Microwave-assisted synthesis of nanosized MoSe$_2$

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A microwave-assisted reaction between Mo(CO)$_6$ and Se has yielded MoSe$_2$ nanoparticles. Nanorods of MoSe$_2$ of lengths ranging from 45 to 55 nanometers are identified in the product mixture. The prepared MoSe$_2$ has been characterized by X-ray powder diffraction measurements, FTIR spectroscopy, photoacoustic spectroscopy (PAS), transmission electron microscopy (TEM) and high resolution TEM (HRTEM).

Introduction

Molybdenum disulfide, diselenide, and ditelluride have attracted attention because of their technological importance as photoactive materials,[1,2] dehydrosulfurization catalysts,[3] solid-state lubricants,[4] and cathode materials for high-energy density batteries.[5] They have a sandwich-layered structure and are used as an intercalation host to derive novel materials with modified physical properties.[4,6–8] This layered structure is also related to their conversion upon heating to the famous anion-like structure known also as inorganic fullerenes (IF).[4,9] Because of their importance, various attempts have been made to find a simple and cheap method for their preparation. Although various methods have been proposed for the synthesis of MoSe$_2$, it is clear that due to the higher negative reduction potential of selenium its preparation is more difficult than that of the corresponding sulfide.

Recently, Woldervanck et al.[10] reported on a 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. The heating lasted for several days. A metathetical reaction between high-valent molybdenum halide and alkali-metal selenides proceeds rapidly and yields a crystalline product. This reaction is known as self-propagating high-temperature synthesis (SHS).[11] Due to self-produced heat, this reaction system may reach a temperature of 1050 °C instantly. In another publication, Zhan et al. described the synthesis of MoSe$_2$ nanocrystallites by a solvothermal conversion from MoO$_3$ and elemental selenium in a reducing environment of hydrazine.[12] The reaction mixture was composed of MoO$_3$, N$_2$H$_4$, water, and Se dissolved in pyridine, and it was heated at 300 °C for 12 hours. A single-molecular-layer (SML) of MoS$_2$ and MoSe$_2$ was synthesized by a hydrothermal method at 150–180 °C.[13] Szabo and Vollath used a microwave plasma to prepare a series of layered selenides in the size range of 5–10 nm.[14] For the formation of the selenides, the chlorides of the metals and SeCl$_4$ were mixed mechanically, and reacted under Ar/4 vol% H$_2$. A short time, in the millisecond range, was required for the reaction to occur. Hershfinkel et al. reported on the preparation of MoSe$_2$ by annealing thin (60 nm) molybdenum oxide films on a quartz substrate in a H$_2$Se/H$_2$/N$_2$ gas mixture for 30 min at 850 °C.[15]

The synthetic route of Chen and Fan was conducted at a relatively low temperature. They have performed a hydro-thermal synthesis of transition metal dichalcogenides. An aqueous solution of Na$_2$Se$_2$O$_3$ and Na$_2$MoO$_4$ was transferred to an autoclave and maintained at 135 °C for 12 h.[16]

Tenne[4,9] has already demonstrated that, as expected, the layered structures when subjected to high temperatures may convert not only to IF but also to nanotubes.[4] Indeed, Rao reported recently on his success in obtaining MoSe$_2$ and WSe$_2$ nanotubes by the reduction of the corresponding triselenides in hydrogen or by the decomposition of the ammonium selenometallates in a hydrogen atmosphere.[17]

In this paper, we report on the synthesis of MoSe$_2$ nanocrystals, which have been prepared by the microwave-assisted polyol method. The polyol method was developed over the past two decades and has been applied to the preparation of submicrometer metallic nanoparticles of the easily reducible transition metals.[18] This method is based on alcohols (such as ethylene glycol, and other glycols) acting as reducing agents of metallic cations to form the corresponding metals. In almost all reactions, the polyol plays the role of the solvent for the same reaction. Generally, the solution reactions for the formation of binary chalcogenides are relatively slow,[19] and are conducted under hydro- or solvothermal conditions in special high temperature and pressure equipment in order to accelerate their rate. Even under these conditions the reaction lasts for many hours, or even days.[20]

Recently, we have found that the application of microwave radiation or ultrasound greatly facilitates the use of the polyol method for the preparation of binary chalcogenides (selenides and tellurides).[21] In most experiments, the microwave reaction is completed within a few minutes, the maximum duration being one hour. The reaction is conducted in a regular domestic microwave oven and does not require the special hydrothermal equipment used in Komarneni's polyol reactions.[22]

Experimental

All the reagents were of the highest commercially available purity. Elemental Se, Mo(CO)$_6$, and ethylene glycol (EG) were purchased from Aldrich Co. and used without further purification. The X-ray diffraction patterns of the products were recorded with a Bruker AXS D8 Advance Powder X-ray Diffractometer (using CuKα λ = 1.5418 Å radiation). Peak fitting and lattice parameter refinement were computed using the Topas and Metric programs (Bruker Analytical X-Ray Systems). EDX measurements were done on an X-ray microanalyzer (Oxford Scientific) built on a JSM-840 Scanning Electron Microscope (JEOL). The transmission electron micrographs (TEM) were imaged on a JEOL-JEM 100SX microscope, using 100 kV accelerating voltage. Samples for TEM were prepared by placing a drop of the sample suspension on a copper grid (400 mesh, Electron Microscopy Sciences) coated with carbon film. The grid was then air-dried. High resolution TEM (HRTEM) images were taken using a JEOL

3010 with 300 kV accelerating voltage. A conventional monochrome CCD camera, with resolution of 768 × 512 pixels, was used to digitize the images. The digital images were processed with the Digital Micrograph software package (Gatan, Inc., Pleasanton, CA, USA). Samples for TEM were prepared by placing a drop of the sample suspension on a copper grid (400 mesh, Elctron Microscopy Sciences) coated with carbon film. The grid was then air-dried. FTIR spectra were recorded in KBr pellets using an Impact 410 Nicolet spectrometer.

The electronic properties of the nanoparticles were measured using photoacoustic spectroscopy (PAS). Photoacoustic measurements were conducted employing a home-made instrument which has been described elsewhere.[23] The signals, which are acquired as a function of wavelength, were normalized against the absorption of carbon black powder, the 100% absorber. The band gap is calculated by the 'knee' method for all the samples.[24]

The microwave-assisted reaction was carried out in a Spectra 900 W microwave oven, with a 2.45 GHz working frequency. The oven was modified to include a refluxing system. In all the experiments, the microwave oven was cycled as follows: on for 21 s, off for 9 s, with total power always at 900 W. This cycling mode was chosen in order to reduce the risk of superheating the solvent. All reactions were conducted under a flow of nitrogen.

Microwave synthesis

Stoichiometric quantities of $Mo(CO)_6$ and Se powder were put in ethylene glycol. The system was purged for a few minutes with nitrogen prior to switching on the microwave reactor. The reactions were conducted for 1 hour under nitrogen. In the post-reaction treatment, the product was centrifuged once with the mother liquid, and a few times with ethanol, at 20 °C and 9000 rpm. The product was then dried overnight under vacuum. We have also tried other routes such as reacting a mixture of ammonium molybdate and molybdenum acetate dimer with Se in ethylene glycol to get $MoSe_2$.

Results and discussion

The colour of the sample after the drying process was black. The sample underwent a series of standard characterization measurements to determine its composition and morphology. In parallel, the sample was heated to 600 °C for 5 hours.

EDX and FTIR studies

EDX measurements of as-prepared and the annealed samples indicate the presence of Mo and Se in the atomic ratios 1 : 2.13 and 1 : 2, respectively. Only small amounts of carbon and oxygen impurities were detected in the EDX measurements. This is in line with previous results[25] that showed that the microwave-assisted polyol reaction yields products with a low level of impurities. Ethylene glycol coated on the $MoSe_2$ particles was found to be the main impurity. This conclusion is derived from the FTIR spectra of the as-prepared product, which revealed the presence of an absorption band at 3500 cm^{-1} assigned to O–H and absorption band at 2900 cm^{-1} assigned to C–H stretching vibrations.[26] The vibrational bands, related to the ethylene glycol, disappeared in the annealed sample.

Powder XRD studies

The X-ray diffraction patterns of the as-prepared material are shown in Fig. 1a. No diffraction bands were detected, indicating that the as-prepared material is amorphous. Diffraction peaks assigned to unreacted Se were the only
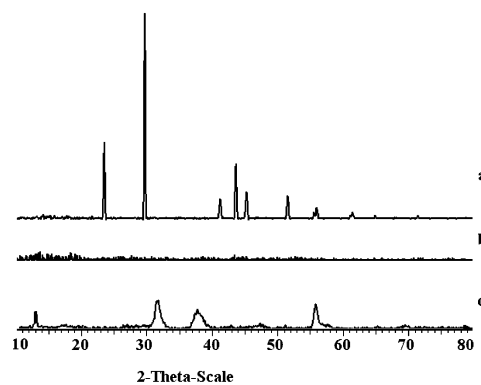
Fig. 1 XRD patterns for the as-prepared product (a), annealed at 300 °C (b) and heated at 600 °C (c).

identifiable diffraction peaks. This is in accordance with the slight excess of Se in the as-prepared material detected by the EDAX measurements.

Fig. 1b illustrates the diffraction peaks of the sample annealed at 300 °C in pure argon for at least 5 hours. It is clear that upon heating the peaks assigned to Se have disappeared, and the annealed sample is still amorphous. The disappearance of the excess Se is due to its evaporation at the annealing temperature (the m.p. of Se is 221 °C). Fig. 1c depicts the XRD diffraction peaks of crystalline $MoSe_2$ obtained when the as-prepared sample was heated at 600 °C for 5 hours in pure argon. The XRD patterns match the literature data of the diffraction peaks of crystalline molybdenum selenide (Powder diffraction file, PDF #77-1715). Fig. 1c shows very broad diffraction peaks for the crystalline product, indicating that the product particles were nanosized. The size of these nanocrystals was calculated by using the Debye–Scherrer (DS) equation[27] and it was found to be in the range of 11–12 nm.

TEM

The TEM images of the as-prepared and annealed samples are illustrated in Fig. 2. In the case of the as-prepared sample, aggregates of nearly spherical morphology were seen, whose sizes varied from 100–400 nm. After heating to 600 °C (Fig. 2b), these aggregates were merged together to form bigger particles. Each aggregate was a highly agglomerated form, consisting of nanocrystals as revealed from the edges of these aggregate particles seen in the TEM images. The size of these nanocrystallites varied from 11–16 nm, in good agreement with the XRD results.

HRTEM

The HRTEM images are depicted in Fig. 3. The images show that the sample is composed of nanorods whose length varies between 45 to 55 nm, while the width of these rods ranges between 2.5 to 6.0 nm. It is difficult to conclude whether onion-like morphologies are part of the structures observed in Fig. 3a. Pictures of higher resolution are depicted in Fig. 3b and c. Fig. 3b shows the detailed structure of the nanorods. The fringes observed are ∼0.65 nm apart, which fits well to the distance between the (002) planes of hexagonal $MoSe_2$. Nath and Rao[17] have synthesized $MoSe_2$ nanotubes. The spacing of the layers of the 002 planes observed by them was ∼0.64 nm. At the edges of the pictures we observe partially crystallized or even amorphous $MoSe_2$. In Fig. 3c we observe, in addition to the rods, elliptical particles whose length is about 10 nm. Fringes spaced by 0.25 nm are observed. Similar features with the same spacing, but less distinct, are also observed in Fig. 3b.
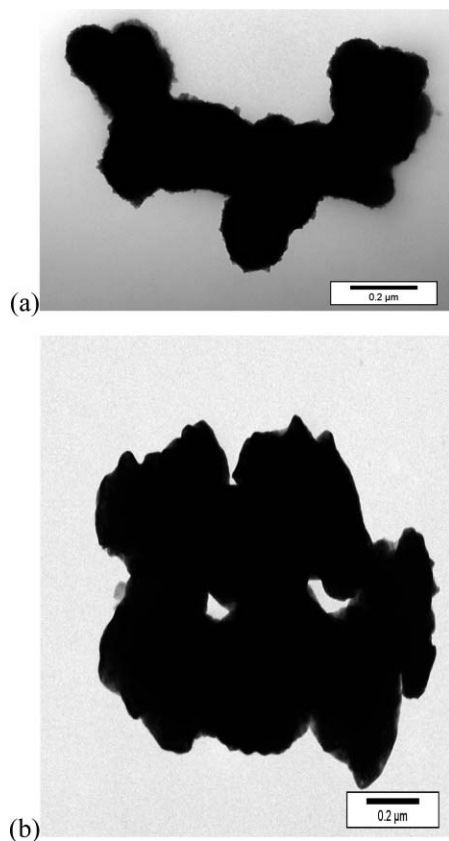
(a)

(b)

Fig. 2 Low resolution TEM images of as-prepared material (a) and sample heated to 600 °C (b).

The 0.25 nm spacing is related to the (103) planes of the hexagonal crystal.

PAS

The PAS spectrum of MoSe$_2$ is shown in Fig. 4. Based on previous results, we assign two band-gaps from the PAS. The first, an indirect band-gap at 1.128 eV, and the second a direct band-gap at 1.385 eV. We chose for the determination of the first band-gap the second PAS peak because it is close to the values of reference 2. If the first peak would have served for the determination of the band-gap the value would be 1.05 eV. The values reported in the literature for MoSe$_2$ are very similar to those obtained in the current study. Hunag and Kelley (H & K),[2] for example, report two band-gaps at 1.09 and 1.35 eV. We cannot assign unequivocally the differences to a quantum size effect, because our HRTEM measurements reveal a mixture of small particles with various morphologies, for which an
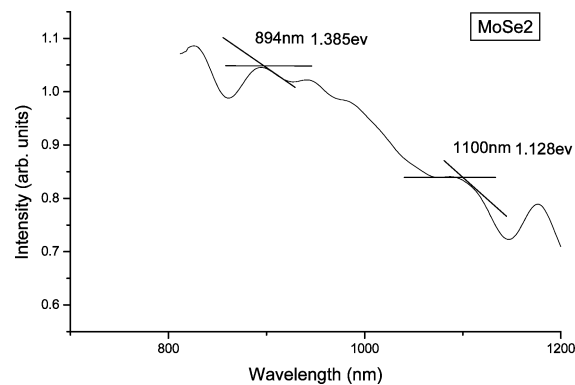

Fig. 4 Photoacoustic measurements of MoSe$_2$.

appropriate comparison with the sizes of H & K particles is not possible.

Proposed mechanism

In the former polyol reactions, which have been carried out in a microwave oven, we have found, like others,[28] that in microwave boiled solvents the solvents themselves can undergo profound overheating.[22,28–30] As a result of such overheating, the metal ion could be reduced to the metal in the zero oxidation state. Such metallic particles may strongly interact with microwave radiation, yielding very high temperatures, which will enhance the reduction of the selenium atom. In order to succeed in obtaining the metallic particles, the reagents must be soluble in ethylene glycol and independently reducible by the solvent.[31] Ions such as Ag$^+$, Cu^{2+}, Ni^{2+}, Pb^{2+}, Bi^{3+}, *etc.* were all reduced to their metallic nanoparticles by ethylene glycol under microwave heating. We therefore conducted a few experiments to probe whether Mo at various oxidation states can be reduced to Mo(0). The solution of [Mo(Ac)$_2$]$_2$ or (NH$_4$)$_2$MoO$_4$ in ethylene glycol or even higher glycols did not yield the corresponding metallic nanoparticles. The same was true for Mo compounds with a higher oxidation state. In the reaction of [Mo(Ac)$_2$]$_2$ with ethylene glycol, no product was obtained. For the reaction of (NH$_4$)$_2$MoO$_4$, MoO$_2$ is obtained.

To further investigate the mechanism of the reaction between Mo(CO)$_6$ and Se, a control reaction was carried out. In this reaction Mo(CO)$_6$ was heated in ethylene glycol without Se. A black amorphous powder was obtained, which upon heating to 1000 °C converted to Mo$_2$C, and metallic Mo. It is therefore clear that, at least partially, the mechanism of the current reaction involves metallic nanoparticles, which are obtained in the mechanism's first step due to the decomposition of the carbonyl to the corresponding metal. The second step follows the regular polyol reaction steps described above. The part of the carbonyl that converts to the carbide will possibly react
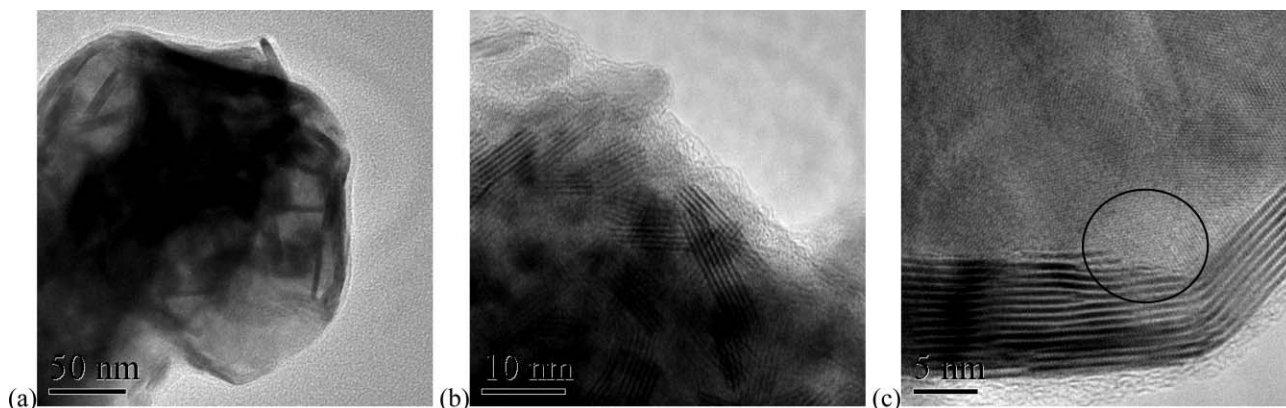

Fig. 3 High resolution TEM images of MoSe$_2$ nanorods.

with the Se according to $Mo_2C + 4Se \rightarrow 2\ MoSe_2 + C$. However, we propose that perhaps in the presence of Se the carbide is not formed, because the reaction of metallic Mo and Se is so fast that it prevents the formation of the corresponding carbide. Indeed, when heating up the product mixture to 1000 °C we could not detect the presence of the carbide.

Acknowledgements

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