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Strong quantum-size effects in a layered semiconductor: MoS_2 nanoclusters

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High-quality, size-selected, nano-size (2–15 nm±10%) clusters of MoS_2 have been successfully grown inside inverse micellar cages and their optical properties have been studied. These clusters exhibit (1) large blueshifts in the optical-absorption features with decreasing cluster size due to quantum confinement, affording great tailorability in the absorption thresholds and (2) a demonstration of the crossover from bandlike (solid) to moleculelike spectra as the size of the clusters becomes smaller than that of the exciton in the bulk.

Clusters are an exciting class of materials whose properties are intermediate between atoms or molecules and bulk materials. They exhibit size-dependent physical and chemical properties largely as a consequence of the confinement of their electrons and their unusual surface morphology. The goal of much recent research on clusters is understanding the evolution of cluster properties with cluster size. Especially interesting are the manifestations of electron and hole confinement in semiconductor clusters as the cluster size decreases below the excitonic Bohr radius, and the electronic band structure gives way to discrete molecule-like electronic states. These effects have been studied experimentally and theoretically mostly in group II-VI semiconductors (CdS, CdSe, CuCl, etc.) and to a much lesser extent in group IV and III-V semiconductors (Si and GaAs).[1]

In this paper we report on the successful synthesis of size-selected nano-size clusters of molybdenum disulfide (MoS_2), a layered-structure material, and on their interesting optical properties. Highlights of the work include the observation of (1) remarkable structure in the absorption spectra reflecting the underlying physics as well as the high quality and size monodispersity of the clusters; (2) large blueshifts in the spectral features with decreasing cluster size affording great tailorability of the bandgap; and (3) a demonstration of the crossover from bandlike (solid) to moleculelike spectra as the size of the clusters becomes smaller than that of the exciton in the bulk.

Our choice of MoS_2 was motivated by both scientific and applied interest. On the scientific side, bulk MoS_2 crystallizes in a hexagonal layered structure ($P6_3/mmc$-D_{6h}^4) composed of sheets of Mo atoms sandwiched between sheets of S atoms in a S-Mo-S arrangement. The S-Mo-S sandwiches are held together by weak van der Waals forces and are stacked along the c axis with two sandwiches per unit cell ($c = 12.3$ Å). Given this interesting layered structure and a synthesis method in which clusters are grown inside inverse micellar cages,[2,3] a number of questions were of interest: will clusters of MoS_2 in the <10-nm size range form? Can the size of such clusters be controlled? Will these clusters exhibit novel properties and strong electron confinement effects?

Previous attempts to produce MoS_2 clusters consisted of growing them in porous glass,[4] dissolution of bulk powder in acetonitrile,[5] and sonication of bulk powders in water under Ar-He atmosphere.[6] Optical-absorption studies of materials produced by the first two methods gave some evidence of a blueshift in the spectrum relative to the bulk, but the absorption spectra were featureless, suggesting a broad distribution of cluster sizes.

The third method also did not allow control of cluster size, producing colloidal solutions with two size distributions achieved by filtration: a distribution of large particles 50 to several 100 nm in size, and a distribution of particles <10 nm in size. Both distributions exhibited optical-absorption features that were similar to, but essentially unshifted from, those of the bulk. This is not surprising because the particles in the first distribution are clearly too large to exhibit quantum-size effects, and the absorption spectrum of the second distribution appears to be also dominated by relatively large particles (which on the basis of our results presented below we estimate to be close to 10 nm in size). The spectrum of the solution with the small size distribution did, however, exhibit stronger absorptions at shorter wavelengths relative to absorption at longer wavelengths, a feature characteristic of the presence of some small particles.

MoS_2 has numerous applications as a catalyst. For example, we are interested in the potential of MoS_2 as a hydrogenation catalyst for the conversion of coal to liquid fuels and as an electrode material for photoelectrochemical solar cells. In the latter application MoS_2 is expected to be highly stable against photocorrosion,[7] and in both applications, clusters have significant advantages over bulk material.

Our clusters were grown inside inverse micellar cages in nonaqueous solvents.[2,3] Inverse micelles are formed when surfactant molecules are dispersed in a nonpolar (e.g., octane, oil) continuous medium. In such a medium, the hydrohilic ends of the surfactant avoid the oil and form cages whose sizes typically range from one to tens of nanometers. MoS_2 clusters are formed by first dissolving a molybdenum (IV) halide salt inside the cages and then combining this solution with another inverse micelle solution containing a sulfiding agent (e.g., metal sulfide or H_2S). All preparations were done in a Vacuum Atmospheres dry box with catalytic oxygen and water removal

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to prevent degradation of the Mo (IV) salt precursor. Both oxygen and water levels were monitored and kept below 1 ppm during the reaction. The Mo:S ratio was chosen to be 1:2 or less.[3] Clear suspensions varying in color from nearly colorless for the smallest clusters (<2 nm in diameter) to deep blue for the larger clusters (~ 15 nm) are obtained. The cluster size is varied by using different sized micellar cages to encapsulate the Mo salt. These cluster suspensions are remarkable for they are homogeneous, stable, and transparent dispersions of MoS_2 clusters in a nonpolar fluid.

The grown clusters were characterized by a variety of techniques including transmission electron microscopy (TEM), x-ray and electron diffraction, optical spectroscopy, dynamic light scattering, and small angle x-ray and neutron scattering. Figure 1 shows a TEM micrograph of 3.0-nm-diam MoS_2 clusters (for now assumed spherical—see later discussion) deposited on a carbon grid. The clusters are remarkably uniform in size. As it is difficult to obtain x-ray diffraction from such small clusters, larger clusters were grown for this purpose. Figure 2 shows an x-ray diffraction spectrum of clusters whose size in solution was 15 nm but which were then deliberately aggregated to form a powder for the x-ray measurements. This aggregation may have caused some grain boundary growth. The lines are broadened somewhat by the small size of the crystallites, but they remain relatively sharp, and their locations agree well with those of bulk MoS_2 indicated by the vertical lines in the figure. Thus these MoS_2 clusters crystallize in the bulk hexagonal layered MoS_2 structure. The electron diffraction pattern in the inset of Fig. 2 shows that 4.5-nm-diam clusters retain the bulk structure also. This evidence does not, of course, guarantee that smaller size clusters will develop the bulk phase, but it shows that bulklike clusters persist down to at least 4.5 nm in size, a fact supported by the optical data to be discussed below.

Figure 3 shows the optical-absorption spectra of 4.5- and 2.5-nm-diam MoS_2 clusters dispersed in acetonitrile at concentrations of $\sim 10^{-3}$ molar and compares the results with those of bulk single crystals (inset). These spectra, which were measured at 290 K, exhibit well-defined features which we now wish to discuss.

FIG. 1. TEM micrograph showing 3-nm MoS_2 clusters.

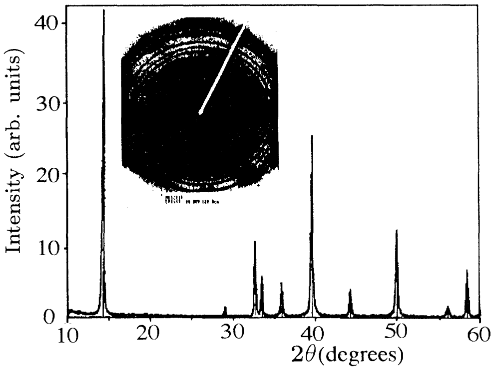

FIG. 2. X-ray diffraction spectrum of 15-nm MoS_2 clusters. The inset shows an electron diffraction pattern on 4.5-nm clusters.

First we review briefly the spectrum of bulk MoS_2. This spectrum, which has been studied extensively[8,9] and compared with results of electronic band structure calculations,[10] consists of a series of absorption thresholds. The first threshold corresponds to weak absorption in the near IR at ~ 1040 nm (~ 1.2 eV) (not shown) 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 and is associated with a direct transition at the K point. The two sharp peaks (A and B) on the high-energy side of this threshold are excitonic transitions ($K_4 \rightarrow K_5$ and $K_1 \rightarrow K_5$, respectively) whose energy separation ($=0.18$ eV) is due to the spin-orbit splitting of the top of the valence band at the K point.[10] A third threshold at ~ 500 nm is due to a direct transition (specifics unknown) from deep in the valence band to the

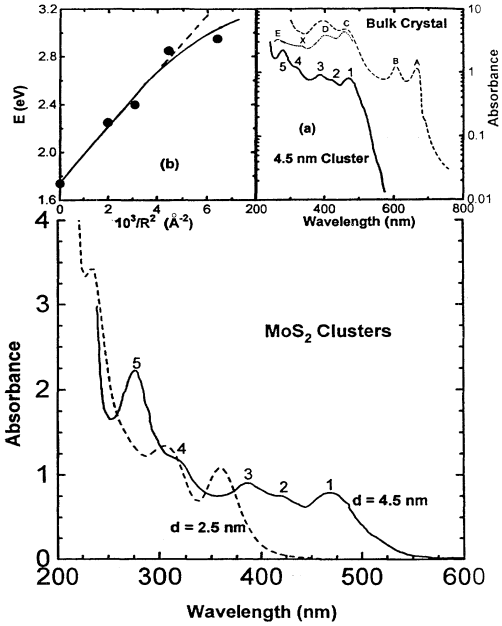

FIG. 3. Optical-absorption spectra of 4.5- and 2.5-nm MoS_2 clusters (absorbance in arbitrary units). Inset (a) compares the spectrum of the 4.5-nm clusters to that of bulk thin (dotted) and thick (dashed) crystals (Refs. 8 and 9). Inset (b) shows the dependence of the absorption threshold at the K point on cluster size.

conduction band. Excitonic features (C and D) are also associated with these transitions. A fourth threshold at ~350 nm is also due to transitions from deep in the valence band. Features on the high-energy side of this threshold (labeled X, our own notation, and E in Fig. 3) are seen in thin samples. The relative intensities of peaks A and B, C and D, and X and E are known to vary with sample thickness as well as quality.[8,9]

The spectrum of the 4.5-nm clusters in Fig. 3 is rich in spectral features, the most prominent of which we have labeled 1–5. Multiple maxima in the absorption spectra of clusters can be due to either specific electronic transitions in monodisperse clusters or to the presence of structured size distribution (e.g., magic numbers) of clusters in a given sample. In the present case, however, comparison of spectra on several samples shows no evidence for structured size distributions, and thus the features in the spectrum are intrinsic properties of monodisperse clusters and attest to the high quality of our clusters.

Comparison of the spectrum of the clusters to that of the bulk crystal reveals two main features: (1) a large blueshift for the clusters, and (2) preservation of the excitonic features in the spectrum of the clusters. In fact, a detailed comparison of this spectrum to that of the bulk crystal allows an essentially one-to-one association of the features in both spectra (inset Fig. 3). First, it seems certain that feature 1 ($\lambda=470$ nm) in the cluster spectrum is associated with excitonic peak A ($\lambda=665$ nm) of the bulk, corresponding to a blueshift of 0.78 eV due to the quantum-size confinement effect of the 4.5-nm clusters. If we then, as a rough approximation, assume that all of the other peaks of the bulk crystalline spectrum are blueshifted by the same amount, then their energies (λ's) in eV (nm) would be $B=2.86$ (434); $C=3.45$ (360); $D=3.90$ (318); $X=4.50$ (276); and $E=5.30$ (234). For comparison, features 2, 3, 4, and 5 in the spectrum of the 4.5-nm clusters have energies (λ's) of 2.92 (425); 3.24 (382); 3.92 (317); and 4.51 (275), respectively. It is seen that these latter energies (λ's) are close to the expected shifted positions of peaks B, C, D, and X (the biggest difference being for peak C), thereby providing an argument for the one-to-one association of these features. Our assumption that all the peaks in the single-crystal spectrum blueshift equally in energy upon going to the clusters cannot, of course, be strictly correct as different parts of the band structure (or Brillouin zone) should be affected differently by quantum-size confinement due to differences in effective masses. In reality, however, the above analysis shows that this assumption is not far wrong for MoS_2 which implies, in the context of simple models, that the effective mass must not vary strongly among the various points in the Brillouin zone involved in the observed optical transitions. Despite any uncertainties in the above association of spectral features, the important point we wish to make is that the absorption spectrum of the 4.5-nm clusters is essentially bulklike.

The above conclusion that features 1–5 in the spectrum of the 4.5-nm clusters derive from features in the bulk single-crystal spectrum is consistent with the fact that these clusters are somewhat larger than the size of the exciton[8–10] (radius $r_B=2.0$ nm) in bulk MoS_2. For these clusters there are apparently sufficiently high densities of states in the conduction and valence bands to make it possible to produce bulk bandlike features in the absorption spectrum and thereby preserve the quasiparticle character of the excitons. Thus the spectrum of the 4.5-nm clusters reflects size quantization of excitonic features in the weak-to-moderate confinement regime (cluster radius $R > r_B$). The above results also strongly indicate that 4.5-nm MoS_2 clusters retain the bulk hexagonal crystal structure of this material.

Turning next to the spectrum of the 2.5-nm clusters in Fig. 3, we note that this spectrum is qualitatively different from that of the 4.5-nm clusters and of the bulk crystal. Specifically, on going to the 2.5-nm clusters, the excitonic features in the spectrum give way to a ladder of three well-defined peaks over the spectral range covered. This is the expected behavior in crossing over from the weak (excitonic) confinement regime to the strong (noninteresting carrier) confinement regime where the cluster size (in this case $R=1.25$ nm) is considerably smaller than the excitonic Bohr radius ($r_B=2$ nm). For these very small clusters the low densities of states prevent observation of excitonic features, and the allowed energy levels change from continuous bands to a ladder of essentially discrete levels as in molecular systems. Figure 4 shows that the spectrum of 3.0-nm MoS_2 clusters is very similar to that of the 2.5-nm clusters reflecting this ladder of discrete levels. This result indicates that the crossover from solidlike to molecularlike behavior occurs at a cluster size between 4.5 and 3.0 nm. Comparison of the spectra in Figs. 3 and 4 shows only relatively small blueshifts of the absorption peaks in going from 3.0- to 2.5-nm clusters. This trend was manifested by a third sample with 2.0-nm clusters. Thus it appears that the absorbance blueshift levels off in this (3–2 nm) size range.

That this leveling off in the shift occurs in the size range where the clusters becomes moleculelike is not surprising and strengthens the assertion that the optical properties of these clusters are indeed molecularlike. The ladder of peaks in the absorption spectra of the clusters in this size range then corresponds to transitions to various excited molecularlike states with some vibrational broadening. We note here that a qualitatively similar leveling off in the blueshift has been reported for small PbS

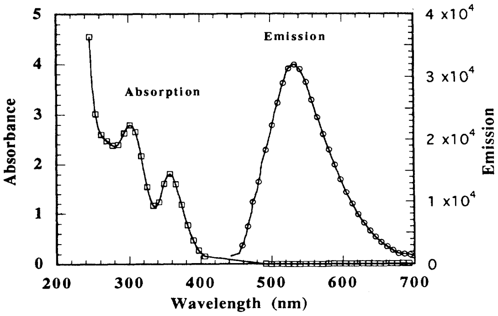

FIG. 4. Room-temperature optical-absorption and emission spectra of 3-nm MoS_2 clusters. (Absorbance and emission in arbitrary units.)

clusters in what is also believed to be the molecular range.[11]

A variety of theoretical models have been used to describe size quantization of the energy spectrum of the carriers in semiconductor clusters. These models, which express the size dependence of the energy of the excited states in terms of the bulk energy gap, the kinetic energy, Coulomb interaction, and correlation energy of the electron-hole (e-h) pairs, have been recently reviewed by Yoffe.[1] They include the initial effective mass (EM) treatment of Efros and Efros[12] and later improvements by Brus,[13] Kayanuma,[14] and others, semiempirical tight-binding treatments, and recent empirical pseudopotential methods.[1] Despite their shortcomings,[1] 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, and in the size regime where quantum confinement effects are prominent, the shift of the absorption edge, or band gap, $E(R)$ of a cluster of radius R relative to that of the bulk is to a reasonable approximation proportional to $1/2\mu R^2$, where μ is the reduced mass of the exciton. A plot of $E(R)$ vs $1/R^2$ should then yield a straight line with slope $\alpha 1/(2\mu)$. Such a plot for the sharp absorption threshold at the K point of the zone ($E=1.74$ eV in the bulk) for our clusters is shown in the inset of Fig. 3 and is linear for clusters larger than 3 nm in diameter. The linear portion yields $\mu=0.16m_0$, where m_0 is the free-electron mass. Interestingly, this value compares favorably with the bulk value of the reduced mass of $0.18m_0$ for the A exciton deduced from optical measurements along the optic c axis of the crystal.[9] While we cannot rule out the possibility that this agreement between the two values of μ may be fortuitous, it suggests that simple EM models capture some of the essential physics for MoS_2 clusters.

Figure 4 also shows the room-temperature emission spectrum for the 3.0-nm-diam clusters excited at 476 nm. In this early study we did not observe any luminescence due to direct e-h recombination near the absorption threshold for any of the clusters. Rather, the spectrum consists of a blueshifted (relative to bulk emission), broad emission peak centered at 537 nm which is characteristic of surface and/or defect recombination. For these 3.0-nm clusters many of the atoms lie at or near the surface, and surface states associated with adsorbed species, dangling bonds and other defects can be expected to play a major role in determining the fate of the carriers produced by light absorption.

Finally, given the layered nature of the MoS_2 structure, it is interesting to speculate about the shape of MoS_2 clusters in the size range of the present study. In its hexagonal phase, the unit cell of MoS_2 contains 2 formula units and has dimensions $a=3.15$ Å and $c=12.30$ Å yielding a unit cell volume equal to 317 Å^3. Assuming spherical clusters and full packing, a 4.5-nm-diam cluster would contain 150 unit cells, or 300 formula units, and a 2.5-nm-diam cluster would contain 26 unit cells, or 52 formula units. However, the shape of the unit cell precludes full packing, and so the number of molecules in these clusters can be expected to be considerably less. As noted above, the 4.5-nm clusters appear to retain the bulk structure, and in a spherical box these clusters will be ≤ 4 unit cells thick. We do not know the structure of the 2.5-nm clusters, but this size is equivalent to 2 unit cells thick. However, it is not likely that these small clusters will have any strong semblance to the bulk structure since a stack of two unit cells does not define a structure; additionally, as already noted, the optical spectrum of these clusters reveal their molecular character. In all cases we envision the clusters to be disk shaped.

In summary, we have successfully grown high-quality, size-selected, nano-size (2–15 nm) clusters of the layered semiconductor MoS_2 and studied their interesting optical properties. The large blueshift in the optical-absorption spectrum with decreasing cluster size affords great tailorability of the band gap. Relatively intense photoluminescence controlled by surface and/or defect recombination is observed at room temperature. Finally, the results provide a demonstration of the crossover from solidlike to moleculelike optical-absorption spectra as the size of the clusters becomes smaller than that of the exciton in the bulk.

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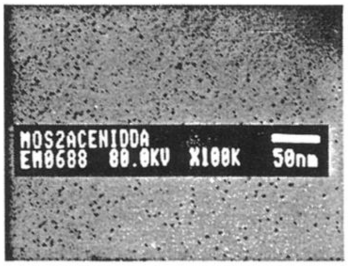

FIG. 1. TEM micrograph showing 3-nm MoS_2 clusters.