (approximately 100 times lower than aqueous electrolytes). Thus, Na_2SO_4 aqueous solution is used as the electrolyte in this study. For supercapacitor electrode materials, transition metal oxides and conducting polymers in pseudocapacitors can achieve higher energy density than that of carbon materials with a capacitive electrochemical double layer [5].

MnO_2 is an environment-friendly and low-cost supercapacitor electrode material with theoretical capacitance that can reach 1370 F g^{-1} in an aqueous electrolyte [6]. However, the kinetic features of ion and electron transport are limited between a MnO_2 electrode and electrode/electrolyte interface. Therefore, excellent electrical conductivity and large specific surface area are important to enhance electrochemical performance. The incorporation of MnO_2 into conductive materials, such as carbon nanotubes, graphene, or conducting polymers, to form hybrid electrodes improves the specific capacitance [7-10]. The addition of organic binders during the preparation of composite electrodes generally decreases the ion diffusion and electronic conductivity of electrodes. Thus, composite coatings on a conductive substrate without binders can improve electrode performance.

Single-wall carbon nanotubes (SWNTs) have excellent potential application in energy storage devices for their high specific surface area, superior electrical conductivity, and excellent chemical stability. Free-standing SWNT macro film is an excellent choice as a substrate to incorporate active materials and as flexible and stretchable supercapacitors [11,12].

Combining MnO_2 and SWNTs to produce macro films has been proven effective to improve specific capacitance [13-15]. However, the dissolution of MnO_2 cannot be prevented during experiments. In this study, a facile and *in situ* method was developed to synthesize SWNTs@MnO_2/PPy hybrid films as supercapacitor electrodes without binders at room temperature. The produced film provides a method to resolve the above two problems. A commercial coin cell system (CR 2032) was assembled with SWNTs@MnO_2/PPy as electrodes. Electrochemical performances, including specific capacitance, cycling stability, energy, and power densities of the electrodes, were investigated, and we found that the SWNTs@MnO_2/PPy films have better electrochemical properties than SWNT@ MnO_2 films.

Experimental

Synthesis of SWNT macro films

The SWNT macro films were synthesized through chemical vapor deposition, as previously reported by our group [16]. The films were annealed and then washed with diluted hydrochloric acid. The films were then washed with deionized water until pH=7.

Preparation of SWNTs@MnO_2/PPy hybrid films

Free-standing SWNT films were immersed in a mixed solution with 10 mL of ethanol and 2 mL of pyrrole monomer. Next, 0.1 M $KMnO_4$ aqueous solution was added dropwise. A layer of nanostructured MnO_2/PPy was co-deposited on the surface of SWNT film within 5 min. The as-prepared SWNTs@MnO_2/PPy hybrid film was rinsed with deionized water and ethanol thrice. Finally, the films were dried at room temperature for 12 h. Then, we obtained the binder-free electrode.

MnO_2/PPy coating measurement

A Mettler Toledo XP6 microbalance with an accuracy of 0.001 mg was used to measure the mass of the MnO_2/PPy films. Briefly, 0.5 in of SWNT macro film plate was measured. After the co-deposition reaction, the SWNTs@MnO_2/PPy hybrid film was weighed, after which the mass of the MnO_2/PPy was determined. On average, 10% of MnO_2/PPy precipitated on the surface of SWNT films, as determined by weighing several SWNT films before and after coating.

Structural characterization

The structure of the obtained hybrid film was characterized by using a Philips X'Pert X-ray diffractomer with Cu-Kα radiation operating at 0.15406 nm. The data were recorded from 2θ=10-80° at a scan rate of 0.02° per step and 0.2 s per point. The infrared (IR) spectra were obtained using an 8400S Fourier-transform IR spectrometer. Morphological characterizations were performed using scanning electron microscopy (SEM, JEOL JSM-7400F) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010F). The Mn contents in SWNTs@MnO_2/PPy and SWNTs@MnO_2/PPy electrode before/after cycling were measured by inductively coupled plasma mass spectrometer.

Electrochemical characterization

Electrochemical characterizations were performed using a standard symmetric 2032 coin cell. Copper foil was used as current collector. The working electrode was a free-standing SWNTs@MnO_2/PPy hybrid film, and 1 M Na_2SO_4 aqueous solution was used as the electrolyte. Wattman glass microfiber paper was punched and used as the separator. Cyclic voltammetry (CV) and electrochemical impedance scanning (EIS) were conducted using a PARSTAT 2273 potentiostat/galvanostat. EIS spectra were obtained with frequencies ranging from 100 kHz to 10 mHz. Galvanostatic charge/discharge (GCD) tests were conducted using an Arbin BT4+ test system. All of the electrochemical measurements were performed at room temperature.