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A robust free-standing MoS_2/poly(3,4-ethylenedioxythiophene):poly (styrenesulfonate) film for supercapacitor applications

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ABSTRACT

Two-dimensional molybdenum disulfide (MoS_2) is a promising energy storage material due to its high surface area and unique electronic structure. Free-standing flexible MoS_2-based electrode is of importance for use in flexible energy storage devices, whereas there are limited reports available. In this work we developed a robust hybrid film, MoS_2 incorporated with highly conductive poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate). This free-standing film possesses excellent mechanical properties with a fracture strength of 18.0 MPa and a Young's modulus of 2.0 GPa. It can deliver a large volumetric capacitance of 141.4 F cm^{-3}, a high volumetric energy density of 4.9 mWh cm^{-3}, and a capacitance retention rate of 98.6% after 5000 charge/discharge cycles. This film has demonstrated its application in an all-solid-state bendable supercapacitor as well.

1. Introduction

Flexible/bendable electronic equipments such as roll-up displays and wearable devices are currently under rapid development, which urgently requires the development of flexible energy storage devices to match [1–3]. As an important energy storage device, flexible supercapacitor has attracted attention due to its ease of large-scale production and promising electrochemical properties (*i.e.* large capacitance, high power density and long cycle life) [4,5]. Free-standing, binder-free films are one very important type of flexible electrodes, since they can be easily processed into different shapes and sizes for simplicity of device fabrication. Two-dimensional (2D) graphene or conjugated polymers films have demonstrated this use [6–9], while the pursuit of new materials with higher performance is still in demand.

Molybdenum disulfide (MoS_2) nanosheet, as a typical inorganic analogue of graphene, has emerged as an excellent material for energy storage applications due to its sheet-like structure providing large surface area for charge storage [10–12]. The centre Mo atom in MoS_2 has a wide range of oxidation state from +2 to +6, offering pseudo-capacitances [13–15]. Moreover, MoS_2 is non-toxic, eco-friendly and of low cost [16].

Li-intercalation exfoliation method is a widely used method to fabricate single- and few-layer MoS_2 nanosheets. The produced high-concentration MoS_2 nanosheets in dispersion are the ideal precursor for fabrication of free-standing MoS_2 films. In addition, these Li-intercalation exfoliated MoS_2 nanosheets contain a high ratio of metallic 1T phase [17], which can electrochemically intercalate with various ions, resulting in high capacitive performance. The 1T-MoS_2 film via filtration delivered a volumetric capacitance ranging from 400 to 700 F cm^{-3} in aqueous electrolytes [17]. However, this film was used with the aid of a mechanical support: a gold coated substrate. Probably the free-standing film was lacking in mechanical robustness and flexibility due to the small lateral size of MoS_2 nanosheets (typically $<1\,\mu m$) and the relatively low aspect ratio [18]. The large size of liquid-crystal MoS_2 may provide a solution [19]. Moreover, the restacking of MoS_2 nanosheets may result in a poor capacitive performance especially for thick films, due to the loss of surface area. The introduction of supportive materials such as graphene can enhance the mechanical as well as electrochemical properties. For example, three-dimensional MoS_2/graphene aerogel prepared by a hydrothermal procedure could deliver a specific capacitance of 268 F g^{-1} at 0.5 A g^{-1}. A free-standing and flexible MoS_2/GO hybrid film via vacuum filtration [18] has shown a high volumetric capacitance (~380 F cm^{-3} at 10 mV s^{-1}).

Conjugated polymers (CPs) are an intriguing class of materials to form high performance composites with a variety of materials (*e.g.* metal oxides, organic conductors, 2D materials) for

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supercapacitor applications [20–22]. The composites based on CPs and 2D materials exhibit properties of each of the individual components with synergistic effect due to the facile charge transfer between these two constituents [23]. The addition of CPs to 2D semiconductors (*i.e.* MoS_2 in this work) is valuable because CPs can function as the conducting platform for charge delivery between 2D sheets. The reported composites include MoS_2/polyaniline [24], MoS_2/polypyrrole [14] and MoS_2/poly(3,4-ethylenedioxythiophene) composites[25], demonstrating high capacitances in the range of 400–700 $F\,g^{-1}$. However, these composites are all in the powder form. The reports on free-standing flexible MoS_2-CPs films are still limited. The widely used poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) possesses all the above mentioned advantages for supercapacitor application [26]. More importantly, it can be easily dispersed into different solvents [27]. This unique character allows it to be easily mixed with MoS_2 dispersion forming MoS_2/PEDOT composites and a free-standing flexible film may be produced via simply casting or filtration.

Herein, free-standing MoS_2/PEDOT hybrid films were fabricated through a simple filtration technique. The resultant MoS_2/PEDOT films were robust, demonstrating a high fracture strength of 18.0 MPa. They could deliver high volumetric capacitances and good cycling stability as well. Moreover, this hybrid film had demonstrated its application in all-solid-state bendable devices. This work provides a step forward to the practical application of MoS_2-based electrodes in flexible supercapacitors.

2. Experimental

2.1. Materials

Molybdenum disulfide fine powder was sourced from Asbury Carbon. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT: PSS) pellets were obtained from Agfa Group. N-butyllithium (2.5 M solution in hexane) was purchased from Sigma-Aldrich.

2.2. Fabrication of MoS_2 nanosheets in aqueous dispersion

Chemically exfoliated MoS_2 nanosheets were prepared using lithium intercalation-exfoliation method developed by Morrison and co-workers [28]. Briefly, dried MoS_2 powder (1 g) was put into a 100 mL round-bottom flask, followed by the addition of 2.5 M n-butyllithium solution (10 mL). This mixture was stirred for 48 h under the protection of argon. Then the Li-intercalated MoS_2 was exfoliated into water (~100 mL) via sonication. The resulting dispersion of exfoliated MoS_2 nanosheets was purified by dialysis with water for 2 weeks, removing the contained lithium ions and organic residues.

2.3. Fabrication of MoS_2/PEDOT hybrid films

The MoS_2 nanosheet dispersion (~1 mg mL^{-1}, 60 mL) was added dropwise to 1.5 wt% PEDOT:PSS dispersions (4 mL, 2 mL or 0.8 mL) under stirring to fabricate the films with a weight ratio of 1:1, 2:1 and 5:1 (MoS_2: PEDOT:PSS). The mixture was then filtered onto a PVDF hydrophobic filter membrane (90 mm diameter, pore size of 0.22 μm) and peeled off. The complete incorporation of PEDOT:PSS can be evidenced by the clear filtrate produced during the filtration process, as the dispersion containing tiny amount of PEDOT:PSS is light blue in color. These films were dried in a vacuum oven at 60 °C overnight. They were denoted as MoS_2/PEDOT-1, MoS_2/PEDOT-2 and MoS_2/PEDOT-5 according to the above-mentioned weight ratio. As control samples, neat MoS_2 films were fabricated using the same amount of MoS_2 nanosheets dispersion via the same procedure but on a 47 mm-diameter membrane instead, due to the difficulty in forming robust freestanding films on a 90 mm membrane. Neat PEDOT:PSS films were fabricated by a simple casting technique.

2.4. Structural and morphological characterization

The topographic data of exfoliated MoS_2 nanosheets were collected by atomic force microscopy (AFM) (Asylum Research, MFP-3D). Transmission electron microscopy (TEM) images of MoS_2 nanosheets were collected using JEOL JEM-2200FS. The morphology of the films was characterized with field emission scanning electron microscopy (FE-SEM) (JEOL JSM-7500FA). Raman spectra were obtained with a confocal Raman spectrometer (Jobin Yvon HR800, Horiba) using a 632.8 nm diode laser. X-ray photoelectron spectroscopy (XPS) data was collected from a hemispherical energy PHOIBOS 100/150 analyser. Tensile tests of the films were conducted using a Shimadzu EZ mechanical tester at a cross-head speed of 1 mm/min.

2.5. Supercapacitors assembly and electrochemical measurements

Symmetrical supercapacitors were assembled into two-electrode Swagelok type cells with filter paper as separator and 1 M Na_2SO_4 as electrolyte. The films were cut into a dimension of 0.5 cm × 0.5 cm for use.

For an all-solid-state supercapacitor, a PVA/H_3PO_4 gel electrolyte (PVA:H_3PO_4, 1:1.5) was used following the previously reported procedure [29]. A film electrode (1 cm × 2 cm) was pasted onto a stainless steel mesh with silver paste (Electron Microscope Sciences Co.), followed by being immersed in the electrolyte overnight. Two electrodes with the semi-dried electrolyte layer were pressed together forming flexible devices.

Cyclic voltammetry (CV) of the device was conducted from 0 to 1 V using a CHI 604D (CHI Instruments). Electrochemical

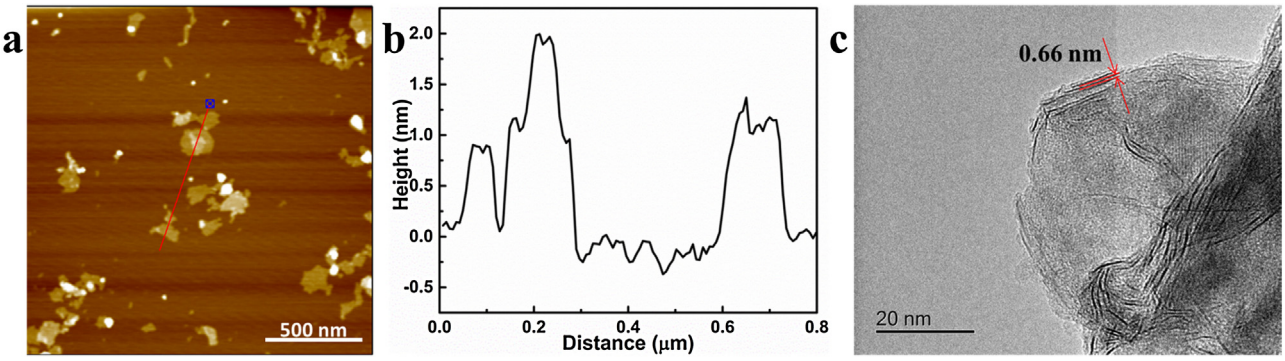

Fig. 1. AFM image (a) and height profile (b) along the line drawn in (a) of exfoliated MoS_2 nanosheets; (c) TEM image of MoS_2 nanosheets.