

## A Novel Route to Obtain Molybdenum Dichalcogenides by Hydrothermal Reaction

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Hydrothermal reactions between aqueous  $\text{Na}_2\text{MoO}_4$ ,  $\text{Na}_2\text{ESO}_3$  (E=S, Se) and hydrazine monohydrate at 135 °C for 12 h produce phase-pure  $\text{MoS}_2$  and  $\text{MoSe}_2$  with good yield of about 90%. X-ray powder diffraction, chemical analysis and X-ray photoelectron spectroscopy were used to characterize the structure and composition of the products annealed at 350 °C. Transmission electron microscopy images show that the samples of  $\text{MoS}_2$  and  $\text{MoSe}_2$  consist of nano-crystallites with average particle size of 4 nm and 7 nm, respectively.

Molybdenum dichalcogenides have drawn considerable attention due to their technological importance as high-energy density battery cathodes,<sup>1</sup> lubricants<sup>2</sup> and hydrodisulfuration catalysts<sup>3</sup> etc. Their sandwich interlayer structure allowed them to act as intercalation host to derive novel materials with modified physical properties.<sup>4</sup> Traditionally, the most straightforward method to obtain molybdenum dichalcogenides is the stoichiometric combination of metal molybdenum powder and elemental chalcogen in an evacuated silica tube at high-temperature, however which demands significant energy input and gives little control in the particle size of products. Besides, a nano-scaled material can exhibit different properties and often performs better than its bulk counterparts in many applications.<sup>5</sup> Some low-energy routes to molybdenum disulfides, such as polar organic solvent based metathesis of molybdenum halides and alkali-metal sulfides or covalence sulfur sources, have been explored.<sup>6</sup>  $\text{MoS}_2$  film has been prepared by deposition reaction of molybdenum carbonyls with various sulfur sources in non-aqueous solution.<sup>7</sup> Kaner et al. reported a rapid solid state synthesis of  $\text{MoS}_2$  from high valence molybdenum halides and sodium monosulfide.<sup>8</sup> But the large extherm results in a local high temperature up to 1050 °C. Zhan et al. reported a solvothermal reaction<sup>9,10</sup> of molybdenum trioxide and selenium powder in pyridine to obtain nano-meter  $\text{MoS}_2$  and  $\text{MoSe}_2$ .

In the present paper, we first report an aqueous solution based route to molybdenum dichalcogenides from  $\text{Na}_2\text{MoO}_4$  and  $\text{Na}_2\text{ESO}_3$  (E=S, Se) assisted by hydrazine. It gives obvious advantages in comparison with previous low-energy methods: (1) it is not necessary to prepare unstable or air-sensitive precursor of high valence halides; (2) water, a convenient and green solvent, is more favored than toxic organic solvents in industrial applications. Our experiment procedure are presented below.

A stoichiometric amount of  $\text{Na}_2\text{MoO}_4$  and  $\text{Na}_2\text{S}_2\text{O}_3$  was put into a Teflon-lined autoclave and dissolved with 35% aqueous  $\text{N}_2\text{H}_4$  solution into a clear, colorless solution. This autoclave was sealed and maintained at 135 °C for 12 h. The black solid precipitate was collected by filtering, washed with distilled water and ethanol, and dried at 60 °C for 3 h. The synthesis of  $\text{MoSe}_2$  was carried out in an analogous procedure by

using  $\text{Na}_2\text{SeSO}_3$  as selenium source.  $\text{Na}_2\text{SeSO}_3$  was prepared by refluxing  $\text{Na}_2\text{SO}_3$  and selenium powder in distilled water for 10 h. The precipitates of molybdenum dichalcogenides were annealed at 350 °C in flowing high-pure  $\text{N}_2$  atmosphere for 9 h to yield crystalline products. Chemical analysis for the composition was conducted according to previous methods.<sup>11</sup>

The precipitates from hydrothermal reaction are amorphous molybdenum dichalcogenides indicated by X-ray diffraction (XRD). The XRD pattern shown in Figure 1a for annealed  $\text{MoS}_2$  can be indexed to hexagonal 2H- $\text{MoS}_2$  structure with lattice parameter  $a = 3.12$  Å and  $c = 12.73$  Å, which is consistent to that in the literature.<sup>8</sup> The composition of this sample was determined by chemical analysis to be  $\text{MoS}_{2.02}$ . XPS spectrum also demonstrated its composition close to its chemical formula. TEM image shown in Figure 2a for annealed  $\text{MoS}_2$  indicates that it consists of homogeneous particles with an average size of 4 nm. While the calculation by Scherrer's equation suggests the size in the direction [001] is larger than that in the direction [h0l]. This is because the layer rotation around the axis perpendicular to the basic planes of (00l), which leads to the lack of constant orientation between sheets. Due to the high surface Gibbs free energy, these nano-crystallites prone to agglomerate and are not easy to divide by supersonic wave.  $\text{MoSe}_2$  obtained was also characterized by XRD pattern shown in Figure 1b to derive its structure to be hexagonal 2H- $\text{MoSe}_2$  type with lattice parameter  $a = 3.22$  Å and  $c = 13.31$  Å. Its composition was determined by chemical analysis to be  $\text{MoSe}_{1.95}$ . However, due to the exchange of  $\text{Na}_2\text{SeSO}_3$  and  $\text{Na}_2\text{SSeO}_3$ , a problem must be proposed that whether the products is pure  $\text{MoSe}_2$  or contains large amount of  $\text{MoS}_2$ . XPS spectrum shown in Figure 3 further convinced the purity of the products of  $\text{MoSe}_2$ . The typical spectrum shows the existence of Mo, Se and unavoided C, O surface contamination from absorbed gaseous molecules. Considering the value of binding energy and relative intensity ratio of different elements, no other impurity peaks can be detected. The peak area in Mo 3d core and Se 3d core were measured and calculated to

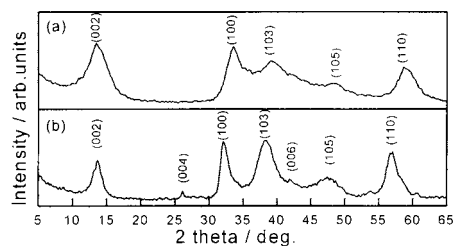
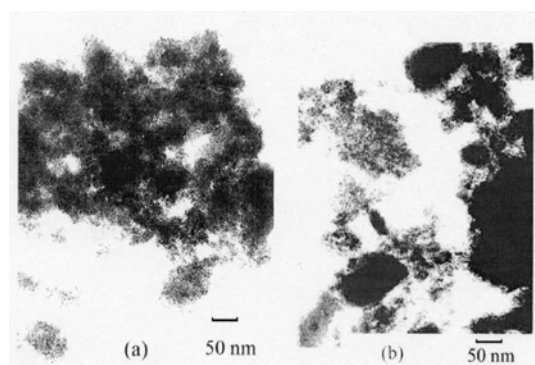
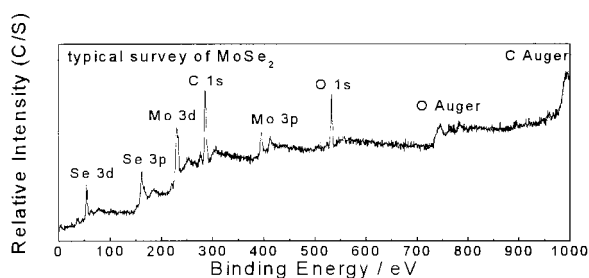


Figure 1. X-Ray diffraction pattern for the samples of (a)  $\text{MoS}_2$  and (b)  $\text{MoSe}_2$  after annealing at 350 °C for 9 h.

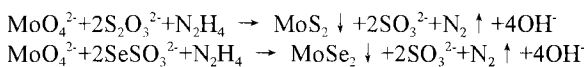


**Figure 2.** the TEM images for nano-particles of (a) MoS<sub>2</sub> and (b) MoSe<sub>2</sub> after annealing at 350 °C for 9 h.



**Figure 3.** X-Ray photoelectron spectrum for annealed MoSe<sub>2</sub>.

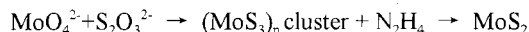
give the ratio of Mo to Se to be 1: 1.90. Infrared spectrum of MoSe<sub>2</sub> obtained recorded in a KBr matrix shows no IR absorbance in the region 930–940 cm<sup>-1</sup> for Mo–O vibration. This confirmed the good purity of MoSe<sub>2</sub> obtained without amorphous MoO<sub>x</sub>. Actually, reduced MoO<sub>x</sub> usually forms in an acid condition, while our hydrothermal reactions were carried out in weak alkaline media. The TEM image shown in Figure 2b for annealed MoSe<sub>2</sub> shows that it comprises of homogenous nanoparticles. The average size is about 7 nm calculated by Scherrer's equation in the direction of [001]. These hydrothermal reactions can be related below:



Besides, we also explored one-step hydrothermal preparation from Na<sub>2</sub>MoO<sub>4</sub>, Na<sub>2</sub>SO<sub>3</sub> and selenium powder assisted by N<sub>2</sub>H<sub>4</sub>. The final product proves to be phase-pure MoSe<sub>2</sub>, too. Some minor unreacted Se powder can be removed readily due to its density less than that of water.

In order to understand the possible mechanism of these hydrothermal reactions, we changed the amount of starting reagents while maintaining other factors constant, such as temperature, reaction period, etc. If Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> is absent, the initial clear solution of Na<sub>2</sub>MoO<sub>4</sub> and N<sub>2</sub>H<sub>4</sub> gives no solid precipitate after hydrothermal process. With the increasing of the amount of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, phase-pure MoS<sub>2</sub> forms without any other solid by-product. So, the formation of MoS<sub>2</sub> is chemically favored in this pathway. No function between the nature of final products

and the stoichiometry of starting materials has been observed. When N<sub>2</sub>H<sub>4</sub> is absent, brown MoS<sub>3</sub> wet gel can be obtained, which can partly convert to MoS<sub>2</sub> by reducing with hydrazine. Thus we infer that MoS<sub>3</sub> cluster may be the intermediate and the reaction procedure can be explained as follows:



However, for a shortened reaction period of 1 h, only product of MoS<sub>2</sub> forms in a smaller yield. Thus, the second step of reduction with N<sub>2</sub>H<sub>4</sub> is a rapid one.

The sample of MoS<sub>2</sub> and MoSe<sub>2</sub> are homogeneous nanoparticles with average size of 4 nm and 7 nm, respectively, which are much smaller than that of the samples prepared by previous solid-state reactions or solvothermal process at 300 °C. Usually, the hydrothermal reactions involve a solid-liquid interaction procedure, in which solid reagents may act as nucleation core for the growth of products. But in our experiment, the initial reaction medium is a clear solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>MoO<sub>4</sub> and N<sub>2</sub>H<sub>4</sub>, which may contribute to the homogeneous nucleation of the product of MoS<sub>2</sub>. Moreover, a greatly lowered reaction temperature gives better control of particle size.

In summary, MoS<sub>2</sub> and MoSe<sub>2</sub> were prepared successfully by a hydrothermal reduction of aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>MoO<sub>4</sub> assisted by N<sub>2</sub>H<sub>4</sub> at 135 °C for 12 h, followed by annealing at 350 °C in an inert atmosphere. The mechanism of these hydrothermal reactions and morphology control are investigated. To our knowledge, many low-temperature solution routes to transition metal dichalcogenides are explored, but all of them are conducted in non-aqueous medium, even moisture in air will influence the formation of products significantly. We first developed an aqueous solution based route to molybdenum dichalcogenides, and it could be applicable for preparing other technologically important transition metal dichalcogenides.

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