Langmuir−Blodgett Film Formation from Fluorescence-Activated, Surfactant-Capped, Size-Selected CdS Nanoparticles Spread on Water Surfaces

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Fluorescence-activated sodium hexametaphosphate stabilized CdS particles have been transferred from water into apolar organic solvents (chloroform and hexane) by dioctadecyldimethylammonium bromide (DODAB) and by cetyltrimethylammonium chloride (CTAC) and spread on water surfaces in a Langmuir film balance. Surface pressure vs surface area isotherm, absorption spectroscopic, emission spectroscopic, Brewster-angle microscopic, reflectivity, and scanning probe microscopic determinations have established the formation of a monoparticulate layer of CdS which contained islands of DODAB monolayers. The surfactant-coated CdS monoparticulate layers have been transferred, layer-by-layer by the Langmuir−Blodgett technique, to solid supports. The fluorescence spectrum of films, built from DODAB-capped CdS nanoparticulate layers, was characterized by a sharp excitonic emission bands at 478 nm, whose intensity dramatically increased upon exposure to water. Fluorescence measurements of DODAB-capped CdS nanoparticulate films, in the 12−140 K range, indicated the predominance of shallow surface traps in the semiconductors. Scanning tunneling spectroscopy of individual DODAB-capped CdS nanoparticles, in the dark and under illuminations, have established them to be n-type semiconductors.

Introduction

Colloid chemical approaches are increasingly utilized for the preparation, stabilization, and supramolecular organization of semiconductor nanoparticles.[1,2] Methodologies have been developed for the in situ formation of relatively monodispersed CdS, PbS, ZnS, CdSe, PbSe, ZnSe, and ZnO particles both in homogeneous solution and in a variety of membrane mimetic systems.[1,3] The size of particles has been controlled by judicious manipulations of the temperature, the solvent(s), and the type, the concentration, and the addition rate of reagents and additives. These measures, in turn, have caused the termination of particle nucleation and the prevention of the Ostwald ripening (the addition of smaller crystallites to the surface of larger particles). Particularly successful has been the shifting of the nucleation−growth equilibrium by capping the incipient semiconductor nanocrystallites by a solvent (tri-*n*-octylphosphine, for example) or a nucleophile (a long-chain thiol, for example).[4−7] The capping agent passivated the surface of the semiconductor particle and permitted size-selective precipitations.[8,9]

Prompted by the importance of nanostructured materials, we have developed techniques for the construction of monoparticulate and multiparticulate layers of semiconductor clusters.[2] Specifically, we have reported the formation of monoparticulate layers of dodecylbenzenesulfonic acid stabilized 34.0-, 29.4-, and 26.5-Å-diameter CdS clusters at the air−water interfaces in a Langmuir film balance.[10] As a continuation of this work, we report here, for the first time, the transfer of fluorescence-activated, sodium hexametaphosphate stabilized CdS particles from water into apolar organic solvents (chloroform and hexane) by dioctadecyldimethylammonium bromide (DODAB) and by cetyltrimethylammonium chloride (CTAC) and the formation of monoparticulate fluorescence-activated, capped and size-selected CdS films on water surfaces. Further, the monoparticulate films formed were transferred, layer-by-layer, from the water−air interface onto solid substrates to yield a stable ultrathin n-type CdS semiconductor superlattice.

Experimental Section

Cadmium perchlorate ($Cd(ClO_4)_2$, >99%, Aldrich), sodium hexametaphosphate ($(NaPO_3)_6$, >96%, Aldrich), hydrogen sulfide (H_2S 99.5%, Matheson), dioctadecyldimethylammonium bromide (DODAB, >99%, Sigma), cetyltrimethylammonium

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chloride (CTAC, 99%, DBH), chloroform (99.9%, Aldrich), and sodium hydroxide (NaOH, 99.99%, Aldrich) were used as received. Doubly distilled water was purified by a Millipore Milli-Q system containing a 0.22-μm Millistack filter at the outlet.

Preparation of aqueous fluorescent CdS nanoparticle sols followed the established procedure.[3] Briefly, a 500 mL aqueous solution of 2×10^{-4} M $Cd(ClO_4)_2$ and 2×10^{-4} M $(NaPO_3)_6$ was bubbled with high-purity Ar gas in a 1000 mL round-bottom flask for ca. 20 min. The starting pH value of this solution was adjusted to 9.4 by adding 1.0 M aqueous NaOH. Calculated volume of H_2S (9 mL) was then quickly injected into the flask under vigorous stirring for 5 min, leading to a turquoise-colored dispersion. The pH of the system was then raised to 11.2 by addition of 1.0 M aqueous NaOH. The fluorescence activation of the dispersion was conducted by dropwise introduction of 1.0 M aqueous $Cd(ClO_4)_2$ until the excitonic fluorescence reached the maximal intensity.[11] This solution is, hereafter, referred to as the CdS stock solution.

The CdS nanoparticles were capped with surfactants and were subsequently extracted into organic solvents such as chloroform and hexane. Typically, solid DODAB (0.082 g) and 5.0 mL of chloroform were placed into a 10 mL CdS stock solution, in a 20 mL screw-capped glass vial, and vortexed vigorously for 5 min, resulting in a milky emulsion which underwent phase separation after 2 h at room temperature. The lower organic phase appeared to be turquoise while the upper aqueous phase turned colorless. No CdS particles could be detected in the aqueous phase by absorption spectrometry (detection limit = 10^{-6} M of Cd^{2+}). Similar methodology was used for the extraction of the CdS nanoparticles into chloroform (or into hexane) by CTAC (0.025 g of CTAC and 5.0 mL of chloroform were added to 10 mL of the CdS stock solution in a 20 mL screw-capped vial).

Size-selective precipitation was accomplished by titration by methanol of the chloroform dispersion of the surfactant-capped CdS nanoparticles until the appearance of opalescent flocculants. The precipitate was separated from the supernatant by centrifugation for 20 minutes at 1000 rpm. Absorption and fluorescence spectra of the supernatant solution were measured at different stages of the precipitation.

Surface pressure (Π) vs surface area (A) isotherms were determined on a Lauda Model P film balance. A calculated amount of a chloroform dispersion of the surfactant-capped CdS nanoparticles was spread evenly on water in the trough. The films were conditioned by repeated compression and expansion cycles, and their behavior was monitored, in situ, by a homemade Brewster-angle microscope. Monoparticulate layers were transferred onto solid substrates (quartz plates for spectroscopic measurements, freshly cleaved mica for atomic force microscopic measurements, highly orientated pyrolytic graphite, HOPG, for scanning tunneling microscopy) by the Langmuir–Blodgett (LB) technique. The substrate was first dipped vertically into the aqueous subphase prior to the spreading of the surfactant-capped CdS particles. Following the compression of the film to a condensed state with surface pressure 35 mN/m, the deposition was started by vertical lifting the substrate at 10 mm/min. Sequential dipping–lifting cycles were carried out to produce a Y-type built-up multilayer films. Overall transfer ratios were 1.0 ± 0.1.

Absorption spectra were taken on a Hewlett-Packard 8452A diode array spectrophotometer, and the fluorescence emission spectra were recorded on a Spex fluorometer equipped with a Tracor Northern 6500 rapid-scan spectrometer detection system.

For low-temperature fluorescence measurements, the surfactant-capped CdS particulate monolayers were transferred, by the Langmuir–Blodgett technique, from the air–water interface onto a quartz plate. The sample plate was then mounted on the copper holder of a HELI-TRAN LT-3 helium flow cryostat which was connected to a DISPLEX CS-208 closed-cycle compressor (Air Products Ltd.). Temperature of the samples were monitored by an indium wire thermocouple inserted between the sample plate and the copper holder. The entire low-temperature cell holder was inserted into the sample compartment of the SPEX fluorometer. Emission spectra were recorded by front face illumination.

A homemade Brewster angle microscope, BAM, was used to image the surfactant-capped CdS particulate films on water surface in the film balance. Incident beam from an Ar^+ CW laser (Ion Laser Technology, 514.5 nm, 30 mW) was directed to the surface at the Brewster angle (ca. 54°). The beam, reflected from the surface, was monitored by an MTI CCD-72 camera.

Atomic force microscopic (AFM) measurements were performed on a Topometrix Explorer 2000 scanning force microscope using a 2 μm^2 scanner and a S_3N_4 tip, with a spring constant of 36–44 N/m, $F_0 = 176$ kHz. Images were taken in air with noncontact mode. Scanning tunneling microscopic, STM, and scanning tunneling spectroscopic, STS, measurements were also carried out on the Topometrix Explorer 2000 with a tungsten tip. All images were obtained with different tips and at least three different sites were examined in a given sample.

Results and Discussion

The CdS nanoparticles, prepared initially in aqueous solutions, were stabilized by sodium hexametaphosphate. This polyanionic stabilizer terminated the crystal growth by electrostatic attachment onto the CdS surface. Equally importantly, it provided a negative surface charge and thereby maintained the CdS nanoparticles in the aqueous dispersion. Added positively charged long-chain DODAB (or CTAC) molecules were attracted to the available anionic sites; thereby, they rendered the CdS nanoparticles hydrophobic and, therefore, to be extractable into apolar solvents. Thus, the nanoparticles extracted into an organic solvent may be perceived as a kind of reversed micelles whose cores are the hexametaphosphate-stabilized CdS. Alternatively, the present system can be described as DODAB (or CATAC) capped CdS nanoparticles in which the precise arrangements of the hexametaphosphate ions, the long-chain surfactants and Cd^{2+}, S^{2-}, or HS^- on the semiconductor surface is somewhat uncertain.

Absorption spectra of the surfactant-capped CdS nanoparticles, taken at different stages of the size-selected precipitation in chloroform, are shown in Figure 1. The initially prepared dispersion gave a featureless absorption band with an edge at 502 nm (see spectrum 1 in Figure 1), corresponding to CdS nanoparticles with an average diameter of 5.2 nm.[3] Dropwise addition of methanol to this dispersion resulted in the flocculation of larger CdS particles, while the smaller ones remained in the supernatant whose spectrum indicated an absorption edge at 498 nm (spectrum 2 in Figure 1). Further size partitioning, by adding methanol to successively harvested supernatant solutions, blue-shifted the absorption edge to 490 and 486 nm (see spectra 3 and 4 in Figure 1) and permitted the isolation of capped CdS nanoparticles with average diameters of 4.0 and 3.6 nm.[8,9] It should be noted that even though there is no maximum in the absorption spectrum of sample 4 (Figure 1) the CdS particles are size quantized. A similar situation has been encountered for semiconductor particulate films.[13]

The concentration of CdS nanoparticles were calculated by assuming the molar absorption coefficient of CdS (in terms of $[Cd^{2+}]$) to be constant at 450 nm within the size range of nanoparticles investigated here. The

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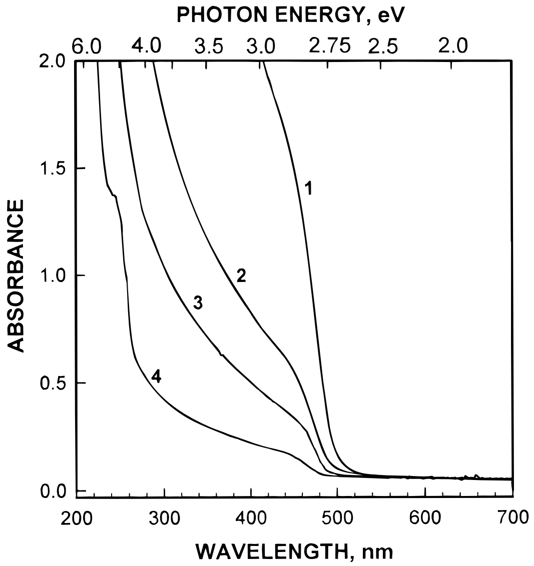

Figure 1. Set of absorption spectra taken during a successive size-selective precipitation. (1) Originally prepared chloroform dispersion of DODAB-capped CdS nanoparticles. The CdS particles were first formed by injection of H_2S in aqueous Cd^{2+}, stabilized by HMP, capped by DODAB, and in turn extracted into chloroform. (2) Spectrum obtained in the supernatant following the first precipitation (about 0.6 mL of methanol was dropped into 5.0 mL of dispersion 1 which resulted in flocculation. Following centrifugation, the supernatant was taken for the absorption measurement). (3) Spectrum obtained in the supernatant following the second precipitation (about mL of methanol was added to sample 2 which resulted in flocculation. Following centrigugation, the supernatant was taken for the absorption measurement). (4) Spectrum obtained in the supernatant following the third precipitation (About 3.5 mL of methanol was titrated in sample 3 which resulted in flocculation. Following centrifugation, the supernatant was taken for the absorption measurement.)

size and size distribution of the CdS nanoparticles, initially produced in aqueous media, were found to be governed by the starting pH of the solution and the concentrations of the stabilizer (HMP) and the cadmium ion. The average diameter of CdS particles, generated in solutions at a starting pH of 9.4, was determined to be 5.2 ± 2.5 nm by absorption spectrophotometry and transmission electron microscopy.[3] In fact, inspection of the absorption spectrum of the initially prepared CdS dispersion (shown in Figure 1) indicated the presence of 12% 3.6 nm (and smaller), 24% 3.6−4.0 nm, and 38%; 4.0−4.6-nm diameter particles. This result is in a good agreement with that obtained by analyzing the transmission electron micrographs of the CdS dispersion prepared in an identical manner.[3] Size-selective precipitations were also carried out on DODAB-capped CdS nanoparticle dispersions in hexane by titration by pyridine, on CTAC-capped CdS nanoparticle dispersions in chloroform by titration by methanol and on CTAC-capped CdS nanoparticle dispersions in hexane by titration by pyridine. Size partitioning by flocculation, on the other hand, is based on interparticle attraction (van der Waals force) which, in turn, is dependent on the nature and on the surface area of the particles.

Fluorescence spectra of DODAB capped CdS nanoparticles are shown in Figure 2. All spectra were normalized to the maximum intensity of the initially prepared CdS nanoparticle dispersion (i.e., to spectrum 1 in Figure 2). The photon energy of the excitonic emission of CdS nanoparticles is known to be size quantized.[1,14] The strong emission peak, centered around 480 nm, was attributed, therefore, to the recombination of excitons constrained within the CdS nanoparticles. With the successive size-selective precipitation, the longer-wavelength band edge underwent a significant blue shift (not shown) while the shorter wavelength edge remained unaltered (Figure 2). This behavior is in accord with the removal of larger sized CdS nanoparticles by the size-selective precipitations.

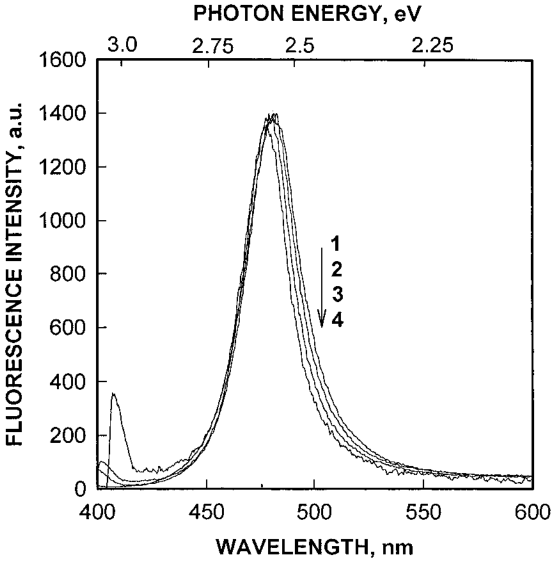

Figure 2. Fluorescence spectra of chloroform dispersions of DODAB capped CdS nanoparticles (see description of 1−4 in Figure 1). The spectra have been normalized to the peak intensity of spectrum 1.

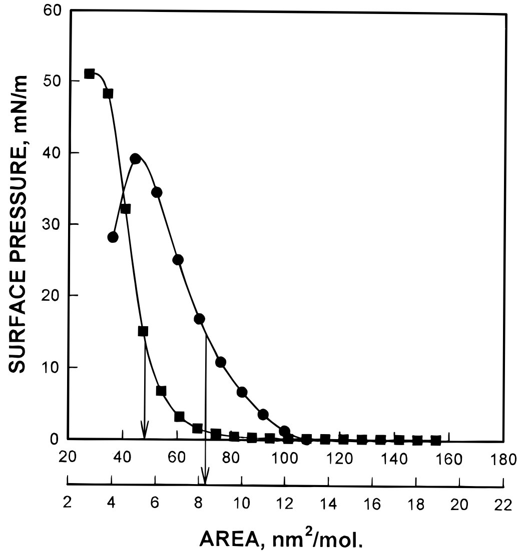

Figure 3. Surface pressure (Π) vs surface area (*A*) isotherms of obtained on spreading DODAB (1) and CTAC (2) capped CdS nanoparticles on water surfaces.

Capped CdS nanoparticles can be spread on the water surface, as evidenced by the observed regular surface pressure (Π) vs surface area (*A*) isotherms (Figure 3). Apparently, DODAB-capped CdS nanoparticles formed a stable layer on the wter surface, which underwent liquidlike state (Π < 15 mN/m) to condensed state (Π > 15 mN/m) transition and collapsed at Π = 50 mN/m. CTAC capped CdS nanoparticles, in contrast, organized themselves on the water surface in a more expanded

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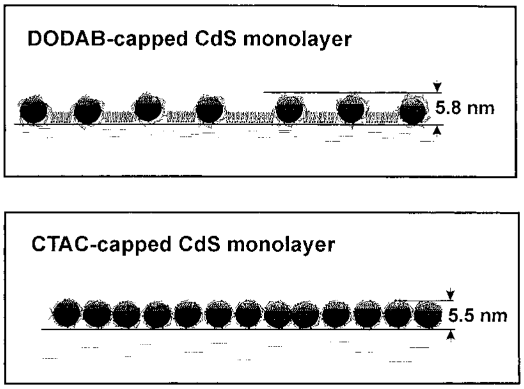

Figure 4. Schematics of DODAB- and CTAC-coated CdS nanoparticles spread on water surfaces.

way. Upon compression, the layer ran over the liquid-expanded state until it collapsed at $\Pi = 40$ mN/m (Figure 3).

Areas occupied by a single CTAC- or DODAB-capped CdS particle were estimated, by extrapolating from the condensed portion of the Π vs A isotherms, to be 11.7 and 58 nm^2, respectively. The obtained area-per-particle value for the CTAC-capped CdS particles corresponds to a hexagonal close packing of 5.2 nm diameter CdS nanoparticles, a value which agrees well with that derived from the absorption spectrum (vide supra). On the other hand, the area per DODAB-capped CdS particle is approximately 4 times greater than that estimated from the absorption spectrum, implying that DODAB molecules occupy an appreciably larger space than CTAC around the semiconductor nanoparticle. In situ reflectivity measurements of the CTAC- and DODAB-capped CdS layers on water surfaces (at $\Pi = 30$ mN/m) resulted in thicknesses of 5.5 and 5.8 nm (using a fitting program and assuming $n = 1.94 \pm 0.05$[15]). These thicknesses correspond nicely to monoparticle spreading of both CTAC- and DODAB-coated CdS and imply the presence of substantial DODAB monolayers between the particles (Figure 4).

Typical BAMs of the surfactant-capped CdS monoparticulate layers on the water surface are shown in Figure 5. Fairly uniform images of the DODAB-capped CdS layers are seen in the condensed region (Figure 5a), although some aggregation was found during the early stages of compression (gaseous and liquidlike states). A homogeneous condensed film appeared as the surface pressure approached 50 mN/m. Domain structures became visible subsequent to reexpansion from the condensed film (Figure 5b). The laterally shaped islands, with sizes ranging from 100 to 450 μm in dimension, resulted apparently from fracture due to some intralayer interactions. Conversely, the CTAC-capped CdS particulate layers were less uniform in the entire compression stage (Figure 5c) than their DODAB-coated counterparts. Reexpansion of the CTAC-covered CdS nanoparticulate layer led to the formation of 50−150 μm islands (Figure 5d). Filling the interparticle space with DODAB molecules led to a more condensed phase.

Monoparticulate layers of fluorescence-activated surfactant-capped size-selected CdS nanoparticles were successfully transferred onto such solid supports as glass, mica, graphite, and quartz plates by the LB technique with excellent transfer ratios. This allows, of course, the characterization of ultrathin organized semiconductor particulate films in the solid state and opens the door to superlattice-based device construction.

The excitonic fluorescence of surfactant-capped CdS nanoparticles was found to be sensitive to surface states. Surface modification by ionic species, water coordination, and, indeed, by capping has been shown to enhance or destroy the fluorescence of LB-film-incorporated CdS nanoparticles.[12] We have reported that water and ionic environments play an important role in activating the excitonic fluorescence of CdS nanoparticle dispersions.[12] Evaporating the surfactant-capped CdS nanoparticulate films to dryness dramatically decreased the emission intensity. Conversely, immersing a film, built from 10 layers of DODAB-capped CdS particles, resulted in a progressive and substantial increase of the excitonic fluorescence (Figure 6). The very weak excitonic emission peak at 478 nm (spectrum 1 in Figure 6) grew 7-fold upon immersion into water for 1.5 min (spectrum 2 in Figure 6). Longer immersions into water led to progressively enhanced fluorescence intensities up to a saturation value (at 15 min immersion) which was 165-fold greater than that obtained in the dry state (see insert in Figure 6). The relatively slow rate of fluorescence increase reflects the rate of water penetration in the surfactant-capped CdS nanoparticulate films. A similar behavior was previously observed for water penetration into LB-film-entrapped semiconductor nanoparticles.[12] The strong emission observed for CdS nanoparticles dispersed in an organic solvent indicates the presence of a considerable amount of water molecules of hydration around the semiconductor.

Modifications of CdS nanoparticles by chemi- or physisorption of simple or complex molecules by capping and by changing the composition or dielectric constant of the dispersing medium have profoundly affected the structures of surface traps.[15−19] Trap structures have been investigated at low temperatures, by steady-state and dynamic luminescence measurements, when the barrier between the trap and the excited states is amplified. Insight was gained on the surface traps, in the present work, by examining the fluorescence spectra of a five-layer film, built from DODAC-capped CdS nanoparticles, at various low temperatures. At low temperatures, the spectra of the film showed a weak broad emission band due to trapped fluorescence, centered in the 550−750 nm region, in addition to the sharp excitonic emission centered at 478 nm (Figure 7). The excitonic fluorescence intensity was found to increase with decreasing the temperature from 130 to 30 K but to decrease with further decreasing temperature to 10 K (see the insert of Figure 7). On the other hand, decreasing the temperature increased the intensity of the longer wavelength fluorescence, but it did not affect the peak position or the bandwidth (Figure 7).

Excitonic fluorescence has been established to originate in the detrapping of trapped electrons.[15−19] The trap energy levels can be located well below (deep traps) or close to (shallow traps) the excited states of the

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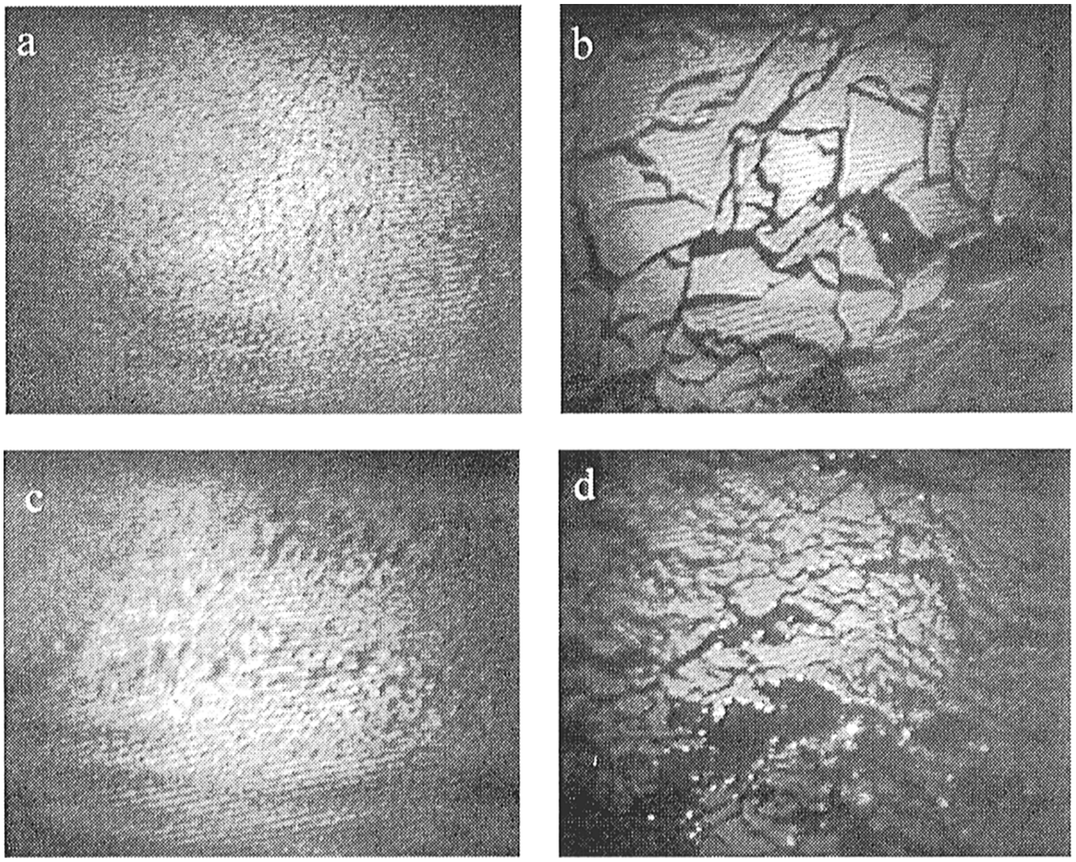

Figure 5. Brewster-angle microscopic images of capped CdS nanoparticles spread on water surfaces at different stages of their compressions and expansions. (a) Condensed phase ($\Pi = 35$ mN/m) of the DODAB-capped CdS nanoparticulate layer. (b) Typical domains observed for the DODAB-capped CdS nanoparticulate layer, subsequent to a compression to 50 mN/m. (c) Liquid-expanded phase of the CTAC-capped CdS nanoparticle layer at $\Pi = 15$ mN/m. (d) Domains of the CTAC-capped CdS nanoparticle layer subsequent to a compression to 50 mN/m.

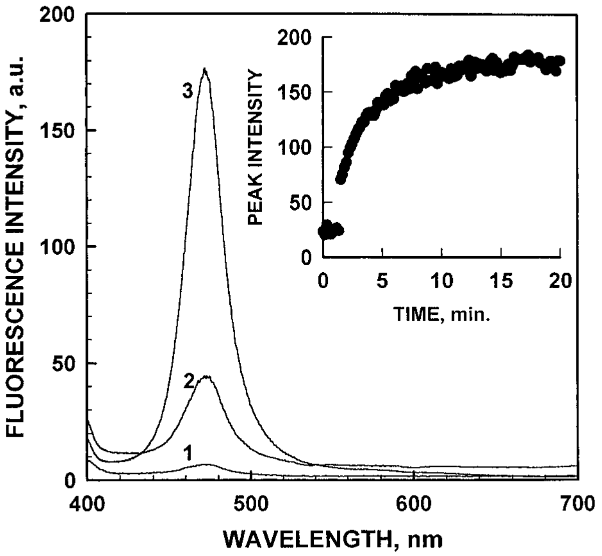

Figure 6. Excitonic fluorescence enhancement of a 10-layer film, built from DODAC-capped CdS nanoparticulates, upon its immersion in water. The spectra given correspond to (from bottom to top) 0-, 1.5-, and 15-min immersion in water. The insert plots the emission peak intensity vs immersion time.

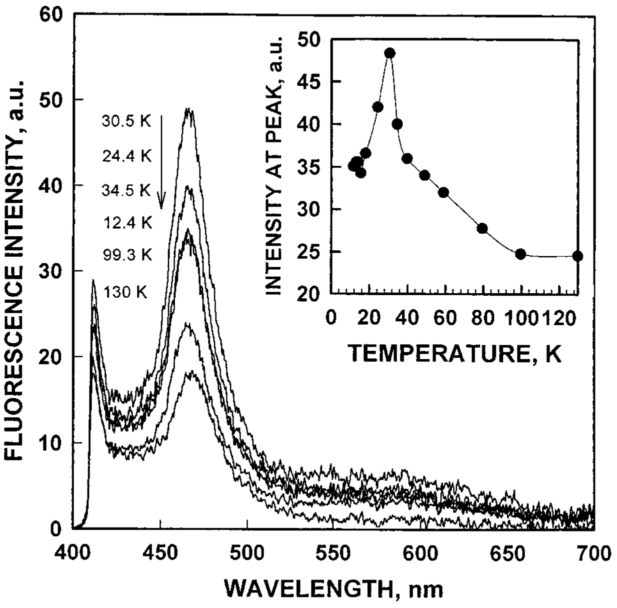

Figure 7. Fluorescence spectra of a five-layer film, built from DODAC-capped CdS nanoparticulates, at different temperatures. The insert plots the emission peak intensity vs temperature.

semiconductors. Two types of low-temperature fluorescence behaviors have been observed for CdS nanoparticles. The significant blue-shift and band narrowing of the fluorescence of HMP-stabilized CdS particles which accompanied the temperature decrease from 220 to 4 K represents the first case. It was attributed to the coexistence of deep and shallow traps with a thermally exceedable barrier between the traps and the conduction band.[9] The second case, due to the presence of shallow traps, is characterized by an increase of the excitonic luminescence intensity with decreasing temperature, down to 8 K, without band shifting and band narrowing. DODAC-capped, HMP-stabilized, CdS nanoparticles, prepared in the present work (see Figure 7), and ammonia-passivated CdS nanoparticles, reported

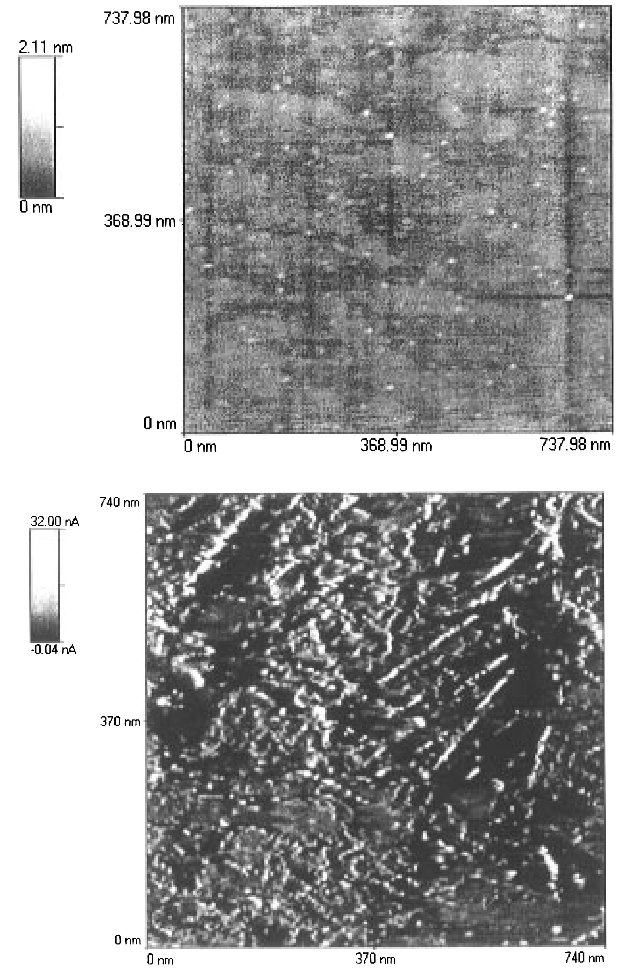

Figure 8. The 700 nm × 700 nm two-dimensional AFM (a, top) and STM (b, bottom) images of a DODAB-capped CdS monoparticulate films.

previously,[16c] are examples of the second case. Interaction of the ammonium groups (of DODAC) with the HMP-covered CdS surface results in the change of surface charges and in the redistribution of surface traps to more shallow regions of the semiconductor. Furthermore, the presence of a peak in the intensity vs temperature plot at around 30 K (see insert in Figure 7) indicates the existence of an energy barrier between the shallow traps and the conduction band which can be overcome thermally when the temperature increases beyond this value.

Atomic force and scanning probe microscopic images provided two-dimension information on the monoparticulate layers of the capped CdS. The CdS particles are seen to be evenly distributed with little aggregation of the particles (Figure 8a). The size of a particle, obtained from the images, was determined to be 8 ± 3 nm. The loose, stringlike arrays of particles, as seen in the STM image (Figure 8b), originate in some weak interparticle interaction. Similar phenomenon was previously observed on growing CdS particulate films under organic monolayers.[1,2] Counting the number of the particles in a given area resulted in an area-per-particle value of 58 nm^2/particle for DODAB-capped CdS particles, in accord with that estimated from the Π vs A isotherm (vide infra). This well-separated morphology of the DODAB-capped CdS particulate film implies that the DODAB molecules, which served as extraction agent, fill up the remaining space between the particles (Figure 4).

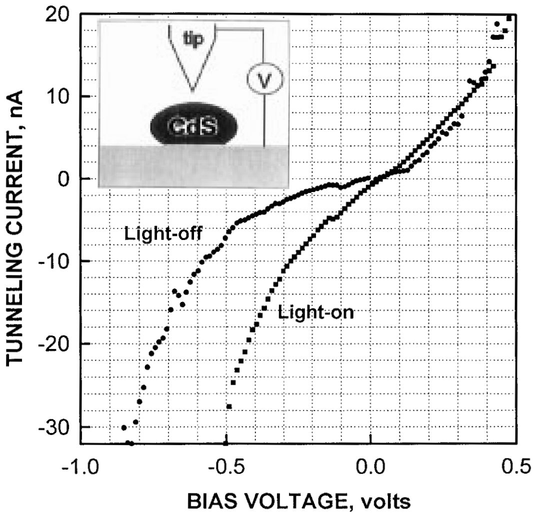

Figure 9. Scanning tunneling spectra of a DODAB-capped CdS nanoparticulate film deposited on HOPG. The measurements were conducted by aiming a tungsten tip at a single particle site on the image obtained prior to the tip approaching. The tip-to-sample distance was controlled by setting a tunneling current of 8 nA at a bias of −30 mV. The light source was a 500 W xenon lamp and was directed to the sample through a glass fiber optics.

Scanning tunneling spectroscopy (STS) provides a wealth of information on the electronic structure of semiconductors.[20] Indeed, we have determined the type of majority charge carriers (n or p type) and the density of surface states for semiconductor nanoparticulate films, generated under monolayers by STS.[21,22] The present system permitted the limitation of STS to a single CdS nanoparticle (see the insert of Figure 9). All the measured $I-V$ curves, both in the dark and under illumination, exhibited a typical n-type Schottky rectification behavior: at a given tip-to-particle distance the cathodic current increased exponentially with a forward bias (positive), while much smaller anodic current flowed under a reverse bias (negative). The anodic current in the negative voltage region (0 to −1.0 V) showed an interesting photoinduced effect. In the dark, the single particle tunneling current was found, as expected, to behave exponentially. When illuminated, however, the anodic tunneling current increased significantly while no change was observed for the cathodic current branch (Figure 9). This fact reveals that the majority carriers in the capped CdS monoparticulate films are negative, and thus this system behaves like an n-type semiconductor. An enhancement of the signal at certain electronic bias level reflects the resonance excitation of the surface at that measurement point. Since the measurement only involved a single CdS nanoparticle, the surface states can be well represented by the interior electronic structure of the particles. Therefore, the observed photoeffect on the tunneling current corresponds to optical transition which increases the transmission coefficient under the reverse voltage. This, once again, is characteristic of n-type semiconductor behavior.

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