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### Preparation and Spectroscopic Characterization of $\text{MoS}_2$ and $\text{MoSe}_2$ Nanoparticles

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## Preparation and Spectroscopic Characterization of $\text{MoS}_2$ and $\text{MoSe}_2$ Nanoparticles

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**Abstract:** In this manuscript, we report an experiment for the upper division chemistry laboratory involving the synthesis and characterization of molybdenum (IV) chalcogenide nanoparticles. The reaction is a straightforward synthesis between molybdenum hexacarbonyl and sulfur or selenium. Students follow the progress of the reaction via monitoring the carbonyl stretch using Fourier transform infrared (FTIR) spectroscopy. The nanoparticles are found to absorb light in the UV region of the spectrum compared with the near IR for bulk molybdenum (IV) chalcogenides. Further, the particles also exhibit a blue fluorescence when excited in the UV region. Students can easily complete the experiment in two 3-hr laboratory periods, one focusing on the synthesis and the other on the spectroscopic characterization.

**Keywords:** Molybdenum (IV) selenide, molybdenum (IV) sulfide, nanoparticles, nanotechnology

### INTRODUCTION

Nanoclusters have become the focus of increased attention in the chemical and materials science literature in recent years because of the unique properties

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they possess as well as the technological advances that have aided their characterization. When particle size is of the order nanometers, the spectroscopic, chemical, and electronic properties of the compound significantly differ from the bulk material because of the effects of quantum confinement. Because of these quantum size effects, the resulting properties are directly related to particle size, in contrast with what is found in bulk materials.

The recent increased focus on nanotechnology research has begun to spill over into the science curriculum. This is evidenced by a number of recent reports where nanotechnology concepts are implemented in undergraduate education.<sup>[1–5]</sup> Previously, we published an overview of a number of experiments implemented in the chemistry curriculum at Armstrong Atlantic State University over the past 3 years, from general chemistry through physical chemistry and biochemistry.<sup>[6]</sup> In addition, we also published a simple, aqueous preparation of ZnS nanoparticles with and without metal ion dopants<sup>[1]</sup> followed by spectroscopic characterization. The paper focused on the elucidation of the nanoparticle band gap energy as well as the luminescent properties of these compounds. The experiments were straightforward; however, they required an in-depth student understanding of molecular orbital theory, band theory of solids, quantum mechanics, and nanomaterials, thus the experiment is best suited for advanced inorganic or physical chemistry.

This current paper focuses on the implementation of a new chemistry laboratory experiment for upper level chemistry courses, highlighting the synthesis and spectroscopic analysis of molybdenum (IV) chalcogenide nanoparticles. The experiments presented require student understanding of nanoparticles and their quantum effects, UV-Vis, fluorescence, and FTIR spectroscopies, as well as kinetics, as would be inherent in an upper level chemistry course.

There is considerable interest in molybdenum (IV) chalcogenides due to their interesting photovoltaic catalysis<sup>[7]</sup> and lubricant abilities.<sup>[8]</sup> These complexes form a stacked interlayer structure loosely bound together by van der Waals forces.<sup>[9]</sup> A number of previous reports have detailed the synthesis, characterization, and photophysical reactivity of  $\text{MoX}_2$  ( $\text{X} = \text{S}^{2-}$  and  $\text{Se}^{2-}$ ) compounds.<sup>[10–23]</sup> These compounds have been synthesized by a variety of techniques including hydrothermal, solvothermal, metathesis, and reduction of Mo(V). Many of these procedures require extreme temperatures, reactive starting materials, and high pressures, all of which are not optimal for an undergraduate chemistry experiment. We have chosen a simpler reaction, appropriate for the undergraduate student, which uses common reagents and moderately priced starting materials to achieve molybdenum (IV) chalcogenide nanoclusters of the order 2.5 nm in particle size. In this paper, we report the synthesis of  $\text{MoX}_2$  ( $\text{X} = \text{S}^{2-}$  and  $\text{Se}^{2-}$ ) from molybdenum hexacarbonyl and the elemental form of the group 16 chalcogen. Furthermore, this reaction can be followed in a straightforward manner by monitoring the disappearance of the carbonyl stretch via FTIR. Finally, the particles size and spectral

properties of the product are examined via UV-Vis and fluorescence measurements. This experiment is most suitable for the undergraduate inorganic chemistry or physical chemistry laboratory.

## MATERIALS AND METHODS

### Materials

Mixed xylenes, molybdenum hexacarbonyl, elemental sulfur, and selenium powder were purchased from a commercial supplier and used without further purification.

### Safety

Students should be instructed to wear goggles and gloves and work in a laboratory hood as the chemicals used in this laboratory carry risk of toxicity and flammability. This laboratory experiment should only be performed by junior or senior chemistry majors with previous experience using reflux techniques and the use of argon or nitrogen to produce an inert atmosphere over their reaction. In order to collect samples during the formation of the nanoparticles and subsequently analyze them by FTIR in a timely manner, students should be instructed to work in pairs.

### Instruments

A Hewlett Packard 8453 Diode Array UV-Vis Spectrometer (Santa Clara, CA, USA) was used to record the absorbance spectrum from 190 to 1100 nm. A Perkin Elmer Spectrum One Fourier-Transform Infrared Spectrometer (Waltham, MA, USA) was used to obtain the carbonyl spectrum. A Shimadzu RF-5301PC Spectrofluorometer (Columbia, MD, USA) was used to record the fluorescence spectrum from 300 to 500 nm.

### Synthesis

#### Molybdenum (IV) Sulfide Nanoclusters

The procedure used in this experiment was modified from a literature reference.<sup>[23]</sup> The experiment was performed in 100 mL of mixed xylenes as solvent. The mixed xylenes solution was degassed with argon for 20 min. While stirring, molybdenumhexacarbonyl (113 mg,  $4.30 \times 10^{-4}$  mol) was added to the xylene under an argon blanket. The mixture was heated to

reflux and maintained at 140°C for 10 min or until complete dissolution of the Mo(CO)<sub>6</sub> was observed. The solution was then cooled to 70°C, maintaining an argon blanket. Sulfur (30.8 mg, 9.60 × 10<sup>-4</sup> mol) was added to the solution. The mixture was heated to reflux and maintained at 140°C for 1 hr under inert atmosphere. The solution was then placed in an ice bath for 20 min. The black precipitate was vacuum filtered and washed with small aliquots of acetone. The MoS<sub>2</sub> nanoclusters were placed in the oven at 140 °C to dry.

#### Molybdenum (IV) Selenide Nanoclusters

The above procedure was followed; however, sulfur was replaced with selenium powder (75.8 mg, 9.60 × 10<sup>-4</sup> mol).

### Analysis

#### FTIR

A 3-μL sample was taken of the Mo(CO)<sub>6</sub> solution, prior to the addition of the sulfur/selenium, and injected into a liquid FTIR cell and the spectrum obtained immediately. This analysis was considered to establish the beginning of reaction as time = 0. After the addition of the sulfur/selenium, a 3-μL sample of the reaction mixture was taken every 10 min for up to 1 hr and analyzed immediately via FTIR.

#### UV-Vis

A small portion of the product was suspended in acetonitrile. The solution was sonicated for 2 min before being analyzed in order to redissolve the precipitate and break apart any aggregates that may form, as the particles are not surfactant stabilized.

#### Fluorescence

A small sample of the product was suspended in water. The solution was sonicated as in the UV-Vis experiment before being analyzed and excited at 260 nm.

## RESULTS AND DISCUSSION

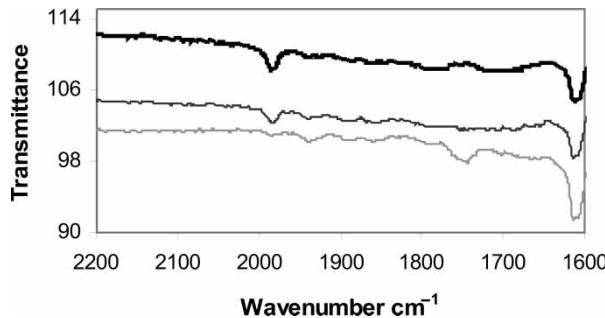
All data shown is data from student experiments.

### Synthesis

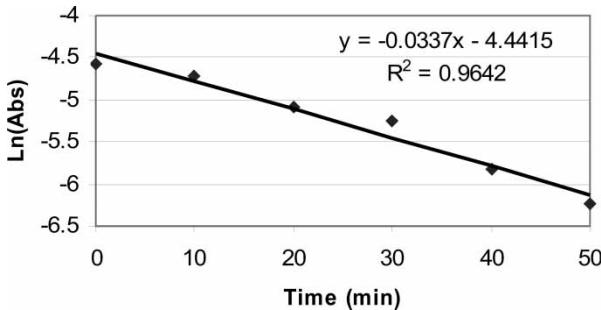
The synthesis of the nanoparticles requires students to work in an inert atmosphere, and the progress of the reaction is followed directly by FTIR. This is accomplished by monitoring the decrease in the area of the peak representing the carbonyl stretch at  $1986\text{ cm}^{-1}$  as shown in Fig. 1. As part of the laboratory report, students are first asked to consider, using group theory arguments, why only one CO stretch is observed for the hexacarbonyl starting material in the IR. The peak is completely gone after 1 hr of reaction time at elevated temperature. After converting the transmittance data to absorbance and subtracting, students plot the first-order integrated rate law for the disappearance of the carbonyl peak and determine that the reaction is first order in the decomposition of  $\text{Mo}(\text{CO})_6$ . It should be noted that the slope of the  $\text{MoSe}_2$  graph is similar to the  $\text{MoS}_2$  graph within experimental error (Fig. 2). Prior reports have outlined this synthesis in reverse<sup>[23]</sup> by first heating the sulfur (or selenium) to  $140^\circ\text{C}$  then cooling the reaction mixture down to room temperature, adding the molybdenum hexacarbonyl, and finally returning the temperature to  $140^\circ\text{C}$  for several hours. However, we have found no major difference in the reaction rate or quality of the product if we perform the reaction in the reverse by adding sulfur or selenium to the hot molybdenum hexacarbonyl. It is, however, easier to monitor the reaction by the loss of the carbonyl in this direction. It is interesting to note that the reaction is reported to proceed through a free elemental form of Mo, which appears to be the rate-limiting step. The fine Mo particles then react readily with the free chalcogen to form the  $\text{MoX}_2$ .

### Spectroscopy

Bulk semiconductors exhibit an absorbance spectrum that corresponds with the bandgap energy, which is defined as the energy equivalent to the



**Figure 1.** FTIR spectra of  $\text{Mo}(\text{CO})_6$  during formation of  $\text{MoS}_2$  nanoparticles. The carbonyl peak at  $1986\text{ cm}^{-1}$  disappears and is used to calculate the rate of the reaction. For clarity, only  $t = 10$  (thick black), 30 (thin black), and 50 minutes (gray) are shown.

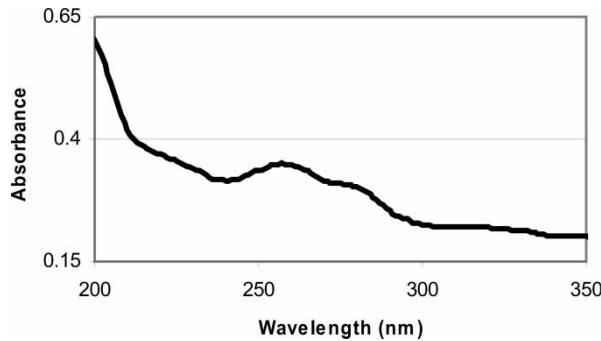


**Figure 2.** First-order plot of the peak absorbance at  $1986\text{ cm}^{-1}$  over the course of the reaction.

separation between the valence band and the conduction band. Promotion of an electron from the valence band to the conduction band is accomplished by light equal to or exceeding the band gap energy. The valence band subsequently contains a hole where the electron was prior to its excitation. Bulk  $\text{MoS}_2$  has a first allowed transition at  $2.07\text{ eV}$  ( $660\text{ nm}$ ) and an indirect band gap energy of  $1.2\text{ eV}$ , corresponding with an absorbance in the near IR of  $1034\text{ nm}$ . Bulk  $\text{MoSe}_2$  has a first allowed transition at  $1.09\text{ eV}$  and bandgap of  $1.36\text{ eV}$  corresponding with  $914\text{ nm}$  and  $1140\text{ nm}$ , respectively. Bulk  $\text{MoS}_2$  can be purchased from Aldrich (St. Louis, MO, USA) and examined if the instructor desires.

For particles of the order or significantly smaller than the size of the bulk band gap, the observed absorbance maxima is blue shifted and related to particle size. As a semiconductor cluster gets smaller, the conduction band moves to more negative potentials, while the valence band moves only slightly to more positive potentials. The result is a larger effective band gap and an observed blue shift. Via microscopy, the  $\text{MoS}_2$  particle size, for particles prepared via the referenced literature method, was found to be in the range  $2.5\text{--}7\text{ nm}$ .<sup>[23]</sup>

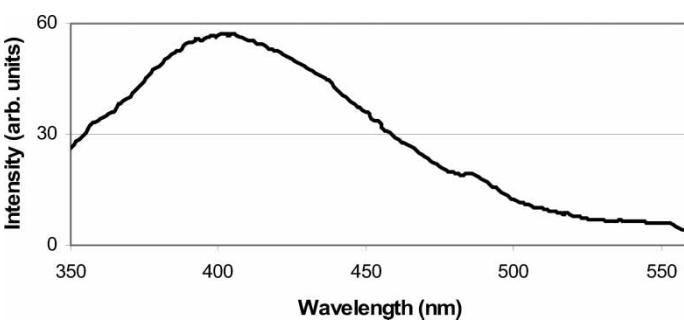
Given that microscopic techniques are not always readily available for undergraduate student use, spectroscopic estimation of the particle size can be used. Student data indicates that the absorbance maxima (Fig. 3) are shifted to  $257$  and  $280\text{ nm}$  for  $\text{MoS}_2$  and  $259$  and  $280\text{ nm}$  for  $\text{MoSe}_2$  compared with the bulk values. From published references, where a series of  $\text{MoS}_2$  particles were synthesized, examined by UV-Vis, and their size confirmed by microscopy, these absorbance maxima correspond with particle sizes of less than  $2.5\text{ nm}$ .<sup>[19]</sup> A number of mathematical models have also been used to predict the particle size from the absorbance spectrum with varying degrees of success. Most often used is the effective mass treatment from Brus, which takes into account the kinetic energy of the electron and the hole, the effective mass of the electron and the hole, and the Coulombic attraction between the two.<sup>[24,25]</sup> Although a discussion



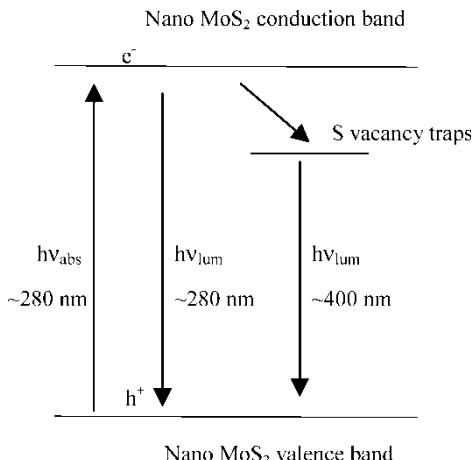
**Figure 3.** Absorbance spectra of the  $\text{MoS}_2$  nanoparticles.

of this equation can accompany the laboratory experiment in the context of a particle-in-a-box,<sup>[1]</sup> the equation can only lead to a qualitative approximation of the size of the  $\text{MoS}_2$  or  $\text{MoSe}_2$  particles, due to the fact that the nanocrystals form a trilayer of X–Mo–X and are not spherical. Thus, the wave vector is not defined satisfactorily to determine the particle size with sufficient accuracy.<sup>[20]</sup> The only way to accurately confirm particle size in this experiment is to use microscopic techniques, if available or via inference from the absorbance spectrum as we have outlined.

The particles, prepared by the students, exhibit a fluorescent emission at 400 nm for  $\text{MoS}_2$  and 420 nm for  $\text{MoSe}_2$  after excitation at 280 nm (Fig. 4). Emission peaks are broad and are the result of electrons decaying back to the valence band from various “shallow” or “deep” traps in the conduction band (Scheme 1). The value of considering the fluorescence spectrum for a student is that it couples the excitation process (UV-Vis) and the band gap energy with the decay process (fluorescence). It introduces the students to a common feature in nanoparticles, the concept of traps that allow the particles to reside in a slightly different energy level than either the conduction



**Figure 4.** Fluorescence spectra of the  $\text{MoS}_2$  nanoparticles.



**Scheme 1.** Molecular orbital diagram for  $\text{MoS}_2$  nanoparticles.

or valence band for a period of time. The quantum “sinks” hold the electron for a brief period either in a lower-level excited state or a high-level ground state.

## CONCLUSIONS

In this experiment, upper level undergraduates are exposed to nanoparticle synthesis, spectroscopy, and theory using the  $\text{MoS}_2$  and/or  $\text{MoSe}_2$  systems. Students use FTIR spectroscopy to follow the reaction progress and can determine the first-order kinetic analysis through a systematic manipulation of the amount of chalcogen starting material, if desired. The reaction product, band gap energy, and particle size can then be inferred through UV-Vis analysis and comparison with the literature values. The absorbance and fluorescence spectra of these two nanoparticles give students exposure to band gap energies for nanoparticles, electron traps, as well as molecular orbital theory of this type of particle.

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