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Facile synthesis of three dimensional MoS_2 porous film with high electrochemical performance

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ABSTRACT

In this work, we report the successful fabrication of MoS_2 nanosheets directly grown on three dimensional porous Mo foil by combining the texturing with hydrothermal reaction. Ascribed to the large surface area, three-dimensional porous structure and low resistance, the porous film exhibits enhanced electrochemical capacity. Moreover, these unique three dimensional structures could effectively weaken the agglomeration and stacking problems during the electrochemical reaction, ensuring high cycling stability.

1. Introduction

Recently, three-dimensional (3D) porous films have received increasingly attention for their potential applications in photocatalysis [1], batteries [2] and electrocatalysts [3]. Several strategies such as templating [4,5], electrodeposition [6] and self-assembly [7–10] have been applied to fabricate 3D porous structures. However, these preparations were limited to bottom-up methods and the traditional top-down ways were confined to electron-beam [11] and photolithography [12] techniques which are complicated and high-cost. Herein, exploring new and convenient strategy to prepare the porous substrate is urgent to be addressed. For electrochemical electrodes, only the parts of active materials which are exposed to electrolyte and connected to current collector can effectively participate in charge storage during the electrochemical process [13,14]. This unique porous film could provide large surface area which is exposed to the electrolyte. Thus preparing the free-standing film directly on porous substrate would remarkably enhance capacitive performance ascribed to the large surface area, short transport pathways of electron and ion. Furthermore, the intrinsic 3D porous structure could relieve the disintegration of the active materials and ensure the longer cycling life. MoS_2 possessing S-Mo-S layers which are separated by van der Walls forces is similar to graphene [15–17]. Therefore, the MoS_2 has been widely studied, and various MoS_2 films have been prepared for enhanced electrochemical performance [18,19]. However, these MoS_2 films were confined to nanosheet array films or layered films and the three dimensional MoS_2 porous film has never been reported and researched.

Herein, the MoS_2 nanosheets directly grown on porous Mo foil (porous Mo-MoS_2) was fabricated which can be used as the binder-free electrode straightly. The preparation of porous Mo-MoS_2 combined texturing with hydrothermal treatment for the first time. Ascribed to the unique 3D nanostructure, it exhibits enhanced electrochemical activity compared to the MoS_2 nanosheets directly grown on smooth Mo foil (smooth Mo-MoS_2). As a result, the porous Mo-MoS_2 shows a specific capacitance of 0.243 F cm^{-2} at 0.6 mA cm^{-2} and 91.7 % retention of initial capacitance value even at high current density of 4 mA cm^{-2} after 1000 cycles, indicating the good capacitive property and excellent cycling stability.

2. Experimental section

Prior to the synthesis, the Mo foil was cleaned and then the surface texture was conducted on the disks by using a commercial pulse Nd:YAG laser. The micropores are prepared with a pulsing frequency of 10 kHz, scanning speed of 5 mm/s and an overlapping rate of 90% for laser spot. Then the textured and un-textured Mo foils after cleaning were respectively transferred

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into an 80 ml Teflon lined autoclave with an aqueous solution of thiourea (0.5 M, 48 ml). Subsequently, the autoclaves were heated to180 °C and kept for 24 h at this temperature (see details in SI).

3. Results and discussion

The structure of porous Mo foil through texturing was revealed by SEM image (Fig. 1A), indicating the three-dimensional porous feature. More specifically, the pores exhibit a uniform dispersion with a diameter of about 15 μm. After sulfureting of porous Mo foil, the Mo foil still remains the porous feature in over-all morphologies of low magnification SEM image (Fig. 1B). Moreover, the porous Mo-MoS_2 electrode shows many protuberances which are conducive to buffer the volume expansion. In the high magnification SEM image (Fig. 1C), it can be clearly seen that the MoS_2 film grows on the surface of porous foil and even on the walls of deep pores. The MoS_2 nanosheets with a thickness of 50 nm also interconnect with each other to form porous. To further investigate the structure and crystallinity of the MoS_2 nanosheet array grown on the porous Mo foil, the transmission electron microscopy (TEM) images of samples peeled off the porous Mo foil were characterized. As shown in Fig. 1E, the samples exhibit a porous network comprising interconnected nanosheets. The HRTEM image of the MoS_2 nanosheets (Fig. 1F) displays the interplanar spacing of 0.27 nm which could be devoted to (100) planes of MoS_2 [20]. It is highly recognized that ordered interconnected MoS_2 nanosheet networks was fabricated and obtained on porous Mo foil by controlled design, manifesting the considerable surface area and porosity.

The X-ray photoelectron spectroscopy (XPS) was conducted on the porous Mo-MoS_2 electrode to confirm the valance states of elements. As shown in Fig. 2A, the survey pattern exhibits the peaks of Mo and S, indicating that the composition of the electrode. Furthermore, in the high-resolution XPS (Fig. 2B) pattern of Mo 3d, the peaks located at 229 eV and 232 eV can be derived from Mo $3d_{5/2}$ and Mo $3d_{3/2}$ of Mo^{4+}. Meanwhile, a single doublet peaks at around 162.0 eV are consistent with the S^{2-} in MoS_2 (Fig. 2C). Ultimately, these XPS results further validate that the MoS_2 was well obtained after texture and hydrothermal treatment. Fig. 2D shows the typical adsorption-desorption isotherms of the smooth Mo-MoS_2 and porous Mo-MoS_2 electrodes, which indicate the monolayer absorption and surface area. Evidently, the porous Mo-MoS_2 electrode possesses a much larger surface area (2.363 m^2/g) than smooth Mo-MoS_2 (0.152 m^2/g) associated with the larger area encircled by the curve.

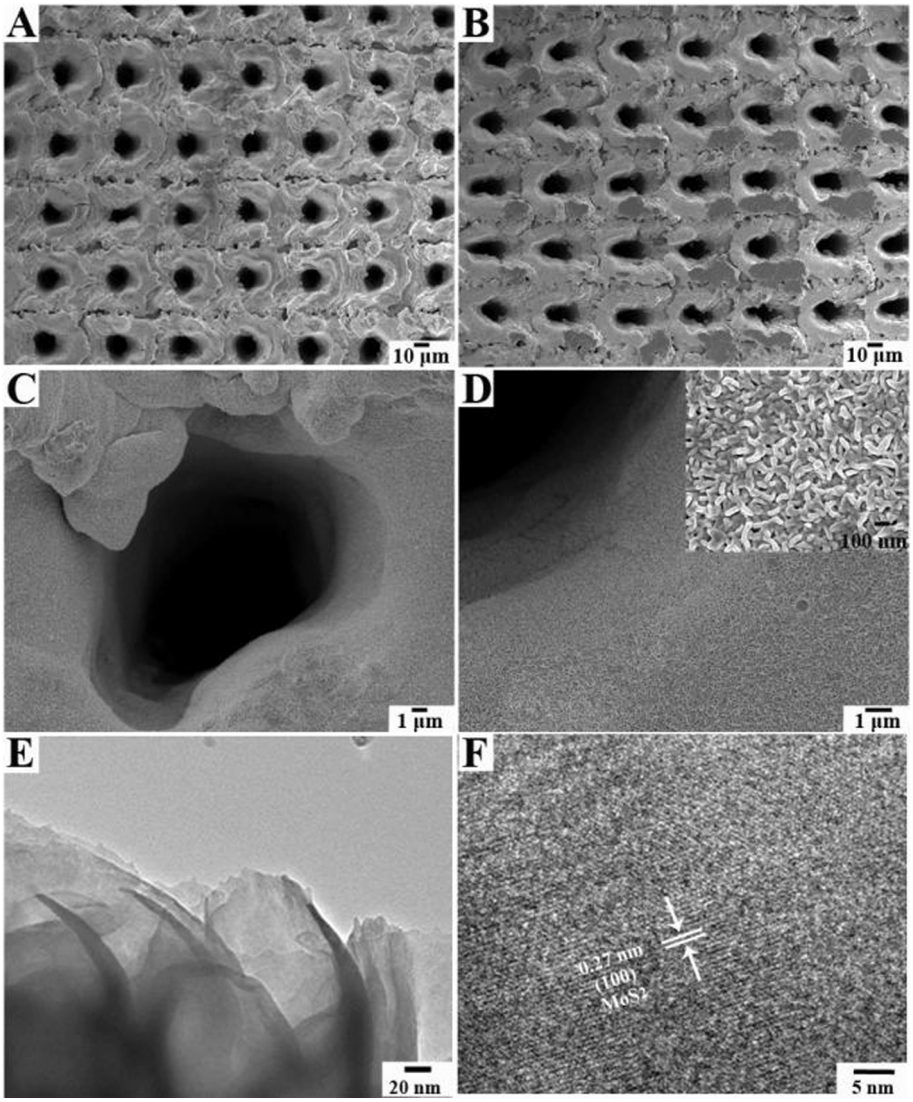

Fig. 1. SEM images of (A) porous Mo foil (B–D) porous Mo-MoS_2 (E) TEM images and (F) HRTEM image of porous Mo-MoS_2 electrode.