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Thiol-modified MoS_2 nanosheets as a functional layer for electrical bistable devices

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ABSTRACT

Molybdenum disulfide nanosheets have been synthesized by one-pot method using 1-ODT as sulfur source and surfactant. The structure, morphology and optical properties of samples were investigated by XRD, FTIR, Abs spectrum and TEM patterns. The XRD pattern indicated that the as-obtained MoS_2 belong to hexagonal system. The as-obtained MoS_2 nanosheets blending with PVK could be used to fabricate an electrically bistable devices through a simple spin-coating method and the device exhibited an obvious electrical bistability properties. The charge transport mechanism of the device was discussed based on the filamentary switching models.

1. Introduction

Two-dimensional (2D) materials have attracted more attentions since the graphene was separated from graphite in 2004 [1–3]. Especially, layered transition-metal dichalcogenides (LTMDs) have similar layered structure and properties like graphene. LTMDS can be obtained via micromechanical cleavage or the "Scotch tape method" due to the weak van der Waals forces interlayers [4,5]. Therefore, LTMDS can be used for sensors, memory devices, and organic thin-film transistors (TFTs), dry lubricant and photodetector, *etc.* [6–10].

Molybdenum disulfide (MoS_2) is one of the most stable layered metal dichalcogenides and a naturally exist molybdenite [11]. Bulk MoS_2 belongs to an indirect *n*-type semiconductor with 1.2 eV band gap. While, its band gap becomes greater with its layers decrease and it transforms to direct semiconductor with 1.8 eV band gap when it turns into monolayer [12,13]. The optical and electrical properties of 2D MoS_2 materials obviously enhance with decreasing of layer. Especially and its mobility is about 200–500 $cm^2/(Vs)$, which make it has potential application in electrical aspects. The size and quality of 2D materials has much difference with inartificial MoS_2, thus it is important to develop synthetic techniques of 2D MoS_2 materials. So far, many methods including chemical vapor deposition (CVD) [14], ion-intercalation [15,16] and exfoliation and colloidal chemical synthesis are employed for preparing MoS_2 [17].

In our experimental, a series of MoS_2 nanosheets (NSs) have been synthesized by direct thermolysis of a mixed solution of molybdenum acetylacetonate ($Mo(acac)_2$) and 1-octadecanethiol (ODT) in non-coordinating solvent octadecylene (ODE). At this case, the products synthesized at 280 °C for different reaction time exhibit a multilayer morphology. Moreover, the electrical bistable devices (EBDs) prepared using MoS_2 and Poly(9-vinylcarbazole) (PVK) as functional layer exhibit better electrical bistable properties.

2. Experimental

2.1. Materials

Molybdenum acetylacetonate (≥99%), 1-octadecanethiol (≥97%) and 1-octadecene (≥90%) were purchased from Aladdin Chemical Reagent Co., Ltd., China. The buffer layer solution poly (3, 4-ethylenedioxy-thiophene): poly-(styrene-sulfonate)-PEDOT:PSS was purchased from Xi'an Polymer Light Technology Corp. PVK was purchased from ACROS ORGANICS and its average molecular weight (M. W.) is 135 600. Other solvents such as chloroform, ethanol and acetone were commercially available products in analytical grade, which were purchased from Tianjin Chemical Reagent, China. ITO glass, silver (Ag) and aluminum (Al) were purchased from Zhongnuo new material Co., China. All the materials were used as purchased without further purification.

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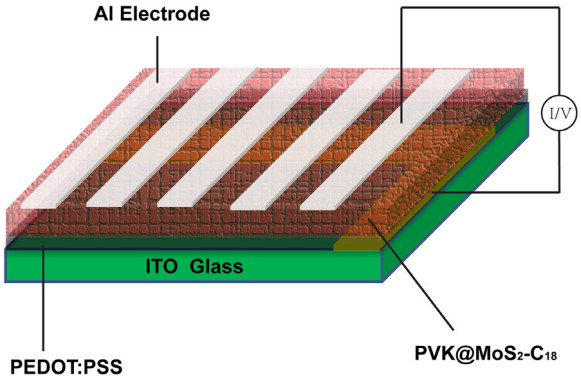

Fig. 1. Diagrammatic sketch of the EBDs based on MoS_2–C_{18} NSs.

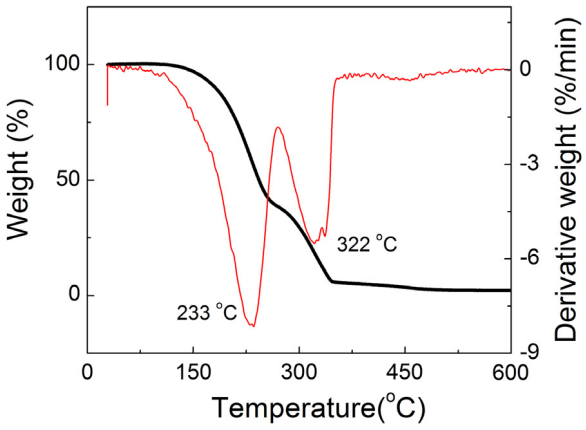

Fig. 2. TGA pattern of MoS_2 NSs.

2.2. *Synthesis of* MoS_2 *NSs*

At the beginning of synthesize reaction, $Mo(acac)_2$ (0.9875 g, 3 mmol) and 1-ODT (5.5158 g, 6 mmol) were mixed with ODE (20 ml) in a 50 ml four-necked flask. In order to drive out the oxygen in the reaction mixture, N_2 glow was applied for 20 min firstly. Then the mixture were heated up slowly to 280 °C under magnetic stirring and kept at this temperature for 240 min. During the reaction process, the mixture gradually became black solution. The samples were collected from the mixture at different reaction time to monitor the size and shape evolution. After the reaction finished, the mixture was cooled to room temperature naturally. Afterwards, the chloroform and absolute ethanol was added to precipitate the samples, which were collected by centrifugation at 7000 rpm for 10 min. The precipitation and purification process was repeated three times, and the final products were dispersed in chloroform or dried for next analyses.

2.3. *Preparation of EBDs based on* MoS_2 *NSs*

The fabrication process of EBDs based on MoS_2 NSs was listed as follows: the ITO (In_2O_3:Sn)-coated glass substrates were cleaned with deionized water, acetone, and absolute alcohol, and then dried using N_2 gas with a purity of 99.99%. Then pre-filtered PEDOT:PSS solution was spin-coated onto the ITO substrate at speed of 2000 rpm. In order to form better film, the ITO substrate should be heated on a 150 °C heating stage for 20 min. Subsequently, the MoS_2 NSs & PVK solution was spin-coated onto the PEDOT:PSS layer at 1800 rpm, in which the weight ratio of MoS_2 NSs and PVK is 1:1 and the concentration of solution is 20 mg/ml. Finally, 100 nm Al electrode was coated on top of device by thermal evaporation under vacuum at a system pressure of 1×10^{-6} Torr. The thickness of PEDOT:PSS, PVK & MoS_2–C_{18} and Al electrode were about 100 nm, 150 nm and 100 nm, respectively. Finally, the device with ITO/PEDOT:PSS/PVK & MoS_2–C_{18}/Al sandwich structure was obtained and the diagrammatic sketch was shown in Fig. 1. In this EBDs, the ITO on the glass substrate was used as anode, which was 0.4 mm width. The cathode was patterned into parallel electrodes with width of 0.4 mm by a shadow mask. The overlap between the column and row electrodes determined the acreage of the EBDs (0.16 mm^2). All the preparation and measurement of the EBDs were actualized in the glove box with high purity nitrogen atmosphere.

2.4. *Characterization*

The thermogravimetric analysis (TGA) was measured by a SDTA851E Thermogravimetric Analyzer. The crystal structure of the samples were measured using a Bruker D8 Discover X-ray Diffractometer with a CuKα radiation source (λ = 1.54056 Å). The X-ray photoelectron spectroscopic (XPS) measurement was performed on an ESCALAB 250 spectrometer with a 300W Al Kα radiation source. The UV–Vis absorption spectra were obtained by a Shimadzu-UV UV3101 spectrometer. Transmission electron microscopy (TEM) was performed using a Tecnai G2 F20 transmission electron microscope at an accelerating voltage of 100 kV. Fourier transform infrared spectra (FTIR) were collected by a Nicolet-6700 spectrometer. The current–voltage (I–V) characteristics of the device were measured by a Keithley 2612 source meter controlled by a computer. All of the operation voltages were applied on the ITO bottom electrode, with which the Al top electrode was grounded. All the measurements were carried out at room temperature.

3. Results and discussions

3.1. *TGA of* MoS_2 *NSs*

In order to investigate the information of the thermal behavior of MoS_2–C_{18} precursor, TGA and differential thermal gravity (DTG) is measured and given in Fig. 2. The TGA plot shows a rapid weight loss from 150 to 350 °C. It can be seen from Fig. 2 that the two main DTG peaks are at 233 and 322 °C, which indicates that the thermal decomposition includes the two steps. The first step from 150 to 280 °C may be caused by volatilization or decomposing of 1-ODT and the second step from 280 to 350 °C is attributed to the decomposition of ODE.

3.2. *XRD patterns of* MoS_2 *NSs*

As stated in previous report that metal-thiolate compounds could be prepared through the reaction of metal salts and thiol [18,19]. In this case, MoS_2 NSs was synthesized using 1-ODT as sulfur source (MoS_2–C_{18}). Fig. 3(a) shows the XRD patterns of MoS_2–C_{18} synthesized at 280 °C for 240 min. There are three obvious diffraction peaks at 2° of 33.5°, 39.5°and 58.3°, which are corresponding to (1 0 1), (1 0 3) and (1 1 0) planes of 2H-MoS_2. The results indicate that 2H phase MoS_2 is synthesized. This MoS_2 phase belongs to hexagonal crystal system with P-6m2 (187) space group (JCPDS card 24-0513) and the crystal parameters is $a = b = 0.3166$ nm, $c = 1.229$ nm. The wider diffraction peaks are attributed to the thinner MoS_2 sheets. As quasi-2D compound, MoS_2 was composed of three atom layers (S–Mo–S) stacked together by weak van der Waals interactions [20–22]. The schematic model for the layer structure of MoS_2 is given in Fig. 3(b), in which it can be seen that Mo atom layer is hold in two S atom layers.

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