Langmuir–Blodgett Manipulation of Size-Selected CdSe Nanocrystallites

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The Langmuir–Blodgett (LB) technique is used to deposit monolayers of nearly monodisperse nanometer-size CdSe crystallites (quantum dots) onto various substrates. Size-selected CdSe nanocrystallites capped with trioctylphosphine oxide are directly applied onto the water surface of a LB trough and serve as the LB-active species. Absorption and luminescence studies of monolayers transferred onto glass slides indicate that the monolayers retain the general optical properties of isolated crystallites. Transmission electron micrographs of monolayers on amorphous carbon show the formation of two-dimensional hexagonal close-packed domains.

Introduction

Submicron semiconductor structures which confine electronic excitations in one or more dimensions are rich in new and interesting physics.[1] Confinement in all three dimensions results in "quantum dots" with an electronic spectrum which is discrete rather than continuous. Nanometer-size crystallites of II–VI semiconductors (also called quantum dots, quantum crystallites, or nanocrystallites) have received much attention both as model systems for probing the development of bulk properties from molecular species and for their size dependent optical properties.[2] Organized assemblies of crystallites should show interesting physical properties. Difficulties in producing and manipulating nearly monodisperse nanometer-size crystallites of arbitrary diameter have prevented the fabrication of such well-defined two- or three-dimensional structures. A recent exception is the special case of single crystals of identical ~15-Å CdS clusters.[3] Self-assembly techniques have also been used to deposit submonolayers of CdS nanocrystallites on metal surfaces.[4] Arrays of significantly larger quantum dots fabricated using lithographic methods show that novel electronic behavior can arise from interdot collective interactions.[5] Lithographic methods are however presently limited to lateral sizes greater than ~100 nm.

This paper describes the Langmuir–Blodgett (LB)[6] manipulation and characterization of locally ordered 2-D hexagonal close-packed monolayers of CdSe nanocrystallites transferred onto various substrates. We combine the LB technique with a recently developed synthesis[7] for nearly monodisperse nanometer-size CdSe crystallites. Crystallites capped with trioctylphosphine oxide are prepared and size selected using the procedure of ref 7. The crystallites are then applied onto the water subphase of a LB trough. In contrast to previous works combining LB methodology with nanocrystallites,[8,9] the crystallites in our work themselves serve as the LB-active species. Room-temperature absorption and luminescence spectroscopies are used to optically characterize monolayers of crystallites deposited on glass slides. Transmission electron microscopy (TEM) is used to image and structurally characterize monolayer films of crystallites deposited on amorphous carbon films.

Experimental Section

Synthesis and Characterization of CdSe Nanocrystallites. Nearly monodisperse CdSe nanocrystallites with diameters tunable from 15 to 120 Å ($\sigma < 5\%$) were obtained following the procedure of ref 7 from the pyrolysis of dimethylcadmium and trioctylphosphine selenide in trioctylphosphine oxide (TOPO), followed by a size-selective precipitation process. Crystallites of various sizes capped with TOPO were recovered as powders which can be dispersed in a variety of solvents. The crystallites were characterized by optical absorption, powder X-ray diffraction and transmission electron microscopy.

Preparation of Spreading Solutions. Spreading solutions of CdSe nanocrystallites for five different sizes (25, 30, 36, 43, and 53 Å diameter) were prepared as follows: Powders of crystallites were first washed with methanol to remove any residual free TOPO. The crystallites were then dispersed in HPLC grade chloroform at concentrations of 5–10 mg/mL and passed through a 0.2-μm PTFE filter (Fisher Scientific) to remove any dust particles or large aggregates of nanocrystallites.

Langmuir Monolayers of CdSe Nanocrystallites. A Lauda FW-2 film balance was used to manipulate CdSe nanocrystallites at the air–water interface. The water in the subphase was purified in a Milli-Q purification system (Millipore Corp.). Small aliquots of the spreading solutions (10–30 μL) were spread dropwise onto the subphase and the barrier was swept at a rate of ~90 mm/min to obtain surface pressure/area (π-A) isotherms for each size at 20.0 ± 0.1 °C.

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(1) Ploog, K. *Angew. Chem., Int. Ed. Engl.* 1988, *27,* 593. Schmitt-Rink, S.; Chemla, D. S.; Miller, D. A. B. *Adv. Phys.* 1989, *38,* 89.

(2) Brus, L. E. *Appl. Phys.* 1991, *53,* 465. Wang, Y.; Herron, N. *J. Phys. Chem.* 1991, *95,* 525. Weller, H. *Angew. Chem., Int. Ed. Engl.* 1993, *32,* 41. Henglein, A. *Top. Curr. Chem.* 1988, *143,* 113. Stucky, G. D.; MacDougall, J. E. *Science* 1990, *247,* 669. Goldstein, A. N.; Echer, C. M.; Alivisatos, A. P. *Science* 1992, *256,* 1425.

(3) Herron, N.; Calabrese, J. C.; Farneth, W. E.; Wang, Y. *Science* 1993, *259,* 1426.

(4) Colvin, V. L.; Goldstein, A. N.; Alivisatos, A. P. *J. Am. Chem. Soc.* 1992, *114,* 5221.

(5) Heitman, D.; Kotthaus, J. P. *Physics Today* 1993, *46(6),* 56.

(6) Blodgett, K. B.; Langmuir, I. *Phys. Rev.* 1937, *55,* 19. Roberts, G. G. *Langmuir–Blodgett Films;* Plenum: New York, 1990.

(7) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* 1993, *115,* 8706.

(8) Zhao, X. K.; Fendler, J. H. *J. Phys. Chem.* 1991, *95,* 3716; Yuan, Y.; Cabaso, I.; Fendler, J. H. *Chem. Mater.* 1990, *2,* 226.

(9) X. Peng, X.; Zhang, Y.; Yang, Y.; Zou, B.; Xiao, L.; Li, T. *J. Phys. Chem.* 1992, *96,* 3412.

0897-4756/94/2806-0216$04.50/0

Langmuir–Blodgett Substrates. Hydrophilic glass slides (Fisher Scientific) cut to 2.5 cm × 2.5 cm and cleaned using standard procedures (see ref 10) were used for the initial dipping experiments. Glass slides coated with a layer of sulfonated polystyrene (SPS) prepared by the method of ref 10 were used subsequently. Magnetic nickel TEM grids (Ernest F. Fullam Corp.) supporting a thin film (50–100 Å) of amorphous carbon were used as is for the TEM imaging. The grids were placed on the front face of a thin rectangular magnet (2.5 cm × 5 cm × 2 mm) for dipping and transferring monolayers.

Langmuir–Blodgett Manipulation. LB substrates were positioned vertically or at a slight angle from the vertical inside the subphase. Aliquots (100 μL) of the spreading solutions were added dropwise via microsyringe at various locations on the trough. The films were compressed to a surface pressure of 30 mN/m and allowed to anneal for 10–15 min. Single monolayers of CdSe nanocrystallites were transferred onto the substrates on an upward stroke at a rate of 20 mm/min.

Optical Characterization. Optical absorption spectra were taken on an Oriel diode array spectrometer. Fluorescence spectra were obtained in a front face geometry using a SPEX Fluorolog-2. Spectra of monolayers on glass slides and corresponding solutions in cuvettes were taken under similar conditions for direct comparison.

Transmission Electron Microscopy. A Topcon EM002B transmission electron microscope operated at an accelerating voltage of 200 kV was used to obtain images of monolayer films deposited onto the TEM grids described above. Objective apertures were used to allow lattice imaging of only the (100), (002), and (101) wurtzite planes.

Results and Discussion

Traditional LB monolayers consist of amphiphilic molecules which are spread on a water surface polar head down, nonpolar tail up, corralled into a monolayer by an adjustable barrier, and then transferred onto solid substrates.[6] Previous LB studies on nanoparticulate materials have generally relied on traditional amphiphiles to form monolayers at the air–water interface.[8,9] The nanoparticles are then grown in situ[8] or dispersed in the subphase and attracted by the monolayer.[9] Our systems here do not rely on classical amphiphiles; the nearly monodisperse crystallites are passivated with loosely bound TOPO molecules with the alkyl chains pointing out. The crystallites have a polar core but present a hydrophobic surface. Consequently, the crystallites themselves serve as the surface-active molecules, much like in the recently reported nontraditional LB films of C_{60} molecules.[11]

Monolayers at the Air–Water Interface. Figure 1 shows surface pressure–area (π–A) isotherms for samples of nanocrystallites with five different sizes (25, 30, 36, 43, and 53 Å diameter). The isotherms display a transition plateau with negligible surface pressure where the crystallites are probably clustered as small islands floating on the subphase. A steep rise in surface pressure follows as the islands begin to touch. The islands merge to form a monolayer which can withstand surface pressures up to ~65 mN/m before collapsing. The isotherms show strong hysteresis indicating that the films are rigid and intercrystallite interactions at the air–water interface are attractive. Areas per crystallite in the rigid monolayers are within experimental error (~15%) of capped crystallite cross-sectional areas, consistent with close packing.

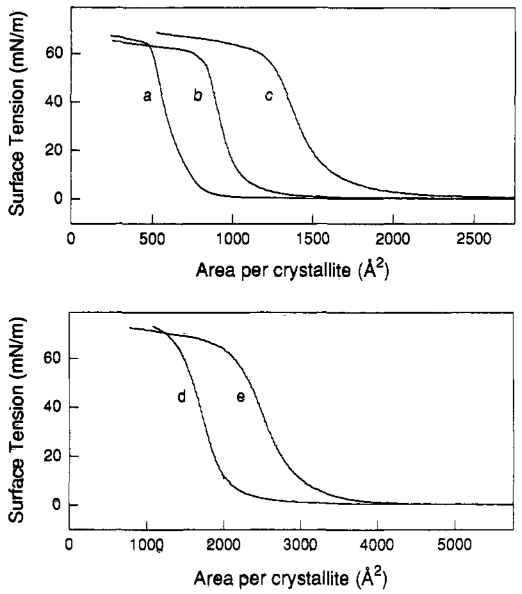

Figure 1. Surface pressure–area (π–A) isotherms for Langmuir monolayers of CdSe nanocrystallites. Diameters are (a) 25, (b) 30, (c) 36, (d) 43, and (e) 53 Å. The area per crystallite is obtained by dividing the total area available during compression by the estimated number of crystallites applied onto the water surface.

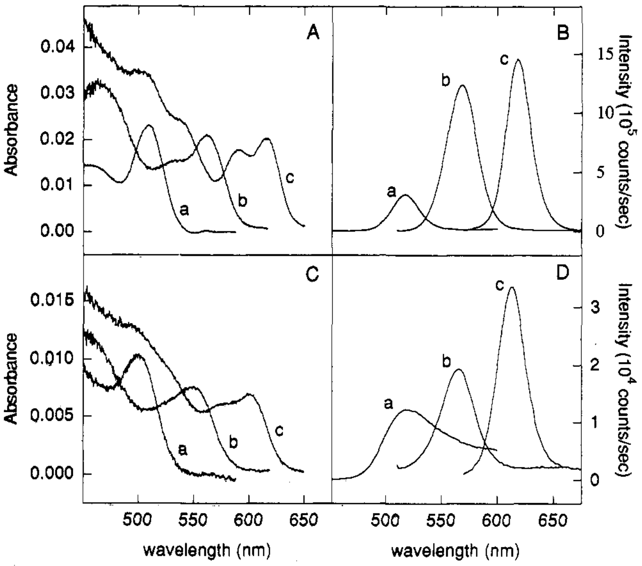

Figure 2. Comparison of optical properties of solutions and monolayers of CdSe nanocrystallites. Optical absorption (A, C) and photoluminescence (B, D) spectra of crystallites in solution (A, B) and as close-packed monolayers on SPS-coated glass (C, D). Crystallite diameters are (a) 25, (b) 36, and (c) 53 Å. Excitation wavelengths for photoluminescence are (a) 430, (b) 490, (c) 540 nm.

Adding 100 μL of the chloroform spreading solution to the surface of the subphase produces monolayers with area >400 cm^2 which are reasonably stable at the air-water interface. After seven hours and at a surface pressure of 30 mN/m, the area of a monolayer of 53-Å diameter crystallites decreased by about 10%, with most of the loss in area attributable to aggregation of crystallites at the interface with the moving barrier. Spreading the crystallites from more dilute solutions results in less stable films, as has also been observed with nontraditional films of C_{60} molecules.[11]

Langmuir–Blodgett Manipulation. Single monolayers of crystallites are transferred onto hydrophilic glass slides by dipping upward. Attempts to transfer a monolayer on the downward stroke resulted in much smaller transfer ratios. Transfer onto the slides, as estimated from

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(10) Decher, G.; Hong, J. D.; Schmitt, J. *Thin Solid Films* **1992**, *210/211*, 831. Ferreira, M.; Cheung, J. H.; Rubner, M. F. *Proceedings of the SPE meeting*, ANTEC '93.

(11) Obeng, Y. S.; Bard, A. J. *J. Am. Chem. Soc.* **1991**, *113*, 6279. Bulhões, L. O. S.; Obeng, Y. S.; Bard, A. J. *Chem. Mater.* **1993**, *5*, 110.

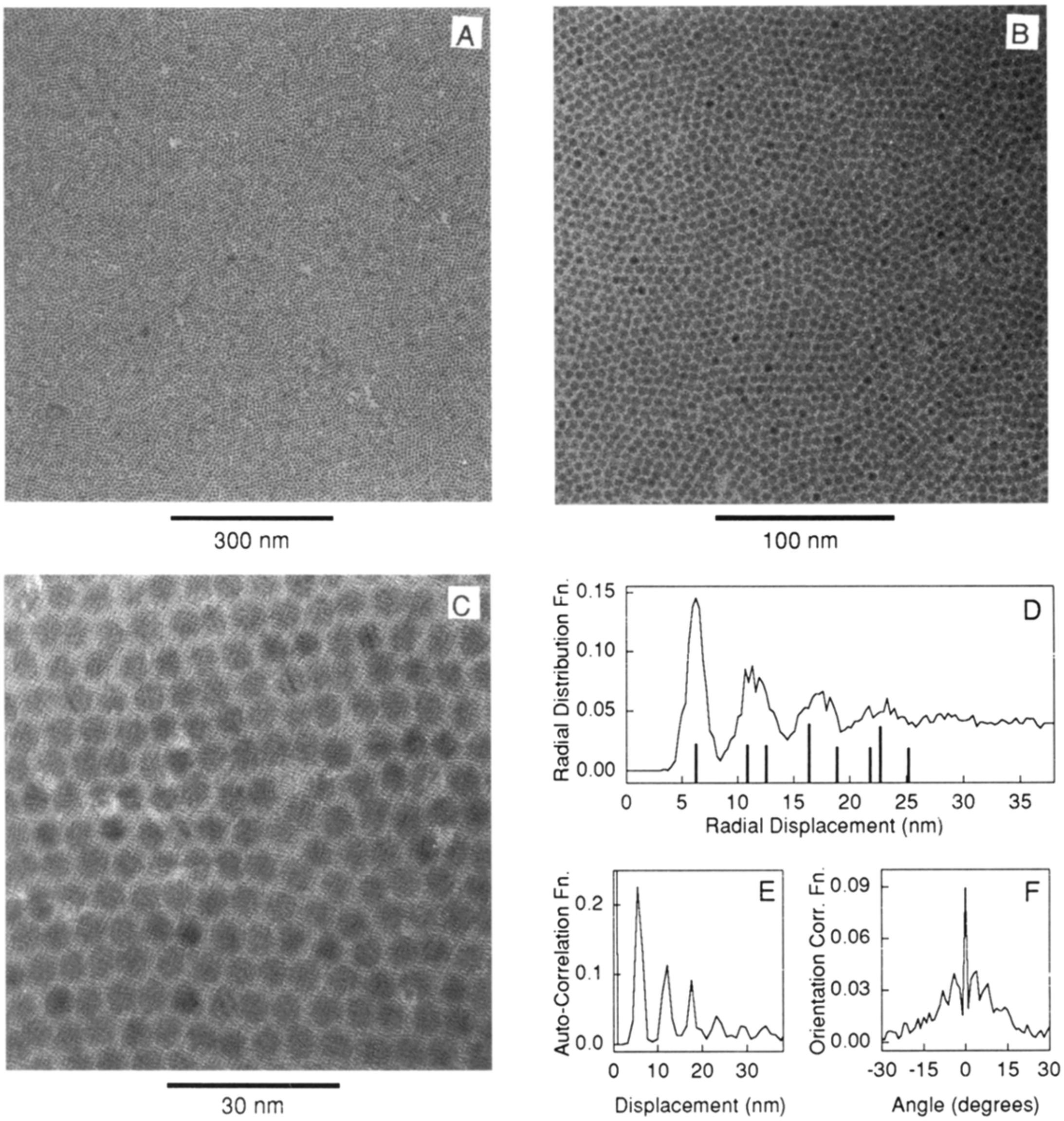

Figure 3. Imaging and structural analysis of a monolayer of CdSe Nanocrystallites. (A–C) TEM micrographs of a monolayer of close packed 53 Å ($\sigma \sim 4\%$) CdSe nanocrystallites at three different magnifications. (D) Radial distribution function of a rectangular patch of ~550 crystallites (0.18 μm × 0.13 μm) obtained from coordinates of the centers of the crystallites. The stick spectrum is the expected RDF for a perfect hexagonal close packed lattice of the same size, scaled to fit below the experimental data. (E) Cross section of the 2-D autocorrelation function along a hexagonal axis. (F) Nearest-neighbor orientation distribution function referenced to a fixed direction and modulo 60°.

changes in surface areas at the air–water interface, is nearly complete (>90%). Transfer onto glass slides coated with a layer of sulfonated polystyrene (SPS) is generally higher (>95%) than for plain hydrophilic slides. This may be due to the reduced surface roughness of SPS-coated slides or to electrostatic interactions between the charged polymer and the polar core of the crystallites. Multilayers of crystallites can also be deposited: An initial monolayer is transferred, the slide is air dried and repositioned in the subphase, crystallites are spread again on the water surface, and a second monolayer is transferred on top of the first.

Optical Characterization. Optical absorption and luminescence spectroscopy of the monolayers deposited on glass shows that the films retain the general characteristics of isolated crystallites. Figure 2A,B shows room-temperature absorption and photoluminescence spectra for dilute solutions of three different size nanocrystallites. The spectra show discrete optical transitions with the lowest transition blue-shifting with decreasing size as a result of quantum confinement.[2] The optical features are inhomogeneously broadened from distributions in crystallite size and morphology. Quantum yields in solution at room temperature can reach 10%.[7] Figure 2C,D shows absorption and photoluminescence spectra of monolayers of the same samples deposited onto SPS-coated glass. The absorption features for the monolayers are slightly broadened and blue shifted from the solution spectra. This may be due to the combination of close packing the crystallites and slight surface degradation of the crystallites due to prolonged exposure to water during the LB procedure. The degradation could cause a broadening of the size distribution and a slight reduction in the average size. Reducing annealing times on the water surface appears to reduce both the blue shift and the broadening to some extent. A nonaqueous subphase, a dark room, or adjustment of the water pH may reduce any degradation further.

The optical density and intensity scales in Figure 2 are absolute scales and excitation energies are the same for solutions and monolayers, allowing for meaningful comparisons. Quantum yields of the monolayers using front face collection are generally 10–20 times smaller than in solution. Monolayer photoluminescence spectra also show a smaller blue shift and less broadening than the corresponding absorption spectra. The quenching of the luminescence and the larger shift between absorption and luminescence for the monolayers may result from a combination of close packing of the crystallites, leading to efficient energy transfer and trapping at nonradiative recombination centers and possibly surface degradation processes from exposure to water.

Transmission Electron Microscopy. The large atomic numbers of Cd and Se and the crystalline nature of the nanocrystallites enable us to readily image the monolayers with high resolution using TEM. Figure 3A–C shows TEM micrographs of a monolayer of 53-Å ($\sigma \sim 4\%$) diameter CdSe nanocrystallites at three different magnifications. The crystallites close pack with local hexagonal symmetry. Analysis of a number of micrographs of different monolayers shows that coverage ranges from 95 to over 99%. Many of the voids look like tears and are probably formed during the transfer process. Dipping with the substrate at a slight angle to the vertical decreases the number of these voids. Figure 3A shows nearly complete (>99%) coverage over a relatively large region (0.9 μm × 0.9 μm). Figure 3B, at an intermediate magnification, shows that the crystallites organize in small nearly crystalline domains. Single rows of over 40 crystallites can be seen. Figure 3C at high magnification highlights the local hexagonal ordering. A centrally located vacancy leads to a dislocation defect and a loss of translational symmetry.

Statistical Analysis. A rectangular patch of $\sim$550 nanocrystallites (0.18 μm × 0.13 μm) which includes the crystallites of Figure 3C is used for statistical analysis of the local ordering. Coordinates of the centers of the crystallites were used to obtain a radial distribution function (RDF), a two dimensional auto-correlation function, and a nearest-neighbor orientation distribution function. Figure 3D shows the experimental RDF and compares it to that of a perfect crystalline lattice of the same size. Four nearest-neighbor shells are visible. The first nearest-neighbor shell is peaked at 6.3 nm, consistent with 53-Å crystallites surrounded by a $\sim$5-Å-thick layer of TOPO capping groups. The integrated area of the first nearest-neighbor shell yields 5.7 nearest neighbors on average, as expected for a similarly sized finite hexagonal close packed lattice.

Figure 3E shows a cross section of the 2-D autocorrelation function along one of the hexagonal symmetry axes. Four peaks are visible with intensities rapidly decreasing, indicating loss of translational symmetry. Nearest-neighbor 6-fold orientational ordering is however preserved as seen in Figure 3F which shows the distribution of nearest-neighbor orientations referenced to a fixed direction and modulo 60°. This distribution function is sharply peaked, indicating the presence of long-range hexagonal orientational ordering. The combination of short range translational order but long-range nearest-neighbor orientational order is a result of dislocation defects as seen in Figure 3C and is the signature of a hexatic phase.[12] The crystallites appear to form hexatic domains on $\sim$0.2-μm-length scales. Grain boundaries and vacancies prevent longer range correlations. Longer annealing at the air–water interface or simply annealing the transferred films at temperatures close to 50 °C (the melting point of free TOPO) may improve long-range order.[13] Figure 4 compares the first shell of the RDF with the measured crystallite diameter distribution function. The distribution of crystallite diameters is peaked at 53 Å with a standard deviation of $\sim$4%. The measured standard deviation for this distribution is an upper bound: the loss of contrast at the edges of the crystallites introduces a measurement error of the same size as the measured width of the distribution. The first shell of the RDF ($\sigma \sim 17\%$) is significantly wider than the diameter distribution function, indicating that the distribution of crystallite diameters is not the major cause of lattice disorder. The large difference in width between these two distributions indicates that longer range order should in fact be possible.

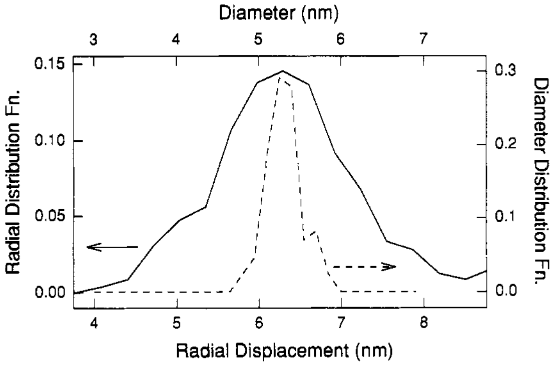

Figure 4. Comparison of the first shell of the radial distribution function (RDF) and the crystallite diameter distribution function. The solid line is the first shell of the RDF of Figure 3D, peaked at 63 Å with a standard deviation of 17%. The dotted line is the distribution function of crystallite diameters, peaked at 53 Å with a standard deviation of 4%.

Conclusion

Langmuir–Blodgett (LB) technology is used to produce close packed monolayers of nearly monodisperse CdSe nanocrystallites with diameters tunable from 25 to 65 Å. The crystallites themselves serve as the LB-active species. The crystallites are capped with a hydrophobic layer of trioctylphosphine oxide (TOPO) and behave like weakly attracting hard balls on the water surface. The spacing between crystallites in the monolayers is fixed by the size of the cap (TOPO) and should be adjustable by changing capping groups (from TOPO to tributylphosphine oxide, for example). The monolayers can be transferred on various hydrophilic substrates and directly imaged by TEM to analyze their structure. Absorption and luminescence bands of the monolayers on hydrophilic glass retain the general properties of isolated crystallites.

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(12) Nelson, D. R. In *Phase Transitions and Critical Phenomena*; Domb, C., Lebowitz, J., Eds.; Academic Press: New York, 1983; Vol. 7.

(13) Annealing of transferred traditional LB monolayers by gently heating has been demonstrated by: Bourdieu, L.; Ronsin, O.; Chatenay, D. *Science* 1993, *259*, 798.