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One-step preparation of layered molybdenum disulfide/multi-walled carbon nanotube composites for enhanced performance supercapacitor

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ABSTRACT

We report a simple strategy to prepare novel 2-dimensional graphene analog MoS_2/MWCNT (molybdenum disulfide/multi-walled carbon nanotube) composites as electrode material for supercapacitor. The MoS_2/MWCNT composites exhibit superior electrochemical performance to pure MWCNT and MoS_2. The composite shows a high specific capacitance of 452.7 F g^{-1} at a current density of 1 A g^{-1}, as compared to 69.2 F g^{-1} for MWCNT and 149.6 F g^{-1} for MoS_2. In addition, the cycling measurements show that the MoS_2/MWCNT composites maintain a specific capacitance of 412.2 F g^{-1} at 1 A g^{-1} after 1000 cycles corresponding to a reduction of capacitance of about 4.2%. The enhancement in supercapacitor is believed to be due to the layered MoS_2/MWCNT conductive network which promotes not only efficient charge transport and facilitates the electrolyte diffusion, but also prevents effectively the volume expansion/contraction and aggregation of electroactive materials during charge-discharge process.

1. Introduction

The ever-increasing energy and power demands in applications have triggered significant research efforts on the development of new electrode materials for advanced energy storage devices. Thereinto, supercapacitors attract tremendous attention due to their superior advantages such as high power/energy density, excellent cycling stability and fast charge/discharge capability [1–3]. They store and release energy based on either the accumulation of charges at the interface between electrode and electrolyte (EDLC (electrical double layer capacitors)) or fast and reversible faradic redox reactions (pseudocapacitors), or both, depending on the nature of activated materials [4]. For EDLC, the typical electrode materials are carbonaceous materials, such as activated carbon, CNT (carbon nanotube), and graphene, which usually contain high surface area and conductivity [4,5].

CNT has a uniform diameter of several tens of nanometers, high surface area and high electrical conductivity, as well as unique properties such as a three-dimensional entangled structure on the nanometer scale [6,7], and it has been studied extensively as electrode material in supercapacitors due to its well-controlled nanostructure, surface functionality and the cyclicity of the power supply [8,9]. However, the poor energy storage capacity and limiting rate capability restrict their applications [4]. Therefore, more and more efforts have been devoted to designing new CNT composites based supercapacitor, which can meet the requirements of high energy density, high power density and high cyclability [10,11].

Layered transition-metal dichalcogenides, such as WS_2, MoS_2, SnS_2 and VS_2, have been established as a new paradigm in the chemistry of nanomaterials during the past decades [12–14]. MoS_2 is a typical family member of transition-metal dichalcogenides. It is composed of the metal Mo layers sandwiched between two sulfur layers and stacked together by weak van der Waals interactions [15]. The layered structure of MoS_2 is expected to act as an excellent functional material because the 2-dimensional electron–electron correlations among Mo atoms would aid in enhancing planar electric transportation properties. Indeed, MoS_2 has been used in capacitor research due to its higher intrinsic fast ionic conductivity [16] (than oxides) and higher theoretical capacity (than graphite) [17]. For example, Soon and Lohz [18] reported the using MoS_2 as electrode material for capacitor. The results showed that the supercapacitor performance of MoS_2 was comparable to CNT array electrodes. However, the electronic conductivity of MoS_2 is lower compared to graphite/CNTs, and the specific capacitance of MoS_2 is still very limited in alone for energy storage applications. The combination of MoS_2 and other conducting materials may overcome these deficiencies, such as CNTs.

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In this work, MWCNTs (multi-walled carbon nanotubes) were bonded to 2D MoS_2 by a simple one-pot L-cysteine-assisted hydrothermal process. Due to the unique morphology and synergistic effects of the different components, this highly conductive MoS_2/MWCNT composite based electrode exhibited high specific capacitance and excellent long-term cycling stability, offering as a new supercapacitor with high performance based on two-dimensional materials.

2. Experimental

2.1. Synthesis of MoS_2/MWCNT composites

The MoS_2 nanosheets were synthesized as follows: 0.30 g $Na_2MoO_4 \cdot 2H_2O$ were dissolved in 40 mL deionized water. After adjusting the pH value to 6.5 with 12 M HCl, 0.80 g L-cysteine was added. The mixture was then diluted with water to 80 mL and violently stirred for about 1 h. Subsequently, the mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 48 h. After cooling naturally, the black MoS_2 was collected by filtration, washed with distilled water and absolute ethanol for several times, and dried in vacuum at 60 °C for 24 h.

The MoS_2/MWCNT composites were prepared as follows: firstly, 0.017 g MWCNTs was ultrasonic dispersed in 40 mL deionized water. Then 0.30 g $Na_2MoO_4 \cdot 2H_2O$ was added and ultrasonic dispersed for 20 min. After adjusting the pH value to 6.5 with 0.1 M NaOH, 0.80 g L-cysteine was added. The resultant mixture was diluted with water to 80 mL and violently stirred for about 1 h. The mixture was then transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 48 h. After cooling naturally, the MoS_2/MWCNT composites were collected by filtration, washed with distilled water and absolute ethanol for three times, and dried in vacuum at 80 °C for 20 h. The procedure for MoS_2/MWCNT composites preparation is illustrated in Fig. 1.

2.2. Characterization

The morphologies of the composites were recorded on a JEM 2100 TEM (transmission electron microscope) and a Hitachi S-4800 SEM (scanning electron microscope). XRD (X-ray powder diffraction) pattern was operated on a Japan RigakuD/Maxr-A X-ray diffractometer equipped with graphite monochromatized high-intensity Cu Kα radiation ($\lambda = 1.54178$ Å). FT-IR (Fourier transform infrared spectroscopy) was measured on a Bruker-Tensor 27 IR spectrophotometer. Raman spectra were recorded at ambient temperature on a Renishaw Raman system model 1000 spectrometer with a 200 mW argon-ion laser at an excitation wavelength of 514.5 nm.

2.3. Electrochemical measurement

CV (Cyclic voltammetry), galvanostatic charge/discharge and EIS (electrochemical impedance spectroscopy) were measured by a CHI 660D electrochemical workstation using a three-electrode electrochemical cell, which consisted of a counter electrode (Pt), an Ag/AgCl reference electrode, and stainless steel (SUS) mesh (1 cm × 1 cm) coated with samples as the working electrode. To obtain working electrodes, the MoS_2/MWCNT composites (MoS_2 or MWCNTs), carbon black, and poly(tetrafluoroethylene) (80:15:5, w/w) were mixed. The mixture was then coated onto SUS mesh and dried at 60 °C for 12 h in a vacuum oven. CV measurements were carried out in 1.0 M Na_2SO_4 solution at scan rates of 2–50 mV s^{-1} in the voltage range from −0.8 to 0.2 V. EIS measurements were done in the frequency range from 0.1 to 100,000 Hz at open circuit potential with an ac perturbation of 5 mV. Galvanostatic charge/discharge curves were measured at different current densities of 1, 1.5, 3, 5 and 10 A g^{-1}. The specific capacitance of electrode material was calculated according to the following equation [19]:

$$C_s = It/\Delta Vm \quad (1)$$

where I, t, ΔV and m are the constant current (A), discharge time (s), the total potential difference (V) and the weight of active materials (g), respectively.

3. Results and discussion

3.1. Characterization of the MoS_2/MWCNT composites

The SEM images of MoS_2, MWCNTs and MoS_2/MWCNT composites are shown in Fig. 2. As shown in Fig. 2A, the MWCNTs are entangled and interconnected. The diameter of the MWCNTs is 20–30 nm. It can be observed from Fig. 2B that the layered MoS_2 is flowerlike with the overlapped or coalesced sheet-like subunits structure. Fig. 2C shows the SEM image of the as-prepared MoS_2/MWCNT composites, illustrating a 3D architecture that MWCNTs insert and entwine the layered MoS_2 nanosheets. The 3D architecture is helpful to increase the specific area of the composites. Furthermore, the overlapping or coalescing of the MoS_2 in the 3D MoS_2/MWCNT composites would form an interconnected conducting network, which facilitates rapid electronic transport in electrode reactions.

The morphology and structure of the MoS_2, MWCNTs and MoS_2/MWCNT composites were further characterized using TEM (Fig. 3). Fig. 3A shows a typical TEM image of MoS_2 nanosheets, which is thin layers folded and tangled together morphology. Fig. 3B shows the interlayer spacing between the MoS_2 sheets in the composites is estimated to be 0.68 nm. Fig. 3C and D further show that the layered MoS_2 with few layers accumulates on MWCNTs. Fig. 3D

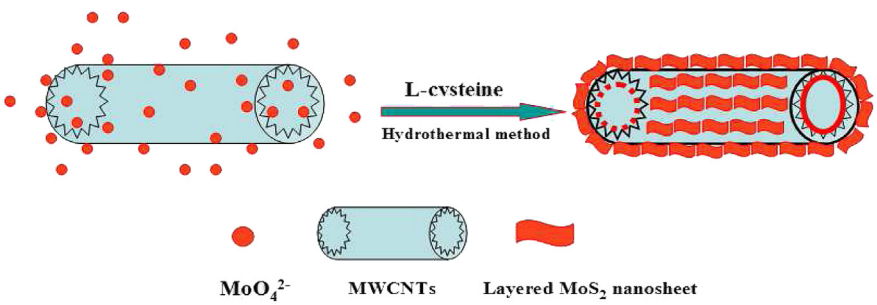

Fig. 1. Illustration of the procedure for preparing the MoS_2/MWCNT composites.