



Graphene/surfactant-assisted synthesis of edge-terminated molybdenum disulfide with enlarged interlayer spacing

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ABSTRACT

The paper presents a facile and effective method to fabricate the new type MoS₂ with expanded interlayer spacing (~9.70 Å) and high-density edges in the presence of graphene oxide (GO) and surfactant. The abundant oxygen-containing groups on GO surfaces can provide nucleation sites through electrostatic interaction with the assistance of surfactant to promote heterogeneous nucleation of MoS₂ on GO surfaces. During reaction, GO was reduced to graphene (rGO) by eliminating the oxygen-containing groups. The nonwettability between MoS₂ and rGO compels the growing MoS₂ nanosheets to stretch out of the rGO surfaces, leading to the high-density edges. Besides, the excess surfactant can insert the interlayer of MoS₂, causing the enlarged interlayer spacing. The obtained MoS₂ could exhibit improved catalytic activity and the synthetic approach presented here may be extended to grow other transition metal dichalcogenide materials.

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1. Introduction

Molybdenum disulfide (MoS₂) has been widely investigated due to its unique properties and anisotropic structure [1], which make it a promising material in various applications such as photocatalysis [2], energy storage [3], and chemical sensors [4]. As a typical transition metal dichalcogenide (MX₂), where M represents a transition metal and X represents a chalcogen (S, Se, or Te), MoS₂ is composed of a layered structure with weak Van der Waals bonding between adjacent sandwiched S-Mo-S layers. Layered MoS₂ usually expose the basal planes as the terminating surface with minimal roughness and dangling bonds, which are ideal for electronic device applications [5,6]. In contrast, less effort has been made to use the edges of MoS₂. The edges of MoS₂ are full of dangling bonds and chemically active to manipulate the catalytic activity of the layered materials. Recently, the enlarged interlayer spacing has also been acknowledged as an important parameter to enhance catalytic properties of MoS₂ [7]. Hence, it is more promising to fabricate MoS₂ that can simultaneously exhibit both high-density edges and expanded interlayer spacing, which can synergistically improve performance of the MoS₂ for many important catalytic reactions including hydrogen evolution reaction, hydrodesulfurization, oxygen reduction reactions, and methane conversion.

However, to date, only a few papers have been reported for the synthesis of high-density edges MoS₂ with normal interlayer spacing through chemical vapor deposition [8]. Here, we propose a scalable and effective method to fabricate nanostructured MoS₂ with high-density edges and interlayer-expanded features. The resulting MoS₂ structure was characterized using a wide range of microscopic and spectroscopic techniques. The possible synthesis mechanism was proposed.

2. Experimental section

All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received. Graphene oxide (GO) was produced by the modified Hummers method [9]. In brief, GO and cetyltrimethylammonium bromide (CTAB) were added in deionized water under vigorous stirring. Then, Na₂MoO₄·2H₂O was dissolved into the mixture, following by addition of thiourea and NaBH₄. The resulting solution was transferred into stainless steel autoclave and maintained at 220 °C for 24 h. To improve the crystallinity, the obtained samples (CTAB-MoS₂/G) were further calcinated at 800 °C in Ar for 2 h (the detailed synthesis procedure was described in the Supporting Information).

The samples were examined by X-ray powder diffraction (XRD, Bruker, Germany). Microstructural characterizations were investigated by scanning electron microscopy (SEM, JSM-7001F, Japan) and transmission electron microscopy (TEM, JEOL-2010, Japan). Raman spectra were performed using a Raman microscope

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(Raman, Thermo Fisher, USA). Fourier transform infrared spectra were measured on a spectrometer (FTIR, iSSO, USA).

3. Result and discussion

Schematic illustration of graphene/surfactant-assisted synthesis of edge-terminated MoS₂ with enlarged interlayer spacing is shown in Fig. S1. At the early reaction stage, the abundant oxygen-containing groups of GO surfaces interact with the positive charged ammonium ion of CTAB to generate cationic-adsorbed GO. Then, the negatively charged MoO₄²⁻ adsorbed on cationic-adsorbed GO surfaces through ionic interaction, which provided nucleation sites to promote heterogeneous nucleation of MoS₂ on GO surfaces. The increased hydrophobicity of GO associated with the conversion of GO to reduced GO (rGO) resulted in the nonwettability between MoS₂ and rGO, which forced the growing MoS₂ nanosheets to protrude out of rGO surfaces, leading to the high density of MoS₂ edges. The subsequent calcination could effectively improve the crystallinity of the obtained samples (Fig. S2).

Fig. 1a presents XRD patterns of the obtained samples. The XRD pattern of pure-MoS₂ can be well indexed to hexagonal 2H-MoS₂ (JCPDS 73-1503). The major XRD peak at 14.2° corresponds to the (0 0 2) reflections of closely stacked layered structure with an interlayer spacing of 6.20 Å. For the XRD pattern of CTAB-MoS₂/G, it can be seen that two peaks at high-angle region (32° and 57°) are well indexed to (1 0 0) and (1 1 0) peaks of the MoS₂, indicating the same atomic arrangement along the basal planes of MoS₂ in CTAB-MoS₂/G. But two new broaden peaks (marked by *) with diploid relationship appears at low-angle region with d spacing of 9.70 Å and 4.85 Å, respectively. This is similar to the XRD pattern of CTAB-MoS₂. The diploid relation between the d spacing clearly indicates the formation of a new MoS₂ structure with enlarged interlayer spacing of 9.70 Å compared with that of 6.20 Å in 2H-MoS₂. Moreover, the calculated XRD pattern

(Fig. 1a, top) of MoS₂ using an interlayer spacing of 9.70 Å along the c axis was found to agree well with experimentally collected CTAB-MoS₂ pattern, revealing the validity of the as-built structural model.

Recent works also reported a large interlayer spacing of 9.50 Å or 9.40 Å in hydrothermally prepared MoS₂, which however were ascribed to oxygen incorporation [10] or DMF species incorporation [7]. Herein, the enlarged interlayer of our sample is likely due to the intercalation of CTA⁺. The insertion of CTA⁺ into the sample was confirmed by FTIR analysis. Fig. 1b displays FTIR spectrum of CTAB-MoS₂/G. Before the calcination, CTAB-MoS₂/G precursor displays two peaks at 2919 cm⁻¹ and 2853 cm⁻¹ which are assigned to C-H stretching vibration of -CH₃ and -CH₂ in CTA⁺. The peak at 1481 cm⁻¹ belongs to the asymmetric δ_{C-H} (rocking vibration) of -CH₃ and -CH₂. All of these peaks corresponding to CTA⁺ disappeared completely after calcination due to the carbonization of CTA⁺.

SEM and TEM analyses were performed on CTAB-MoS₂/G. As shown in Fig. 1c–e, the surface of CTAB-MoS₂/G is terminated by MoS₂ edges. From HRTEM image (Fig. 1f), the S-Mo-S layers with a curved stripe-like feature can be observed and the layer-to-layer spacing is about 9.70 Å, which is consistent to XRD results. The selected-area electron diffraction pattern shows the polycrystallinity of CTAB-MoS₂/G with concentric rings (Fig. S3). EDX spectrum indicates that the obtained sample mainly contains Mo, S, and C elements (Fig. S4). To better characterize the sample, the microstructures of pure-MoS₂, CTAB-MoS₂, and pure-MoS₂/G are also characterized. As shown in Fig. 2a, pure-MoS₂ exhibits a bulk-like morphology. The interlayer spacing is found to be 6.20 Å (Fig. 2g). The obtained CTAB-MoS₂ nanosheets that are tightly stacked together (Fig. 2b) and the interlayer spacing (9.70 Å, Fig. 2h) is the same to that of MoS₂ synthesized in existence of CTAB and GO. In addition, without CTAB, almost no MoS₂ nanosheets can be found on the surface of rGO (Fig. 2c and f) due to the absence of nucleation sites.

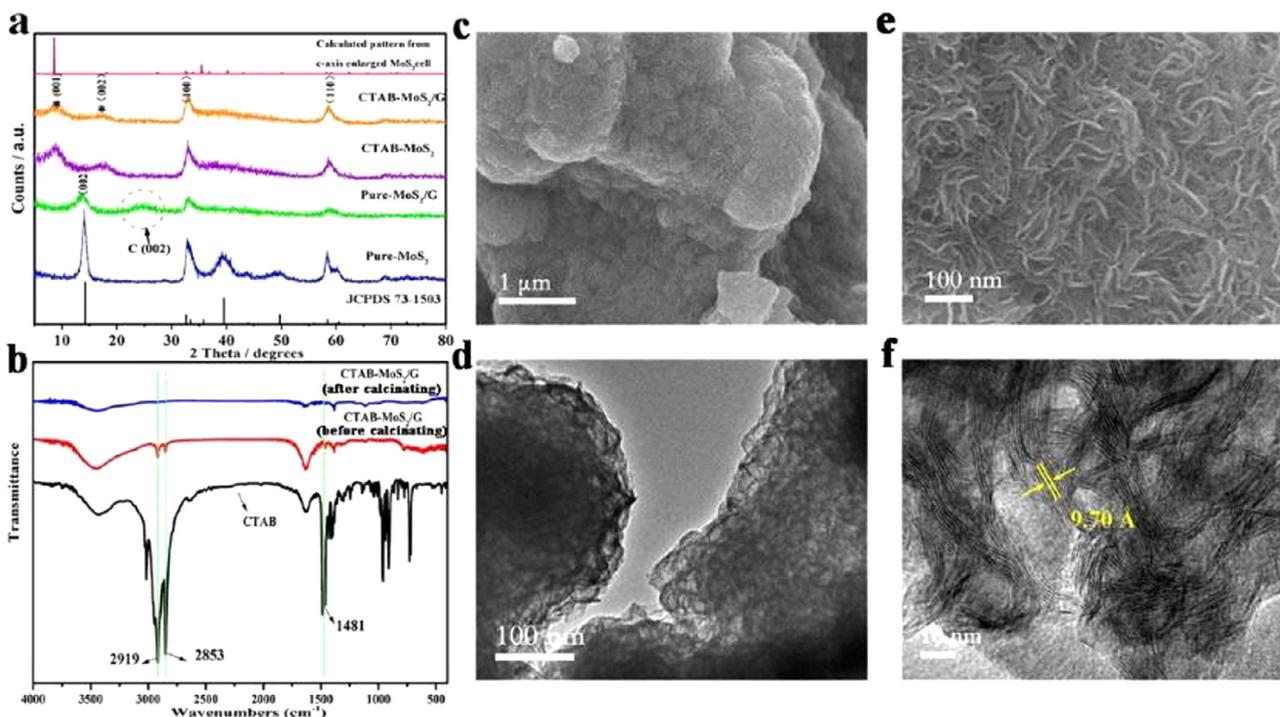


Fig. 1. (a) XRD patterns of samples. (b) FTIR spectra of CTAB-MoS₂/G. (c, e) SEM images (d, f) TEM images of CTAB-MoS₂/G.

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