Charge Overlap Interaction in Quantum Dot Films: Time Dependence and Suppression by Cyanide Adsorption

Shaibal K. Sarkar and Gary Hodes*

Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

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Chemical bath deposited films of CdSe nanocrystals (<4 nm) are shown to exhibit time-dependent spectral red shifts, caused by increasing overlap of the electron wave functions in adjacent nanocrystals. Treatment of these "aggregated" films with aqueous KCN solution results in repulsion of the wave functions due to the strongly adsorbed negatively charged cyanide and thus electronic decoupling of the physically connected nanocrystals. The previously reported band gap increase due to cyanide adsorption on nominally uncoupled nanocrystals is also described here in more detail.

Introduction

The optical absorption spectra of very small (<2 nm) semiconductor quantum dots have been found to red shift upon transfer from a colloidal solution to an aggregated film. In most cases, this has been explained by overlap interaction between electrons in neighboring quantum dots which reduces the degree of electron localization in each dot.[1−4] More recently, it has been suggested that such shifts may be caused by dipole−dipole interaction between the optically generated electron−hole pair and an induced pair in a neighboring dot.[5] In these previous studies, the quantum dots were capped with molecules, which maintained a certain separation between adjacent dots. Due to this separation, the interaction between dots was less than if they were in direct contact.

In precipitates of aggregated CdSe quantum dots, which do not have any capping layer, we have found that this overlap interaction occurs for considerably larger dots (the effect is large for dots ca. 3 nm in size). Furthermore, the interaction increases as a function of time.[6] It was suggested that the particles become more tightly aggregated with time, therefore increasing the overlap interaction.

In this paper, we report a similar time-dependent red shift for *films* of CdSe quantum dots deposited by chemical bath deposition (CBD) when the CdSe crystal size is small (<4 nm). In this case the crystals in the films are already aggregated and not expected to be mobile, and so the time-dependent red shift is unexpected. This effect was observed during a study of the effect of cyanide adsorption on the CdSe quantum dot films. We have previously shown that adsorption of ionic cyanide on CdSe quantum dot films increases the band gap of the CdSe.[7] This effect increases with decrease in dot size and is reversible if the cyanide is rinsed off. The band gap increase was explained by compression of the electron wave function in the dot by the negative cyanide which chemisorbs strongly on both Cd and Se sites on the CdSe surface. Adsorption of various species on semiconductor nanocrystals has long been known to affect the emission properties of the nanocrystals, usually through passivation or activation of intragap surface states that control emission. However, optical absorption is much less strongly dependent on these surface states, and normally, no appreciable effects are seen in the absorption spectra due to surface adsorption. A blue shift in the absorption spectrum of very small (1.6 nm diameter) CdSe quantum dots was observed by adsorption of amines and attributed to size and/or structural changes in the quantum dots due to exothermic adsorption.[8] This effect was not found on 3.2 nm dots and, from the explanation, is presumed to be irreversible.

We first describe, in more detail than previously, this cyanide treatment of CdSe quantum dot films. We then describe how this study led us to observe the time-dependent red shift in small crystal size, as-deposited, CBD CdSe films. Finally, we show how adsorption of cyanide on these red-shifted films of CdSe quantum dots not only increases the band gap as described previously, but additionally suppresses the electron interaction between neighboring dots which is believed to be the cause of this red shift.

Experimental Section

Film Deposition. Films were deposited by CBD onto microscope slide glass (for Kelvin probe measurements, on SnO_2-coated glass) from an aqueous solution containing $CdSO_4$ (80 mM), potassium nitrilotriacetate (120−180 mM), and sodium selenosulfate (for CdSe, 80 mM) or thiourea (for CdS, 80 mM) at a pH between 10.0 and 10.5. The films were typically 70−90 nm thick. The crystal size was varied depending on the deposition temperature (lower temperature gives a smaller crystal size; for example, at 0 °C, the crystal size in the film was 3.3 nm, while at 5 °C it was 3.7 nm) and the nitriloacetate: Cd ratio (which controls the deposition mechanism), described in detail in ref 9. The films were comprised of aggregated, sphalerite CdSe crystals of approximately spherical shape and typical standard size deviation of 15−20%.[9,10] The term "crystal size" in this paper refers to the diameter of the crystals.

As described under Results and Discussion, films made up of small crystals (<4 nm) underwent changes in their optical spectra within ca. 1 h after removal from the deposition bath. Films measured immediately after deposition are termed "as-deposited", while those measured after the spectra had stabilized are termed "stabilized".

Cyanide Treatment. For the cyanide treatment, the films were immersed in 0.8 M aqueous KCN solution for 3 min except where otherwise stated.

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* Corresponding author. E-mail: gary.hodes@weizmann.ac.il.

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Physical Measurements. *Optical Spectroscopy.* The optical transmittance spectra of the films were recorded using a double-beam JASCO V-500 UV/vis spectrophotometer, fitted with an integrating sphere (the integrating sphere is part of the standard setup of our instrument; the films were visually very transparent). The transmission measurements were made using the same type of substrate used in the sample (microscope glass or SnO_2 glass) as reference. No correction for reflectance was made. For investigation of the time-dependent spectral changes for small-crystal (<4 nm) films, initial measurements of the as-deposited films were made on samples that were not dried after rinsing (wet films did not undergo these spectral changes—see below). This prevented irreproducibility that might arise from changes in the film during measurement. Films measured after these changes were dried; however, immersion of these dried and spectrally shifted samples in water resulted in no further change in the spectra (other than possible minor changes in reflectivity due to adsorbed water[11]) and certainly not to the measured band gap.

Band gaps were estimated from these spectra by measuring the absorption coefficients, α, derived from the spectra and using the Tauc plot method to derive band gap for a direct band gap semiconductor by plotting $(\alpha h\nu)^2$ vs $h\nu$, where $h\nu$ is the illumination energy in electronvolts, and extrapolating to $(\alpha h\nu)^2 = 0$. While this derivation is not necessarily valid for low-dimensional semiconductors, in the case of the present samples we have found it to give values that are consistent with other band gap vs crystal size measurements as well as with visual estimation of the band gap based on the spectra.

X-ray Powder Diffraction. Powder X-ray diffraction (XRD) spectra of the films were recorded on a Rigaku RU-200B Rotaflex diffractometer operating in the Bragg configuration using Cu Kα radiation. The accelerating voltage was set at 50 kV with a current of 150 mA. Scatter and diffraction slits of 1° and a 5 mm collection slit were used. Coherence length (assumed equal to crystal size) was estimated using the Scherrer equation based on XRD peak broadening.

Kelvin Probe/Surface Photovoltage Spectroscopy. The Kelvin probe/surface photovoltage spectroscopy (SPS) measurements were made using a commercially available Kelvin probe (Besocke, Delta-Phi) with a sensitivity of ~1 mV. All measurements were performed in ambient atmosphere. The sample was illuminated by a 600 W Xe lamp passing through a 0.5 m grating monochromator (Jobin-Yvon 270M).

Results and Discussion

Cyanide Adsorption on As-Deposited Films. As we showed previously,[7] treatment of CBD CdSe (and CdS) films by cyanide resulted in a blue shift of the optical transmission spectra. The magnitude of this shift as a function of measured band gap of as-deposited CdSe films is shown in Figure 1. (The data in the rectangular box near the top of the figure are from a different set of experiments and will be discussed later: they should be ignored for now). An example of the shift of the spectrum for one film (crystal size ca. 3.5 nm) is shown in the inset. The effect is reversed if the sample is rinsed with water, thereby removing the adsorbed cyanide, as seen in the inset. It is also slowly reversed on exposure to air as shown in Figure 2. CN^- can be oxidized to cyanate (CNO^-), which, unlike CN^-, has no measurable effect on the spectra of as-deposited films. In accordance with this mechanism, exposure to argon instead of air does not cause reversal of the cyanide-induced blue shift.[12] CdS films show a similar effect although less pronounced as expected from the smaller Bohr diameter of CdS, therefore with less quantization for any specific crystal size.
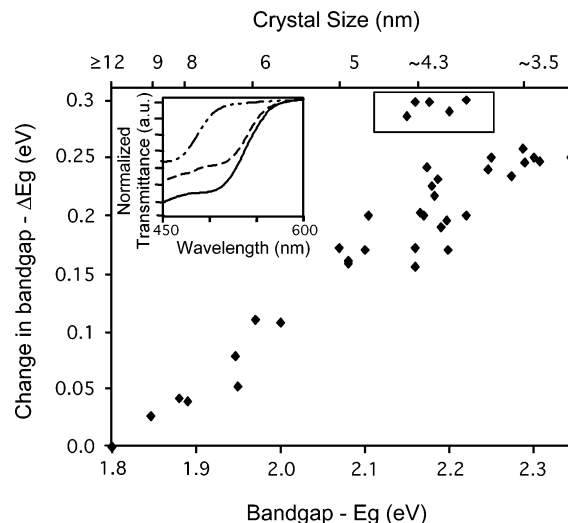

Figure 1. Increase in band gap of as-deposited CdSe films due to cyanide treatment as a function of measured band gap of the (untreated) films. The approximate crystal size, measured by XRD line broadening, is given on the upper scale. The inset shows an example of the spectrum of an as-deposited film with crystal size ca. 3.5 nm (solid line), after cyanide treatment (dashed−dotted line), and after subsequent rinsing with water (dashed line). The data in the rectangular box near the top right side of the figure are from measurements on stabilized films.
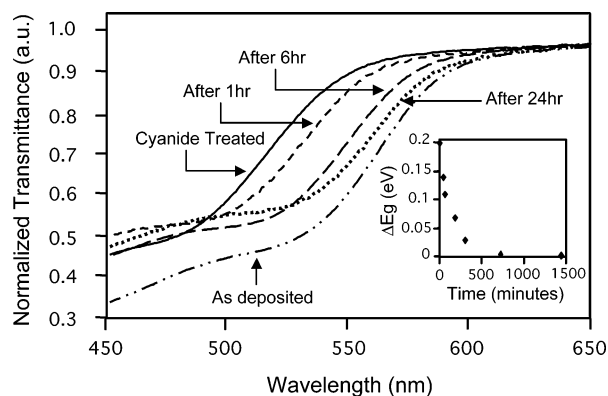

Figure 2. Transmission spectra of a CdSe film (4 nm crystal size) as-deposited (dashed−dotted line), after cyanide treatment (solid line), and with subsequent exposure to ambient conditions for times shown. The inset shows the bandgap increase compared to the as-deposited film as a function of time of exposure to ambient.

The blue shift increases with increasing cyanide concentration and then gradually tails off for higher concentrations, as shown in Figure 3. On the basis of this behavior, we chose 0.8 M as the standard concentration because the additional increase in band gap was very modest at higher concentrations and stronger solutions were more liable to remove the films, particularly for small crystal sizes.

We explained this blue shift as arising from electrostatic compression of the electron wave function in the individual nanocrystals by the strongly chemisorbed negative CN^- [7] as represented schematically in Figure 4. (The major part of the size quantization in CdSe and CdS is due to localization of the electrons rather than holes, due to the smaller effective mass of the electron compared to that of the hole.) Cyanide is strongly bonded both to Cd and to Se (S) (Cd forms strong cyanide complexes and elemental Se (S) reacts to form selenocyanate (thiocyanate)). We believe this strong bonding to both constituents of the nanocrystals to be important, since the resulting close packing of the cyanide on the crystal surface will sterically hinder adsorption of K^+ adsorption on the surface. Such
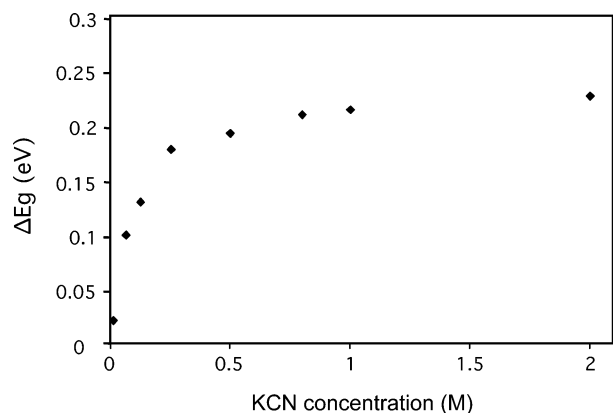
Figure 3. Spectral blue shift of ca. 4 nm crystal size CdSe film as a function of KCN concentration (for 3 min treatment time).
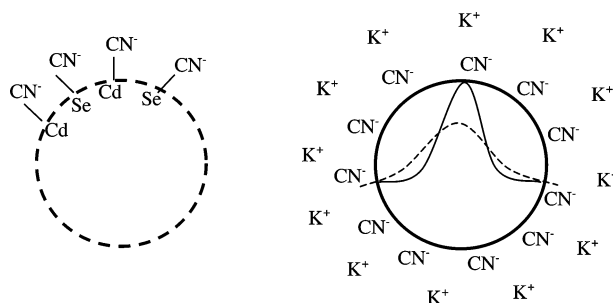

Figure 4. Schematic diagrams showing (left side) bonding of CN^- to surface Cd and Se atoms and (right side) separation of ionic charges and effect of cyanide adsorption on electronic wave function of a photogenerated electron in a particle. Broken trace, before cyanide adsorption; solid trace, after cyanide adsorption.

adsorption would screen the negative charge of the CN^-, thus preventing the electrostatic localization of the electron. It should also be noted that the cyanide-induced blue shift only occurs for nanocrystals that are small enough to exhibit size quantization (smaller than the Bohr diameter of 11 nm for CdSe), as seen in Figure 1. This observation provides a direct connection between the cyanide-induced blue shift and size quantization. The increase in blue shift with decreasing crystal size can be related to the supralinear (between linear and parabolic) increase in band gap as a function of decreasing size.

According to our model shown in Figure 4, the work function of the cyanide-treated films should decrease compared to the corresponding nontreated films. This expectation reflects the outer positive K^+ shell which should make it easier for electrons to leave the crystal. Figure 5 confirms this expectation; the work function measured by the Kelvin probe decreases after cyanide treatment (more negative CPD is equivalent to a decrease in work function). As an interesting side issue, surface photovoltage spectroscopy (using the Kelvin probe with monochromatic light excitation of the film to measure potential changes on illumination) showed a strong passivation by adsorbed cyanide of the subband-gap response from the nontreated films (Figure 5). This passivation may be caused by the strong surface bonding of the cyanide which would saturate dangling bonds and/or removal of Cd−O and Se−O species from the crystal surface (removal of Se−O is clearly seen in XPS measurements). We note that passivation of defect states in Si by cyanide resulting in improved photovoltaic cells has been previously reported.[13] As for the transmission spectra, the surface photovoltage spectrum also can be reversed to the nonpassivated state by removal of the cyanide by rinsing with water, as seen in Figure 5.
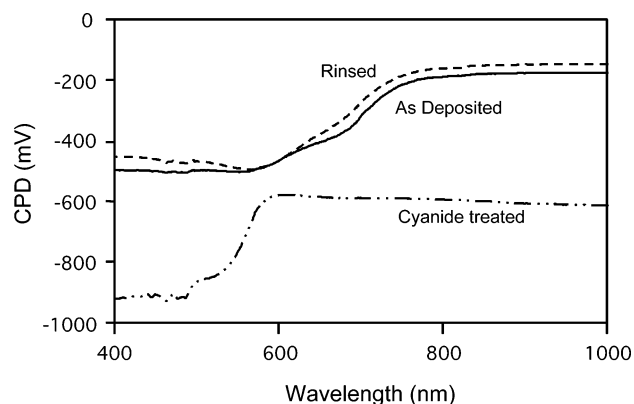

Figure 5. Contact potential difference (CPD), as a function of illumination wavelength, of a cyanide-treated CdSe film (4 nm crystal size). Solid line − as-deposited: dash-dot line − after cyanide treatment (0.1 M KCN for 3 min; lower concentrations of KCN are required to passivate the films than to shift the bandgap: dotted line − after rinsing with water).
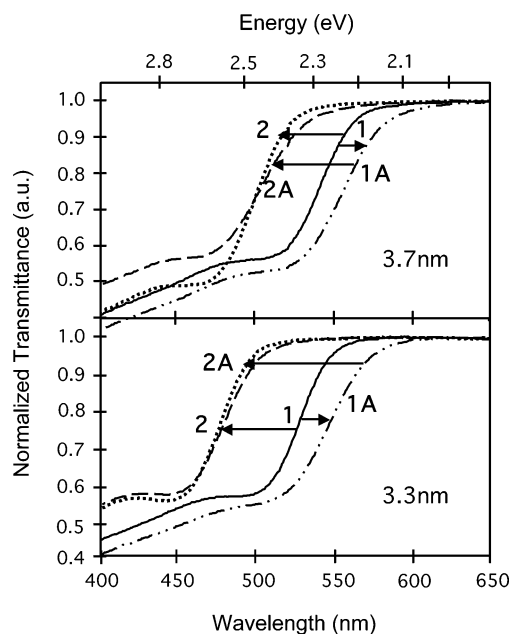

Figure 6. Changes in (normalized) transmission spectra of CdSe films, deposited by chemical solution deposition, and with XRD-measured crystal sizes of 3.7 nm (5 °C deposition), top figure, and 3.3 nm (0 °C deposition), bottom figure. The as-deposited film is designated by "1", and the same film after cyanide treatment (3 min in 0.8 M aqueous KCN) is designated by "2". Separate as-deposited films (closely similar in the band gap region to the previous ones, therefore not shown separately to simplify the figures), after spectral stabilization (1A) followed by cyanide treatment (2A).

Time-Dependent Spectral Changes in the Films. Films deposited at a temperature of ≥10 °C (crystal size ≥ 4 nm) showed very little time-dependent red shifts in the spectrum after deposition (shifts of 2−3 nm, corresponding to a maximum of 10 meV in this spectral region, were measured for films deposited at +10 °C). However, for lower temperature depositions (smaller crystal size), the transmission spectra of the films red shifted with time and to a degree which increased with decreasing deposition temperature. Figure 6 shows these spectral changes for two films deposited at 5 °C (3.7 nm size) and 0 °C (3.3 nm). The red shift is shown by the spectra 1 (as-deposited) to 1A (stabilized − after steady-state spectrum reached) for the two films. The red shift for the 3.3 nm crystal size film is 85 meV, and that for the larger 3.7 nm crystals is 60 meV. We
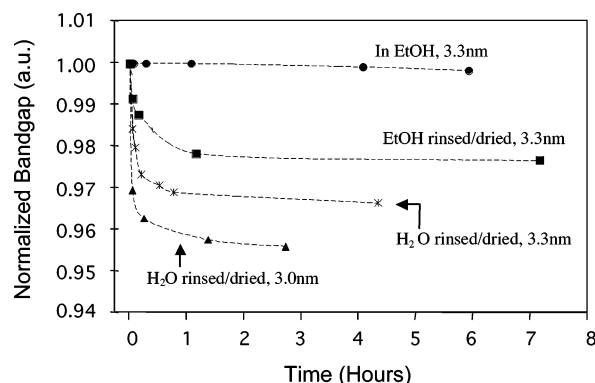
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Figure 7. Time-dependent band gaps (normalized to the same arbitrary value and shown as a fraction of the initial band gap) of CdSe films. Closed triangles: deposited at −10 °C (ca. 3 nm), water rinsed, and dried. Crosses: as before but deposited at 0 °C (3.3 nm). Closed squares: as crosses and rinsed with ethanol, then dried. Closed circles: as squares but kept and measured in ethanol instead of in air. 5−10% ethylene glycol was added to the solution for the ≤0 °C depositions as antifreeze. Control experiments with ethylene glycol added to 5 °C films deposition showed no effect of the ethylene glycol on the spectra of the films.

also note that the stabilized spectra are somewhat less steep than the as-deposited ones.

We assume at this point that the red shift is due to some change in the films that increases the charge overlap. The crystal size in these films is considerably larger than sizes from previous studies[1−4] which suggested charge overlap as the cause for the red shift when a colloid was aggregated into a film. However, in contrast to those studies, there is no capping agent on the present samples, and therefore the intercrystal distance will be less. We also stress the difference between those previous studies, where the spectral changes occurred when colloids were converted from a dispersed phase into a film, and the present case, where no dispersed phase is considered and the changes occur in the film itself as a function of time.

The change in shape of the spectra after stabilization is also expected based on overlap interaction. In an ideal case, splitting of levels due to the interaction would broaden the transition.[5] In the present samples, this broadening is seen as a reduction in the steepness of the absorption onset.

Samples in this study were normally rinsed with water and dried in a stream of nitrogen. Under these conditions, most of the red shift occurred within 30 min and the final band gap value was reached in a few hours. Figure 7 shows some examples of the fractional change in band gaps, normalized to a common value of unity for ease of comparison, as a function of time for different films and for different rinsing regimes. Looking first at the normal water rinsed and dried samples, films with smaller crystal size exhibited a greater fractional shift than those with larger crystals (compare 3.0 and 3.3 nm H_2O/dried).

Films rinsed with ethanol instead of with water red shifted less (within the time scale of the measurements) than those rinsed with water (filled squares in Figure 7). A major reduction in the red shift was obtained when the films were stored immersed in ethanol instead of in air (filled circles in Figure 7). We have previously found that CdSe precipitates (<4 nm crystal size), when prepared under certain conditions, also undergo a red shift and this red shift is slowed if the precipitate is kept in pure water or even suppressed completely by various organic solvents, including ethanol.[6] This shift was believed due to increasing strength of aggregation of the crystals in the precipitate with time (and therefore increased charge overlap, resulting in reduced quantization), in particular since

shaking a stabilized precipitate resulted in a temporary blue shift that could be explained by decreasing strength of aggregation by shaking. However, there are important differences between the two studies: in ref 6, the "free-floating" precipitates were always immersed in a liquid, while in the present study they are "immobilized" on a substrate and sometimes dry. It was previously mentioned (in the Experimental Section) that stabilized films were measured dry, but that even if the dried films were subsequently moistened with water and measured wet no further change in the absorption onset occurred. The red shift in the as-deposited films is therefore apparently connected with drying of the films, and this suggests that capillary forces which act to pull the crystals together as the water (or other solvent) evaporates, forming a meniscus connecting crystals,[14] may be the cause of the red shift. This is also supported by the reduction in red shift if the films are rinsed in ethanol, since the surface tension of ethanol, and thus the capillary forces involved as it evaporates, will be less. Since the neighboring crystals in the as-deposited film are already in some degree of contact (otherwise the film would fall apart), the very small difference in separation caused by the capillary forces could be enough to influence the charge overlap between crystals (this overlap is exponentially dependent on distance).

Since the capillary forces can also be reduced by very slow drying, we rinsed an as-deposited film in ethanol and then placed it in a vessel containing some ethanol (i.e., in an atmosphere of ethanol vapor) which slowly evaporated over a time span of hours. After 17 h, the (then dry) sample was remeasured and very little difference (a few nanometers red shift at most) was found compared with the original, as-deposited film. The film was then rinsed with water, dried, and remeasured. The normal red shift that would have been expected if the original as-deposited sample had been dried quickly now occurred. This observation supports our assignment of the capillary forces upon drying being responsible for the red shift.

While the above results and arguments constitute reasonable evidence for the cause of the red shift being closer contact between crystals due to capillary forces, we will also consider other possibilities in decreasing order of what we believe to be likely as alternate explanations.

There was no difference in crystal size (measured by XRD peak broadening) before and after these spectral changes. Therefore, the change is probably not due to room temperature annealing of the crystals into larger ones. We say "probably" since XRD would not reveal a slight coalescence of the crystals that might lead to a small loss of quantization. (The as-deposited and stabilized films could not be compared using TEM since the as-deposited films would have stabilized by the time they had been prepared for TEM measurements.) Such slight coalescence can be considered an extension of the capillary explanation with the difference that instead of simply pulling the crystals fractionally closer, the strength of the capillary forces may actually cause a morphological deformation leading to some coalescence at the interface between two crystals.

It is possible that there is a change in the surface of the individual nanocrystals (in this respect, we note that substituting argon for air when the film dries has no effect on the red shift; therefore oxidation is not likely to be the chemical reaction were this hypothesis to be correct). Chemical changes could lead to differences in potential barriers at the interfaces between crystals which might then be responsible for changes in quantization.

The dipole−dipole interaction that has been suggested in ref 5 as a cause for the red shifts of close-packed colloidal particles is unlikely to be a major factor causing the red shift in the

present system. There are several reasons for this. One is that the films are already aggregated in the as-deposited state; any change in distance between neighboring crystals from the as-deposited state to the stabilized state would be very small indeed. A very small difference in quantum dot separation would still have a noticeable effect on overlap interaction which depends exponentially on this distance, as mentioned previously. However, the main parameter in defining the average dipole−dipole distance is the size of the particles themselves. Since the particle sizes in this study are considerably larger than those used in ref 5, the resulting dipole interactions will be much smaller (scaled as a function of r^{-6}, where r is the particle radius). A second reason is based on the rationale of the authors of ref 5, where they expect spectral changes due to overlap interaction to be accompanied by broadening in the absorption peak (in our case, where there is no peak, the broadening will be of the absorption onset), which we do observe, while dipole−dipole interaction should cause no change in shape of the absorption. A weaker argument, based on the (small) possibility that the red shift is connected with chemical changes at the crystal surfaces, is that such changes should not have a strong effect on the dipole−dipole interaction but may be critical for overlap interaction.

Cyanide Adsorption on Stabilized Films. Returning to Figure 1, we now consider the points in the rectangular box (top of figure under the 4.3 nm crystal size marker; the particle size scale above these points is *not* valid for these points, because they are actually smaller). These points show the change in band gap after cyanide treatment for stabilized films (in contrast to as-deposited films for the rest of the data in that figure). It is of interest to note that these points were not deliberately taken on stabilized films: We were not aware of the time-dependent spectral changes at that time. In fact, it was in trying to understand why this group of data behaved differently that we noticed the time-dependent red shift. In retrospect, we observed this shift for very small crystal size films a long time ago: films deposited at −10 °C, for example, are almost yellow (band gap ca. 2.4 eV) but turn orange within a short time when removed from the cooling bath. At the time, we thought this was due to room-temperature annealing (i.e., coalescence) of the very small crystals, but never checked this supposition.

As seen from Figure 1 and also Figure 6, cyanide treatment of the stabilized films results in a larger blue shift of the spectra compared to as-deposited films. This can be seen in Figure 6 by the change in spectra from as-deposited films (1) to cyanide-treated films (2), and from fully aggregated films (1A) to cyanide-treated, fully aggregated films (2A). Of particular importance is the fact that the spectra of the cyanide-treated, as-deposited, and stabilized films are essentially identical, even though the spectra of the respective nontreated films are different.

These results can be explained by a decrease in electron overlap in neighboring crystals due to cyanide adsorption. In essence, the electrons are relocalized on the individual crystals; i.e., the neighboring crystals are electronically decoupled.

It is important to stress the difference between this decoupling and the effect of cyanide on as-deposited films. Figure 8 shows a schematic representation of the effect of cyanide on as-deposited and stabilized films. In both cases, the negatively charged cyanide adsorption results in compression of the electron wave function and increased localization (higher band gap). This effect is in principle not dependent on the state of aggregation of the nanocrystals and should operate also for
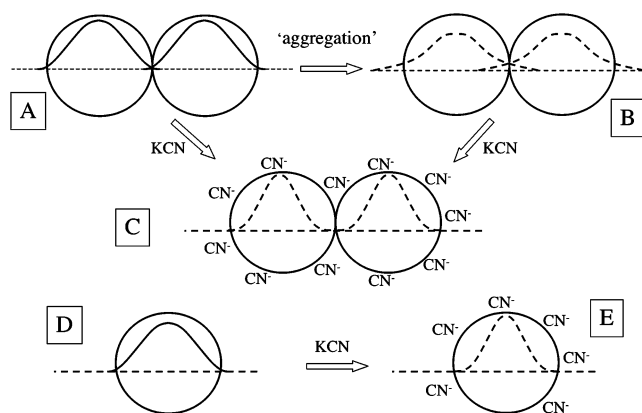

Figure 8. Cartoon showing the effect of aggregation and cyanide adsorption on the electron wave function in CdSe quantum dots. (A) Two neighboring, as-deposited dots, which couple more strongly with time, resulting in increased interaction of the individual wave functions (B) and some loss in quantization. Treatment of the paired dots, either as-deposited (A) or stabilized (B) by cyanide results in compression of the wave function to the same extent (C). The effect of cyanide on an isolated dot (D to E) is the same as that of a freshly prepared (assume nonelectronically interacting) coupled system.

isolated crystals (Figure 8D,E). For as-deposited films, the effect was also seen on relatively large quantum dots (>6 nm). In the present case, however, while this same effect occurs, *additional* localization occurs due to the decoupling of the aggregated dots, and only for small dots (≤4 nm) where appreciable overlap occurs in the first place. Thus, in films of 6 nm dots, where localization due to cyanide is still clear,[5] there is no appreciable overlap between neighboring dots and therefore clearly no overlap suppression. The final localization due to adsorbed cyanide will be the same for an isolated dot (Figure 8D to 8E), for the same dot size in the as-deposited film (Figure 8A to 8C), and for the dots in the stabilized film, where the pre-cyanide band gap is less than that of the as-deposited film (Figure 8B to 8C).

There is another possible explanation for the larger effect of cyanide on stabilized films: it is that adsorption of cyanide causes repulsion between neighboring crystals. The cyanide treatment does result in reduced adhesion of the films, particularly in the smaller crystals where the adhesion is less to begin with. To test this possibility, a film that was allowed to aggregate and then treated with cyanide (for a shorter time than used in Figure 6) was then rinsed with water to remove the cyanide (Figure 9, top). If the cyanide resulted in repulsion between crystals, then removal of the cyanide would be expected to regenerate the spectrum of the as-deposited film, which would then gradually red shift due to aggregation. However, as seen in Figure 9, rinsing regenerates the spectrum of the aggregated film, which then does not change further. On the other hand, if an as-deposited film is treated with cyanide and then rinsed, the spectrum returns to the original as-deposited one and then gradually red shifts due to aggregation (Figure 9, bottom). These experiments show that the effect on cyanide on aggregated films is not to physically separate the crystals and therefore reduce electron overlap for this reason.

Finally, we note that red spectral shifts have been reported for CdSe colloids due to solvent-induced changes in polarization energy of the confined exciton.[15] Shifts of a few millielectron-volts were found from solvent to solvent. Larger values were anticipated for uncapped particles (such as used in the present study), but still much smaller than those measured here. More
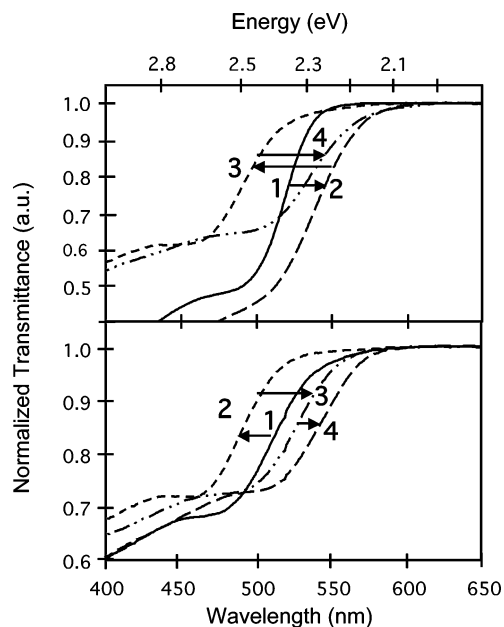
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Figure 9. Normalized transmission spectra of CdSe films (deposited at 0 °C, ca. 3.3 nm). Top figure: as-deposited film (1) allowed to aggregate (2), then treated with cyanide (1 min in 0.4 M aqueous KCN) (3) followed by rinsing off the cyanide with water (4). No further change in spectrum 4 occurred with time. Bottom figure: as-deposited film (1) treated with cyanide (2), which was then rinsed off by water (3) and allowed to stand until the spectrum stabilized (4). (A shorter cyanide treatment time than that required to obtain the maximum blue shift in these experiments was used since the adherence of the films and their stability to cyanide decreases as the crystal size decreases.)

importantly, however, the present results show red shifts in the absence of any change of solvent.

Conclusions

CBD CdSe films where the crystal size is less than the Bohr diameter of CdSe (11 nm) exhibit size quantization and increase in band gap. Treatment of these films with aqueous KCN solution results in a further increase in band gap which can be reversed either by rinsing with water or by slow air oxidation. This increase in band gap is larger as crystal size decreases and does not occur for a crystal size larger than the Bohr diameter. The band gap increase is explained by electrostatic compression of the localized electron by the negatively charged, strongly adsorbed cyanide.

For CdSe films with crystal size below 4 nm, a time-dependent decrease in band gap occurs after removal from the deposition solution together with a noticeable broadening of the transmission spectrum. This is explained by drying of the films and the resulting capillary forces causing better contact between crystals in the aggregated film and thus increased charge overlap between neighboring crystals.

Treatment of these red-shifted films with cyanide results not only in an increase in band gap as for as-deposited films, but also in an additional increase due to suppression of electron overlap between neighboring dots. This results in electronic decoupling of the dots from each other, even though they are in physical contact.

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(11) Since measurements were carried out in ambient atmosphere, which contains water vapor, even "dried" films will contain some adsorbed water.

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