Spectroscopic Study of Electronic States in an Ensemble of Close-Packed CdSe Nanocrystals

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Nearly monodisperse CdSe quantum dots of 1.8 nm in size were synthesized and capped with a surface monolayer of 1-thioglycerol. The optical properties of thin films made from these matrix-free close-packed quantum dots were studied at different temperatures and electric field strengths and compared with isolated quantum dots of the same size embedded in a PMMA matrix. The broadening and red shift of the optical transitions observed in absorption and excitation spectroscopy for the ensemble of close-packed quantum dots is explained by the formation of collective electronic states between interacting nanocrystals. The reversible collapse of these extended electronic states into localized states was demonstrated for the close-packed quantum dots by applying an external electric field.

Introduction

At present, the optical properties of II–V semiconductor nanocrystals are intensively studied, and the various observed phenomena are well-described in terms of single isolated quantum dots.[1,2] However, only a few studies exist that deal with collective phenomena in ensembles of interacting nanocrystals. For example, the energy transfer from wide- to narrow-band gap close-packed CdSe nanocrystals has been observed in photoluminescence experiments.[3] First signs for a transition from individual to collective electronic states were obtained in ref 4 by comparing the absorption spectra from ensembles of CdSe nanocrystals of the same size but with varying interparticle distances. In ref 4 it was found that the room-temperature absorption of 1.8 nm CdSe nanocrystals shows an evolution from a sharp peak at 3.25 eV toward a broad absorption band centered at approximately the same energy with increasing density of the close-packed nanocrystals. A first theoretical approach based on a statistical analysis of the energy overlap integrals demonstrated a steady increase of the number of delocalized states in ensembles of interacting quantum dots when the size of the CdSe nanocrystals and the interparticle distance are smaller than ∼2 nm and ∼4 nm, respectively.[5] Delocalization of electron–hole states has clearly been observed until now only for ultrasmall, nearly monodisperse nanocrystals having small electron or hole effective mass. The larger the nanocrystals and their effective masses are, the smaller the probability is that electron (hole) wave functions overlap for neighboring nanocrystals.

In the paper presented here, we investigate the optical properties of close-packed and isolated ultrasmall CdSe nanocrystals using various spectroscopic techniques such as absorp-

tion, photoluminescence (PL), photoluminescence excitation (PLE), and electroabsorption. Ultrasmall CdSe nanocrystals were chosen for the following reasons: (i) CdSe has small effective masses for both electrons and holes, (ii) the band-gap energy of CdSe is in the visible spectral range, which simplifies the optical detection, (iii) the synthesis of very small monodisperse CdSe nanocrystals of so-called "magic size" is well-established (see e.g., ref 6 and references therein). Distinct differences were observed in the optical properties of isolated and close-packed CdSe nanocrystals, which will be explained by the existence of delocalized electronic states developing within ensembles of interacting semiconductor nanocrystals.

Experiments

Sample Preparation. Nearly monodisperse CdSe clusters with an average diameter of 1.8 nm were synthesized in colloidal solution. Ten milliliters of 2×10^{-2} M cadmium acetate (commercially available cadmium acetate dihydrate) solution in dry pyridine (Ferak) was heated to 80 °C and stirred under nitrogen flow (magnetic stirrer, 600 rpm). To this solution, 1 mL of selenourea (Aldrich) in pyridine was rapidly added, resulting in an instantaneous yellow color of the colloidal solution of CdSe nanocrystals. The entire Cd:Se molar concentration was 2:1. Then, the colloidal solution was cooled to room temperature and 0.1 mL of 1-thioglycerol (Aldrich) was added dropwise. While the initially fabricated CdSe nanocrystals are stabilized by pyridine molecules, the last procedure results in a replacement of the surface pyridine monolayer into a thioglycerol layer. The thioglycerol-stabilized CdSe nanocrystals are no longer soluble in pyridine and precipitate from the solution. The CdSe nanocrystalline phase was centrifuged, washed twice with methanol, and redispersed in a fresh pyridine solution by ultrasonic treatment. For optical measurements, thin films of close-packed CdSe nanocrystals were prepared by placing a drop

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of the final colloidal solution onto quartz glass and drying it at room temperature in air. To prepare the thin films of isolated CdSe nanocrystals, an appropriate amount of poly(methyl methacrylate) (PMMA) was added to a colloidal solution before drying. The polymer PMMA is readily soluble in pyridine and creates a transparent matrix of excellent optical quality.

X-ray Diffraction. Wide-angle X-ray diffraction data (XRD) of powdered close-packed CdSe nanocrystals were collected using a Cu K_α diffractometer. The powder of close-packed nanocrystals was prepared by drying the final colloidal solution with thioglycerol-stabilized CdSe nanocrystals at room temperature and depositing it on a PMMA substrate for analysis.

Optical Measurements. For spectroscopic studies, two types of samples were prepared, namely, a PMMA film containing about a 5% mass of CdSe nanocrystals labeled as the isolated-dot sample and a thin film of close-packed CdSe nanocrystals without any stabilizing polymer, labeled as the close-packed quantum dot sample. For the isolated nanocrystals in PMMA, the average wall-to-wall interparticle distance estimated from the volume concentration of nanocrystals was 8 to 10 nm, which is much larger than the size of the nanocrystals. The intrinsic absorption of PMMA in the near-UV region is small enough and does not interfere with the absorption of the CdSe nanocrystals. The absorption spectra of both colloidal solutions and thin solid films were recorded using a CARY 2300 spectrometer equipped with a home-built cryostat for low-temperature measurements. The spectral resolution was better than 0.5 nm. Photoluminescence (PL) and PL excitation spectra (PLE) were recorded with an experimental setup consisting of a Xe lamp as excitation source, two monochromators for excitation and emission spectra, a cryostat, and a CCD camera. Fourier transform infrared spectra (FTIR) of the close-packed nanocrystals deposited on Si wafers were recorded with a Perkin-Elmer spectrometer 1000.

Electroabsorption. Glass covered with transparent conductive SnO_2:Sb (100 Ω cm^{-1}) layers was used as a substrate for electroabsorption measurements. Conducting layers were prepared by standard spray pyrolysis of $SnCl_4\cdot5H_2O$:$SbCl_3$ solution on glass slides heated to 600 K. Then, thin films of both isolated and close-packed CdSe nanocrystals of 250 and 100 nm thickness, respectively, were deposited at room temperature as described above. A second, metallic mirror electrode was formed by vacuum evaporation of a 200-nm layer of Al atop the CdSe films. The less-than-a-micron thin SnO_2/CdSe/Al sandwich structure allows high internal electrical field strengths of $\sim10^5$ V cm^{-1}, using external bias below 50 V. The electroabsorption spectra were obtained by measuring the beam intensity after passing the sample twice. The incident light passed the glass substrate, the transparent conductive layer, and the thin film of CdSe nanocrystals and was then reflected back from the Al mirror. The reflected light was collected under a reflection angle of 20°. The reflection spectrum of the Al mirror itself was nearly constant in the spectral range of interest.

Results and Discussion

Morphology of Films. The CdSe nanocrystals possess a surface-stabilizing cap layer based on thiol groups strongly bound to cadmium atoms. The replacement of the pyridine surface-stabilizing monolayer into a thioglycerol one results in CdSe nanocrystals that are more stable against oxidation and recrystallization when forming close-packed films. Additionally, the precipitation by thioglycerol and the redispersal of nanocrystals in a fresh pyridine solution results in a very small
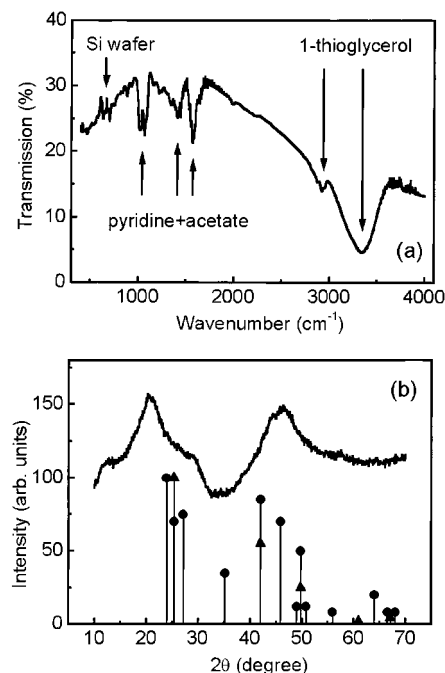

Figure 1. Room-temperature FTIR spectrum (a) and wide-angle X-ray diffractogram (b) of close-packed CdSe nanocrystals. For comparison, the data are shown for bulk CdSe of sphalerite (circles) and wurtzite (triangles) structures.

amount of residual ions. Comparing the absorption spectra of the CdSe colloidal solution before and after addition of thioglycerol, we did not observe any significant changes, that is, the chemical replacement of the surface layer had no influence on the electronic states. The presence of thioglycerol groups in the film was examined by FTIR spectroscopy. Figure 1a shows the room-temperature FTIR spectrum of a thin film of close-packed CdSe nanocrystals. The bands at 2930 and 3350 cm^{-1} can be assigned to OH groups of thioglycerol (Aldrich FTIR catalog, no. M560-7). The average size of the nanocrystals was determined by fitting the line broadening of the XRD peaks, and a diameter of 1.8 ± 0.1 nm is obtained. Based on the model of an array of randomly distributed hard spheres, an estimate of the interparticle distance between neighboring nanocrystals (center-to-center distance) was made, resulting in a value of about $2(R + l) \approx 2$ nm, where R is radius of the nanocrystal core and l is the thickness of the surface monolayer of thioglycerol. The measured XRD pattern does not allow us to assign unambiguously the crystallographic structure to either the wurtzite or sphalerite type of nanocrystal because of the very large size-dependent broadening of reflexes (Figure 1b). Our X-ray data point to a slightly distorted hexagonal (wurtzite) crystalline structure of the nanocrystals. We suppose that the approximately 100 core atoms of these ultrasmall CdSe nanocrystals are arranged in a "small piece" of bulk wurtzite rather than in large supermolecules. For a clear assignment, however, XRD data on larger monocrystals are needed. Such monocrystals are difficult to prepare from our colloidal solution of thioglycerol-capped CdSe nanocrystals. During the slow evaporation of pyridine, a transparent gel was first obtained, which then tranforms into a powder of randomly packed nanocrystals. XRD data obtained for similar films of clusters have been published in refs 6–10, and different concepts have been proposed to describe the crystalline structure of close-packed films, such as supercrystals or Koch-pyramids. Thus, the crystalline structure of close-packed films is presently still an open and intensively discussed question.

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Optical Absorption. An indication of the delocalization of electronic states in an ensemble of close-packed nanocrystals is spectral broadening and a small red shift of the discrete optical transitions in the absorption spectra. Figure 2 shows the optical absorption of both close-packed and isolated CdSe nanocrystals of the same size. Whereas the sample with isolated nanocrystals shows two very pronounced peaks due to discrete absorption of the lowest confined electron–hole pair states, the absorption peaks of the close-packed CdSe-sample are broadened and show a red shift. In particular, the spectral broadening of the second peak at higher energy is much stronger, which can be qualitatively understood within the simple model of a "particle-in-a-box" with finite potential walls. The energetically higher electronic states in the box exhibit a larger extension of their wave functions into the barriers. This gives rise to a stronger overlap of the electron (hole) wave functions between neighboring nanocrystals. Therefore, the delocalization of the higher energy levels involved in the optical transitions has a much higher probability.

Both close-packed and isolated CdSe nanocrystals show pronounced blue shifts when the temperature is decreased. The temperature-dependent energy shift $\delta E/\delta T$ was calculated for a temperature interval between 70 and 300 K, both for close-packed (3.82×10^{-4} eV K^{-1}) and isolated nanocrystals (3.54×10^{-4} eV K^{-1}). Since these values are in agreement with the bulk data, that is, the phonon-mediated gap-shift is similar for nanocrystals and bulk CdSe, we conclude that the crystal lattice of the CdSe quantum dots shows bulklike lattice properties already for very small sizes of nanocrystals.

Photoluminescence. Delocalization of electronic states should cause a similar spectral broadening and red shift in photoluminescence to that observed in absorption. For such ultrasmall nanocrystals, however, photoluminescence might be caused by different processes. For example, for thiol-stabilized CdS nanocrystals, a deep trap PL is reported due to the large number of surface states associated with thiol groups.[11] PL caused by direct transitions of confined electron–hole pairs can be activated by creating a surface shell of ZnS or CdS that covers the CdSe core,[12,13] or by depositing Cd(OH)$_2$ on CdS.[14] Also, absorption of amines at the surface of CdS nanocrystals was found to increase the band-edge PL yield.[15,16]

High PL efficiency is necessary to measure, for instance, PL excitation spectra (see below). To increase the direct electron–hole radiative recombination rate, we modified the surface of CdSe nanocrystals correspondingly. Figure 3 shows the low-temperature PL spectra of the close-packed CdSe nanocrystals for different excitation energies. Two PL bands are clearly resolved in the spectra. Whereas the blue-green PL band is attributed to the direct electron–hole recombination, the red band is caused by deep traps. The relative contribution of the band-edge-related recombination is higher for excitation directly into the absorption peaks. When exciting in the tail of the absorption, the trap-related luminescence is enhanced. The spectral position of the band-edge PL peak slightly follows the excitation energy, whereas the deep-trap PL band is insensitive with respect to the excitation, since its energy is determined rather by the electron configuration of the surface states.

PL Excitation Spectroscopy. PLE is a widely used method to study excited-state energies by detecting the emission intensity I_{lum} in the ground state or in a deep-trap state. For a fixed detection energy $\hbar\omega_{det}$, the photon energy of the excitation $\hbar\omega_{exc}$ is varied, keeping the incident intensity almost constant. Provided that the relaxation process is fast, the peaks in the PLE spectrum, that is, in the curve $I_{lum}(\hbar\omega_{det}) = f(\hbar\omega_{exc})$,
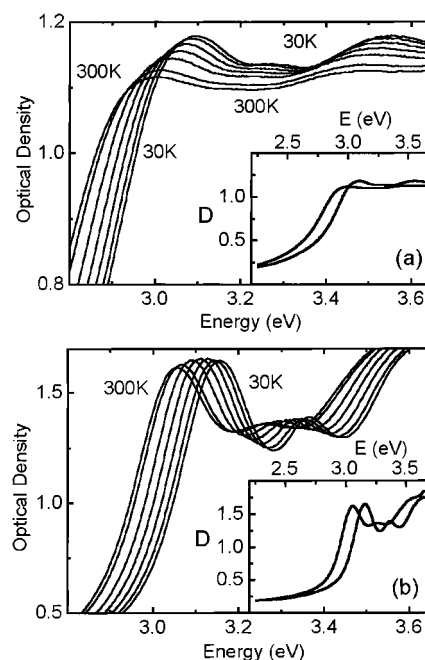
Figure 2. Absorption spectra of thin films of close-packed (a) and isolated (b) CdSe nanocrystals at different temperatures (from right to left curves): 30 K, 80 K, 130 K, 180 K, 230 K, 280 K, and 300 K. The insets show the full-range spectrum of optical density D for lowest and highest temperature.
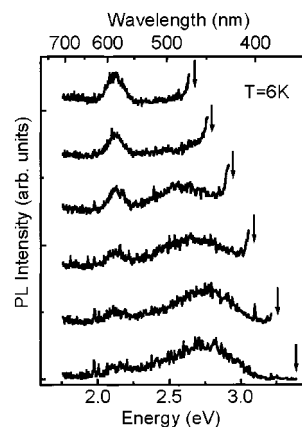
Figure 3. Low-temperature PL spectra of surface-passivated close-packed CdSe nanocrystals excited at different energies, indicated by arrows at the corresponding curves.

indicate the energies of enhanced absorption, because of being in resonance with excited states. PLE spectra have been analyzed for systems of isolated CdSe quantum dots to assign the excited states of the quantum dot as a function of size.[17,18] In these experiments, one makes use of the *size-selectivity* of the PLE when detecting at different energies within the inhomogeneously broadened PL band. The experimental approach in the work here is to study the change in this size-selectivity during the transition from individual, isolated quantum dots toward an ensemble of coupled quantum dots exhibiting a collective state. A sample with well-separated noncoupled dots slightly varying in size should show different excited-state energies for every detection energy, because the tuning of the detection energy every time selects another size of quantum dots. In contrast, a collective state is homogeneously broadened and the excited state is independent of the detuning of the detection energy within an energy range of homogeneous line width.

In the following, we compare the PLE spectra for the two samples of isolated and close-packed CdSe QDs described
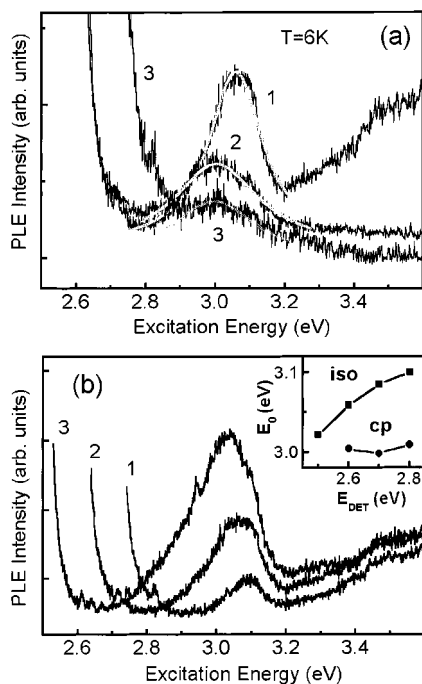
Figure 4. (a) PLE spectra at 6 K of isolated (1) and close-packed CdSe nanocrystals (2, 3) at detection energies 1 and 2−2.6 eV and 3−2.7 eV. (b) PLE spectra at 6 K of isolated nanocrystals at detection energies 1−2.7 eV, 2−2.6 eV, and 3−2.5 eV. Insert: PLE peak position vs detection energy for isolated (**iso**) and close-packed (**cp**) nanocrystals.

above. At fixed detection energy close to the absorption band edge (for our example here, 2.6 eV was chosen), the PLE signal is expected to reflect the behavior obtained in absorption (see Figure 2); that is, the small red-shift and broadening of the lowest resonance should be observed in the case of the close-packed quantum dots, whereas the resonances of the isolated QDs should be blue-shifted and of a smaller homogeneous broadening. Figure 4a shows the corresponding result: a Lorentzian fit of the PLE bands results, for the close-packed QDs, in a peak energy of $E_0 = 3.004$ eV and a line width of $\Gamma = 294$ meV (curve 2 in Figure 4a)). For the sample of isolated QDs, the values $E_0 = 3.059$ eV and $\Gamma = 190$ meV are obtained (curve 1, detection energy $E_{Det} = 2.6$ eV). Additionally, the PLE spectrum is shown for the close-packed sample for $E_{Det} = 2.7$ eV (curve 3). For both detection energies of 2.6 eV and 2.7 eV (curves 2 and 3, respectively) the Lorentzian fit clearly results in similar peak energies and line widths (for 2.7 eV, $E_0 = 2.997$ eV and $\Gamma = 290$ meV), that is, *no dependence on the detection energy* was obtained. In contrast, the PLE spectra of the sample containing isolated QDs is characterized by a shift of the PLE peak when the detection energy is varied (Figure 4b)). The inset of Figure 4b summarizes the results and shows the different behavior in the excited state properties: the size-selectivity is maintained for the inhomogeneously broadened PL of isolated QDs, as indicated by the continuous shift of the PLE peak when the detection energy is changed, whereas no shift is observed for the sample of close-packed QDs when changing E_{Det} over a range corresponding to the homogeneous broadening Γ. The increase in the homogeneous line width and the loss of size-selectivity in the PLE signals demonstrate the formation of a collective state having a wave function that is extended over many QDs. The increase in homogeneous line width represents the first step toward the formation of miniband states similar to a 2-dimensional superlattice but here in all three dimensions.[19]

Finally, it should be mentioned that films of close-packed quantum dots do not automatically develop coupled states. An important requirement is their resonance in energy, that is, the size distribution must be minimized. In case this condition cannot be fulfilled, the PLE spectra reflect this by strong peaks at the energy of the LO-phonon replica[20] caused by phonon-assisted relaxation processes. Within the close-packed ensemble of quantum dots (but with very different transition energies), the excited electron−hole pairs relax to the locally lowest-energy states by emission of LO-phonons. Most often during that relaxation, a spatial wandering of the charged carriers also occurs.

Electroabsorption. The application of strong $(10^4 − 10^6$ V cm$^{-1})$ external electrical fields to an ensemble of isolated semiconductor nanocrystals results in the quantum-confined Stark effect (QCSE). The optical transitions are broadened and shifted to the red due to gradual field-induced ionization of excitons.[21] In the case of ideal quantum dots, the potential wells created by the nanocrystal surface prevent the complete electron−hole pair dissociation. For ensembles of close-packed interacting nanocrystals, however, we expect just the opposite effect when applying an external electrical field, an analogy we know from semiconductor superlattices. Above a certain applied bias, the electric field-dependent band bending results in a breaking of the minisubband structure and localization of electronic states within the wells. In the thin layers of close-packed nanocrystals studied here, the electron states are delocalized over several nanocrystals. With increasing electric field strength, the localization of electronic states in the single nanocrystals should be restored. Hence, under external bias, the absorption spectrum of close-packed nanocrystals should develop into that of isolated nanocrystals in the absence of electric fields. As we demonstrated earlier,[4] the formation of delocalized states within an ensemble of close-packed CdSe nanocrystals results in a broadening of optical bands and in a decrease in their intensity. We may expect that the reverse process of field-induced decoupling of delocalized states will result in an increase of the intensity of optical bands.

Figure 5a shows the change in optical density of isolated CdSe nanocrystals for various values of applied external bias. The measured data for ΔD correspond to a broadening and red shift of the first absorption peak, as expected for isolated nanocrystals. A careful analysis of Figure 5a allowed us also to resolve the negative signals from the second and third optical transitions at 3.26 and 3.47 eV. The peak data coincide with the corresponding energies of the room-temperature linear absorption spectrum of Figure 2b. In the inset of Figure 5a, the peak energy E of the first confined optical transition is plotted versus the squared external bias U. The nearly linear dependence $E \sim U^2$ is characteristic for the quantum-confined Stark effect.

In contrast, the close-packed nanocrystals exhibit only a positive Stark signal and no red shift with increasing electric field (Figure 5b). Such a positive signal in ΔD without zero-crossing cannot be explained by a broadening of the absorption peak due to field-induced ionization of electron−hole pairs. As a consequence of the decrease in oscillator strength, a negative ΔD signal should be observed. For the positive Stark signal observed here, we suggest an increase of absorption because of stronger localization of the electron−hole pair states, that is, a reverse effect compared to the delocalization effect due to the spatial overlap of the wave function in the close-packed structure. Even when taking into account the more complex behavior of electric field effects (the appearance of former forbidden transitions and the Franz-Keldysh effect of the
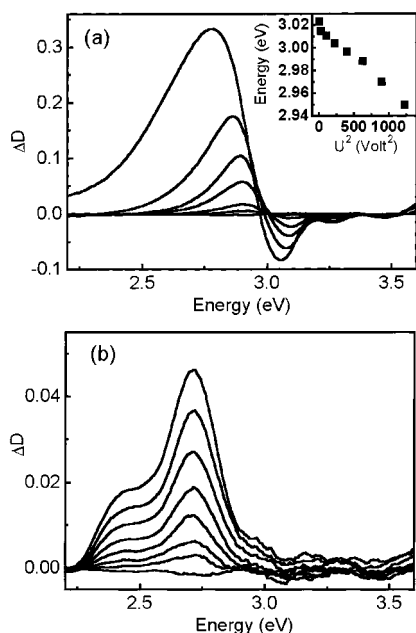
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Figure 5. Room-temperature Stark signals from thin films of isolated and close-packed CdSe nanocrystals. (a) Change in optical density of isolated nanocrystals at different biases (from top to bottom): 35, 30, 25, 20, 15, 10, and 0 V. Inset shows energy of the first optical band vs the squared bias. (b) Change in optical density of close-packed nanocrystals at different biases (from top to bottom): 10.03, 9, 8.11, 7.02, 6, 5, 4, and 0 V.

delocalized eh pairs), the observed changes fit well with our qualitative picture. The electroabsorption response from both isolated and close-packed films is fully reversible, and initial absorption spectra were restored after the bias was turned off.

Conclusions

We compared room- and low-temperature optical spectra of isolated and close-packed CdSe quantum dots to prove the existence of delocalized electronic states in a dense ensemble of ultrasmall quantum dots. The absorption spectra demonstrate a distinct broadening and a red shift of optical bands in the close-packed quantum dot ensemble versus isolated nanocrystals, a result of delocalization and formation of collective electronic states. The presence of collective states results in loss of the detection energy dependence of the photoluminescence excitation spectra due to the larger homogeneous broadening of collective optical transitions. However, for isolated quantum dots we observed the well-known effect of a size-selective shift of the PLE band due to size-dependent inhomogeneous broadening. Using the electroabsorption technique, we demonstrated that collective states in close-packed ensembles can collapse, and

primary localization of electronic states can be restored under strong electric fields. The comparably large electroabsorption response in thin films of ultrasmall CdSe quantum dots could be used for the development of large-area electrooptic elements.

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(19) Notice that the measured line width in PLE overestimates the homogeneous line width because a spectral window of 20 meV is used for the detection.

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