

# Hydrothermal Synthesis of MoS<sub>2</sub> and Its Pressure-Related Crystallization

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**Crystalline, poorly crystalline, and single-layer MoS<sub>2</sub> were synthesized using a hydrothermal method at low temperature (170–200°C) through changing pressure and time. XPS, XRD, and TEM were used to study the products. It was found that the stacking of the single layers was closely related to the pressure in the autoclave. A model was presented to explain this phenomenon.**

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**Key Words:** MoS<sub>2</sub>; single-layer; pressure-related; hydrothermal.

## INTRODUCTION

The structure and properties of molybdenum disulfide are of special interest because of their enormous potential as lubricants (1) and as hydrodesulfurization catalysts (2). Crystalline MoS<sub>2</sub> has a sandwich interlayer structure formed by stacking of the (S–Mo–S) layers in the direction [001] (3). The layers are loosely bound to each other only by van der Waals forces, which account for easy cleavage of (S–Mo–S) layers in the direction [001]. Compared with the crystalline 2H, 3R, and 1T-MoS<sub>2</sub> (3, 4, 5), there exist three kinds of ill-crystallized MoS<sub>2</sub> based on XRD patterns, namely, amorphous (6), single-layer (SL) (7), and poorly crystalline MoS<sub>2</sub> (8). According to Chianelli *et al.* (6), the main difference between amorphous and poorly crystalline MoS<sub>2</sub> was considered to be the appearance of the 002 and 110 diffraction or not in their XRD patterns. The two kinds of MoS<sub>2</sub> usually have unique catalytic and electrochemical properties not present in the corresponding crystalline phases (9, 10) and the activity generally increases with decreasing crystallinity. SL MoS<sub>2</sub> has an XRD pattern different from those of the amorphous and poorly crystalline MoS<sub>2</sub> (7). The absence of the 002 diffraction and the appearance of the 110 diffraction indicate that the SL MoS<sub>2</sub> is an aggregate of

S–Mo–S single layers and that the stacking of them has not taken place (7, 11). Crystalline MoS<sub>2</sub> powders have been prepared by the elemental reaction in vacuum at high temperature (12) or by self-propagating high-temperature synthesis (13). Calcinating amorphous and poorly crystalline MoS<sub>2</sub> in vacuum or in an inert atmosphere can produce crystalline MoS<sub>2</sub>, too (14–16). Amorphous and poorly crystalline MoS<sub>2</sub> can be prepared not only by thermal decomposition of ammonium thiomolybdates at relatively low temperatures (14–16) but it can also be synthesized by metathesis reactions between molybdenum halides and alkali-metal sulfides or covalent sulfating agents in organic solvents at moderate temperature (17, 18). SL MoS<sub>2</sub> was often prepared using the exfoliation method (7). Recently, Afanasiev *et al.* synthesized single layers of MoS<sub>2</sub> by a simple method and the single layers had to be stabilized by a surfactant (19).

Here, we report the synthesis of crystalline, poorly crystalline, and single layers of MoS<sub>2</sub> by a hydrothermal method at low temperature through changing reaction pressure and time. A model is presented to explain the relation between pressure and crystallization.

## EXPERIMENTAL

### Preparation of Samples

All the reagents used were of analytical grade purity (Shanghai Chemistry Co.) and were used without further purification. A typical procedure is as follows. Four Teflon-lined stainless steel autoclaves of capacity 25 ml were used in the synthesis. Ammonium molybdate [(NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O], 1 g, elemental sulfur, 0.35 g, and 8 ml of hydrazine monohydrate (86%) were put in each autoclave. The autoclaves were then filled with distilled water to 70–80% of the total volume. Two autoclaves were tightly sealed and maintained at 170–200°C for 72 h and 30 days, separately. The corresponding two samples were named M1 and M2. The other two autoclaves, which were also heated at the same

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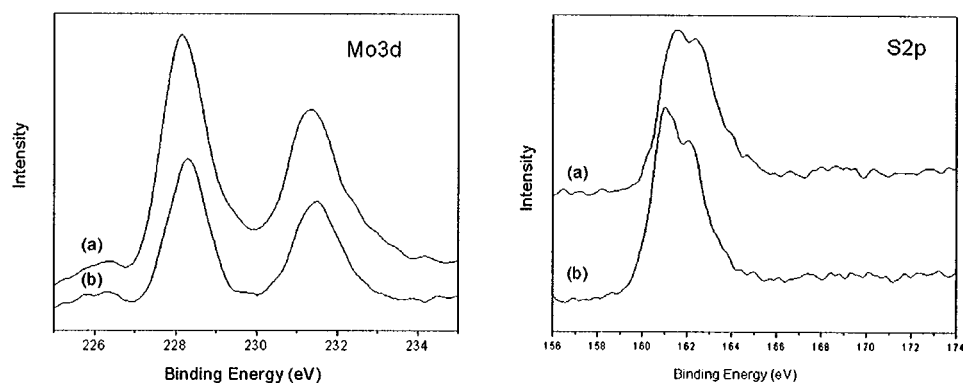


FIG. 1. Mo3d and S2p XPS spectra of (a) **M1** and (b) 2H-MoS<sub>2</sub>.

temperature (170–200°C) for 72 h and 30 days, were sealed in such a way that the gases could gradually leak out of the autoclaves in the process of heating and a lower pressure (compared to the two tightly sealed autoclaves) was maintained. The corresponding two samples were called **M3** and **M4**. After heating, the autoclaves were cooled naturally. The resulting deep-colored powder was filtered and washed with water, diluted hydrochloric acid, and ethanol, successively. The final products were dried in vacuum at 80°C for 2 h.

#### Characterization of Samples

The X-ray photoelectron spectra (XPS) were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer with an exciting source MgK $\alpha$  (1253.6 eV) in high vacuum ( $5 \times 10^{-9}$  Pa). X-ray powder diffraction (XRD) patterns were recorded with a MAX 18 AHF X-ray diffractometer (MAC Science Co. Ltd) with CuK $\alpha_1$  radiation ( $\lambda = 1.54056$  Å). The morphologies of the final products were observed by transmission electron microscopy (TEM) using a Hitachi H-800 transmission electron microscope. XPS spectra and XRD patterns of analytically pure 2H-MoS<sub>2</sub> reagent were recorded in order to compare them with those of the samples.

### RESULTS AND DISCUSSIONS

XPS measurements of the so-prepared samples indicated that the binding energies of Mo ( $3d_{5/2}$ ) and Mo ( $3d_{3/2}$ ) are ca. 228.1 and 231.1 eV, and that of S ( $2p_{3/2}$ ) and S ( $2p_{1/2}$ ) are ca. 161.6 and 162.8 eV, the same as that for 2H-MoS<sub>2</sub> (20). The binding energy of S ( $2s$ ) at ca. 226.4 eV is characteristic of S<sup>2-</sup>. Figure 1 shows the binding energies of Mo3d and S2p of **M1** and 2H-MoS<sub>2</sub>, other samples have similar XPS spectra. Analysis of the Mo ( $3d$ ) and S ( $2p$ ) peak intensities gave a S/Mo atomic ratio of 2.00 to 2.08. Chemical analysis of sample **M1**, **M2**, **M3**, and **M4** gave a S/Mo atomic ratio

range of 2.0 to 2.1, which is in agreement with the XPS measurement. Thus, the so-prepared samples should be MoS<sub>2</sub>.

Figure 2a is the XRD pattern of sample **M1**, which shows only a broad, weak envelope beginning at about  $2\theta = 30^\circ$  and continuing out above  $60^\circ$ , the two maxima approximately locate at the 100 and 110 positions of bulk 2H-MoS<sub>2</sub> (21). The XRD pattern resembles that of the single-layer MoS<sub>2</sub> prepared by the exfoliation method (7). The absence of the 002 reflection suggests the absence of stacking, thus, sample **M1** should be an aggregate of single sheets of MoS<sub>2</sub> (11, 19). Figure 2b shows the XRD pattern of sample **M2**, which is almost the same as Fig. 2a. Sample **M1** had a dark gray color and sample **M2** had a pure black color.

Figure 2c shows the XRD pattern of sample **M3**. The appearance of the  $2\theta = 14.4^\circ$  hump suggests the stacking of the single layers (11, 19). Thus, sample **M3** should be the poorly crystalline MoS<sub>2</sub>. It was found that this hump did not appear except when a leakage took place. The leakage of the autoclave indicated a decrease of pressure in it, which probably meant that low pressure in the autoclave was helpful in the stacking of single layers. Figure 2d is the XRD pattern of sample **M4**, which can be ascribed to the XRD pattern of 2H-MoS<sub>2</sub> (21). Figure 2d shows that sample **M4** had a fairly good crystallization just like the MoS<sub>2</sub> prepared at relatively high temperature (11, 19). Comparing Fig. 2c with Fig. 2b, it is even clear that pressure played an important role in the crystallization of the MoS<sub>2</sub>-stacking of the single layers. At high pressure, the single layers were difficult to stack and at low pressure the stacking became easy. Sample **M4** had a silvery dark gray color in sharp contrast with sample **M2**. Sample **M3** had a dark gray color just like sample **M1**. Under TEM, all the samples had similar “rag” morphology just like those reported by Chianelli *et al.* (8). Figure 3 shows the TEM images of samples **M2** and **M4**. It can be seen that the “rag” of **M2** is smaller than that of **M4**.

Considering the structure of the single-layer MoS<sub>2</sub> prepared by the exfoliation method (22), a model was put

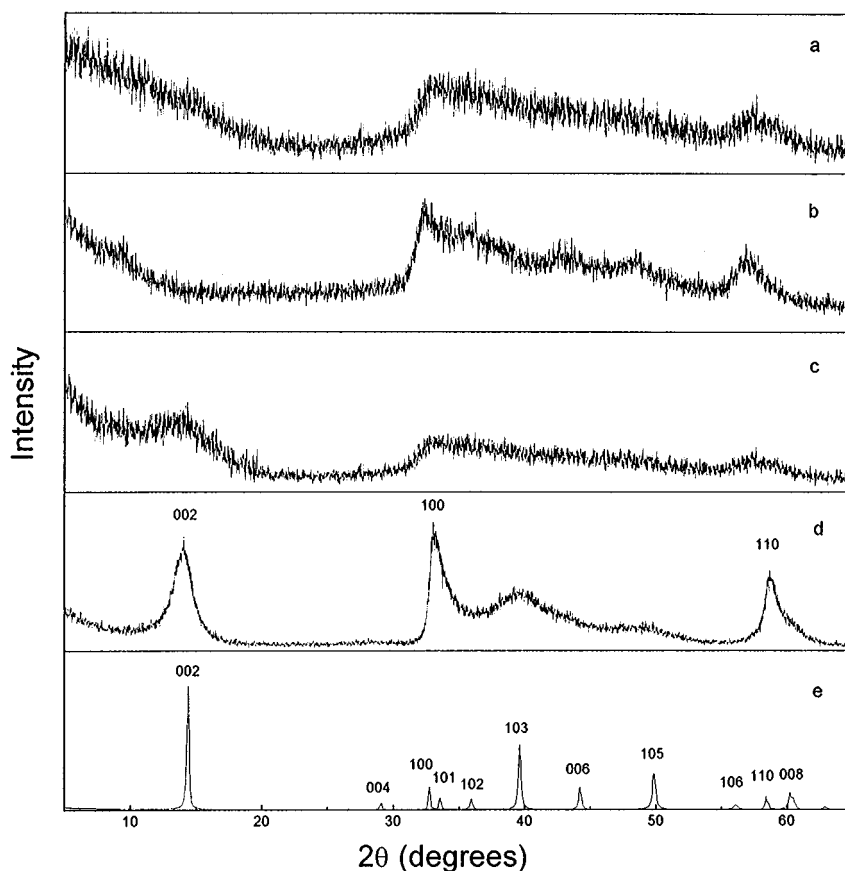


FIG. 2. XRD patterns of (a) M1, (b) M2, (c) M3, (d) M4, and (e) 2H-MoS<sub>2</sub>.

forward to explain the above experiments. It was thought that the single layers of the so-prepared MoS<sub>2</sub> had the ability to adsorb substances on them, such as H<sub>2</sub>O and NH<sub>3</sub>. In other words, it could be considered that some substances could stabilize the single layers. The interaction between the adsorbed substances and the single layers themselves became strong under high pressure, which prevented the single layers from stacking. When a gradual leakage took place in the autoclaves, due to the lower pressure and the loss of the adsorbed substances, this interaction became weak and the single sheets were able to stabilize mutually by stacking into a crystalline structure.

If the model actually reflects what happened in the autoclaves, it seems to indicate that when a pressure is acted on an ultra thin film (for example, a single layer of MoS<sub>2</sub>), the effects may be different from the bulk. Thus, studies about amorphous materials, especially those with a layered structure, under high pressure in solvents (organic and inorganic) may be of special importance. New properties of materials, even new structures, may be found through this method.

In conclusion, crystalline, poorly crystalline, and single-layer MoS<sub>2</sub> were synthesized by hydrothermal method at low temperature (170–200°C) through changing reaction

pressure and time. It was found that the stacking of the single layers was closely related to the pressure in the autoclave. At high pressure, the single layers were difficult to stack and at low pressure the stacking became easy. A model, which assumes that the pressure-modulated inter-

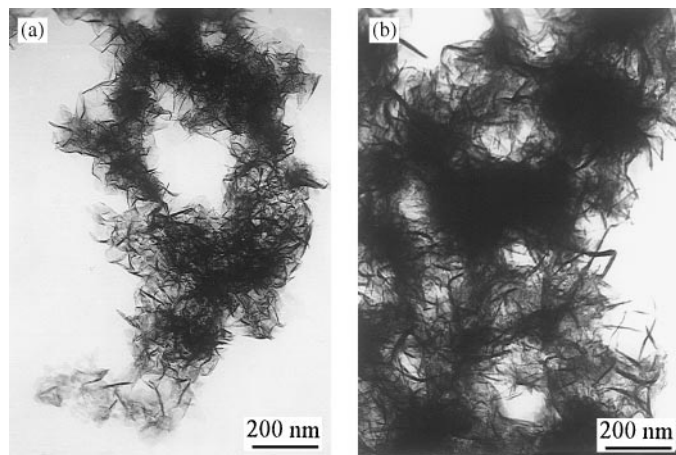


FIG. 3. TEM images of (a) M2 and (b) M4.

action between the adsorbed substances on the single layers and the single layers themselves controlled the stacking, was presented to explain this phenomenon.

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