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Sandwiched MoS_2/polyaniline nanosheets array vertically aligned on reduced graphene oxide for high performance supercapacitors

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ABSTRACT

MoS_2/polyaniline/reduced graphene oxide hierarchical nanosheets (denoted as MoS_2/PANI/rGO HNSs) with novel structure of sandwiched MoS_2/PANI nanosheets array vertically align on rGO are successfully synthesized and investigated as supercapacitor electrode in aqueous electrolyte (1 M H_2SO_4). In this hierarchical nanosheets, PANI chains are intercalated into MoS_2 interlayers constructing sandwiched MoS_2/PANI nanosheets and restrict the volume change itself, meanwhile the sandwiched MoS_2/PANI nanosheets array vertically align on rGO nanosheets creating intimate and sufficient hetero-interface between PANI, MoS_2 and rGO layers. Thus excellent conductivity and ultrahigh reactive surface area are achieved and leads to superior supercapacitance. In the three-electrode system, the MoS_2/PANI/rGO-300 HNSs show a capacitance of 330.7 F g^{-1} at current density of 10 A g^{-1} at first cycle, and have capacitance retention about 81.9% after 40,000 cycles. Assembled as MoS_2/PANI/rGO-300//MoS_2/PANI/rGO-300 symmetric supercapacitor, it exhibits a capacitance of 97.8 F g^{-1} at current density of 2 A g^{-1} at first cycle. After 20,000 cycles, 84.2% of initial capacitance is retained. When assemble asymmetric supercapacitor using MoS_2/PANI/rGO-300 HNSs as cathode and active carbon (AC) as anode, it still shows a high capacitance of 73.3 F g^{-1} at current density of 2 A g^{-1} at first cycle, retains 87.9% after 20,000 cycles.

1. Introduction

Supercapacitors is considered to be one of the most promising energy storage devices because of their high power density, fast charge/discharge process and long cycle life [1–3]. Since the electrode materials play the key role in supercapacitors, many efforts have been devoted to the research and development of excellent performance electrode materials for supercapacitors in recent years [4–10]. Typically, electrode materials for the electrochemical double layer capacitors (EDLCs) are made of carbon-based materials, such as carbon nanotube, activated carbon and graphene, which can withstand a huge number of charge-discharge cycles, up to 1,000,000 cycles with small decrease [11]. However, the capacitance which delivered in the aqueous and organic electrolytes are only about 200 F g^{-1} and 100 F g^{-1}, respectively [12,13].

In this situation, transition metal sulfides [14], such as MoS_2 [4,15–20], have attracted great attention as electrode material. MoS_2 nanosheets are analogue of graphene, which stacked by S–Mo–S layers under van der Waals force [21,22]. Therefore, MoS_2 can be effortless intercalated by foreign invaders. Because of its special layered structure and enormous theoretical capacitance (~1000 F g^{-1}), MoS_2 is considered to be a competitive electrode material for supercapacitors [6]. Nevertheless, the poor electronic and ionic conductivity between two contiguous S–Mo–S layers results in an unsatisfactory capacitance delivery, especially at the high current density [23–25]. Generally, design and construction of hierarchical structures with conductive materials is an effective method to solve this problem [26–30]. The synergistic effects of all individual constituents can combine high capacity and long cyclic performance for supercapacitor. Though many researches have been conducted about the composite of MoS_2 and conducting polymer or carbon materials, the simple coating PANI onto the surface of MoS_2 or growing MoS_2 on the carbon skeleton materials cannot take full advantages of the conductivity of PANI or carbon materials and the mechanical stability of MoS_2. For instances, Ma et al. [31] coated MoS_2 nanosheets by polypyrrole and obtained a capacitance of 553.7 F g^{-1} in 1 M KCl electrolyte at a current density of 1 A g^{-1}, but suffer from a severe capacitance fading (declined by 10% only after 500 cycles). This simple method of polypyrrole coating on the surface of MoS_2 not only cover a large proportion of

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active sites of MoS_2, but also could not be able to solve the problem of the poor cyclic stability of polypyrrole. Similarly, Li et al. [32] synthesized MoS_2/RGO@PANI by coating PANI on MoS_2/RGO composite and obtained a capacitance of 1224 F g^{-1} in 1 M H_2SO_4 electrolyte at a current density of 1 A g^{-1}. Although the cycle performance is improved to some extent, it's still unsatisfactory (82.5% capacitance retention after 3000 loops). Until now, realizing both high capacity and good cycling performance in MoS_2-based supercapacitor is still a great challenge. On the basis of the 2D structural features of MoS_2, it may be feasible to intercalate PANI into the interlayers of MoS_2 which can not only form sufficient PANI-MoS_2 hetero-interfaces without great losses of the surface active sites of MoS_2, but also restrict the volume change of PANI in the charge/discharge process. Moreover, adopting graphene [17,33,34] which possesses large specific surface area, ultra high mechanical strength and high electrical conductivity as a template to support the formed MoS_2 nanosheet arrays is expected to construct a conducting network and then improve the charge transfer conductivity between the adjacent MoS_2 nanosheet, increase the specific surface area and stabilize the nanostructure of MoS_2.

Herein, we design and synthesize hierarchical nanosheets of sandwiched MoS_2/PANI nanosheets array vertically aligned on rGO nanosheets based on our previous work [35]. PANI chains are intercalated into MoS_2 interlayers constructing sandwiched MoS_2/PANI nanosheets, meanwhile the sandwiched MoS_2/PANI nanosheets array vertically aligned on rGO creating intimate and sufficient hetero-interface between PANI, MoS_2 and rGO layers. Thus excellent conductivity and ultrahigh surface area are achieved and leads to superior supercapacitance. The electrochemical tests indicates that the MoS_2/PANI/rGO HNSs exhibit a high capacity (330.7 F g^{-1} at 10 A g^{-1}) and excellent cyclic stability (retains 81.9% after 40,000 cycles) compared with the conventional carbon based and MoS_2 based electrode materials.

2. Experimental section

2.1. Preparation of GO and synthesis of MoS_2/PANI/rGO HNSs

The synthesis of GO was based on a typical Chemical Oxidation method [36]. To synthesize 3D MoS_2/PANI/rGO HNSs, $Mo_3O_{10}(C_6H_5NH_3)_2{\cdot}4H_2O$/GO precursor was firstly prepared referring to our previous report [35]. 300 mg GO was dispersed in 100 mL deionized water by ultrasonication for 5 h to form a homogeneous suspension. Meanwhile, 1.65 g $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ and 1.75 g aniline were added into above GO suspension after dissolved in 140 mL deionized water. Then, 1 M HCl was drop added to precisely adjust the pH value to 4.0 under the monitor of pH-meter. After stirring at 50 °C in oil bath for 5 h, the product of $Mo_3O_{10}(C_6H_5NH_3)_2{\cdot}4H_2O$/GO were collected, washed and dried at 60 °C. Secondly, $Mo_3O_{10}(C_6H_5NH_3)_2{\cdot}4H_2O$/GO were transformed to MoO_x/PANI/GO. 1.35 g $Mo_3O_{10}(C_6H_5NH_3)_2{\cdot}4H_2O$/GO were dispersed in 100 mL deionized water, then 1 M HCl was dropwise added until the pH value was adjusted to 1.7. Afterwards, 60 mL of HCl solution (pH 1.7) containing 2.4 g $K_2S_2O_8$ was added into the suspension. After stirring for 6 h, gray product of MoO_x/PANI/GO was obtained. Lastly, the MoS_2/PANI/rGO HNSs were synthesized using hydrothermal method, in which 0.5 g MoO_x/PANI/GO nanocomposite were dispersed in 30 ml deionized water containing 0.5 g thiourea. After stirring for 30 min, the solution was transferred to a 50 ml Teflon-lined stainless-steel autoclave and heated at 200 °C for 48 h. After that, the black product were centrifuged, washed with deionized water and ethanol, and finally dried at 60 °C. The as-prepared product was called MoS_2/PANI/rGO-300 HNSs according to the weight of GO.

For comparison, the MoS_2/PANI/rGO-200 HNSs and MoS_2/PANI/rGO-400 HNSs were also synthesized with the weight of GO are 200 mg and 400 mg, respectively. MoS_2/rGO and MoS_2/PANI were synthesized in the control experiment: 0.5 g $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ and 0.5 g thiourea were dissolving in 30 ml GO suspension which contained 37.5 mg GO, then stirring for 30 min. After heated at 200 °C for 48 h in a 50 ml Teflon-lined stainless autoclave, the MoS_2/rGO was synthesized. MoS_2/PANI was synthesized by the same procedure as MoS_2/PANI/rGO-300 HNSs with the absence of GO.

2.2. Materials characterizations

Morphology and structure of samples were analyzed by using field-emission scanning electron microscope (FESEM, Carl Zeiss, Supra 40), transmission electron microscope (TEM, JEOL-2100) at 200 kV, and X-ray diffractometer (XRD, Rigaku, MiniFlex 600) with Cu-Kα radiation. Infrared spectra analysis was made using Fourier transform infrared spectrometer (FT-IR, Nicolet iS50). The surface area was calculated by Brunauer–Emmett–Teller (BET) method using an Autosorb iQ2014 analyzer. The Raman analysis was conducted by a laser Raman spectrometer (Raman, Horiba) with an excitation wavelength of 632.8 nm.

2.3. Electrochemical measurements

To fabricate working electrodes, each as-synthesized active materials, acetylene black and polyvinylidene fluoride (PVDF) with a ratio of 80:15:5 were stir in ethyl alcohol for 24 h to form slurry. Then the slurry was coated onto the graphite paper substrate (1 cm × 1 cm) and dried at 60 °C in a vacuum oven for 12 h to remove the solvent. The weight of the active material in per working electrode is about 1 mg. A typical three-electrode system used the measured materials as working electrode, a Pt plate as counter electrode and a saturated Ag/AgCl electrode (0.1981V vs. SHE) as reference electrode. In a typical two-electrode configuration, MoS_2/PANI/rGO-300 HNSs were used as the cathode and activated carbon (AC) or MoS_2/PANI/rGO-300 HNSs were used as anode. All the electrochemical measurements were conducted with 1 M H_2SO_4 as electrolyte. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed on an electrochemical work station (Gamry Interface1000). EIS was carried out in a frequency range of 100 kHz to 10 mHz at an open circuit potential with an perturbation potential of 5 mV. Galvanostatic charge/discharge measurements were performed on a supercapacitor test system (SCTS, Arbin).

3. Result and discussion

The synthesis process is schematically displayed in Fig. 1. Firstly, a typical organic/inorganic hybrid $Mo_3O_{10}(C_6H_5NH_3)_2{\cdot}4H_2O$/GO precursor (Fig. S1) was synthesized base on previous report [35]. After the in-situ polymerization of aniline in the $Mo_3O_{10}(C_6H_5NH_3)_2{\cdot}4H_2O$/GO precursor, the obtained MoO_x/PANI/GO (Fig. S2) was subsequently sulfurized, and GO was reduced (Fig. S3) at 200 °C in a hydrothermal reaction, resulting in MoS_2/PANI/rGO HNSs.

To investigate the structure, the MoS_2/PANI/rGO-300 HNSs were firstly characterized by XRD. Fig. 2 (a) shows the structure characteristics of MoS_2/PANI, MoS_2/rGO and MoS_2/PANI/rGO-300 HNSs. Compared with MoS_2/PANI, the diffraction peak of (002) planes of MoS_2 in MoS_2/PANI/rGO-300 HNSs shifts from 9.5° to a higher angle (12.7°). It means that the enlarged interlayer spacing of MoS_2 caused by the intercalation of PANI has been shrunk from 0.92 nm to 0.70 nm [37–39], which may due to the existence of rGO affects