



SYNTHESIS OF MoSe₂ NANOCRYSTALLITES BY A SOLVOTHERMAL CONVERSION FROM MoO₃

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ABSTRACT

Nanocrystalline 2H-MoSe₂ was prepared from MoO₃, N₂H₄·H₂O, and Se in pyridine at 300°C for 12 h by a solvothermal method. A gray-black product was collected and characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis. The XRD pattern showed that a phase-pure product was prepared. TEM analysis showed that the product was polycrystalline and had plate-shaped particles with a diameter of about 40 nm. The conversion process from MoO₃ to MoSe₂ is discussed. © 1999 Elsevier Science Ltd

KEYWORDS: A. chalcogenides, A. nanostructures, A. layered compounds, B. chemical synthesis

INTRODUCTION

MoSe₂ has a layered sandwich structure, which is isostructural with MoS₂ [1]. Layers of Se–Mo–Se interact with each other by van der Waals forces, which allow adjacent layers to slide. It is easy for ions such as Li⁺ or Na⁺ to intercalate in the interlayer gaps, due to a large d-spacing between two layers. All these properties cause layered MoSe₂ to have special applications in precursors of intercalation superconductor [2], materials for conversion of sunlight into electrical energy in a photoelectrochemical cell [3–5], and solid-state lubricants [6]. On the other hand, a material can exhibit different properties when the size of its particles reach nanometer level. For example, transition-metal (Mo, W) dichalcogenide nanoparticles outperform their bulk counterparts as solid-state lubricants [7].

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Traditionally, crystalline molybdenum diselenide was synthesized by solid-state reaction between a stoichiometric amount of elemental molybdenum and selenium in a sealed evacuated tube at a temperature of at least 900°C for several days [8]. A metathetical reaction between high-valent molybdenum halides and alkali-metal selenides proceeds rapidly and yields crystalline product. This reaction is known as self-propagating high-temperature synthesis (SHS) [9]. Due to self-produced heat, this reaction system may reach a high temperature of 1050°C instantly. A similar reaction between molybdenum halides and alkali-metal selenides in organic solvents has also been explored [10], to produce amorphous MoSe₂ at room temperature. Recently, Feldman *et al.* [11] reported that MoO₃ and H₂S can be converted to nano-MoS₂ in a reducing atmosphere of hydrogen at high temperature of 800°C [11], but there is no report on the conversion from MoO₃ to nanocrystalline MoSe₂ by this method.

As a developing synthetic technology, solvothermal synthesis has gained much attention [12,13]. It is generally conducted at intermediate temperatures (100–400°C) in a sealed system. In this paper, we report the solvothermal synthesis of nanocrystalline MoSe₂ by the conversion of molybdenum trioxide and elemental selenium in a reducing environment of hydrazine (N₂H₄).

EXPERIMENTAL

Molybdenum trioxide (99.5%) and selenium (99.95%) in powder form were purchased from Shanghai Chemical Co. Analytical-grade hydrazine monohydrate (N₂H₄·H₂O) and pyridine were also obtained from this supplier.

A stoichiometric amount of MoO₃ and Se powder was put into a stainless steel autoclave with a 50 ml capacity. Then an appropriate amount of N₂H₄·H₂O was added into the tank. Pyridine was added to fill the autoclave up to 75% of the total volume. The autoclave was sealed and maintained at 250–300°C for 12 h, then cooled to room temperature naturally. A gray-black precipitate was collected. After being washed with absolute ethanol and distilled water, the final product was dried in a vacuum box at 60°C for 4 h.

The final product was characterized by powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD analysis was conducted on a Rigaku D/max γA X-ray diffractometer at a scanning rate of 0.05° s⁻¹ with 2θ ranging from 10° to 70°, using graphite-monochromatic Cu Kα radiation (λ = 1.54178 Å). A Hitachi H-800 transmission electron microscope operating at 200 kV was used for TEM analysis. Content of Mo and Se in this sample was determined by ICP-AES (inductive coupling plasma-atomic emission spectroscopy) after oxidation of the sample in aqua regia and then dissolution of caustic soda.

RESULTS AND DISCUSSION

Figure 1a shows the XRD pattern of the as-prepared sample. Four broadened peaks, which correspond to the (002), (100), (103), and (110) planes of 2H-MoSe₂, respectively, are observed. These broadened peaks suggest that there is a small amount of amorphous product. The TEM microphoto (Fig. 2a) of the sample showed that the MoSe₂ particles were in uniform platelet shape, with an average size of about 40 nm. Also, this microphoto showed that there was a small fraction of amorphous product. Electron diffraction circles (Fig. 3) revealed the polycrystallinity of the sample.

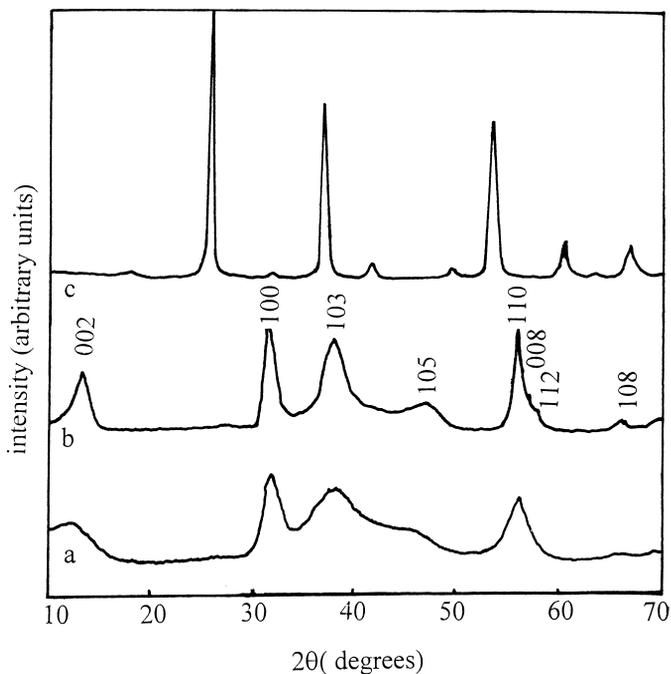


FIG. 1

Powder X-ray diffraction patterns for (a) the sample prepared by the reaction of MoO_3 , Se, and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in pyridine at 300°C for 12 h; (b) the sample after annealing in nitrogen atmosphere at 500°C for 2 h; and (c) MoO_2 prepared by the reaction between MoO_3 and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ at 300°C for 12 h.

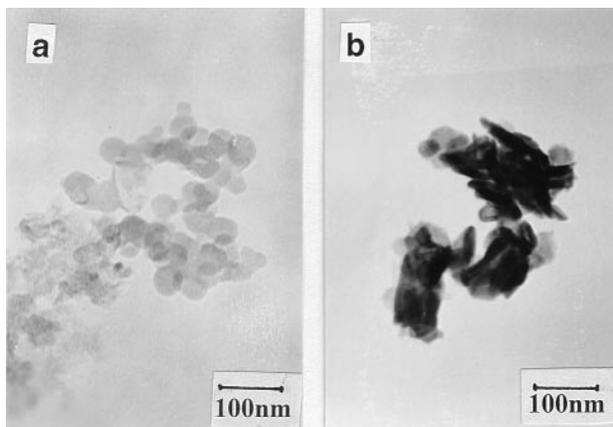


FIG. 2

TEM image showing (a) the main morphology of the as-prepared sample and (b) the aggregation of the sample after annealing at 500°C .

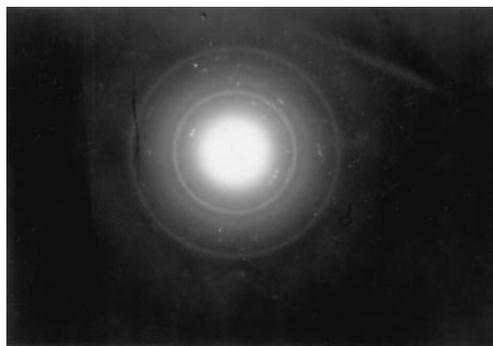


FIG. 3
Electron diffraction pattern for the as-prepared sample.

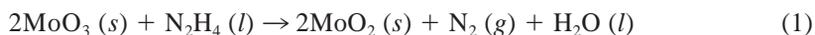
When the sample was annealed in nitrogen atmosphere at 500° for 2 h, all diffraction peaks could be indexed to hexagonal MoSe₂ (space group *P6₃/mmc*) (Fig. 1b). After refinement, the calculated cell constants ($a = 3.29$, $c = 12.93\text{Å}$) were close to those reported on JCPDS card 29-914. Annealing may have led to aggregation of the sample, as shown in Figure 2b.

The content of Mo and Se for this sample was MoSe_{2.07}, as determined by ICP-AES experiments. The sample annealed in nitrogen atmosphere had an obviously different composition.

2H-MoSe₂ nanoparticles were formed by the reactions between MoO₃ and Se in a reducing environment of hydrazine. The formation of MoSe₂ undergoes a bi-step conversion from MoO₃ to MoO₂ and from MoO₂ to MoSe₂. If no elemental Se is present in the system, MoO₃ is rapidly reduced to monoclinic MoO₂ by N₂H₄ (Fig. 1c). When MoO₂ is in place of MoO₃, it also is converted to MoSe₂.

Hydrazine acts as a reducing reagent in the conversion process of MoO₃. If we assume H₂ to be an intermediate, there are two possible routes for the decomposition of hydrazine [14]. It can decompose thermally to produce N₂, H₂, and NH₃ ($\text{N}_2\text{H}_4 \rightarrow 1/2 \text{N}_2 + \text{NH}_3 + 1/2 \text{H}_2$); however, at sufficiently high temperatures, N₂ and H₂ are the only products ($\text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 2\text{H}_2$). In this work, the reaction was conducted at 300°C. This may be the main reaction.

MoO₃ is converted to MoSe₂ via MoO₂ in the reducing environment of N₂H₄. The conversion process may be schemed as follows:



Pyridine has an important role in the conversion of MoO₃ to MoSe₂. Although there is no report that elemental selenium can dissolve in pyridine, it is possible that pyridine can cause a small fraction of selenium to dissolve in the solution phase at 300°C. On the other hand, pyridine activates the surface MoO₃ and Se powder effectively and provides a fresh surface for the reaction.

The effect of temperature on the conversion of MoO₃ to MoSe₂ was also studied. Lower temperature leads to more amorphous product. Higher temperature is helpful in crystallization of the product, but may lead to decomposition of the solvent pyridine. Thus, we selected a moderate temperature range (250–300°C), which is below the critical temperature (346.8°C) of pyridine [15].

CONCLUSIONS

MoO₃ and Se were converted to 2H-MoSe₂ nanocrystallites in the environment of N₂H₄·H₂O via the pyridine-thermal route, in the temperature range of 250–300°C. The product yield obtained was good (90%) according to the amount of Se. Solvothermal conversion perhaps affords a simple route to synthesize nanometer-sized 2H-MoSe₂. The conversion of MoO₃ and Se to MoSe₂ is a two-step process via MoO₂. Pyridine plays an important role in the conversion of MoO₃ to MoSe₂. It activates Se, provides fresh surfaces for the reaction, and promotes the reaction.

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