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Solvothermal Synthesis of Nanocrystalline MoS_2 from MoO_3 and Elemental Sulfur

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Molybdenum disulfide crystallites has been synthesized from MoO_3, S, and $N_2H_4H_2O$ in pyridine at 300°C for 12 h with good yield (> 90%). The product is characterized by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). XRD and IR analysis show that pure MoS_2 has been prepared. TEM shows that these nanoparticles are in the form of platelets. Here, a bi-step transition process from MoO_3 to MoO_2 and from MoO_2 to MoS_2 is proposed.

INTRODUCTION

Molybdenum disulfide (MoS_2) crystal has a sandwich interlayer structure formed by stacking of the (S–Mo–S) layers in the direction [001] (1). These layers are loosely bound to each other only by van der Waals forces, which accounts for easy cleavage of (S–Mo–S) layers in the direction [001]. Due to this structure, laminar molybdenum disulfide has numerous applications as a solid state lubricant (2), as a hydrodesulfurization catalyst (3), nonaqueous lithium batteries (4), and for special applications in space (5). Recently, many efforts have been contributed to prepare materials on a nanometer scale, since nanometer-sized materials can display optical, electronic, and structural properties that are seldom present in either isolated molecules or macroscopic materials. MoS_2 on a nanometer scale performs better as a solid lubricant and possibly as a catalyst or in other applications.

Traditionally, MoS_2 powders have been prepared by the solid state reaction of stoichiometrically mixed molybdenum and sulfur powders in vacuum at high temperature (6) or by thermal decomposition of ammonium tetrathiomolybdate (7). Metathesis reactions between molybdenum halides or carbonyls and alkali-metal sulfides or covalent sulfating agents in organic solvents to produce finely dispersed amorphous products at moderate temperature have been explored (8, 9). Kaner *et al.* (10) synthesized crystalline MoS_2 by self-propagating high-temperature synthesis (SHS), which is an exchange reaction between molybdenum halides and alkali-metal sulfides. Recently, Feldman *et al.* reported that MoS_2 could be prepared from MoO_3 and H_2S in an H_2 reducing atmosphere at a temperature above 800°C (11). Their method involved the production of nested inorganic fullerene-like nanoparticles. A mechanism of MoO_2 particle conversion into IF-MoS_2 was also demonstrated.

Solvothermal technology at moderate temperatures (100–400 °C) has gained increasing attention currently (12, 13). Here, we report the synthesis of nanocrystalline MoS_2 by the reaction between MoO_3 and elemental sulfur with hydrazine as reducing reagent in pyridine at moderate temperature.

EXPERIMENTAL

Molybdenum trioxide (> 99%) and elemental sulfur (99.9%) were obtained in powder form from Shanghai Chemistry Co. Analytical pure hydrazine monohydrate and pyridine were also obtained from this commerical supplier.

Preparation of samples. Powders of molybdenum trioxides, 0.576 g (4 mmol), and elemental sulfur, 0.256 (8 mmol), were ground together sufficiently. This mixture was put into a sliver-lined stainless steel autoclave of capacity 30 ml. A sufficient amount of hydrazine monohydrate (1 ml) was added into the tank. Pyridine was used to fill the tank to 70% of the total volume. The autoclave was maintained at 300°C for 12 h, then allowed to cool to room temperature. A spongy dark-gray precipitate was collected, which was washed with distilled water three times. The final product was desiccated in a vaccum box at 60°C for 5 h. It was characterized by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). Experiments with MoO_3 and S in various ratios were also carried out under the same conditions. These results are listed in Table 1.

Characterization of the sample. XRD analysis were conducted on a Rigaku Dmax γA X-ray diffractometer at

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a scanning rate of $0.05^\circ\ s^{-1}$ with 2θ raning from 10° to 70°, using graphite-monochromatic Cu$K\alpha$ radiation ($\lambda = 0.154178$ nm). A Hitachi H-800 transmission electron microscope operating at 200 kV was used for transmission electron microscopy (TEM). Imaging was collected in a bright field. Copper grids (300 mesh) coated with an amorphous carbon film were obtained commerically. Samples were prepared by placing drops of a dilute alcohol

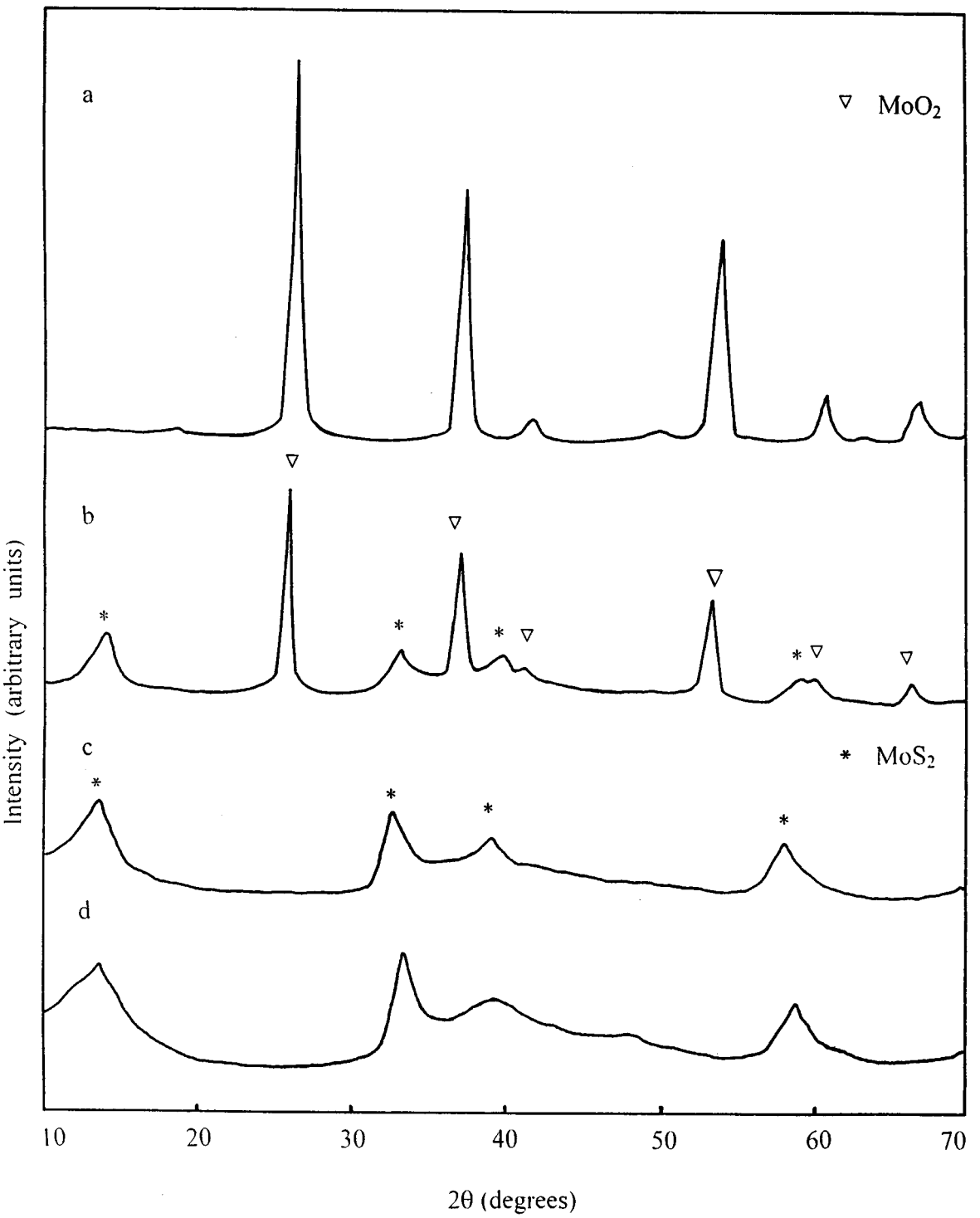

FIG. 1. XRD pattern of products with MoO_3 and S at various molar ratios at 300°C for 12 h: only MoO_3 as reactant (a); MoO_3: S = 1 : 1 (b); MoO_3 : S = 1 : 2 (c); MoO_3 : S = 1 : 3 (d).

TABLE 1
Products with MoO_3 and S at Various Molar Ratios under the Same Conditions

	Reactant (molar ratio)	Product
(a)	MoO_3	MoO_2
(b)	MoO_3 : S (1 : 1)	$MoO_2 + MoS_2$
(c)	MoO_3 : S (1 : 2)	MoS_2
(d)	MoO_3 : S (1 : 3)	MoS_2

dispersion of nanocrystallites on the surface of grids. The composition of the sample was determined by chemical analysis (14). The infrared spectrum was recorded in KBr pressed discs on a Magna IR-750 FT spectrometer.

RESULTS AND DISCUSSION

By XRD analysis, Figs 1c and d shows the XRD patterns of samples c and d. All the peaks can be indexed to 2H-MoS_2 [space group $P6_3/mmc(194)$], which correspond to the (002), (100), (103), and (110) plane of 2H-MoS_2. After refinement, the cell constants ($a = 3.16$ Å, $c = 12.40$ Å) are close to the reported data ($a_0 = 3.1616$ Å, $c_0 = 12.2985$ Å) in the JCPDS cards (37-1492). TEM observations show that MoS_2 crystallites are mainly in the uniform shape of thin platelets with diameters of about 100 nm (Fig. 2). Single particles have regular morphology. Figure 2b shows a single 200-nm-diameter particle.

The composition of the sample was determined by chemical analysis. Ratios of the starting materials have little effect on the composition of the products. Two compositions were $MoS_{1.99}$ (MoO_3 : S = 1 : 2) and $MoS_{2.02}$ (MoO_3 : S = 1 : 3).

MoS_2 adopts kind of packing structure, which can act as an intercalation host to form new material (15). Infrared spectroscopy was utilized to detect guest materials in the

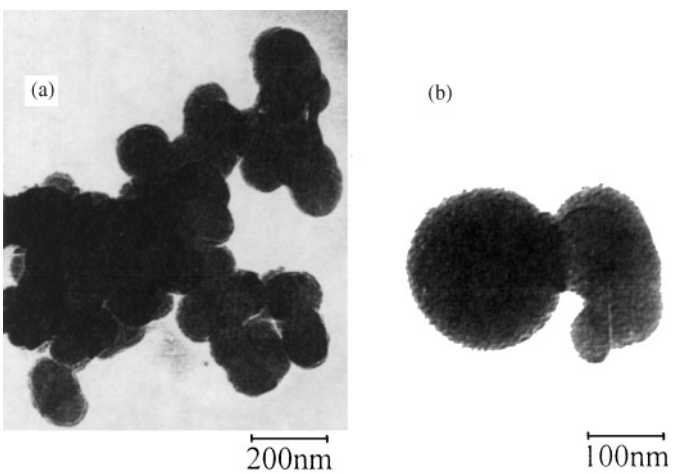

FIG. 2. TEM images of as-prepared MoS_2: (a) the main morphology of MoS_2 nanocrystallites; (b) the morphology of a single MoS_2 nanocrystallite.

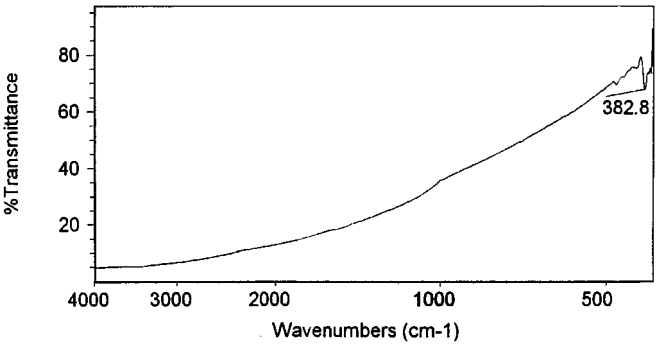

FIG. 3. IR spectrum of MoS_2 powder.

as-prepared MoS_2. Figure 3 shows the IR spectrum collected for the molybdenum disulfide mulled in KBr wafer. The absorption band at 382 cm^{-1} is due to molybdenum disulfide. No absorption bands appear in the range from 500 to 4000 cm^{-1}, indicating there is no guest molecule such as pyridine intercalated between two adjacent S–Mo–S layers.

MoS_2 forms by the reaction between MoO_3 and S in the reducing atmosphere of hydrazine. In the reaction system, hydrazine can reduce MoO_3 to MoO_2 rapidly. After addition of elemental sulfur, MoS_2 forms in the final product regardless of the primitive ratios of MoO_3 and S. If the ratios is 1 : 1, the final product is a mixture of MoS_2 and MoO_2 (Fig. 1b). If the ratio is 1 : 3, the final product is still MoS_2 (Fig. 1d). The excess of sulfur has been dissolved in pyridine. When sufficient sulfur is added to the sample in Fig. 1b, the final product is MoS_2. On the other hand, MoS_2 can also be obtained by this method with MoO_3 replaced by MoO_2. Therefore MoO_2 may be the intermediate of the transition from MoO_3 to MoS_2. As to the formation of MoS_2, the following reactions are related:

$$2MoO_3\,(s) + N_2H_4\,(l) \rightarrow 2MoO_2\,(s) + 2H_2O\,(l) + N_2(g) \quad [1]$$

$$MoO_2\,(s) + N_2H_4\,(l) + 2S\,(l) \rightarrow MoS_2\,(s) + 2H_2O\,(l) + N_2(g) \quad [2]$$

Temperature is another factor in the transition from MoO_3 to MoS_2. Reactions below 250°C require a long time. But high temperatures above 350°C may lead to decomposition of pyridine and cannot greatly improve the crystallinity of MoS_2. Thus 300°C and 12 h were chosen as reaction conditions. Pyridine is used as a solvent in this solvothermal synthesis, because it is stable to heat and can dissolve elemental sulfur similarly to benzene. Moreoever, pyridine, a heterocyclic organic compound, can mix with hydrazine.

In conclusion, nanocrystalline MoS_2 has been synthesized successfully from very crystalline molybdenum trioxide (> 2 μm in size) and sulfur in a hydrazine reducing

environment by the solvothermal method. The IR spectrum showed that MoS_2 did not form intercalating material under this solvothermal condition. MoS_2 particles were in the form of thin platelets with a narrow particle size distribution. This morphology of thin platelets is well suited to applications in solid state lubricants.

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