the fact that the measurements were made at different extremes of concentration and, at these extremes, the detection process is fundamentally different. At low concentration ($\phi < 10^{-3}$), the detection mode is essentially heterodyne whereas at high concentration ($\phi > 10^{-1}$), homodyne detection occurs. In between these extremes, the ACF will contain both heterodyne and homodyne components, their relative strength being determined by the intensity of the scattered light compared with the local oscillator signal. The local oscillator is inherent to the fiber optic system and arises from reflections at the terminal end of the fiber and from the coupler assembly.

The present work shows clearly that it is incorrect to assume that heterodyne detection occurs, as has been done previously.[2,4] Furthermore, it is apparent that the change in the heterodyne/homodyne mix with ϕ may be the predominant reason for the variation of D_{app} with ϕ except at the highest concentrations, where the actual dynamics of the concentrated dispersion will be dominant.

A full fiber optical system remains an attractive and convenient way to perform dynamic light-scattering measurements on concentrated dispersions. However, it is evident from the present work that one has to account correctly for the heterodyne/homodyne mixing problem before the fundamental dynamics of the concentrated system can be studied.

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Scanning Tunneling Microscopic Imaging of CdS Q Particles Prepared in Acetonitrile Solution

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Stable, small, colloidal particles of CdS (<5 nm) were prepared directly by reaction of $Cd(SCN)_2$ with H_2S in MeCN. The absorption spectrum of the colloid prepared at –42 °C showed a plateau at 380 nm, with a large blue shift in the apparent absorption edge compared to bulk CdS. A dispersion prepared at –5 °C showed a smaller blue shift. Both scanning tunneling microscopic (STM) and transmission electron microscopic (TEM) images of particles cast on suitable substrates were examined. The STM image of CdS colloids prepared at higher temperature and cast on highly ordered pyrolytic graphite showed a greater extent of aggregation than an image of CdS colloids prepared at lower temperatures, although the size of the individual particles still ranged from 15 to 40 Å (almost the same as the sample prepared at lower temperature).

Introduction

We report here the production of very small (Q or quantum) particles of CdS by precipitation in MeCN solutions in the absence of added stabilizer and their imaging by transmission electron microscopy (TEM) and scanning tunneling microscopy (STM). Interest in small semiconductor particles, such as CdS, can be traced to their use as photocatalysts[1,2] and pigments and to fundamental studies of photoreactions and electron-transfer reactions at the semiconductor/liquid interfaces.[1,3] While the early investigations utilized particles with diameters of the order of 0.1–1 μm, which had band gaps (E_g) and properties of the bulk material,[2] more recent studies have been concerned with the preparation and characterization of very small particles (<100-Å diameter).[4] These particles, sometimes designated as quantum or Q particles, have optical band gaps, $E_{g,opt}$ (estimated from the spectroscopic absorption edge) that are larger than

E_g of the bulk material; E_g increases as the particle size decreases. These size effects on the energies of the orbitals have been treated by "particle-in-a-box" models.[5,6] Excess charge on small particles can also affect the absorption edge shift.[7-9]

Stabilization and determination of the size of Q particles are often difficult. Because small particles tend to aggregate and grow via Ostwald ripening, stabilizers (e.g., metaphosphate or organic surface-active substances) are frequently added during particle synthesis. These can participate in reactions of photogenerated carriers and may complicate particle characterization, e.g., when forming dispersions on surfaces for microscopic examination. One goal of the work reported here was the preparation of quantum particles of CdS (Q-CdS) without an added stabilizer. Small particles are frequently examined by TEM. However, contrast in the TEM image is poor and often does not permit resolution of fine structure in a particle distribution. Agglomeration of the particles dur-

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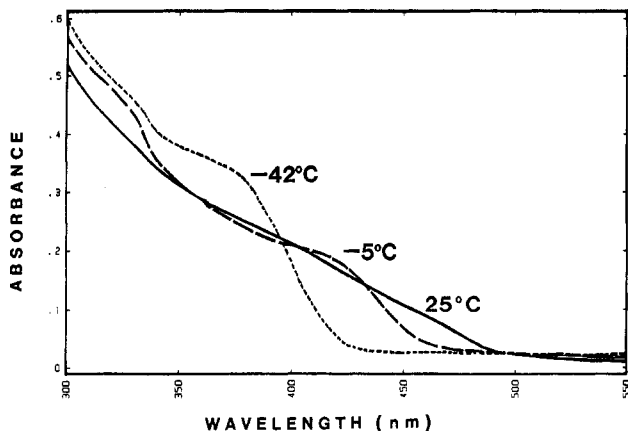(9) Liu, C.-Y.; Bard, A. J. *J. Phys. Chem.* 1989, *93*, 3232.

Figure 1. Visible absorption spectra for 2×10^{-4} M colloidal CdS crystallites prepared in acetonitrile at different temperatures: 25 (—), -5 (- - -), -42 °C (···).

ing preparation of a TEM sample may also be a problem. In this work, we compare the TEM images with the STM images of particles (<5 nm) cast on a highly oriented pyrolytic graphite (HOPG) substrate.

Experimental Section

Materials. Chemicals of analytical grade were used without further purification. $Cd(SCN)_2$ was synthesized by metathesis. Equimolar amounts of aqueous solutions of $CdSO_4$ (Baker, Phillipsburg, NJ) and $Ba(SCN)_2$ (Fisher, Pittsburgh, PA) were mixed to produce a precipitate of $BaSO_4$ and a solution of $Cd(SCN)_2$. The clear solution was separated by filtration and then rotatory-evaporated to dryness. The compound was dried in a vacuum oven at 90 °C for 2 h. H_2S (Linde, Austin, TX) and spectrograde MeCN (Baker) was used as supplied by the vendors. Quartz slides were purchased from ESCO (Oak Ridge, NJ).

Preparation of Colloidal Particles. A stock solution of 2×10^{-4} M $Cd(SCN)_2$ in MeCN was prepared under vacuum. A 125-mL sample of this solution was placed in a 250-mL reaction vessel and degassed under vacuum (aspirator). The solutions were held at the desired temperature, and CdS dispersions were generated by admitting H_2S into the reaction vessel above the solution while it was stirred with a magnetic stirrer. For the sample prepared at room temperature, the rapid appearance of a yellow color indicated the formation of CdS. The same procedure was used to prepare the CdS solutions at 25, -5, and -42 °C. The color of the solution became lighter and lighter as the preparation temperature decreased.

Characterization of CdS Solutions. Particles were characterized by both STM and TEM. The sample for the TEM was prepared by placing a drop of the colloidal dispersion on a carbon film supported on a Cu grid and was examined on a JEOL (Tokyo, Japan) transmission electron microscope (Model JEM-1200 EX). The sample for the STM was prepared by placing two drops of the CdS colloidal dispersion on a freshly cleaved HOPG substrate, which provided a conductive substrate that was atomically flat over thousands of angstroms. The low-temperature samples were prepared by the same procedure, except the substrate was first cooled and was maintained at a low temperature as the MeCN was removed by freeze-drying under vacuum.

Apparatus. The scanning tunneling microscope used here was modified from an earlier design.[10a] A micrometer-driven differential spring assembly was used for sample movement and a piezoelectric tripod to scan the tip. A Compaq Deskpro 286 was used for data acquisition and processing.[10b] Either electrochemically etched tungsten or Ir–Pt (FHC Co., Brunswick, ME) tips were employed. No significant difference was observed in the images obtained with the two kinds of tips. The images
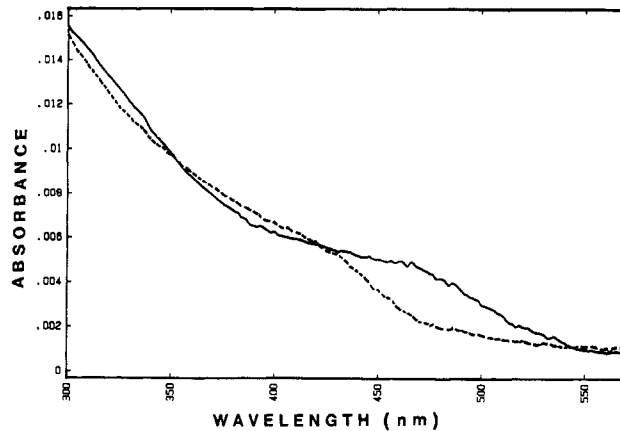

Figure 2. Visible absorption spectra of colloidal CdS crystallites cast on quartz slides at 25 (—) and -5 °C (···). The CdS solution for the 25 °C sample was 3 months old.

were obtained in air by using a constant-current, slow-scan (ca. 1 Hz) technique. The imaging conditions were -600-mV tunneling voltage (tip vs substrate) and 0.5-nA tunneling current. UV–visible absorption measurements were carried out with a HP8451A diode array spectrophotometer (Hewlitt-Packard, Palo Alto, CA).

Results and Discussion

Dispersions of Q-CdS colloids are usually prepared by adding a stabilizer (e.g., hexametaphosphate, poly(vinyl alcohol)) to the solution. Such colloids are stabilized against aggregation and sedimentation in the presence of the additives, which adsorb on the particles. However, we wanted to prepare colloidal Q-CdS without additives. There have been several reports[6c,11,12] of CdS colloids prepared directly in an organic solvent such as MeCN. Since CdS has a low solubility in these solvents, rapid Ostwald ripening and particle growth are hindered. However, compared to aqueous suspensions, CdS colloids in MeCN show poor stability in the absence of stabilizing agents. One approach to stabilization in MeCN is the formation of an electrostatic charge on the particle surface by ionic adsorption.[6c] In this case, electrical double-layer repulsion serves to stabilize the CdS colloids in MeCN against aggregation and sedimentation. For example, double layers on the CdS crystallites are formed, with either Cd^{2+} or S^{2-} chemisorbing on the particle surface, when one of these ions is in excess during synthesis. In this case, a diffuse layer of oppositely charged counterions is attracted to each charged crystallite. Low temperature also has a pronounced effect in stabilizing small particles.[6c] An alternative way of stabilizing the CdS colloids is directly through the strong adsorption of the counterions. For example, Weiser and Durham[13,14] showed that Cl^- adsorbed onto the CdS particles. The present study and others[15] indicate that adsorption of halide or thiocyanate anions (X^-) on CdS particles establishes a negatively charged surface producing an electrostatic repulsive force that discourages flocculation.

When colloidal particles of CdS were prepared directly by reaction of $Cd(NO_3)_2$ with H_2S in MeCN in the presence of potassium halide, the stabilizing effect appar-

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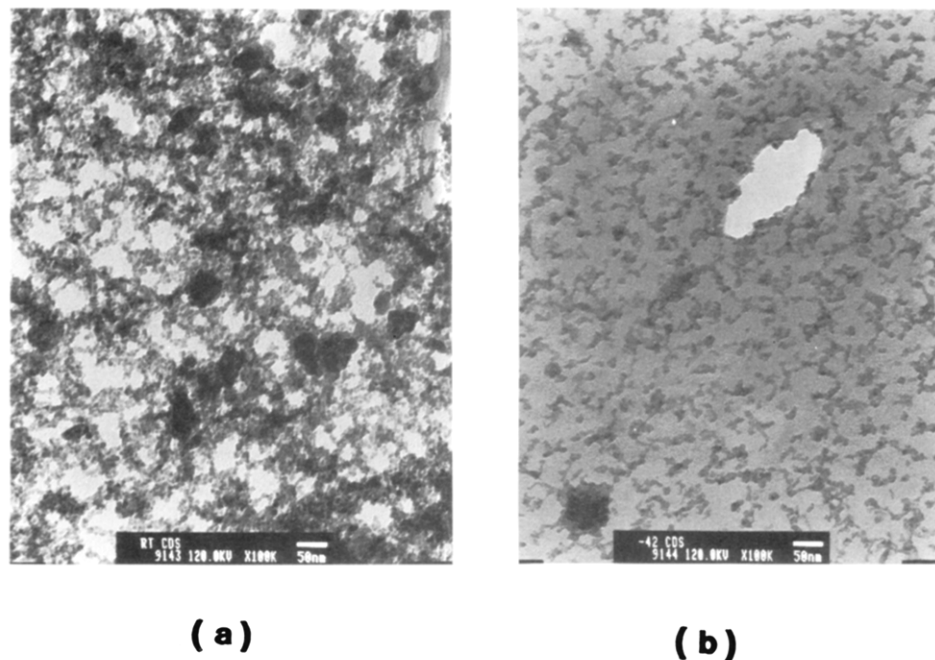
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(a)   **(b)**

Figure 3. TEM images of CdS colloids prepared at (a) 25 and (b) −42 °C.

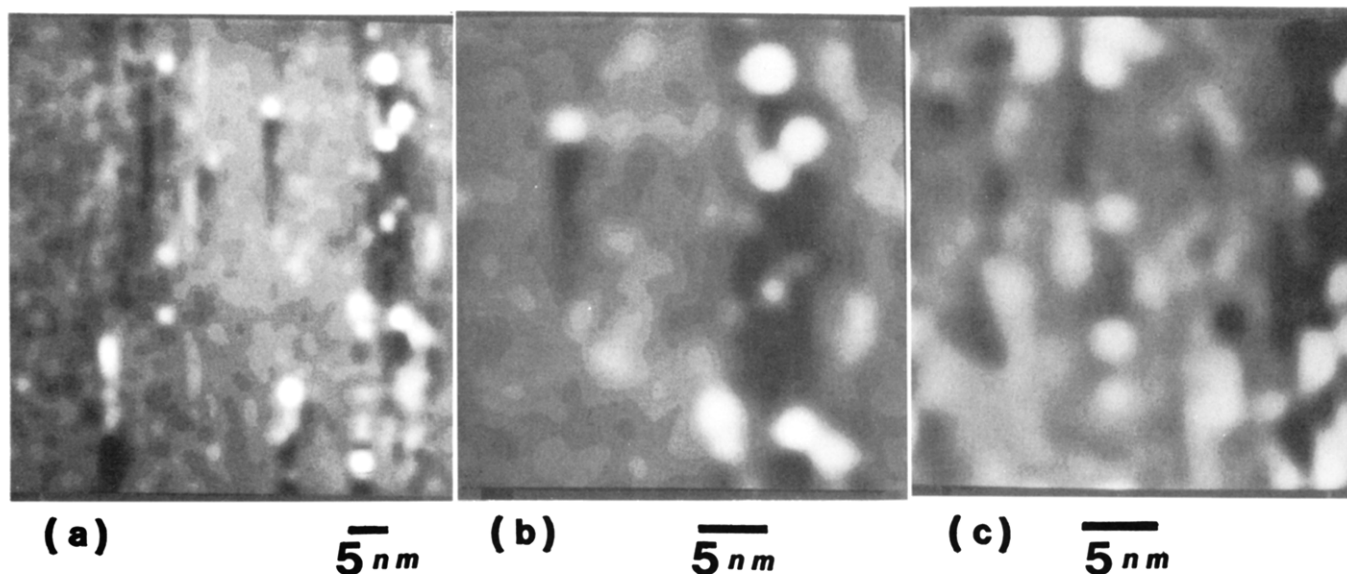**(a)**   5 nm   **(b)**   5 nm   **(c)**   5 nm

Figure 4. Constant-current STM images of CdS Q-particles on HOPG recorded at −600-mV tunneling voltage (tip vs substrate) and 0.5-nA tunneling current. The rastering rate is ca. 1 Hz. Postacquisition image processing consisted of fast Fourier transform filtering to remove high-frequency components: (a) 600 Å × 680 Å image for particles prepared at −42 °C; (b) magnified view of part of a, area 330 Å × 360 Å, total height range 45 Å; (c) 310 Å × 340 Å image for particles prepared at 25 °C, total height range 45 Å.

ently depended on the strength of adsorption of X^- on the surface of the CdS particles. For a given concentration of CdS suspension (e.g., 0.2 mM), the stabilizing effect of the different halides, under identical conditions, was in the order $SCN^- > Br^- > I^- > Cl^-$. However, colloids prepared from these reactants had particle sizes much larger than 10 nm, the upper limit of size of CdS Q-particles. Similar results were obtained by Grätzel et al.,[12] for the preparation of CdS in MeCN. The use of $Cd(ClO_4)_2$ or $Cd(NO_3)_2$ as starting material resulted in precipitation. If $CdCl_2$ was employed, the colloid turned strongly turbid. Only $CdBr_2$ and CdI_2 gave stable CdS colloids. They reported particle sizes in the range of 2–3 nm.

In the results reported here, $Cd(SCN)_2$ was used as a starting material to prepare the CdS colloids. Extremely stable small colloidal particles of CdS were prepared by

direct reaction of $Cd(SCN)_2$ with H_2S in MeCN. The dispersion was stable for more than 4 months after preparation. The particle size depended upon the temperature at which the reaction was carried out, as shown by the absorption spectra of colloidal CdS crystallites prepared at different temperatures (Figure 1). The colloid prepared at −42 °C was stable and transparent in the visible region but turned yellow when the dispersion was warmed to room temperature. The spectrum of this colloid showed a plateau at 380 nm, with a large shift in the apparent absorption edge compared to bulk CdS. A dispersion prepared at −5 °C showed a smaller blue shift.

Both STM and TEM were used to image the CdS particles. The samples were prepared by evaporating drops of the MeCN dispersions on substrates. One problem associated with this sample preparation technique is the possible clumping of the CdS particles upon evapora-

tion into larger aggregates that might not exist in the solutions used for the spectroscopic measurements.[6c] Evaporation at a higher temperature than those used in the precipitation of the dispersion might also lead to growth of the CdS particles. To investigate these possibilities, samples were prepared on quartz slides in the same way as those for microscopic examination, as described in the Experimental Section, at different temperatures, and the absorption spectra were examined. The absorption spectra (Figure 2) still showed essentially the same blue shift of the absorption edge as the solution samples prepared at lower temperature. This result indicates that the colloids on the substrate are of comparable size to those in solution.

The TEM images of CdS colloids prepared at 25 and –42 °C are shown in Figure 3. For the higher temperature preparation, more aggregation of the tiny crystallites occurred; however, individual particles still can be clearly seen. With the lower temperature preparation, the aggregation was less pronounced, but the size of the individual particles was essentially the same. The contrast in these micrographs is poor and does not permit the resolution of the fine structure of the size distribution.

Figure 4a shows an STM image of CdS particles on HOPG prepared at –42 °C. The image, part of a larger area image (1000 Å × 1000 Å), shows many isolated particles of size ca. 15 Å, as well as some clusters of larger

size. It also shows several isolated larger particles of size ca. 45 Å. In the middle section of this image, there are some particles that appear to be undergoing stepwise displacement along the scan direction of the tip. Such motion could be induced by the tip motion and might be associated with the poor conductivity of the particles and their weak interaction with the substrate. Unfortunately, such instability often reduces the reproducibility of the STM image from scan to scan. Figure 4b is a magnification of part of Figure 4a, which clearly reveals that the large clusters are mainly composed of aggregates of particles of size ranging from 15 to 40 Å. As suggested in Figure 4c, which shows an STM image of CdS particles prepared at room temperature, the extent of aggregation of the particles seems to be greater at higher temperature, although the size of individual particles still ranges from about 15 to 40 Å. It is still not clear whether the observed clustering is induced by the sample preparation technique, as mentioned previously, or is an intrinsic property of CdS particles in MeCN solution.

Orientational Ordering in a Monolayer of Hard Oblate Spheroids

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The Onsager theory of orientational ordering is applied to a monolayer of hard oblate spheroids. The spheroids are free to rotate, but their centers are confined to a plane. Order parameters and configurational free energy are calculated, within the Onsager theory. It is found that orientational ordering occurs in two steps, as density is increased from zero. First the spheroids' symmetry axes gradually tip into the plane. Then, in a second-order transition to a nematic phase, the spheroids' major axes align. The second transition shifts to lower density as spheroid eccentricity increases.

Introduction

We present a study of the orientational behavior of a monolayer of hard oblate spheroids. Oblate spheroids of various eccentricities represent shapes from thin disks to spheres. Spheroids are inherently orientable, so an assembly of spheroids may exhibit cooperative orientational ordering. We have studied spheroids with their centers confined to a plane. The system studied crudely represents the shape-induced orientational behavior that may be expected in a monolayer of disklike molecules

(e.g., porphyrins at an air–water interface).

Liquid-crystalline phases of disklike molecules have been observed experimentally in three-dimensional systems.[1–5] Strongly first-order orientational transitions were observed.[1,4] The orientational properties of disklike molecules, and of chlorophylls in particular, dissolved in liquid crystals have been studied. Effects of chlorophyll

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