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Free-standing porous Manganese dioxide/graphene composite films for high performance supercapacitors

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ABSTRACT

A simple hard template method and hydrothermal process have been employed to fabricate a self-standing hierarchical porous MnO_2/graphene film. Thus-constructed electrode materials for binder-free supercapacitors exhibit a high specific capacitance of 266.3 F g^{-1} at the density of 0.2 A g^{-1}. Moreover, the two-electrode device demonstrates an excellent rate capability and cycling stability with capacitance retention of 85.1% after 2000 charge–discharge cycles at a current density of 1 A g^{-1}. The porous nanostructured design can effectively improve the specific surface areas and account for the shorter relaxation time for the electrodes, resulting in a high electrochemical performance.

1. Introduction

The emerging supercapacitors with high power density, exceptional cycle life, high reversibility, good pulse charge–discharge characteristics and environmental friendliness (no heavy metals used) [1–3], are promising energy storage devices, which have potential applications in many potable systems and hybrid electric vehicles. The design of free-standing electrodes without any active and binder is becoming more and more important for high performance supercapacitors due to the avoidance of the 'dead surface' in traditional slurry-derived electrode and allowance for more efficient charge and mass exchange [4]. Because of the unique properties, such as high specific surface area up to 2675 m^2 g^{-1} [5], excellent chemical stability, superior electrical and mechanical properties [6], as well as feasibility for large-scale production, graphene has been regarded as a potential candidate for a kind of ideal free-standing supercapacitor electrode material. Much effort for special graphene structure materials such as graphene paper [7], planar graphene [8], graphene gel [9], has already been investigated. However, large interlayer van de Waals attraction and strong π–π interaction make graphene sheets easily aggregate or re-stack, leading to incomplete utilization of graphene surface. To prevent the stacking, various sandwich and three-dimensional (3D) porous graphene structures have been developed. For instance, Yu and co-workers [8] made graphene-based planar supercapacitors by a self-assembled process. Xie et al. [10,11] designed a three-dimensional graphene structure by CVD and template method. Although some progresses have been achieved, studies on three-dimensional free-standing porous graphene-based films directly used as electrodes are still few.

Unfortunately, the capacitance for pure graphene material is relatively low because of its intrinsic charge storage mechanism. The way of adding pseudo-capacitance materials, which has higher capacitance due to reversible Faradaic redox reaction, is an alternative solution to combine the advantages of the two types of materials. Among the available electrode materials, MnO_2 has proved to be an outstanding candidate for its low cost, environmental friendliness, natural abundance and high theoretical specific capacitance (1370 F g^{-1}) [12–14]. In present work, a new hard template-directed assembly for a three-dimensional porous graphene (3D-RGO) film loaded with MnO_2 by a hydrothermal method has been explored. The facile way can produce controllable and hierarchical porous composite films by using polystyrene (PS) colloidal particles as sacrificial templates. The binder-free MnO_2/graphene-based supercapacitor with MnO_2 loaded on the inner surface of the hollow structure films demonstrates a high rate capability, mechanical flexibility and enhanced capacitance.

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2. Experimental part

2.1. Synthesis of 3D hierarchical porous MnO_2/graphene composite films

Synthesis of PS@PDA spheres: All the reagents were of analytical grade and used without further purification. Monodispersed polystyrene (PS) spheres with an average diameter of 300 nm were synthesized according to the procedure reported elsewhere [15]. Then, 100 mg as-prepared PS spheres were dispersed in 2 mg of dopamine (DA) per 1 mL of 10 mM Tris–HCl buffer solution (pH ≈ 8.5) [16,17]. The solution was vigorously stirred for 15 h at room temperature to generate PS@PDA composite particles [18]. Thus-prepared spheres were harvested by alternatively centrifugating and washing with the mixture of deionized water and ethanol several times, followed by drying at 60 °C. The PS@PDA spheres were re-dispersed in deionized water to obtain aqueous suspensions (10 mg mL^{-1}) for further application.

Synthesis of free-standing hierarchical porous MnO_2/graphene films: Graphene oxides (GO) were initially prepared from natural flaked graphite by the modified Hummers method [19]. An approximate 1.25 mg mL^{-1} GO hydrosol was prepared by dispersing solid GO in water using an ultrasonication process. The GO hydrosol (10 mL) was mixed with PS@PDA sphere suspension (1 mL) and sonicated for 40 min to get a homogeneous colloidal suspension, which was then vacuum filtrated to realize the sandwich PS@PDA@GO film. The free-standing 3D-GO films were obtained by peeling them off from the millipore filter membrane, and then were annealed at 500 °C (heating rate 5 °C min^{-1}) in Ar gas (120 sccm) and located in a tubular furnace for 5 h so as to remove the PS sphere templates. The final 3D hierarchical porous MnO_2/graphene composite films were obtained in a typical process as follows: $KMnO_4$ (15 mL, 5 mM) was added into a 20 mL Teflon-lined stainless steel autoclave lines with the as-prepared films immersed into the reaction solution. The autoclave was sealed and maintained at 180 °C for 20 min. The free-standing porous MnO_2/graphene films were obtained by washing with deionized water, followed by cooling the autoclave under water flow for 10 min.

2.2. Structural characterization

SEM images were obtained by using a field emission scanning electron microscopy (Hitachi S4800). Transmission electron microscopy (TEM) observations were performed on a Tecnai G2 F20 U-TWIN instrument operated at 200 kV. The X-ray diffraction (XRD) data were collected using a Shimadzu X-ray diffractometer (XRD-6000) with Cu Kα radiation ($\lambda = 0.154178$ nm). X-ray photoelectron spectroscopy (XPS) spectra were measured using an ESCALAB 250 electron spectrometer from Thermo Scientific Corporation.

2.3. Electrochemical measurements

All electrochemical characterizations of the free-standing hierarchical porous MnO_2/graphene films were performed in an electrochemical workstation (CHI 660D) using Swagelok-type cells with two symmetrical electrodes, a glass fiber as separator (Whatman Cat No.1823 047) and 1.0 M sodium sulfate aqueous solution as electrolyte at room temperature. The two-electrode test cell configuration is found to provide more reliable and practical data for evaluating the material performance for supercapacitors.

Cyclic voltammograms were recorded between 0 and 0.8 V at various scan rates ranging from 2 to 300 mV s^{-1}. Galvanostatic charge–discharge tests were conducted between 0 and 0.8 V at different current densities from 0.2 to 40 A g^{-1}. The electrochemical impedance spectroscopy (EIS) measurements were performed over a frequency range from 10^5 to 10^{-2} Hz at the amplitude of the sinusoidal voltage of 5 mV. The specific capacitance (C_s) can be calculated from CV and galvanostatic charge–discharge curves according to the following formulas, respectively:

$$C = \frac{\int_a^b I(V)dV}{\Delta V \times v \times m} \quad (1)$$

$$C = \frac{2 \times I \times \Delta t}{\Delta V \times m} \quad (2)$$

where $\int_a^b I(V)dV$ is the integrated area of CV curve in one cycle, υ is the scan rate, I is the constant charge–discharge current, Δt is the discharging time, ΔV is the potential change during discharge process, and m is the mass of one piece of the whole film electrode.

3. Results and discussion

The scheme in Fig. 1 illustrates the preparation process of porous MnO_2/graphene composite film. The PS@PDA spheres were obtained by vigorously stirring the solution of PS and DA for 15 h at room temperature. The mixture of the as-prepared spheres and GO hydrosol was subsequently vacuum filtrated to realize the sandwich type assembly of PS@PDA@GO film. When PS was removed by annealing at 500 °C in Ar atmosphere, a bendable 3D-rGO skeleton was produced. MnO_2 nanoparticles were grown on the inner surface and margin of 3D-rGO through hydrothermal process, thus yielding porous MnO_2/graphene composite films. Fig. 2(a–e) demonstrate the typical SEM images of the PS@PDA, PS@PDA@GO, 3D-rGO, and porous MnO_2/graphene. It can be seen that the PS@PDA spheres were uniform in size with an average diameter of 300 nm (see Fig. 2(a)), which is well agreed with the average size of holes in the 3D-rGO (see Fig. 2(c)). In Fig. 2(b), the PS@PDA spheres were observed to be coated by wrinkled GO sheets. This is probably originated from strong interactions such as hydrogen bonds and electrostatic interactions between the PS@PDA spheres and GO flakes.

The coating process is very important for the preparation of the porous MnO_2/graphene film. The shell thickness of the PS@PDA is determined by the coating time and the concentration of the DA solution. In this work, the coating time is 15 h and the concentration is 2 mg of DA per 1 mL of 10 mM Tris–HCl buffer solution (pH ≈ 8.5) [16]. Due to the PDA shell, the coating spheres were positively charged. GO were synthesized by a modified Hummers method and dispersed in water by ultrasonication. Thus-prepared GO suspension was negatively charged owing to the introduction

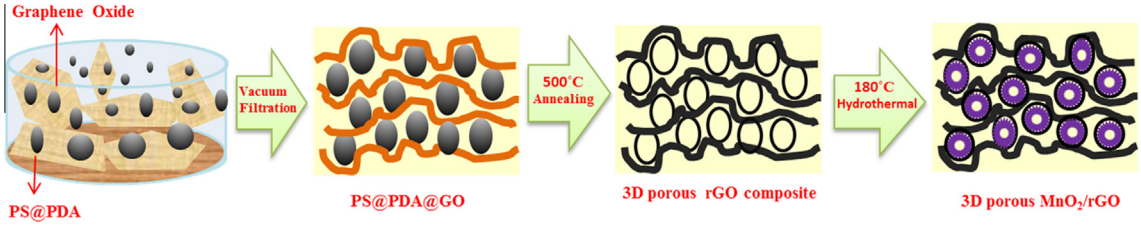

Fig. 1. Schematic illustration of the fabrication process for 3D porous MnO_2/graphene composite film.