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Hydrothermal preparation of MoS_2 nanoflake arrays on Cu foil with enhanced supercapacitive property

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ABSTRACT

Hexagonal MoS_2 nanoflake arrays (h-MNFs) have been synthesized directly via hydrothermal route with Cu foil as substrate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ as the molybdenum source, CN_2H_4S as the sulfur source and reductant, and $(CH_3)_2CHOH$ as the dispersant. The micro morphology and crystallinity of MNFs are analyzed by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Raman microscopy (RM). The morphological change and growth process of MNFs are investigated, basing on the samples at different hydrothermal reaction times. Moreover, the supercapacitive properties of MNFs have been examined. It is found that MNFs has a good cycling invertibility (93%) and stability (90%) after 5000 cycles, a relatively high specific capacitance (420 $F g^{-1}$), a low charge transport resistance (1.8 Ω) and available energy densities ranging from 21 to 17 W h kg^{-1} with corresponding practical power densities ranging from 150 to 3000 W kg^{-1}.

1. Introduction

Entering the twenty first century, efficient, clean, sustainable and renewable sources of energy and its storage and conversion systems are going to be a desired use, because of energy issue on a global scale coupled with limited fossil fuel reserves and other environmental issue [1]. Supercapacitor can effectively store energy owing to advantages of long service lifetime [2], excellent energy and power densities [3], high rate of charge/discharge behavior [4], green and pro-environment [5]. As effective energy storage devices, they have been widely adopted in multiple fields such as electric vehicles [6], public transportations [7], consumer electronics [8], digital telecommunication systems [9] and military devices [10]. Supercapacitors are classified into two types according to the energy storage method: one is electric double-layer capacitor accumulating of charges at the interface between electrode and electrolyte and the other is faradic pseudocapacitor occurring fast and reversible faradic redox reactions [11].

A diverse of carbonaceous material, conducting polymers, metal oxides and metal chalcogenides are used in supercapacitor applications [12]. Transition metal oxides or sulfides (such as RuO_2 [13], MnO_2 [14], Co_3O_4 [15], V_2O_5 [16], WS_2 [17], Ni_2S_3 [18], MoS_2 [19], etc.) are potential pseudocapacitive materials on account of their various valences, excellent electrochemical stability and invertibility, considerable specific capacitances, energy densities and power densities. Among the large number of transition metal compounds, molybdenum disulfide (MoS_2) becomes one of the most important compound semiconductor materials due to its layered structure (three-atom S—Mo—S layers) with strong interlayer covalent bonds separated by weak van der Waals forces [20,21], resulting that MoS_2 could be easy to exfoliate to a lamellar structure. And the two-dimensional (2D) MoS_2 nanosheet, which is similar to grapheme, has been widely applied in each field of hydrogen storage [22], lubricant [23], sensing [24], Li-ion battery [25], and especially supercapacitor [26] owing to its outstanding lubricity, good corrosion resistance and charge storage ability.

The supercapacitive performance of MoS_2 nanostructures with different morphologies had been widely studied. Wang et al. [27].

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reported that 3D flower-like MoS_2 nanostructures had a specific capacitance of 168 F g^{-1} and a good capacitance retention of 92.6% over 3000 cycles as electrode materials for supercapacitors. Few layered-structure MoS_2 was obtained and then assembled into device by Krishnamoorthy et al. [28]. And they found that MoS_2 supercapacitor presented a specific capacitance of 119 mF cm^{-1} with an energy density of 8.1 nW h cm^{-1}. Acerce et al. [29]. exfoliated and restacked MoS_2 nanosheets film. The capacitance values of this film ranged from 400 to 700 F cm^{-3}. Oriented semiconductor nanostructure arrays built on conducive substrate have been demonstrated to be the optimal electrode structure since electrons could transfer between current collector and electrode quickly, resulting in the decrease of inner resistance.

Although a vast number of literatures have reported MoS_2 nanostructures with different morphologies and their supercapacitive performance, most of them synthesized MoS_2 nanopowders firstly, and then prepared working electrode by mixing MoS_2 nanopowders, carbon black and poly to press onto the current collector [30]. However, few literature studies reported 2D MoS_2 nanostructure arrays synthesized directly on conductive materials to study their supercapacitive properties. In this paper, Hexagonal MoS_2 nanoflake arrays (h-MNFs) grown directly on Cu foil was prepared by means of a facile hydrothermal route. The obtained MNFs were stacked by multi-layed MoS_2 nanosheets. The morphological change and growth mechanism of MNFs were investigated and explained systematically. The circulatory stability and invertibility, specific capacitance, energy density, power density and alternating-current impedance of MNFs were studied in detail. And we give a reasonable explanation for the reason why MNFs has a good supercapacitive performance.

2. Experimental sections

2.1. Preparation of MNFs

All chemical reagent (analytical grade) were purchased from China National Pharmaceutical Group Corporation. The precursor solution was prepared as follows: 0.5 mmol of ammonium molybdate ($(NH_4)_6Mo_7O_{24}$) and 15 mmol of thiourea (CSN_2H_4) were dissolved in 15 mL deionized water and agitated magnetically. Then, 0.25 mmol isopropanol was dissolved in the solution. After stirring for 30 min, the as-prepared mixture (15 mL) was transferred into a polytetrafluoroethylene-lined stainless steel reactor. A piece of Cu foil ($1.0 \times 3.0\ cm^2$) was put into the reactor and kept at 180 °C for 24 h. After cooled to room temperature naturally, the MNFs grown on Cu foil was taken out, cleaned several times and stoved at 80 °C. To investigate the formation mechanism of MNFs, the samples were taken out at different times (1, 2, 4, 12 and 24 h). Also ammonium molybdate, thiourea and isopropanol were replaced by a certain mass of sodium molybdate (3.5 mmol), thioacetamide (15 mmol) and ethanol (0.25 mmol), respectively. And the effect of substrate on the morphology was also investigated by using ITO, FTO and Ni foam as substrates.

2.2. Characterization of MNFs

The micro-morphologies, crystallinity, elementary composition, valence state of MNFs were characterized by using X-ray diffractometer (Rigaku Dmax-2550), field emission scanning electron microscope (FESEM, JEOL-JSM-7500), high-resolution transmission electron microscope (HRTEM, JEOL-JEM-2010F) and X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific China., Ltd, ESCALAB 250Xi). The XPS fitting was studied by means of XPS-peak software with Gaussian function. Raman spectroscopy for the MNFs was carried out using a Raman spectrometer (RM, Renishaw, In-via) with a laser at 633 nm. The N_2 adsorption-desorption was measured on a Quantachrome NOVA touch LX4 sorption analyzer.

2.3. Electrochemical measurements of MNFs

The supercapacitive properties were measured on a CHI760E electrochemical workstation with a three-electrode configuration. The working, counter, reference electrodes and electrolyte are MNFs grown directly on Cu foil, Pt foil, Ag/AgCl electrode and 1 mol L^{-1} Na_2SO_4 solution, respectively. Cyclic voltammetry (CV) tests were carried out at different scan rate (5, 10, 20, 50 and 100 mV s^{-1}) and galvanostatic charge-discharge (GCD) curves were recorded at different current densities (0.5, 1, 2, 5, 10 A g^{-1}) in a potential window of 0–0.6 V. The AC impedance spectrum (1 M Hz–1 Hz) was conducted on the same workstation. The mass of the MoS_2 was calculated via the different values of the total Cu foil mass before and after the synthesis reaction. The deposition mass is 2 mg after reaction for 24 h.

3. Results and discussion

3.1. Synthesis and characterization of MNFs on the Cu foil

Fig. 1a–c show the FESEM images of MNFs grown directly on Cu foil at 180 °C for 24 h. It can be seen that these MoS_2 nanoflakes with an average length of 2 μm, thickness of 50–80 nm and height of 1–2 μm grow perpendicularly to the substrate at low magnification, high magnification and cross-sectional view, respectively. In addition, the morphology of most nanoflakes might look like a hexagon and they are made up of a large number of nanoparticles. And these nanoflakes are rooted in the substrate, indicating a tight connection between the MNFs and the Cu foil. Brunauer-Emmett-Teller (BET) calculation reveals that the surface area of MoS_2 flakes is 4.1 $m^2\ g^{-1}$ from the N_2 adsorption-desorption isotherm (Fig. S1). Energy-dispersive X-ray spectroscopy (EDS) in Fig. 1d is used to analyze the element composition of these nanoflakes. The spectrum shows that the components of the nanoflakes are molybdenum (Mo) and sulphur (S). The peaks of Cu and Pt originate from the Cu foil and metal spraying.

The crystalline structure and crystallinity of the MNFs grown on Cu foil were determined by XRD measurements. From Fig. 1e, the main peaks appear at 14.4°, 32.7°, 35.9°, 44.2°, 58.3°, which could be originated from the (002), (100), (102), (006) and (110) crystal faces of the hexagonal MoS_2 structure (JCPDS 00-37-1492) [31], suggesting that a pure MoS_2 is obtained. In addition, the pattern of the MNFs has a broadening of full width at half maximum (FWHM), illuminating that the MNFs contain numerous nanoparticles with small grain size, which is consistent with the SEM images in Fig. 1b. And the strongest peak of pattern appear at 14.4°, indicating a well-stacked layered structure along the c axis [32].

The Raman spectrum in Fig. 1f is decomposed into in-plane E^1_{2g} and out-of-plane A_{1g} modes [33] of the hexagonal MoS_2, whose frequency separation is indicative of the number of MoS_2 layers [34]. As the number of MoS_2 layers increases, the E^1_{2g} mode redshifts whereas the A_{1g} mode blueshifts [35]. Thus, the separation between these two peaks increases with thickness and is routinely used to identify the number of MoS_2 layers. The two modes are centered at 405 and 377 cm^{-1}, with a frequency difference of 28 cm^{-1}, which is much wider than that of the other reported (24 cm^{-1}, 4 layers) [36].

The micro-morphologies and crystalline structures of these MoS_2 nanoflakes were further examined by HRTEM measurements. Fig. 2a displays the morphology of these MoS_2 nanoflakes after ultrasonic treatment. It can be observed that these nanoflakes could be decomposed into many curly and straight nanosheets, which means that the as-synthesized MoS_2 nanoflakes are a stake