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Simple solution route to uniform MoS_2 particles with randomly stacked layers

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Abstract

MoS_2 particles of uniform size (ca. 70 nm) consisting of random and loosely stacked layers have been synthesized from hydrazine solution with $(NH_4)_2Mo_3S_{13}$ as the precursor at 180 °C for 16 h under hydrothermal conditions. The particles were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HREM). The influences of reaction conditions are discussed while a mechanism is proposed to explain the formation of this peculiar morphology.

Keywords: A. Inorganic compounds; A. Chalcogénides; B. Chemical synthesis

1. Introduction

There has been considerable interest in the transition metal dichalcogenide layered compounds, a group of anisotropic materials with strong bonding within the layers and weak interlayer interactions [1]. As one of the members of this family, MoS_2 has numerous applications as a hydrodesulfurization catalyst [2], as a solid-state lubricant [3], as an electrode in high-energy density batteries [4], and as an intercalation host to form new materials [5].

Conventionally, the synthesis of MoS_2 powders involves thermal decomposition of ammonium tetrathiomolybdate [6], or by the reaction of stoichiometrically mixed molybdenum and sulfur powders in vacuum at high temperature [7]. Metathesis reactions [8], gas-phase decomposition of $Mo(CO)_6$ in the presence of H_2S [9], and even sonochemical [10] or γ-irradiation methods [11] to produce finely dispersed MoS_2 have been explored. Afanasiev et al. [12] synthesized single-molecular-layer (SML) MoS_2 in aqueous solution in the presence of an organic surfactant. Recently, Feldman et al. [13]

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reported that nested inorganic fullerene-like MoS_2 could be prepared from the reaction between MoO_3 and H_2S in a H_2 atmosphere at about 800 °C. Liao et al. [14] have also fabricated MoS_2 fibers at room temperature.

Herein, we report the preparation and characterization of 2H-MoS_2 in a new morphological structure. The products were uniform particles that exhibited randomly stacked layers at high magnification.

2. Experimental

All the reagents used were of analytical grade purity (Shanghai Chemistry Co., Ltd.) and were used without further purification.

The precursor $(NH_4)_2Mo_3S_{13}$ was prepared according to the literature [15]. The preparation process of MoS_2 was as follows: 0.5 g $(NH_4)_2Mo_3S_{13}$ and 10 ml hydrazine monohydrate ($N_2H_4{\cdot}H_2O$) were put in a Teflon-lined stainless steel autoclave of 50 ml capacity (caution: excess hydrazine is dangerous because of the sudden production of gas in a confined space). Distilled water was used to fill the tank to 60% of the total volume. The autoclave was maintained at 180 °C for 16 h, then allowed to cool to room temperature. The resulting dark-gray powders were filtered and washed with distilled water and anhydrous ethanol. Then the final products were dried in a vacuum at 50 °C for 5 h. The solids were annealed for 2 h under a Ar flow at 300, 450, and 600 °C, respectively.

Phase identification was performed by X-ray powder diffraction (XRD) using an MXP18AHF X-ray diffractometer (MAC Science Co., Ltd.) with Cu Kα radiation ($\lambda = 1.54056$ Å). The samples were scanned at a scanning speed of 0.02 s^{-1} in the 2θ range of 5–65°. X-ray photoelectron spectroscopy (XPS) spectra were recorded with a VGESCALAB MKII X-ray photoelectron spectrometer, using nonmonochromatic Mg Kα X-ray as the excitation source. Morphology and size information of the precipitates were observed on a Hitachi Model H-800 transmission electron microscopy (TEM), using an accelerating voltage of 200 kV.

3. Results and discussion

The reactions involved here can be described as follows:

$$(NH_4)_6Mo_7O_{24} \cdot 4H_2O + (NH_4)_2S_x \underset{160\,^\circ C}{\overset{H_2O}{\rightarrow}} (NH_4)_2[Mo_3S(S_2)_6] \cdot nH_2O \; (n = 0\text{–}2) \tag{1}$$

$$(NH_4)_2Mo_3S_{13} + 3N_2H_4 \underset{180\,^\circ C}{\overset{H_2O}{\rightarrow}} 3N_2 + 3MoS_2 + 2NH_3 + 7H_2S \tag{2}$$

First, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ reacted with $(NH_4)_2S_x$ in aqueous solution, forming the precursor $(NH_4)_2Mo_3S_{13}$ [15]. Second, $(NH_4)_2Mo_3S_{13}$ was reduced by hydrazine at 180 °C and finally MoS_2 precipitated from the solution. As a reducing agent, hydrazine is volatile and easily decomposes. It can decompose thermally to produce N_2, H_2 and NH_3 ($N_2H_4 \rightarrow (1/2)N_2 + NH_3 + (1/2)H_2$) [16]. Thus the as-produced H_2 could react with the precursor.

The TEM image of the sample prepared at 180 °C is shown in Fig. 1a. It indicates that the product is composed of uniform particles with an average diameter of 70 nm. These particles are dispersed without aggregation. The electron diffraction (ED) pattern shows that they are amorphous. The TEM

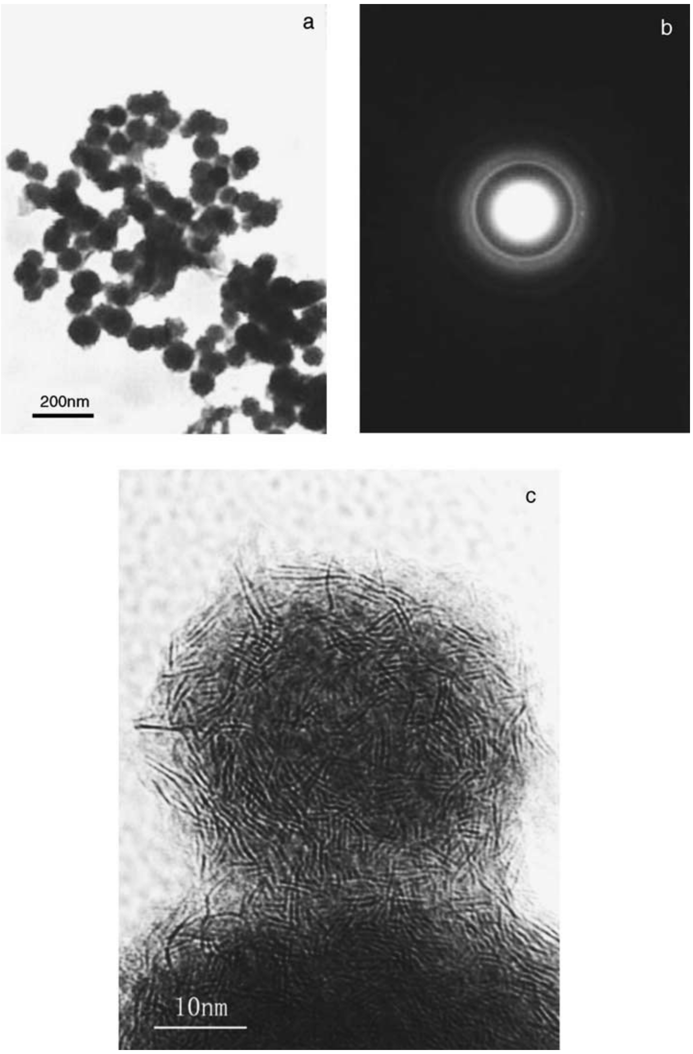

Fig. 1. TEM images of MoS_2: (a) prepared at 180 °C; (b) the electron diffraction pattern of MoS_2 after annealing at 450 °C; (c) HREM image of the sample after annealing at 450 °C.

image of the sample after annealing at 450 °C was similar to Fig. 1a. It is obvious that the morphology and the size of the product are kept during the annealing process. The typical electron diffraction pattern (Fig. 1b) reveals the polycrystallinity of the annealed sample while all of the electron diffraction rings could be indexed to the pattern of 2H-MoS_2. Fig. 1c shows the high resolution image of the sample after annealing at 450 °C. Unlike the image of highly ordered planes of MoS_2 along the *c*-direction which is expected in the 2H-MoS_2, the micrograph of the sample exhibits domains of short-range layered arrays stacked in a fairly chaotic fashion. The stacking number varies from 2 to 6, and the interlayer distance is close to 0.6 nm, which corresponds to the (0 0 2) d-spacing of the 2H-MoS_2 lattice fringe [10]. This suggests that the MoS_2 constitutes a new morphology between amorphous material and the thermodynamically stable 2H allotrope.

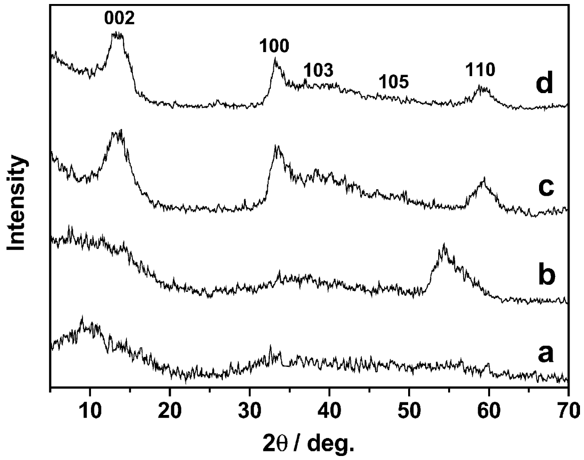

Fig. 2. X-ray diffraction pattern of MoS_2: (a) prepared at 180 °C; (b) annealed at 300 °C; (c) annealed at 450 °C; (d) annealed at 600 °C.

The disordered stacking was also demonstrated by the XRD analysis. Fig. 2a shows the XRD pattern of the product prepared at 180 °C for 16 h in the mixed solution of hydrazine and distilled water under hydrothermal conditions. As no obvious diffraction peak was recorded in the pattern the sample was virtually amorphous. The XRD patterns of the samples annealed at 300, 450 and 600 °C in a flow of argon are shown in Fig. 2b–d. At 300 °C, the (1 1 0) reflection emerged (Fig. 2b), though it shifts to lower angle. At 450 °C, three main diffracting lines are clearly observed (Fig. 2c). This XRD pattern is consistent with the literature report of the 2H-MoS_2 phase (JCPDS 37-1492) and can be indexed to a hexagonal cell with lattice parameters $a = 3.159$ and $c = 12.162$ Å. The XRD pattern of the sample annealed at 600 °C (Fig. 2d) is quite similar to Fig. 2c, indicating the relative stability of the crystallinity in an appropriate temperature range. The most pronounced evidence for the disordered stacking is the (1 0 0) reflection (Fig. 2c and d), which exhibits a characteristic sawtooth shape comprising asymmetrically broadened peaks [17]. Besides, the near-absence of the (1 0 3) and (1 0 5) lines, the small (0 0 2) peaks as well as the strong diffuse background are also indicative of low stacking and highly disordered packing of 2H-MoS_2 layers [18].

XPS were also measured to derive composition information of the product. From the XPS spectra (Fig. 3), the binding energy values of the as-prepared MoS_2 are 231.6 eV for Mo (3d) and 161.6 eV for S (2p), which were close to previous report [19]. The quantification of the peaks gave the ratio of Mo:S of 1:2.1, close to the stoichiometry of MoS_2.

We found that higher temperature is helpful in crystallization of the product as well as for the formation of uniform particles. The experiment carried out at lower temperature (<160 °C) leads to a more amorphous product with an irregular shape. Hydrazine is another factor in the crystallization of MoS_2. Increasing the amount of hydrazine was beneficial for the crystallinity of the product. This was due to the large quantity of N_2, H_2, and NH_3 formed by the decomposition of hydrazine [16], which could produce high pressure in the autoclave. Changing the reaction time does not change the product significantly.

It is well known that MoS_2 has a layered, graphite-like structure consisting of S–Mo–S sandwiches held together by weak van der Waals forces. It is easy for alkali metals and organic bases to intercalate in the interlayer gaps, due to a large d-spacing between two layers [1]. In our experimental conditions,

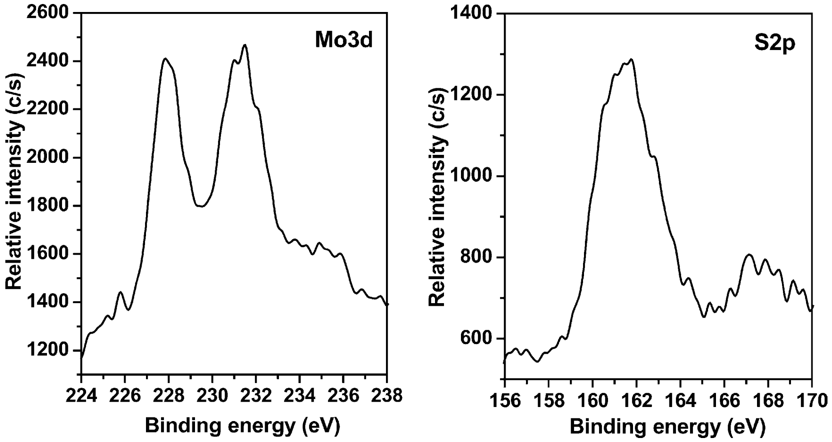

Fig. 3. XPS curves of the sample prepared at 180 °C.

H_2O and NH_3 may be inserted. The interaction between the inserted substances and the MoS_2 layers became strong under high pressure, which prevented the layers from stacking, and thus caused the limited number of these layers. Besides, the reduction step with N_2H_4 is a rapid one, thus, the time is too short to allow for particles to transfer to appropriate positions. As a spherical shape is optimal from an energetic point of view [20], disordered stacking of MoS_2 particles precipitated from the mixed solution of hydrazine and water in the autoclave.

To verify the above-proposed mechanism, a series of experiments were performed. When N_2H_4 was absent, brown MoS_3 precipitated from the solution together with a trace of MoS_2 after 14 h. Addition of hydrazine (10 ml) to the solution containing MoS_3 produced precipitation of molybdenum sulfide powders in 2 h. Obviously, the step of reduction with N_2H_4 is faster than the step of forming precursor $(NH_4)_2Mo_3S_{13}$. If H_2O was absent, the precursor could not completely dissolve in hydrazine. If the reaction was carried out at 100 °C without using an autoclave, the initial solution gave no MoS_2 precipitation.

4. Conclusions

This work describes a simple route leading to molybdenum disulfide with special morphology and properties. The product is composed of uniform (ca. 70 nm) particles, consisting of randomly and loosely stacked MoS_2 layers. This disordered stacking was also confirmed by XRD analysis. The reaction conditions and the formation mechanism were explored. The intercalation of H_2O and NH_3 as well as the rapid step of reduction with hydrazine may explain the morphological formation. This method is expected to apply for the preparation of other layered chalcogenides.

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