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SYNTHESIS AND OPTICAL PROPERTIES OF MoS_2 NANOCCLUSERS

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ABSTRACT

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Highly crystalline nanoclusters of MoS_2 were synthesized and their optical absorption and photoluminescence spectra were investigated. Key results include: (1) strong quantum confinement effects with decreasing size; (2) preservation of the quasiparticle (or excitonic) nature of the optical response for clusters down to ~ 2.5 nm in size which are only two unit cells thick; (3) demonstration that 3-D confinement produces energy shifts which are over an order of magnitude larger than those due to 1-D confinement; (4) observation of large increases in the spin-orbit splittings at the top of the valence band at the K and M points of the Brillouin zone with decreasing cluster size; and (5) observation of photoluminescence due to both direct and surface recombination.

INTRODUCTION

This paper deals with the synthesis and optical properties of size-selected nanoclusters of the layered compound, molybdenum disulfide (MoS_2). Bulk MoS_2 has been studied extensively because it approximates a 2-D system. Understanding how this 2-D character influences the synthesis, structure and electronic properties of nanoclusters of these materials represents a serious challenge. On the applied side there is a need to develop semiconductors for use as photocatalysts for solar fuel production and detoxification of chemical waste. In such applications the semiconductor spectrum must be resistant to photochemical degradation and must have a bandgap that is matched to the solar spectrum. Early work² has suggested that bulk MoS_2 is a good, stable candidate for solar photoelectrochemical applications, and subsequent bandstructure calculations³ have shown that this stability derives from the fact that the relevant state at the top of the valence band is an antibonding state. While the stability of MoS_2 against photocorrosion is attractive, a limitation to its potential as solar a photocatalyst is the fact that in bulk form it is a black solid with indirect bandgap in the near infrared (~ 1.0 eV)^{1,3} and its valence and conduction band energies are not sufficiently large to allow desired chemistry (e.g., water splitting). This limitation can, in principle, be overcome by tailoring the electronic structure by forming clusters. Space limitations restrict this paper to the presentations of few of the results. A more detailed account will appear elsewhere.⁴

EXPERIMENTAL DETAILS

The clusters were grown inside inverse micellar cages in non-aqueous solvents.^{4,5} They are formed by first dissolving a molybdenum (IV) halide salt inside the cages and then combining this solution with another inverse micellar solution containing a sulfiding agent (e.g., metal sulfide or H_2S). The cluster size is varied by using different sized micellar cages. Electron diffraction and x-ray diffraction show the expected bulk hexagonal structure,^{4,6} and high resolution TEM fringe imaging reveals that clusters down to ~ 3 nm are highly crystalline with no defects.⁴ Cluster size was determined by TEM and estimated from dynamic light scattering (which measures the hydrodynamic radius) and from the chromatographic elution time in

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calibrated columns (for the smallest clusters). As grown cluster samples were purified using high pressure liquid chromatography.

RESULTS AND DISCUSSION

Optical Absorption of MoS₂

Figure 1 shows the absorption spectra of different MoS₂ cluster samples and compares these spectra to those of two bulk crystalline samples taken from Refs. 7 and 8. The spectrum of bulk MoS₂ consists of a series of absorption thresholds the first of which corresponds to weak absorption in the near IR at ~1040 nm (~1.2 eV) associated with an indirect gap between Γ and the middle of the Brillouin zone between Γ and K. The second threshold occurs at ~700 nm (~1.8 eV) and is associated with a direct transition at the K point.³ The two peaks (A₁ and B₁) on the short wavelength (λ) side of this threshold are the first (n=1) members of two excitonic Rydberg series corresponding to the transitions K4→K5 and K1→K5, respectively, whose energy separation (~0.20 eV) is due to the spin-orbit splitting of the top of the valence band at K.^{3,7} A third threshold at ~500 nm (~2.5 eV) is due to a direct transition from deep in the valence band to the conduction band. Excitonic features (C and D) are also associated with this transition. A fourth threshold at ~350 nm (~3.5 eV) is also due to transitions from deep in the valence band. Features on the high energy side of this threshold (e.g., E in Figure 1) are seen in thin samples as illustrated in curves 2' and 2".^{7,9}

The cluster results in Fig. 1 show that the main absorption features in this spectral region remain essentially unaltered, but exhibit large blue shifts with decreasing cluster size. Because our measurements were made on dilute solutions (10⁻⁴ to 10⁻³) molar, and because of the inherent weak absorption characteristic of indirect transitions, the signal-to-noise ratio for the cluster samples did not allow measurements in the region of the indirect gap. Nevertheless, the shape of the cluster spectra on the short λ side of this gap suggests that the gap remains indirect. Figure 1 shows the evolution of the room temperature absorption spectrum with decreasing size reveals a one-to-one correlation between the bulk and cluster spectra.⁴

The resolved features in the spectra of the purified samples in this figure make it clear that the bulk-like excitonic features are retained to smaller cluster sizes than originally thought.⁶ The earlier spectra of unpurified samples suggested that a bulk-like to molecule-like crossover occurs in the 3 to 2.5 nm size range. The present results on purified samples suggest that this expected crossover occurs below 2.5 nm.⁴ This is a remarkable result which indicates that clusters which are only two unit cells thick have enough densities of states to reproduce bulk-like absorption properties, a feature undoubtedly related to the 2-D nature of MoS₂.

A variety of theoretical models have been used to describe size quantization in semiconductor clusters.¹ They include effective mass (EM) treatments, semi-empirical tight binding treatments and recent empirical pseudo-potential methods. Despite their shortcomings, the EM models contain some of the essential physics and provide a qualitative framework for examining experimental data and their trends. In terms of these models, the shift of the absorption edge, E(R), of a cluster of radius R relative to that of the bulk is to a reasonable approximation proportional to 1/2 μ R², where μ is the reduced mass of the exciton.¹ A plot of E(R) vs. 1/R² should then yield a straight-line with slope $\propto 1/(2\mu)$. Figure 2 shows such a plot for the various spectral features in the absorption spectrum of MoS₂. The curves show the now familiar deviations from linearity for small clusters, highlighting the inadequacy of EM theory in

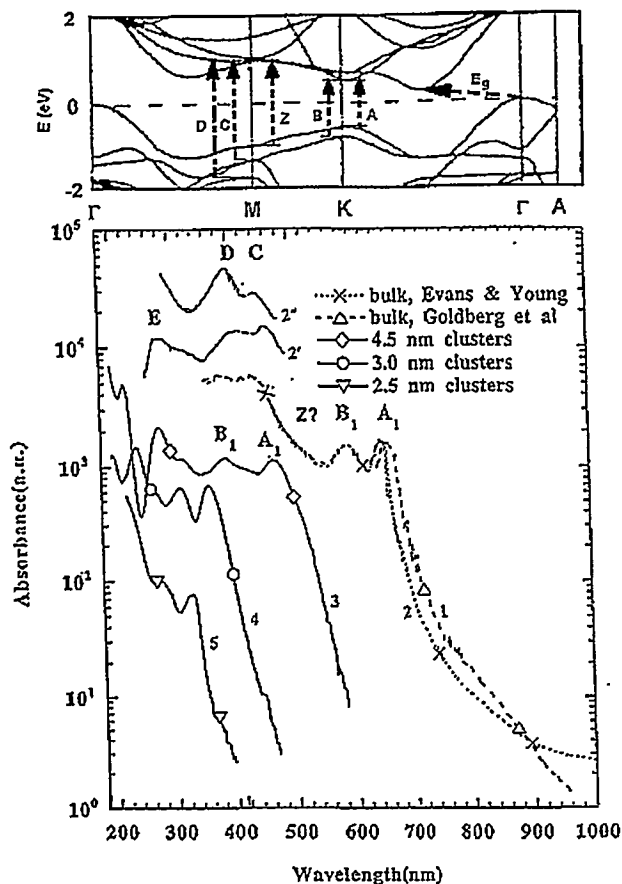
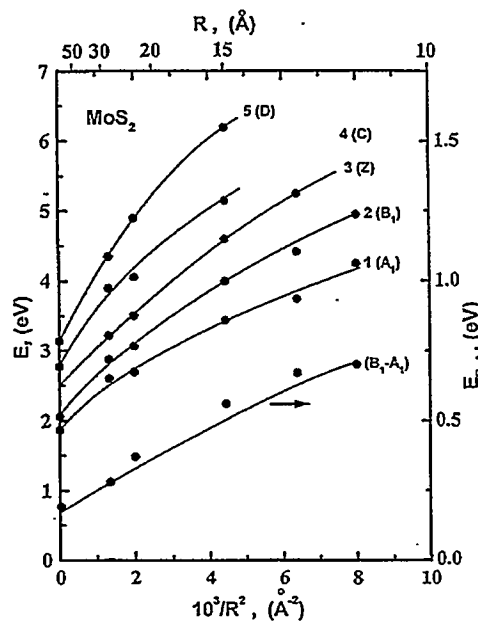


Fig. 1

Optical absorption spectra of two bulk crystalline samples (curve 1 synthetic crystal, Ref. 8; curve 2 natural crystals, Ref. 7) showing various absorption features discussed in the text. Curves 2' and 2'' (from Ref. 9) provide better resolution of the high energy features. For comparison, long wavelength spectra for three cluster sizes are shown. The top of the figure is a portion of the band structure of MoS₂ (taken from Ref. 3) showing the proposed transitions which correspond to the various features in the optical absorption spectra.

Fig. 2

Shifts of the various features observed in the optical absorption spectra of MoS₂ clusters. Also shown (right ordinate) is the increase in the spin-orbit splitting of the A₁ and B₁ excitonic peaks.



this regime. For the larger clusters the initial slope in Fig. 2 yields for the A₁ exciton μ in the range $(0.1-0.2) m_0$, where m_0 is the free-electron mass. This value of μ is comparable to the bulk value of $0.18 m_0$ for the A exciton deduced from optical measurements.⁷ Figure 2 also shows the influence of cluster size on the separation of the excitonic peaks A₁ and B₁, i.e., $E_{B_1-A_1}$ which is due to spin-orbit splitting at the top of the valence band at the K point. This splitting increases from 0.19 eV in the bulk to 0.67 eV for the 2.5 nm clusters.

Consistent with their being weakly bound (i.e., delocalized) Wannier excitonic peaks, the bulk excitonic Bohr radius (r_B) for the $n=1$ Rydberg states of A and B is $r_B=2.0$ nm.^{7,9} Thus, our

4.5 nm (diameter) clusters are only slightly larger than the size of the exciton in the bulk, and the 3.0 nm and 2.5 nm clusters are smaller. Theoretical considerations¹ suggest that when $R/r_B > 4$, the quasiparticle characteristics of the excitons are preserved, whereas for $R/r_B < 2$ these characteristics are lost leading to individual confinement of the electron and hole which then behave like independent particles. Clearly, the data in Fig. 2 show that for MoS₂ clusters the quasiparticle nature of the A and B excitons (as well as the C-D excitons) is preserved to much smaller cluster sizes. No specific assignment of peaks C and D in bulk material have been made; however, using Coehoorn et al's³ band structure results, we assign⁴ these peaks to direct transitions from the spin-orbit-split valence band to the conduction band at the M point (see Fig. 1). The spin-orbit splitting of the top two valence band states at M in the bulk is about twice as large as that at K (0.37 vs. 0.19 eV), and the data in Fig. 2 clearly show that quantum confinement has a strong influence on this splitting. For the 3 nm clusters $\Delta_{D-C} \approx 1.05$ eV. The large increases in the spin-orbit splittings with decreasing cluster size reflect the influence of quantum confinement on the split-off energy levels and to some degree changes in the degree of hybridization among the various Mo and S atomic orbitals. Understanding these changes requires detailed electronic structure calculations.

Photoluminescence of MoS₂ Nanoclusters

In our earlier work on unpurified MoS₂ clusters⁶, the photoluminescence (PL) was dominated by surface recombination. Chromatographic purification has led to significant improvement in the quality of the PL spectra and to the observation of both band edge (direct) as well as surface e-h recombination. Figure 3 shows the room temperature absorption and PL spectra of a 3.0 nm cluster sample. For excitation at $\lambda=450$ nm, which is seen to be a slightly longer λ than the first absorption threshold at ~ 420 nm, a single PL peak centered at 520 nm is observed. Clearly this PL is associated with surface recombination. Excitation at 348 nm (i.e., near the A₁ excitonic peak), however, leads to a PL spectrum consisting of two overlapping peaks. The more intense peak is centered at 420 nm which is seen to be the first absorption threshold for these clusters, and is attributed to direct band (K) edge recombination. Decomposition of the PL spectrum into its two components reveals the second peak which is centered at ~ 520 nm. This much less intense peak is at the same λ as the PL observed for 450 nm excitation, again pointing to its surface recombination character. For excitation at 225 nm (not shown), the PL spectrum consists of two overlapping peaks. The more intense PL is centered at 354 nm which is near the absorption threshold for the B₁ excitonic peak and thus represents direct band-edge recombination. The less intense peak is centered at 420 nm which is again the first absorption threshold for these clusters. For excitation at 425 nm, i.e., just above the first absorption threshold (not shown), the main PL is again due to surface recombination and is centered at 520 nm.⁴ In an earlier collaboration¹⁰, we studied the PL emission kinetics of as-prepared ~ 3.0 nm and ~ 4.5 nm clusters. These samples exhibited weak PL peaks close to the first excitonic thresholds (A₁ peak). The PL decay times were nonexponential having components with time constants ranging from <100 ps to >10 ns. The small values of these time constants are consistent with direct e-h recombination as found in our data on purified samples.

1-D vs. 3-D Quantum Confinement

The above results have clearly illustrated strong three- dimensional (3-D) quantum confinement effects. Because the chalcogen-metal-chalcogen layers in MoS₂ and its Mo and W

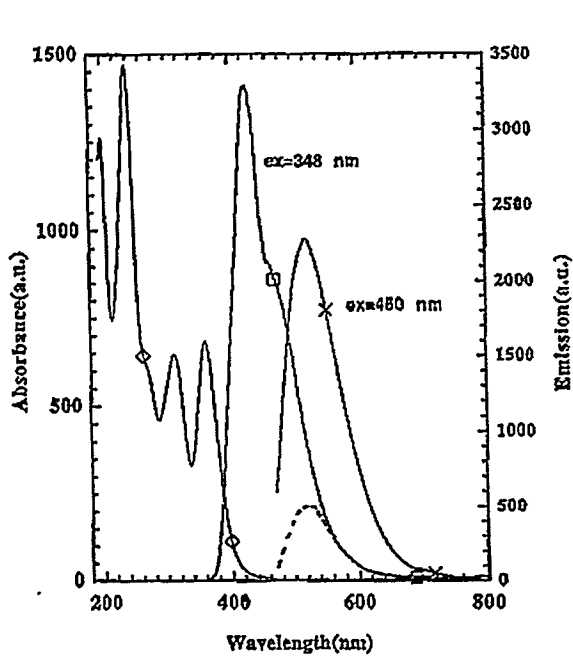


Fig. 3

Optical absorption and PL spectra of 3.0 nm MoS₂ clusters. The two PL spectra were measured for excitation wavelengths of 450 nm and 348 nm. The 348 nm PL spectrum is decomposed into its two components.

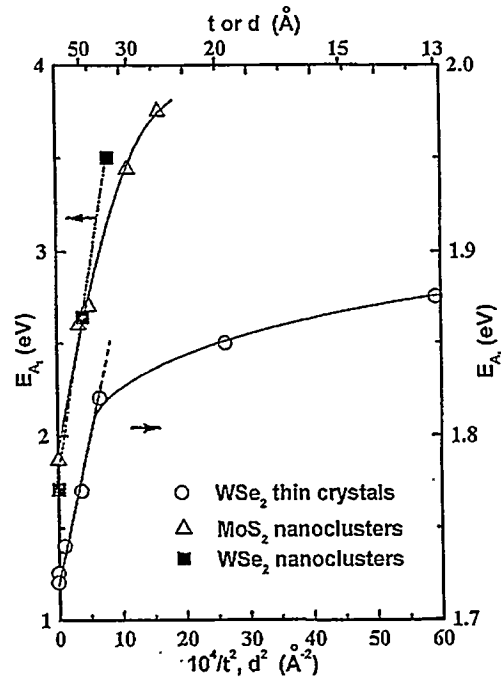


Fig. 4

Influence of dimensionality on the strength of quantum confinement of A₁ exciton in WSe₂ and MoS₂. Shown is the large difference between 1-D (thin crystals) and 3-D (clusters confinement).

isomorphs are held together by weak van der Waals forces, it is easy to cleave bulk crystals parallel to the layer planes. Remarkably, it has been possible to cleave bulk samples down to thicknesses of $\sim 13\text{\AA}$ (which corresponds to 1 unit cell thick) and measure the effects of quantum confinement (one-dimensional, 1-D, in this case) on their optical properties.

Consadori and Frindt¹¹ investigated the effects of crystal thickness (t) down to 13\AA on the A₁ excitonic peak of WSe₂ at 77K. Their results, E_{A_1} vs. $1/t^2$ (Fig. 4), effective mass-like behavior down to $t \approx 40\text{\AA}$, but deviate strongly at smaller thicknesses. The total shift in E_{A_1} between thick and 13\AA thin crystals is, however, only 0.15 eV. For comparison, we have also plotted our results (3-D confinement) for MoS₂ and WSe₂ as E_{A_1} vs. $1/d^2$, where d is cluster diameter. For WSe₂ we have data on only two cluster sizes, ($d=50\text{\AA}$ and 35\AA), but clearly the trend in the WSe₂ data is the same as for the more extensive MoS₂ data. Note that our data are read against the left ordinate and Consadori and Frindt's thin crystal data are read against the right ordinate. The comparison reveals a dramatic difference between 1-D and 3-D confinement. For sizes down to 40\AA , the shift in E_{A_1} is over an order of magnitude larger for 3-D than for 1-D confinement. The difference becomes even larger for smaller sizes. The large magnitude of the difference is undoubtedly related to the quasi 2-D structural properties of these materials. Furthermore, the very large difference between the behavior of the 13\AA (1 unit cell thick) thin crystal and our smallest clusters ($d \approx 25\text{\AA}$) clearly demonstrates that lateral confinement of the carriers within the X-M-X layers is much stronger than confinement in the direction perpendicular to the layers, again emphasizing the 2-D character.

CONCLUDING REMARKS

We have produced high crystalline quality nanoclusters of MoS₂ and demonstrated great tailorability of its optical absorption and photoluminescence properties with change in cluster size -- features that bode well for its potential as a solar photocatalyst. MoS₂ exhibits strong 3-D quantum confinement effects which reflect the 2-D nature of the structure and bonding. The quasiparticle (or excitonic) nature of the optical response is preserved down to clusters ~2.5 nm in size (~2 unit cells thick) and there are large increases in the spin-orbit splittings at the top of the valence band at the K and M points of the BZ with decreasing cluster size. Calculations of the electronic structure as function of cluster size are needed to more fully understand these features.

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