Conf-941144--49

SAND94-3001C

Optical Features of Nanosize Iron and Molybdenum Sulfide Clusters

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Abstract:

In the bulk state FeS_2 and MoS_2 are optically opaque, narrow bandgap semiconductors with no optical applications. We demonstrate that nanosize FeS_2 and MoS_2 have bandgaps that can be adjusted to the visible and even UV region of the spectrum by control of the cluster size. This opens up a host of applications of these materials as inexpensive solar photocatalysts. We demonstrate that the band-gap of both materials shifts to the blue with decreasing size but ceases shifting when a size of ~ 3 nm (in the case of MoS_2) is attained. We interpret this observation as a change from bulk quantum confinement of the hole-electron pair of a tiny semiconductor to a set of discrete molecular-like transitions more characteristic of a whopper molecule. Room temperature photoemission studies of these clusters demonstrate that, while photoemission shifts to the blue with increasing bandgap for large clusters, small clusters have photoemission exclusively from trapped sub-bandgap surface states. Chemical modification of the surface to introduce hole or electron traps can result in either an enhancement or a decrease in the photoluminescence. In addition, we report our results concerning chemical purification and preliminary surface characterization of MoS_2 clusters by chromatography.

Introduction:

FeS_2 and MoS_2 materials in bulk form have significant technological applications. For example, cubic iron sulfide is considered to be the most important mineral present in coal formations and likely plays a critical catalytic role in the hydrogenolysis of coal[1]. It has also been suggested as an inexpensive material for photovoltaic applications. MoS_2 is the most widely used catalyst for the removal of sulfur from crude oil and coal and, due to its graphite-like two-dimensional structure, is widely used in lubrication applications (e.g. axle grease).

However, because both materials are optically opaque and have bandgaps in the near IR, photochemical applications of these materials are non-existent. As with other nanosize semiconductor materials, however, we have shown that in nanosize form the bandgaps of both materials can be shifted into the visible and even UV region of the optical spectrum and thus matched to the solar spectrum[2]. The concomitant shifts in the valence and conduction band potentials theoretically allow chemical oxidation and reduction of a wide range of reactants. This opens up a host of possibilities for these materials as photooxidation catalysts for destruction of chlorinated hydrocarbons in water and H_2 fuel production via splitting of water or H_2S. It should be noted that compared to the only other extant material available for these applications, TiO_2, covalent materials such as MoS_2 and WS_2 can be much better matched to the solar spectrum and, unlike II-VI semiconductor materials such as CdS, are chemically robust and stable in the presence of molecular oxygen. FeS_2, while oxygen sensitive, can be coated with a thin layer of inert metal such as gold as we demonstrate and so is also potentially useful as a photocatalyst.

In this paper we discuss our measurements of size, structure, optical absorbance and photoemission for these new nanosize materials. We also briefly outline our synthetic procedures and novel methods for chemical processing of these nanoclusters.

Synthesis and Processing: It is well known that size control during colloidal growth requires the distinct separation of nucleation from growth. If nucleation occurs continuously in either space or time a highly disperse (power-law distribution) of cluster sizes will inevitably occur. Such processes are typical of growth in a continuous medium whether gas or liquid.

However, if confinement of the reactant precursors can be achieved to limit growth to a restricted region of space a narrow size distribution of clusters will occur. Examples include cluster growth in mineral zeolites and emulsion polymerization to form latexes (the latter process produces the most highly monodisperse objects yet grown). In our synthetic method[3] we achieve this desired spatial restriction by the confinement of the reactants (i.e. metal salts such as Li_2S or $Fe(BF_4)_2$) in the hydrophilic interior of surfactant aggregates called inverse micelles.

Surfactant molecules, the bisexuals of the molecule world can literally go either way solubility-wise (i.e. they like water but they're also comfortable in oil). However, in either case they prefer a bit of molecular apartheid to total integration and thus usually form segregated droplet-like aggregates called micelles whose dimensions are typically 1-10 nm. The modifier "inverse" refers to the negative curvature between the surfactant-oil interface (the oil is the continuous medium). Nucleation only in the micelle interior is guaranteed by the total lack of solubility of the charged metal ions in the low dielectric constant inert oils used as the continuous media. The micelles essentially function as "nano-glassware" to grow the clusters. Since there are roughly 10^{18} such micelles per cm^3 a lot of identical clusters can be grown! The size of these molecular reactors is determined by the chemical structure of the surfactants and their interactions with the oil.

Of course, after formation of the clusters it's time to clean the "glassware". However it would be a little pointless to use soap, right! Instead reaction byproducts are removed at the molecular level by high pressure liquid chromatography, which separates products (clusters) from reactants (surfactants, oils, and inorganic salts). This cleaning process is quite important to allow measurement of the inherent optical features of the clusters, especially features in the UV.

Size/Structure Determination: One of the most significant questions in the area of nanoclusters is the relationship of optical features such as the bandgap to the average mass of the cluster. No single technique is ideally suited to measure cluster size. We rely on direct imaging techniques such as TEM as well as scattering techniques such as dynamic light scattering (DLS) (which measures the z-average cluster diffusion constant and degree of polydispersity), and small-angle scattering using x-rays (SAXS) or neutrons (SANS) (the latter measures the radius of gyration and size distribution). It should be remembered that TEM measures only the two-dimensional projection of the cluster so disc-like clusters cannot be readily distinguished from spherical ones, an important issues for layered materials like MoS2. Thus, for this material we use DLS measurements of size.

In the case of both Fe and Mo sulfides the reaction stoicheometry controls the phase of the final nanoclusters. In both cases we have used x-ray and electron diffraction to establish that semiconductor cubic iron pyrite and hexagonal layered MoS_2 forms only if the Fe:S ratio is 1:2 or less.

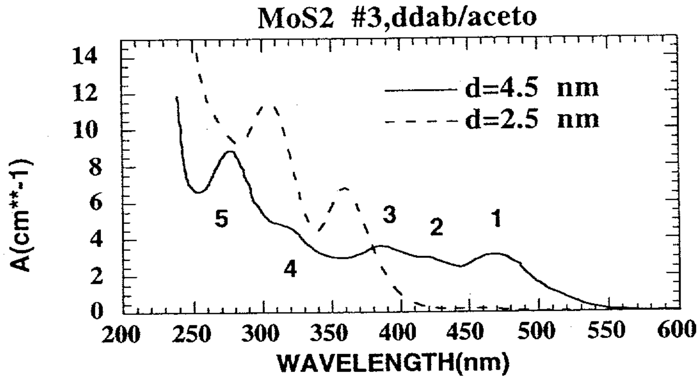

Figure 1. Absorbance Spectra of two different size MoS2 nanoclusters. The labeled features of the 4.5 nm clusters corresponds to those found in the bulk material but significantly blue-shifted as described in the text.

Optical Features: The absorbance spectra of two samples of MoS_2 clusters are shown in figure 1. The first absorbance threshold in the bulk material corresponds to the indirect transition in the bulk at ~1040 nm (1.2 eV). The corresponding bandgap in figure 1 has obviously been blue shifted by quantum confinement to ~520 nm (2.4 eV). The feature labeled 1 in figure 1 can be identified with the first excitonic transition of the bulk material. If all other features are blue shifted by about the same amount then all other transitions can be identified with known bulk features.[2] For example, features 4 and 5 are direct transitions from deep in the valence band to the conduction band.

In addition to the obvious further blue shift of the spectrum which occurs in the 2.5 nm clusters of figure 1, qualitatively different spectral features emerge which we have associated with the low density of states likely in a 2.5 nm cluster which prevent the observation of excitonic features. The transitions are consistent with a change from the continuous bands of a solid material to the discrete levels found in a molecular system[2]. We note that in this case the cluster is significantly smaller than the excitonic Bohr radius of 2 nm for bulk MoS_2. We also caution that the cluster size here is the cross-sectional area as determined by TEM, and, if the clusters have a plate-like morphology the size deduced from TEM may not be the only significant length scale in this problem (i.e. the clusters might have structural anisotropy).

In figure 2 we illustrate the advantages of cleaning up the system by use of liquid chromatography. A 3.0 nm cluster parent solution is compared to the daughter product monitored in the single dominant cluster elution peak. The entire spectrum is obtained on-line in real-time by a photodiode array. These purified, HPLC grade clusters can then be collected for further studies. The bandgap of both samples and the position of the spectral features of both are identical, but removal of UV-absorbing impurities (by-products of the reaction) allows many addition features to be observed.

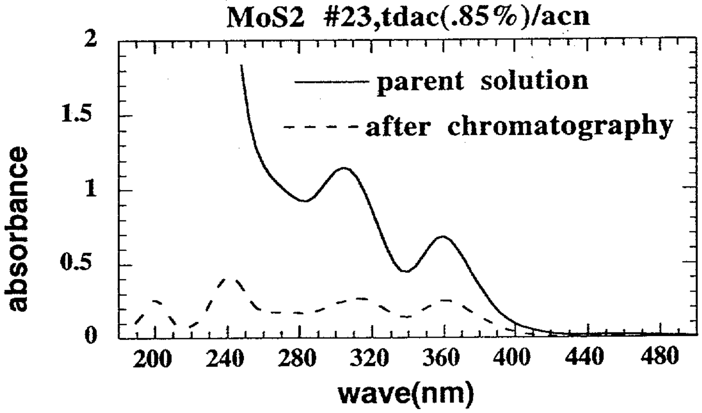

Figure 2. Optical absorbance of 3.0 nm MoS_2 clusters before and after liquid chromatography to remove chemical impurities and excess surfactant.

In figure 3 we show the absorbance and photoemission from 3.0 nm MoS_2 clusters. The broad emission band centered at 537 nm we have identified as resulting from recombination from surface defect states. We find that this feature is present in all clusters from 2.0 to 3.5 nm in size and does not shift in position, consistent with the present interpretation of the origin of this emission.

The blue shifts with decreasing size and cross-over from solid-like to molecular spectra are also observed in the cubic iron sulfide system In this system spectral features analogous to MoS_2 are observed starting at 640 nm as shown in figure 4. As high quality, single phase crystals are next to impossible to grow in bulk form, we have not yet identified the nanosize cluster spectrum with that of the bulk. However, we have begun investigations of the effect of metal coating on the cluster optical features. The 4.5 nm clusters of figure 4 were coated with gold at the atomic ratio shown in the figure. The upper spectrum has been vertically shifted by an arbitrary amount for clarity. The semiconductor features were retained but were blue shifted by ~10 nm. We have made similar observations in the CdS and PbS systems.

Metal coatings on semiconductor nanoclusters may significantly enhance the photocatalytic properties of these materials by increasing the trapping of electrons at the cluster surface. Such increased trapping is advantageous if the clusters are intended to serve as oxidizing nanoelectrodes for organic molecules such as chloroform. We are initiating experiments with a photoreactor which simulates the solar spectrum to test these ideas.

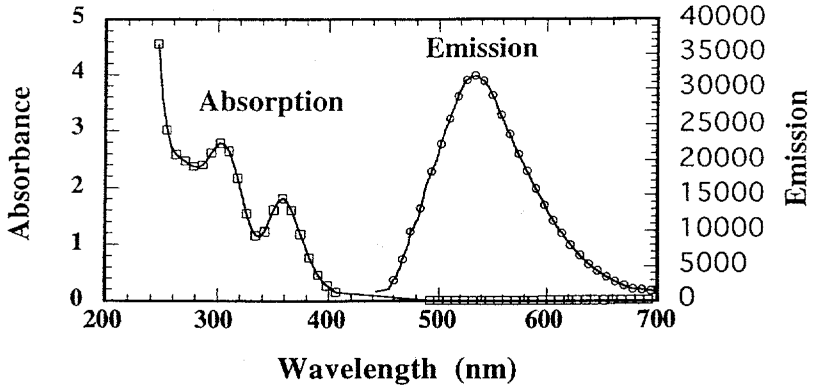

Figure 3. Absorbance of photoemission of 3.0 nm MoS2 clusters. There is little difference in either band-gap or photoemission energy for clusters with sizes between 2 and 3.5 nm.

Finally, given the layered nature of the MoS_2 structure, we might expect some significant structural alterations in the smallest clusters. Assuming spherical clusters and complete packing, a 4.5 nm diameter cluster would contain 300 formula units while a 2.5 nm cluster would contain only 52 formula units. The latter would only be 2 unit cells thick if it retained the bulk symmetry, which would not define a solid structure. Thus, a molecular interpretation of its spectra is quite reasonable, and we strongly suspect major shape alterations in the smallest clusters.

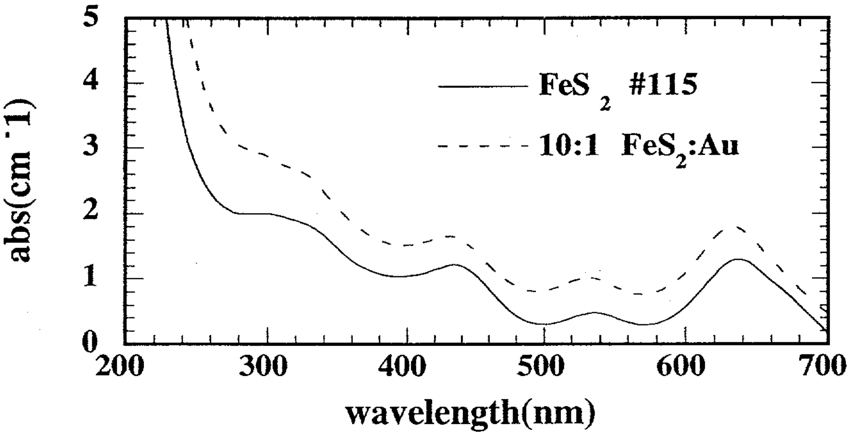

Figure 4. Application of a thin coating of gold to nanosize FeS_2 leads to a blue shift of the first excitonic feature.

Acknowledgment:

This work was performed at Sandia National Laboratories, Albuquerque, NM and supported by the U.S. Department of Energy under Contract No. DE-04-76DP00789.

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