Size-Dependent Spectroscopy of MoS₂ Nanoclusters

V. Chikan and D. F. Kelley*

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506-3701 Received: May 16, 2001; In Final Form: December 17, 2001

The synthesis and characterization of 3.5, 4.5, and 8 nm diameter MoS_2 nanoclusters are described. Each size is characterized by TEM images, electron diffraction, and optical spectroscopy. These nanoclusters can be synthesized directly or may be synthesized from samples of polydisperse nanoclusters. Obtaining larger or smaller discrete sizes from polydisperse samples indicates that these nanocluster sizes are thermodynamically favored, that is, these sizes correspond to free-energy minima. Electron diffraction and static spectroscopic results indicate that the particles are three atoms thick, specifically, single S-Mo-S trilayer disks. Static and time-resolved absorption and emission spectroscopy were used to determine the polarizations of the lowest energy allowed transitions in each case. We find that the 8 nm particles have a lowest energy absorption maximum at 473 nm that has mixed x - y and z polarizations, 4.5 nm particles have absorption maxima at 400 and 440 nm that are x - y and z polarized, respectively, and 3.5 nm particles have an absorption maximum at 362 nm that is z polarized. These results indicate that the polarization of the lowest decreases.

Introduction

One of the central motivations for the study of semiconductor nanoclusters is that many of their properties are size dependent. When the particle size becomes comparable to or less than that of the exciton, the optical and electronic properties vary strongly with the particle size. Properties such as the optical absorption and emission spectra and the electrochemical redox potentials change as a result of "quantum confinement" of the conduction band electrons and valence band holes.^{1–3} Thus, by varying the particle size, it often possible to tune the properties of the semiconductor. Small semiconductor particles generally have larger band gaps, more negative reduction potentials, and more positive oxidation potentials than does the bulk material. Several different treatments of semiconductor nanocluster electronic structure have been developed and have recently been reviewed.⁴ The simplest semiquantitative description of how quantum confinement alters these properties is given by treatments using the "effective mass" approximation, in which the properties of the conduction band electrons and valence band holes are calculated from a simple particle-in-a-box model using the effective masses of each carrier in the bulk semiconductor.^{2,3} The effective mass of each carrier depends on the band structure of the solid and is given by $m_{\rm eff} = \hbar^2 (\partial^2 E / \partial k^2)^{-1}$. It is important to note that the effective mass of a carrier depends on the electronic state of the carrier; different electronic states are characterized by different effective masses. Highly localized electron or hole states have large effective masses. In the effective mass model, the extent of the size-dependent shift of the band gap is proportional to the inverse of the effective mass. Thus, quantum confinement causes localized states to shift less than delocalized states. One could imagine that in some cases this could cause the ordering of different excited states to reverse as the particle size is decreased. Such a reversal involving the lowest excited states would cause the nature of the lowest excited state to change with particle size. Below, we present

results that show that just such a reversal occurs in the case of MoS_2 nanoclusters.

Examination of the size-dependent spectroscopy of any type of nanocluster requires the synthesis of particles having different sizes. Nanoclusters are often synthesized as free-standing particles in solution using colloid chemistry methods. There are several different methods that can be used to control the size distributions of semiconductor and metal nanoparticles and obtain monodisperse samples. These methods fall into three broad classes, although there is considerable overlap between them. Monodisperse nanoclusters may be obtained by (1) controlling the kinetics of nucleation and subsequent crystal growth,^{5,6} (2) synthesizing polydisperse samples and selecting a portion of that distribution, $^{7-9}$ or (3) adjusting the synthetic conditions so that a monodisperse size distribution corresponds to a thermodynamic minimum.¹⁰ The crystal growth kinetics and stability may be strongly influenced by the nanocluster thermodynamics.⁵ Thus, thermodynamics may play a key role in all three methods. The particle surface energy is usually positive, making larger particles thermodynamically more favorable. In addition, the surface free energy increases with the surface curvature, which is the Gibbs-Thomson effect.⁶ This variation of surface energy with particle size leads to the wellknown phenomenon of Oswald ripening, in which larger particles grow at the expense of smaller ones. By controlling the solution monomer concentration, it is possible to vary the growth rates of different-sized particles, thereby focusing or defocusing the size distribution.⁵ Size-dependent thermodynamics affecting the kinetics of particle growth is a rather general and often observed phenomenon. However, thermodynamic control of the static, equilibrium nanocluster size distribution requires that there be a free-energy minimum corresponding to a specific nanocluster size and that the particles be sufficiently labile that this distribution is realized. This situation occurs in surface-supported nanoclusters^{11,12} and in solution-phase metal nanoclusters.^{10,13-15} The most extensively studied example of a thermodynamically controlled nanocluster size distribution is

^{*} Corresponding author. E-mail: dfkelley@ksu.edu.

that of thiol capped gold particles. When polydisperse nanoclusters are heated in the presence of thiols in solution ("digestive ripening"), monodisperse particles are formed, with their average size determined by the thiol concentration. In this case, the free-energy minimum results from a combination of the surface energy, the thiol binding energy, and the Gibbs— Thomson effect. The basic theory is simple and well understood and is discussed below. However, thermodynamic control of solution-phase semiconductor nanoclusters is rarely observed. Below, we present spectroscopic, dynamical, and imaging results indicating that under some circumstances the size distribution of MoS_2 nanoclusters is controlled by thermodynamics rather than by the kinetics of nucleation and crystal growth.

There has recently been considerable study of MoS₂ and related (WS₂, MoSe₂, and WSe₂) nanoclusters¹⁶⁻²⁴ and "inorganic fullerenes" $^{25-35}$ of these materials. The first solution-phase MoS₂ nanoclusters were synthesized by Wilcoxon and coworkers.¹⁶ Subsequently, we have synthesized and characterized WS₂, MoSe₂, and WSe₂ nanoclusters.^{20,21} We have also studied the electron and hole-trapping dynamics in MoS₂ and WS₂ nanoclusters^{20,23} and the trapped electron and hole recombination dynamics in MoS₂ nanoclusters.^{19,24} In addition, we have studied the interfacial electron-transfer dynamics between MoS2 nanoclusters and adsorbed electron acceptors and the electron injection dynamics between MoS2 nanoclusters and adsorbed dyes.^{18,23} The optical properties of MoS₂ nanotubes (inorganic fullerenes) have also been studied and compared to band structure calculations.^{27,36} These systems are much larger and therefore show much smaller quantum confinement effects than do the colloidal nanoclusters.

Despite the above dynamical and spectroscopic studies, a systematic study of the size-dependent spectroscopy of MoS_2 nanoclusters has not been reported. In this article, we report the synthesis of several different sizes of MoS_2 nanoclusters and show that these sizes correspond to thermodynamic minima. We also use static and time-resolved absorption and emission spectroscopy to determine the polarizations of the lowest allowed excited states in each case. These results indicate that the polarization of the lowest observed transition is size dependent and that the ordering of the lowest excited states changes as the particle size decreases.

Experimental Section

Materials. Dodecyltrimethylammonium chloride (DTAC) (99%) and didodecyldimethylammonium bromide (98%) were purchased from Fluka and recrystallized from ethanol. Tridodecylmethylammonium iodide (TDAI) was obtained from Aldrich and repeatedly washed with ether and stored in the glovebox in the dark. Tridodecylmethylammonium chloride (TDAC) was synthesized by the reaction of tridodecylamine (Aldrich) and chloromethane (Aldrich), recrystallized from hexane, and stored in the glovebox. Octane (reagent grade) was purchased from Fisher and distilled in a nitrogen atmosphere from sodium. Hexanol (99%, anhydrous) and ammonium sulfide (20% solution) were purchased from Aldrich and used without further purification. DQTCI dye was obtained from Exciton and used without further purification. Molybdenum(IV) chloride was synthesized by using standard methods.^{37,38} Specifically, MoCl₅ was refluxed in tetrachloroethylene in an evacuated and sealed vessel for 3 days. The resulting product was repeatedly washed with carbon tetrachloride in an inert-atmosphere glovebox to remove starting material. Acetonitrile was distilled from phosphorus pentoxide in a nitrogen atmosphere. Following purification, all the reagents except H_2S and $(NH_4)_2S$ were kept in a glovebox. Typical sample volumes in all syntheses were 10 mL.

Time-Resolved Spectroscopy. Time-resolved emission results were obtained by time-correlated single photon counting. In the apparatus used in these studies, the sample is excited with 7 ps pulses from the second harmonic or the fundamental of a synch-pumped, cavity-dumped cw dye laser (Spectra-Physics 3500), which is pumped by a cw-mode-locked YAG laser (Spectra-Physics 3800). Detection is accomplished with a Hamamatsu 6m MCP PMT and time-correlated single photon counting electronics. Wavelength selection is accomplished using a 0.25 m monochromator with a 150 groove/mm grating. The emission kinetics reported here are taken at 450 nm, with a bandwidth of about 10 nm. The excitation wavelength is varied in the range of 292-315 nm, with pulse energies of about 1.0 nJ focused to a spot size of about 0.5 mm. This combination of low pulse energies and relatively large spot sizes results in fluences that are sufficiently low that multiphoton excitations are completely avoided. Polarized emission detection is accomplished using a 1 cm Glan-Taylor excitation polarizer and a Polaroid emission polarizer in a collinear geometry. Appropriate corrections are made for the polarization-dependent throughput of the detection system.

The apparatus used to obtain the femtosecond one-color polarized transient absorption results is similar to that previously described.²³ The brief description of the apparatus is as follows. The femtosecond light source is based on a Clark-MXR CPA-2001, which produces 775 nm, 130 fs, 800 μ J pulses at a repetition rate of 1 kHz. The pulses are used to pump an OPA (Clark-MXR, Vis-OPA) producing pulses between 450 and 495 nm or are put through a frequency-doubling crystal to produce 387 nm pulses. In the one-color polarized bleach experiments, about 10% of the pulse intensity is split off and used for the sample probe. The remainder is used for sample excitation. The pump beam is reflected through a corner cube on a delay stage to control the relative arrival time of the pump versus the probe at the sample. This is followed by a Glan-Taylor polarizer to ensure that the excitation pulse is completely linearly polarized. The pump beam is typically focused to a spot size of 0.5-1.0mm at the sample. The power density can be varied by changing the position of the sample with respect to the focal point of the pump beam, thereby changing the focal spot size. In the results presented here, variation of the power density by a factor of about 10 has no detectable effect on the observed kinetics. The low-intensity probe beam is attenuated and then split into reference and sample probe components. The sample probe component is then passed through a half-wave plate and a Glan-Taylor polarizer, which is adjusted to obtain equal amounts of vertically and horizontally polarized light. The intensity of the probe pulses is less than 1 μ J at the sample. After the sample, the probe beam is split into horizontal and vertical polarization components and imaged onto the detectors. Alternatively, in the two-color transient absorption experiments, a portion of the 775 nm light is focused onto a sapphire window to generate a white light continuum. A spectral portion of the continuum is selected using interference filters and used as the sample probe. In all cases, the reference and polarized probe beams are imaged onto UDT Sensors PIN 10D photodiodes, biased at -15 V. The photodiode outputs are amplified and input into a Stanford Research Systems gated integrator. The gated integrator output is measured using a National Instruments 16 bit A/D converter in the data acquisition computer. The A/D converter and gated integrator triggering and reset are synchronized with the CPA 2001 Q-switch and controlled by home-built timing electronics. Data acquisition and movement of the delay stage is controlled by LabView software running on a Pentium II computer.



Figure 1. Absorption and emission spectrum of 3.5 nm MoS_2 nanoclusters following extraction into acetonitrile.

Electron Microscopy and Diffraction. The sizes of the different nanoclusters are determined with transmission electron microscopy (TEM) using a Philips CM-100 TEM operating at 100 kV. A small fraction of the nanocluster solution (either acetonitrile or octane phase) is diluted by a factor of 5, and a drop of the diluted solution is spread over a copper grid (300 mesh size) supporting a thin film of amorphous carbon. To reduce the damage from the electron beam, the sample is cooled to liquid nitrogen temperature during data collection. Electron diffraction results were obtained with the same instrument and on the same samples.

Synthesis and Characterization

3.5 nm Nanoclusters. The 3.5 nm nanoclusters are synthesized using the same methods as in previous studies.^{16,18,19,24} MoCl₄ is dissolved in a ternary tridodecylmethylammonium iodide (TDAI/hexanol/octane, 8/8/84 wt %) inverse micelle solution at a concentration of 1.0×10^{-3} M. H₂S (4.0 molar equiv) is added via a gastight syringe to the solution. Reaction occurs within a few minutes. Following reaction, the inverse micelle solution, along with the MoS₂ nanoclusters, are extracted with an equal volume of acetonitrile. The nanoclusters partition approximately equally between the octane and acetonitrile phases.

These nanoclusters are characterized by optical spectroscopy, TEM, electron diffraction, and time-resolved emission depolarization of adsorbed DQTCI dye. The absorption and emission spectra of these nanoclusters are shown in Figure 1. Previous studies by a different group have characterized similar nanoclusters with TEM and optical spectroscopy and have chromatographically purified the particles.^{16,17} The absorption spectrum has a maximum at 362 nm, in agreement with previously reported absorption spectra. The absorption spectra obtained from the octane and acetonitrile phases exhibit the same absorption maximum. The emission spectra are almost featureless and peak at about 420 nm. TEM images of these nanoclusters are shown in Figure 2 and indicate that the average particle diameter is about 3.5 nm. The average size may also be determined by rotational diffusion measurements of an adsorbed cyanine dye, DQTCI. This dye absorbs and emits at about 580 and 650 nm, respectively, which is far to the red of the MoS₂ nanocluster absorption and emission. The rate of emission depolarization is indicative of the rotational diffusion rate and thus the nanocluster/dye hydrodynamic radius. In these studies, a small portion of the nanocluster/micelle sample is



Figure 2. TEM image of 3.5 nm MoS₂ nanoclusters.

transferred into a gastight vial. The solvent is evaporated, and the nanoclusters are subsequently redissolved in acetonitrile in the presence of DQTCI. Repeated evaporation of the solvent followed by dissolution in acetonitrile results in complete removal of the hexanol and in the DQTCI adsorbing onto the particles. The nanoclusters with adsorbed DQTCI are then redissolved in pentane. DQTCI is almost completely insoluble in pentane, ensuring that all of the dye in this solution is indeed adsorbed onto the MoS₂ nanoclusters. The DQTCI/nanocluster solution shows a small spectral shift of the dye absorption, also indicating that the dye is absorbed on the nanoclusters. The static emission is of comparable intensity to that of an equal concentration of DQTCI in ethanol, indicating a lack of quenching by electron transfer. The rotational diffusion dynamics of the DQTCI absorbed on the nanoclusters are determined by time-correlated single photon counting, with sample excitation at 580 nm and emission detection at 650 nm. Both parallel and perpendicular polarizations of the emission are determined. Typical anisotropy decays are shown in Figure 3. The anisotropy of DQTCI in acetonitrile (no MoS₂ nanoclusters) decays very rapidly, in about 100 ps. The average nanocluster size is calculated from these results, on the basis of the Navier-Stokes equation³⁹ that is solved for an oblate rotor using stick boundary condition. Two very reasonable assumptions are made to facilitate these calculations. It is assumed that the thickness of the nanocluster corresponds to that of a single layer of MoS₂ (see below) and that the transition dipole of the absorbed dve is perpendicular to the principal axis of the disc-shaped MoS₂. A Gaussian constraint on the particle-size distribution is also assumed. The temperature of the experiment is 298 K, and the solvent viscosity of *n*-pentane is 0.224 cP. The probability of dye absorption is taken to vary with the particle size and to be proportional to the circumference of the particle. The first 50 ps is not considered in order to neglect the stimulated emission during the excitation pulse duration. A calculated curve corresponding to 3.4 ± 0.6 nm is also shown in Figure 3. Agreement between the observed and calculated depolarization kinetics is quite good. This approximately 3.4 nm average size is also in good agreement with the TEM results.



Figure 3. Emission anisotropy of DQTCI adsorbed on 3.5 nm (MoS₂/TDAI) (lower curve) and polydisperse (MoS₂/DDAB) (upper curve) nanoclusters. Also shown are curves calculated for the rotational diffusion of 3.4 ± 0.6 nm and 4.5 ± 1 nm MoS₂ particles.



Figure 4. TEM image of polydisperse MoS_2 nanoclusters synthesized in DDAB/hexanol/octane micelles. Nanoclusters ranging in size from ~ 2 to ≥ 15 nm can be seen.

Nanoclusters having diameters of 3.5 nm can also be synthesized from a polydisperse sample simply by the addition of iodide ions. The polydisperse sample is synthesized using the same procedure as above except that the ternary inverse micelle solution consists of DDAB/hexanol/octane (6/10/84 wt %), where DDAB is didodecyldimethylammonium bromide. $MoCl_4$ is dissolved in this solution at a concentration of 10^{-3} M and 4.0 molar equiv of H₂S is added via a gastight syringe. Reaction occurs within a few minutes. The absorption spectrum of this solution is featureless beyond 300 nm and decreases smoothly with increasing wavelength, extending out to about 520 nm. This solution is stable for days but will eventually form a precipitate. A TEM image of these particles is shown in Figure 4. The image shows that the sample is highly polydisperse, having particle sizes ranging from about 2 nm to greater than 15 nm. Extraction of these polydisperse MoS₂ nanoclusters with acetonitrile results in the nanoclusters going into the octane phase. The extracted solution is less stable than the micelle solution, and the particles are usually left in the micelle solution.



Figure 5. Absorption spectra of $DDAB/MoS_2$ nanoclusters before (dotted line) and after (solid line) addition of TDAI.

The broad size distribution of these samples is also confirmed by rotational diffusion measurements. DQTCI dyes may be attached to these particles, and a typical emission depolarization decay is shown in Figure 3. The decay is multiexponential and considerably longer than that obtained for the 3.5 nm particles. This decay can be fit assuming particle sizes of 4.5 ± 1 nm.

Following the above synthesis, 0.5 g of TDAI surfactant is added to 10 mL of polydisperse nanocluster inverse micelle solution. The absorption spectrum of this mixture is shown in Figure 5. The reaction mixture remains sealed under a nitrogen atmosphere and left in the dark for several days while further reaction occurs. The resulting spectrum has a well-defined peak at 362 nm, indicating the presence of 3.5 nm particles. At this point, DQTCI dye may be attached to the nanoclusters, and the emission depolarization decay is very similar to that of the 3.5 nm particles (see Figure 3). TEM images also show that the particle-size distribution has narrowed and become smaller.

Samples were also synthesized using TDAC (tridodecylmethylammonium chloride) or mixtures of TDAI and TDAC as the surfactant. The use of TDAC as the surfactant usually results in polydisperse samples similar to those obtained using DDAB as the surfactant. In some cases, a shoulder in the 360-362 nm region is obtained. Previous studies have shown a resolved 360-365 nm peak in MoS2 nanocluster samples synthesized in TDAC/hexanol/octane inverse micelles.^{16,18} This is an important observation in considering the origin of the 362 nm peak, discussed below. The reason that our present samples do not show a resolved peak, while the previous syntheses do, is not known. However, we note that the previous syntheses were done with commercial MoCl₄, and the syntheses reported here were done with freshly synthesized, highly purified MoCl₄. (To the best of our knowledge, MoCl₄ is no longer commercially available.) The presence of small amounts of other molybdenum oxidation states in the commercial MoCl₄ may affect the particle-size distribution.

Several samples were synthesized using a mixture of TDAI and TDAC surfactants. The resulting absorption spectra were superpositions of the polydisperse and 3.5 nm particle spectra. Increasing the fraction of TDAC increases the polydisperse component of the spectrum. Subsequent extraction with aceto-nitrile results in the polydisperse component going into the octane phase and the component having the absorption maximum at 362 nm going into the acetonitrile phase. Little or no shift of this absorption maximum is observed as the TDAI/TDAC ratio is varied.

It is necessary to comment on the possibility of spectral interferences caused by the formation of I_3^- . We note that the absorption spectrum of I_3^- has a peak at about 366 nm, which could interfere with the 362 nm peak observed here. Indeed, it has been suggested that the peaks near 366 nm in the PbI₂ nanocluster absorption spectrum may be assigned to ionic species such as I_3^- rather than to the nanoclusters,⁴⁰ although counterarguments have been given.⁴¹ Independent of any controversy in the PbI₂ case, the results of blank experiments rule out such an assignment or the possibility of significant spectral interference in the present cases. Specifically, performing the synthesis without the metal chloride results in baseline absorption in the 330-500 nm range. As long as the sample remains sealed and in the dark, this blank spectrum is stable. Subsequent exposure to air and light results in an increase of absorption in the 366 nm region, presumably because of the oxidation of I^- to I_3^- . With this in mind, exposure of the samples used here to air and light was avoided. It is also possible to imagine that solution-phase I_3^- could be formed by a redox reaction with MoCl₄, specifically, MoCl₄ + $3I^- \rightarrow MoCl_2$ + $2Cl^{-} + I_3^{-}$. This possibility is also eliminated by blank experiments. No peaks in this spectral region are formed in the absence of H₂S. The only conceivable way that I_3^- could be formed is if the above redox reaction becomes favored in the presence of MoS₂ particles (i.e., if I₃⁻ is stabilized by being formed directly on the nanocluster surfaces). I_3^- is known to have a great affinity for metal atoms on the edges of MoS₂type surfaces, 4^{42-44} which could stabilize I_3^- formed in this way. This possibility cannot be eliminated by any simple control experiments, and it is possible that some I_3^- is formed in this way, resulting in spectral interference. However, as noted above, syntheses using TDAC as the surfactant and the commercial MoCl₄ also give a resolved 360-365 nm peak having an intensity comparable to that observed here.^{16,18} The commercial MoCl₄ may have impurities corresponding to other molybdenum oxidation states, but the synthesis of MoCl₄ does not involve any iodine-containing reagents^{37,38} so it surely does not have iodide ions. In this case, the 360-365 nm peak can have no I₃⁻ spectral interference. The observation that the peak observed in the spectrum of nanoclusters synthesized with commercial MoCl₄ has comparable intensity to the 362 nm peak reported here indicates that the majority of this feature is not due to I_3^- . We also note that 4.5 and 8 nm MoS₂ nanoclusters may be synthesized in a somewhat basic TDAI micelle (see below), without the formation of a 362 nm peak. This synthesis is quite analogous to the procedure described above and therefore serves as another control for the formation of I_3^- . We conclude that we cannot exclude the possibility of some spectral interference from adsorbed triiodide formed by an in situ surface redox reaction. However, we emphasize that there is no reason to suspect any spectral interference and that the TDAC synthesis results show that most or all of the resolved 362 nm peak is due to absorption of the nanocluster itself rather than to $I_3^$ chemisorbed on the nanocluster edges.

4.5 and 8 nm Nanoclusters. The 4.5 and 8 nm nanoclusters are synthesized as follows. MoCl₄ is dissolved in a ternary inverse micelle solution of either dodecyltrimethylammonium chloride (DTAC/hexanol/octane, 3/8/89 wt %) or tridodecylmethylammonium iodide (TDAI/hexanol/octane, 8/8/84 wt %) at a concentration of 1.0×10^{-3} M. Aqueous (NH₄)₂S (100 µL of a 20% solution) is injected into the rapidly stirring solution. Reaction occurs within about a minute. The absorption spectrum of this solution is shown in Figure 6. The presence of a well-defined 400 nm absorption peak indicates nanocluster formation.



Figure 6. Absorption spectrum of a sample produced by the injection of $(NH_4)_2S$ into a $MoS_2/DTAC$ inverse micelle solution. The solid curve is obtained immediately after injection and corresponds to a mixture of 4.5 and 8 nm MoS_2 nanoclusters. The dotted curve is obtained a day later and corresponds to mostly 8 nm MoS_2 nanoclusters.

TEM images taken from grids prepared at this point are shown in Figure 7 and show that these particles have an average diameter of about 4.5 nm. As the samples age, the 400 nm peak slowly loses intensity and is replaced by a well-defined peak at 473 nm. TEM images taken from grids prepared at this point indicate the presence of 8 nm nanoclusters (see Figure 7). The latter TEM image shows that there remains a small but nonnegligible population of 4.5 nm particles. Consistent with this observation, there remains a small 400 nm peak in the latter spectrum in Figure 6. It is important to note that the 400 nm peak does not gradually shift to 473 nm. Rather, the 473 nm peak grows at the expense of the 400 nm peak, with an isosbestic point at 455 nm. This process occurs on the time scale of several hours and reaches equilibrium in about a day. Following the reaction, the inverse micelle solution, along with the MoS₂ nanoclusters, may be extracted with an equal volume of acetonitrile. We find that if TDAI is used as the surfactant then the nanoclusters go into the octane phase. Alternatively, if the same synthesis is performed using DTAC as the surfactant, the nanoclusters go into the acetonitrile phase.

Samples of 8 nm nanoclusters may also be synthesized from samples of polydisperse nanoclusters. Samples of polydisperse nanoclusters are synthesized as described above. Addition of a nonaqueous base, such as NaCN or Na₂S, to this solution results in formation of a well-defined peak at 470 nm. TEM images taken at this point indicate a similar size distribution to that obtained from the $(NH_4)_2S$ synthesis, centered at about 8 nm.

Electron Diffraction Results. Electron diffraction patterns have been obtained for the 3.5 and 8 nm nanoclusters as well as bulk 2H-MoS₂. These results can be interpreted by comparison with electron diffraction simulations. MoS₂ commonly exists as one of two different polytypes, 2H and 3R, which differ in stacking of the S-Mo-S sheets. The more common is the 2H polytype, in which the unit cell consists of two S-Mo-S trilayers with the molybdenum atoms of one layer situated directly above the sulfur atoms of the adjacent layer.⁴⁵ The experimental and calculated diffraction patterns show complete agreement for the bulk 2H-MoS₂; all reflections within a scattering angle of 4° for 100 keV electrons can be assigned. This result serves as an accurate calibration of the TEM instrument on which the diffraction patterns are obtained. Electron diffraction simulations show that the diffraction patterns for the 2H and 3R crystal structures converge as the size of the

(a)



Figure 7. TEM images of mixtures of 4.5 and 8 nm MoS₂/DTAC nanoclusters. The upper panel corresponds to a sample immediately following synthesis and is almost exclusively 4.5 nm particles. The lower panel corresponds to a day after synthesis and is mostly 8 nm particles.

structures decreases along the crystallographic c axis. These electron diffraction simulations show that within a scattering angle of 4° for 100 keV electrons four reflections having indices of (1,1,0), (3,0,0), (2,2,0), and (4,1,0) remain as the crystal thickness is decreased to a single unit cell. Other very intense reflections calculated for bulk 2H-MoS₂ (specifically, (0,0,2), (1,0,0), and (1,0,2)) broaden out and are lost. This result matches the experimental result for both the 3.5 and 8 nm nanoclusters. Diffraction rings at radii corresponding to the (1,1,0), (3,0,0), (2,2,0), and (4,1,0) reflections are observed, and nothing is observed at radii corresponding to the (0,0,2), (1,0,0), and (1,0,2)reflections. We therefore conclude that the MoS₂ nanoclusters

consist of a single trilayer type of structure. This same conclusion was reached for WS₂, MoSe₂, and WSe₂ nanoclusters of comparable size.^{21,22} This conclusion makes good sense in terms of the bonding; the only thing holding the trilayer sheets to each other are comparatively weak van der Waals forces. When the particles are sufficiently small, this binding is weak, and the sheets will spontaneously exfoliate. This result is also consistent with studies of other layered materials, which exfoliate into single covalently bound sheets.^{46,47}

Thermodynamic Control of Nanocluster Sizes. The above results may be summarized as follows. Polydisperse samples, synthesized from DDAB/hexanol/octane micelles, have particle sizes ranging from ~ 2 to ≥ 15 nm and featureless absorption spectra. These samples may be treated with either iodide ions or with a nonaqueous base. In the former case, TEM images show that a relatively monodisperse sample of 3.5 nm particles is formed and that the absorption spectrum develops a resolved peak at 362 nm. In the latter case, relatively monodisperse 8 nm particles are formed, and the absorption spectrum develops a resolved peak at 470 nm.

The above observations indicate that the nanocluster size distributions are controlled by thermodynamics rather than by the kinetics of nucleation and crystal growth. This is an unusual situation for semiconductor nanoclusters, but it is well documented for metal nanoclusters. In most semiconductor syntheses, narrow size distributions are obtained by separating the time scales of nucleation and subsequent crystal growth. Conditions are adjusted such that a burst of nucleation occurs upon mixing the reactants, followed by much slower growth. Because all nucleation occurs simultaneously and growth occurs at the same rate for all of the nascent nanoclusters, a narrow size distribution is obtained in the kinetically controlled limit. In contrast, under some circumstances, the size-dependent thermodynamics determines the size distribution of gold nanoclusters. This is not a "magic number" consideration resulting from the filling of structural or electronic shells but results from classical considerations of the free energies of bound and solution-phase ligands and of curved surfaces. The theory of how thermodynamics controls the size distribution of gold particles in the presence of alkanethiols has been considered in detail.¹⁰ The basic idea is as follows. Particles establish a size distribution that minimizes the free energy of the entire system. Thiols bind quite strongly to the surface of the gold, and the total free energy has contributions from both the surface energy of the gold particles and the adsorbed thiols. How this results in a thermodynamic minimum can be seen from simple scaling arguments. The surface free energy of the gold particles varies with the number of atoms per particle for a constant total number of gold atoms. Specifically,

 $\mu_{\text{surf}} = (\text{number of particles}) \times$ (number of surface atoms/particle) \times (energy/surface atom) (1)

We may define $N \equiv$ total number of atoms (which is constant) and $n \equiv$ number of atoms per particle. We have that (number of particles) = N/n and that the (number of surface atoms/ particle) scales as the square of the particle radius, or as $n^{2/3}$. Thus, the product of the first two terms in eq 1 is related to the total surface area and scales as $n^{-1/3}$. The surface energy per area (or the energy per surface atom) depends on the surface radius of curvature through the Gibbs-Thomson effect.⁶ This surface energy is taken to be C + D'/R or $C + D/n^{1/3}$, where C, D, and D' are constants and R is the particle radius. Thus, we get $\mu_{\text{surf}} = A/n^{1/3} + B/n^{2/3}$, where *A* and *B* are constants. Producing surface and decreasing the surface radius of curvature both cost energy, and *A* and *B* are positive constants. The thiol binding energy is given by

$\mu_{\text{bind}} = (\text{no. of bound thiols}) \times (\text{binding energy/thiol})$ (2)

The number of bound thiols is proportional to the total surface area and hence scales as $n^{-1/3}$. If the thiol binding energy is taken to be surface curvature-independent, then $\mu_{\text{bind}} = A'/n^{1/3}$. Binding of the thiols is energetically favorable, and A' is a negative constant. Thus, combining eqs 1 and 2, the total free energy depends on the particle size and $\mu_{\text{tot}} = \mu_{\text{surf}} + \mu_{\text{bind}} =$ $(A + A')/n^{1/3} + B/n^{2/3}$. If A + A' is negative, then μ_{tot} has a minimum at $n = (-2B/(A + A'))^3$, which corresponds to the thermodynamically favored nanocluster size. It is important to note that the free-energy minimum results from the combination of thiol binding favoring a high surface area and therefore small particles along with the Gibbs—Thomson effect favoring a flat surface and therefore larger particles.

The same basic idea may be applied to the 2-D MoS₂ nanoclusters studied here. In this case, the edge of the (assumed circular) nanoclusters plays the role of the surface in the 3-D gold nanoclusters. The nanocluster edges have exposed molybdenum atoms that may bind to ligands in solution. We suggest that in the neutral pH synthesis using TDAI as the surfactant the ligand that binds to the surface is I⁻ and in the syntheses using (NH₄)₂S or other bases (Na₂S or NaCN) the edge-binding ligand is SH⁻. Because MoS₂ particles are 2-D, the edge area per particle (i.e., the circumference) scales as $n^{1/2}$, and the total edge area at constant N scales as $n^{-1/2}$. By analogy to the 3-D case, the Gibbs-Thomson effect gives an energy term that scales as 1/R. The total free energy may be evaluated for the 2-D case, and we get $\mu_{\text{tot}} = \mu_{\text{surf}} + \mu_{\text{bind}} = (A + A')/n^{1/2} + B/n$. The presence of a strong binding ligand will result in the quantity A + A' being negative, and the free energy will have a minimum at $n = (-2B/(A + A'))^2$. A stronger binding ligand will result in a more negative value for A' and thus smaller particles. We suggest that I⁻ lowers the surface free energy of the nanocluster edges more than does SH⁻, resulting in smaller particles.

An obvious experiment is to try to vary the nanocluster size by varying the iodide ion concentration. One could imagine that this would vary the iodide ion chemical potential and thus vary the extent to which the nanocluster edges are bound by iodide ions. The effect of this would be to vary the magnitude of the A' constant (above) and thereby change the size corresponding to the minimum in the total chemical potential. It has been shown that varying the thiol concentration varies the gold particle size in the gold/thiol system. However, as described above, the result of this type of experiment is to obtain a welldefined peak at 362 nm as well as a broad absorption characteristic of a polydisperse sample. As indicated above, acetonitrile extraction of the nanoclusters synthesized in these mixed surfactant solutions results in a polydisperse sample in the octane phase and a 3.5 nm sample in the acetonitrile phase. The relative concentrations of these components depend on the TDAC/TDAI ratio, with more TDAC favoring a larger polydisperse component. This result may be understood in terms of the inverse micelle solution being a microheterogeneous environment, resulting in more complicated phase-dependent chemistry. We suggest that adsorption of iodide ions results in changing the nanocluster charge as well as the edge energy. Consider the following equilibrium



Figure 8. Absorption spectra of 3.5 nm (dashed curve), 8 nm (dotted curve) and a mixture of 4.5 and 8 nm (solid curve) MoS_2 nanoclusters. The mixture curve corresponds to a $MoCl_4/(NH_4)_2S$ synthesis shortly after injection. A difference curve corresponding to just the 4.5 nm nanoclusters is shown in the insert. The assigned polarizations of the absorption transitions are also shown.

where [MoS₂] refers to an MoS₂ particle and "exterior" and "interior" refer to the nanocluster being in the nonpolar and polar environments on the exterior and interior of the inverse micelles, respectively. MoS₂ particles on the exterior of the micelles (in the hydrocarbon phase) are uncharged and have few iodide ions adsorbed on their edges. We suggest that in the absence of adsorbed iodide ions there is no thermodynamic minimum in the size distribution and these nanoclusters are polydisperse. Decreasing the iodide ion concentration (in the mixed-surfactant syntheses) shifts this equilibrium to the left, increasing the fraction of polydisperse nanoclusters. In this model, nanoclusters on the interior of the micelle are in an environment that is close to saturated with iodide ions, and these nanoclusters always have the same minimum in their size distribution.

The above model considers the surface energy in terms of iodide ion adsorption. However, the same effects should be seen for any species that binds tightly to the nanocluster edge, thereby reducing its chemical potential. The media can be made basic by using (NH₄)₂S as the sulfiding agent in the synthesis or by the addition of Na₂S or NaCN following the synthesis of polydisperse particles. In all of these cases, SH⁻ is formed and can adsorb onto the nanocluster edges. We suggest that the extent to which the chemical potential is lowered by HS⁻ adsorption is somewhat less than that in the case of I⁻. Thus, the quantity A + A' is not as negative in the SH⁻ case, and larger (8 nm) particles are formed. Why the synthesis with (NH₄)₂S initially produces metastable 4.5 nm particles and only later gives the more stable 8 nm particles is not well understood at this point. The initial formation of 4.5 nm particles must be due to both kinetic and thermodynamic factors, but no detailed mechanism can be determined from the results presented here.

Size-Dependent Polarization Spectroscopy

The absorption spectra of the 3.5 nm MoS_2 nanoclusters and the mixture of 4.5 and 8 nm MoS_2 nanoclusters taken shortly after and a day after the $(NH_4)_2S$ injection are collected in Figure 8. As discussed above, injection of $(NH_4)_2S$ into an $MoCl_4$ inverse micelle solution immediately results in the formation of 4.5 nm particles, which later form almost exclusively 8 nm particles. Thus, at long times, there are mostly 8 nm particles, and their spectrum can be obtained with minimal spectral



Figure 9. Time-resolved total emission and emission anisotropy of 3.5 nm MoS_2 nanoclusters excited at 310 nm and detected at 425 nm.

interference from the 4.5 nm particles. The spectrum of the 4.5 nm particles (without spectral interferences of the 8 nm particles) can be obtained by subtracting the long-time spectrum from that obtained shortly after injection. Because there is some concentration of 8 nm particles in the sample shortly after synthesis, this subtraction is scaled to eliminate the 473 nm peak. This subtracted spectrum (Figure 8) shows the well-defined peak at 400 nm and a prominent shoulder at about 440 nm, both of which may be assigned to the 4.5 nm particles.

It is tempting to assume that the 473, 400, and 362 nm peaks correspond to the same transition in the 8, 4.5, and 3.5 nm particles, respectively, and that this transition correlates to the lowest allowed transition (the A exciton) in bulk MoS_2 . The lowest allowed transitions in the bulk material, the A and B excitons, are polarized perpendicular to the crystallographic caxis, so polarization studies of the nanocluster absorptions can determine if this is the case. Both time-resolved polarized emission and one-color time-resolved polarized absorption (transient bleach) studies can reveal the polarization of the absorption oscillator. The 8 nm particles are only very weakly emissive, making time-resolved emission polarization measurements problematic. However, the polarization of the 473 nm peak can be determined only by a polarized bleach measurement. The 3.5 nm particles are emissive, and the polarization of several of the lowest transitions may be determined from polarized emission measurements. The 4.5 nm particles are also only weakly emissive, and we have determined the polarization of the 400 nm peak and the 440 nm shoulder by polarized bleach measurements.

3.5 nm Nanoclusters. Time-resolved total emission and emission anisotropy decays for the 3.5 nm particles are shown in Figure 9. These data were obtained following 310 nm excitation using 450 nm detection. The anisotropy starts out at close to 0.4 and subsequently decays. The dynamics following excitation have been discussed in a previous article.²³ Photoselection theory gives the anisotropy for an incoherent pump/ probe emission experiment as^{48,49}

$$r = (I_{\text{par}} - I_{\text{perp}})/(I_{\text{par}} + 2I_{\text{perp}}) = \frac{2}{5}P_2(\cos\theta) = \frac{1}{5}(3\cos^2\theta - 1).$$

where θ is the angle between the pump and probe oscillators. A value of 0.4 can be obtained only when both pump and probe oscillators are linear and $\theta = 0^{\circ}$. If both oscillators are in a plane, then one must integrate over all orientations in the plane, and an anisotropy of 0.1 is obtained. The other situation relevant to disklike particles is if one oscillator is in-plane and the other is perpendicular to the plane. In this case, $\theta = 90^{\circ}$, and the anisotropy is -0.2. Thus, the initial anisotropy of 0.4 indicates that the absorbing and emitting oscillators are both linear and aligned. Because the only unique axis is the crystallographic caxis, we conclude that the absorption at 310 nm and the emission are both z-polarized. The initial anisotropy is excitation wavelength-dependent. We find that the anisotropy decreases with decreasing excitation wavelength in the 290-315 nm range and approaches 0.0 with 290 nm excitation. This result indicates the presence of an overlapping x - y polarized transition in the blue part of this range.

The combination of static absorption, time-resolved emission, and emission quantum yield measurements suggests that the emitting state is not the same state as that giving rise to the 362 nm absorption peak. The 362 nm peak has an absorbance of about 1.0 in a 0.2 cm path-length cell. These nanoclusters have on the order of 100 Mo atoms, and the original solution has $[Mo] = 10^{-3}$, making the nanocluster concentration about 10^{-5} M. Thus, these nanoclusters have an extinction coefficient at 362 nm of roughly 5×10^5 L mol⁻¹ cm⁻¹. In the strong quantum confinement limit, the excited state (exciton) does not have translational degeneracy, and we conclude that the observed transition is allowed. The emission lifetime is several nanoseconds, and a high emission quantum yield would be expected from an allowed transition. However, the emission quantum yield is observed to be about 10^{-3} . We therefore conclude that emission is from a low oscillator strength, z-axis-polarized transition buried under the red edge of the 362 nm peak. The static polarized excitation spectrum shows small, positive anisotropy throughout the 330-400 nm excitation wavelength range, indicating that the emitting state and the 362 nm peak have the same polarization, that is, they are both z-axis polarized. The exact magnitude of the splitting between these states cannot be determined from the results presented here. These assignments are summarized in Figure 8.

4.5 and 8 nm Nanoclusters. The polarizations of the lowest transitions of the 4.5 and 8 nm particles may be determined from one-color transient bleach measurements. Similar polarization considerations apply to these studies as apply to the case of the time-resolved emission studies, described above. In the bleach experiments, the sample is excited with polarized light, and the decrease of the absorbance at the same wavelength is measured. This may be thought of as a "polarization holeburning" experiment. The anisotropy of the absorbance change will be 0.4 or 0.1 for linear or planar polarized transitions, respectively. In these experiments, the bleach anisotropy was determined using femtosecond pulses, with the probe delayed a few picoseconds from the pump. The results reported here were obtained in acetonitrile solvent, which relaxes quite quickly, within a few picoseconds. This delay ensures electronic and vibrational relaxation as well as relaxation of optical Kerr effects induced in the solvent. One caveat about these transient bleach measurements need to be mentioned. The results could be confused by the presence of an excited-state absorption. To address this question, transient absorption experiments were performed with excitation at 475 nm and detection at 550 nm. This detection wavelength is to the red of the wavelengths at which a bleach would be observed and provides a measure of the transient absorption intensity in this general spectral range. An extremely small transient absorption is observed, which is at least a factor of 10 smaller than the magnitude of the observed bleach signals. We therefore conclude that the polarization of the bleach transients gives an accurate indication of the polarization of the transition being excited.

The transient bleach results indicate that excitation of the 4.5 nm nanoclusters at 387.5 nm induces a transient anisotropy very close to 0.10, which means that the 400 nm peak is x - ypolarized. Determining the polarization of the 440 nm shoulder of the 4.5 nm particles is somewhat problematic because of the spectral overlap with the blue edge of the 473 nm peak (assigned to the 8 nm particles). However, this interference is minimized by taking the bleach results immediately after injection of $(NH_4)_2S$, when the sample has almost exclusively 4.5 nm particles. In this case, excitation at 450 nm induces a transient anisotropy that is very close to 0.40, indicating that the 440 nm shoulder is z-axis polarized. As the sample ages, the 450 nm absorption of the 4.5 nm particles is replaced by a weaker one assigned to 8 nm particles. As this process occurs, the anisotropy decreases, and the bleach becomes essentially unpolarized when the 400 nm peak is completely gone. Consistent with this result, bleach anisotropy measurements following excitation at 475 and 490 nm also show little or no anisotropy. We conclude that the 473 nm peak, assigned to the 8 nm particles, is close to isotropic, which could be due to x - y- and z-polarized transitions that are either overlapping or mixed. It is unlikely that the differently polarized transitions would be exactly overlapping, and if the lack of anisotropy were due to overlapping transitions, then some wavelength dependence of the anisotropy would probably be seen. The band is observed to be isotropic from 450 to 490 nm, and we suggest that the most likely explanation of the lack of polarization is that there is mixing of x - y- and z-polarized transitions at comparable energies. These assignments are also summarized in Figure 8.

Spectral Assignments. The polarization results presented above make it possible to establish the correlations of the transitions observed in these nanoclusters and in bulk MoS₂. In particular, these results show how quantum confinement affects the ordering of the excited states. The lowest allowed transitions in bulk MoS₂ are the A and B excitons at about 660 and 602 nm, respectively.50 Both of these absorption features are polarized perpendicular to the z axis in the x - y plane. Band structure calculations indicate that these two features correspond to the same transition, with the approximately 1500 cm^{-1} splitting caused by the interaction of adjacent trilayer sheets.^{27,36} Thus, only a single transition is expected for the present case of single trilayer nanoclusters. The spectroscopy of MoS₂ thin films and inorganic fullerenes shows that z-axis quantum confinement has only a small effect on this transition energy. The A and B excitons shift only about 0.1 eV (about 800 cm⁻¹) from the bulk energy in the thinnest (a few trilayers thick) inorganic fullerenes or thin films.^{27,51} Thus, in the absence of quantum confinement effects, interlayer interactions split a single transition at about 15 900 cm⁻¹ (630 nm) into the observed A and B exciton transitions.

Although these lowest x - y-polarized transitions are comparatively well understood, assignment of the lowest *z*-polarized transition is somewhat problematic. The *z*-axispolarized transitions in bulk MoS₂ are at an energy higher than that of the A and B excitons and have not been studied. Polarized absorptions in MoS₂ and related materials are typically studied using reflection spectroscopy of single crystals. Related literature on this subject indicates that producing MoS₂ single crystals,

 TABLE 1: Observed Transition and Quantum Confinement

 Energies

	x - y (observed)		z (observed)		$\Delta(x-y)$	Δz
	nm	$/1000 \ cm^{-1}$	nm	$/1000 \ cm^{-1}$	$/1000 \text{ cm}^{-1}$	$/1000 \text{ cm}^{-1}$
bulk 8 nm 4.5 nm	660, 630 473 400 200	15.88 ^a 21.1 25.0	$\approx 540^{b}$ 473 440 262	18.5 21.1 22.7	0 5.3 9.1	0 2.6 4.2

 a Taken from the average of the A and B excitons at 660 and 602 nm, respectively. b Estimated from the broad onset in the amorphous bulk MoS₂ spectra.

cut perpendicular to the basal plane and of sufficient optical quality, is difficult.^{52,53} However, the approximate energy of the lowest *z*-polarized transition may be inferred from the unpolarized amorphous thin film or colloidal particle spectra^{54,55} by knowing the energies of the x - y-polarized transitions from single-crystal spectra. Specifically, while the single-crystal x - y-polarized spectrum shows no transitions in the 500–600 nm region, the unpolarized amorphous thin film and colloidal particle spectra show a broad shoulder at wavelengths less than 570 nm. Assigning the energy of this transition is uncertain because these spectra are quite broad and no peak assignable to the *z*-polarized transition is resolved. However, on the basis of these unresolved spectra, there is probably a *z*-polarized transition in the (approximately) 540 nm region.

Quantum confinement is expected to affect the energies of the x - y- and z-axis-polarized transitions very differently. Photoexcitation produces a nodal plane that is perpendicular to the polarization of the light. We expect that the presence of a nodal plane will increase the spatial extent of the wave function perpendicular to that nodal plane. Thus, an excited state corresponding to an x - y-polarized transition will have a larger x - y spatial extent than will one corresponding to a z-polarized transition, that is, changes in x - y quantum confinement will have the largest effects on x - y-polarized transitions. On the basis of this expectation, an important prediction can be made: reducing the x - y dimensions of these 2-D particles will cause a larger blue shift of the transitions that are x - y polarized than of those that are z polarized. This differential quantum confinement effect can be seen by comparing the absorption spectrum of bulk MoS₂ with that of the 8, 4.5, and 3.5 nm particles. These comparisons are summarized in Table 1. The quantum confinement shifts of the lowest x - y- and z-polarized transitions are given as $\Delta(x - y)$ and Δz , respectively. These shifts are calculated by taking the lowest x - y-polarized transition in bulk MoS₂ to halfway between the A and B excitons. This is appropriate because the nanoclusters are single trilayers, and this value represents the energy of the zerothorder state in the absence of splitting from the interactions of adjacent trilayers. The lowest z-polarized transition in bulk MoS₂ is taken to be at 540 nm, as discussed above. In all cases, the lowest x - y-polarized transition correlates to the A and B excitons, and the lowest observed z-polarized transition correlates to the shoulder at 540 nm in bulk MoS₂. Table 1 shows that as the x - y dimensions of the particle are reduced quantum confinement causes both the x - y- and z-polarized transitions to move to higher energies. As expected from the above arguments, quantum confinement in the x - y plane has a larger effect on the energies of the x - y-polarized transition than on those of the z-polarized transition. The values in Table 1 indicate that the effect of changes in x - y quantum confinement is about twice as large for x - y-polarized transitions. We note that a reversal of the ordering of the excited states occurs upon quantum confinement. In particles smaller than 8 nm, the lowest allowed transition is z polarized, whereas in bulk MoS_2 it is x - y polarized. We suggest that the crossover occurs in particles that are about 8 nm in diameter.

We note that the spectra presented here are consistent with the conclusion made from the electron diffraction results: the particles are single trilayer disks. This result is seen from the comparison of the A and B exciton spectrum of bulk MoS₂ with the spectrum of the 8 nm particles. The splitting between the A (660 nm) and B (602 nm) excitons in bulk MoS₂ is about 1500 cm⁻¹. These transitions are of roughly comparable intensity. In contrast, the spectrum of the 8 nm particles shows a single, well-resolved peak at 473 nm, with the next transition at about 340 nm. The separation between these transitions is about 8000 cm^{-1} . A peak 1500 cm^{-1} to the blue of 473 nm would be at about 442 nm. Figures 6 and 8 show no evidence in the 8 nm particle absorption spectrum of the sort of splitting that gives rise to the A and B exciton in bulk MoS2. Because band structure calculations indicate that the A-B exciton splitting is due to interlayer interactions,27,36 this result also indicates that these particles are single trilayers.

Finally, it is of interest to compare the results presented here with the morphology-dependent spectroscopy of CdSe. The sizedependent emission polarization observed here is somewhat analogous to that observed in CdSe quantum dots and rods. Emission from CdSe quantum dots is planar polarized, with the unique axis established by the crystal structure.⁴ CdSe rods grow along the unique axis, and when the rods are sufficiently long, the emission is linearly polarized.^{56,57} In both the present case and the case of CdSe, it is the change in the particle aspect ratio that changes the amount of *z*-axis versus x - y-plane quantum confinement and thereby causes the ordering of the states to reverse.

Conclusions

Several conclusions may be drawn from the results presented here.

(1) 3.5, 4.5, and 8 nm MoS_2 nanoclusters can be synthesized using inverse micelle methods. Electron diffraction and optical spectroscopic results indicate that these particles are a single trilayer (S-Mo-S) thick. The 3.5 and 8 nm diameter particles are stable, whereas the 4.5 nm particles are metastable, forming 8 nm particles in a matter of hours.

(2) The 3.5 and 8 nm particles may be synthesized directly or from previously synthesized polydisperse samples. The observation that the average size of a polydisperse distribution can be either increased or decreased by the addition of iodide ions or an increase of the pH indicates that these sizes are controlled by thermodynamics and correspond to free-energy minima.

(3) The free-energy minima corresponding to the 3.5 and 8 nm particles may be understood in terms of the particle-edge energies, the ligand (I^- or SH⁻) adsorption energies, and the Gibbs—Thomson effect. This situation is completely analogous to thermodynamic control of the size distribution of gold particles with adsorbed thiols.

(4) The combination of transient bleach and emission studies permits assignment of the polarization of the lowest observed transitions in each case. We find that the lowest transition in the 8 nm particles is at 473 nm and is a mixture of x - y and z polarizations. The 4.5 nm particles have transitions at 440 nm (z polarized) and 400 nm (x - y polarized). The 3.5 nm particles have *z*-axis-polarized allowed transitions at about 310 and 362 nm and a *z*-axis-polarized forbidden transition at

somewhat longer wavelengths. The lowest x - y-polarized transition is at about 290 nm.

(5) The lowest observed transition in bulk MoS_2 is x - y polarized, and we conclude that the ordering of this transition and the lowest *z*-polarized transition reverse for particles smaller than about 8 nm.

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