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Optical Properties of CdSe Superlattices

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Abstract: Three-dimensional, faceted assemblies of CdSe nanocrystals were grown to microscopic sizes sufficient for identification and direct characterization. Analyses made by optical, fluorescence, and transmission electron microscopy showed that individual, faceted superlattices are composed of nearly single-size nanocrystals assembled into fcc lattices. Photoluminescence was measured in individual superlattices, and the results were compared to the same measurements made in amorphous solid layers and solutions of nanocrystals. Differences in the shape and peak positions of photoluminescence spectra are explained by energy transfer processes determined by nanocrystal size distribution, structure of solid layers, and presence of aggregates in solutions.

Introduction

Size-selective optical properties of semiconductor nanocrystals (NCs) have been intensively studied both in solutions and in solid structures. Much progress has been made recently in understanding the optical properties of isolated NCs dispersed in solutions and changes due to interactive phenomena in solid structures.[1–4] Since pioneering work a decade ago[1] showed that, in solid state, colloidal CdSe NCs could form not only random "amorphous" arrays but also perfectly organized assemblies, special attention has been paid to colloidal superlattices (SLs), which now are routinely observed at nanoscale for different kinds of NCs.[5–8] The possibility of controlled assembly of crystallographically organized solids from NCs opens new opportunities for both fundamental studies and engineering of advanced materials, making structural and physical characterization of SLs an important part of research in this direction. As shown previously,[1,2] in solution, NCs act as large molecules that form ordered assemblies, or even faceted, colloidal[9–12] crystals, by the classical Frank–Cabrera mechanism.[13] With

sufficiently narrow size and shape distribution of the NCs, such structures can be extended to several tens of microns,[2,4] which makes them available for studies of their physical and optical properties. Substantial investigations into long-range and internal structural ordering using transmission electron microscopy (TEM), wide-angle X-ray scattering (WAXS), and small-angle X-ray scattering (SAXS) were reviewed.[2] Absorption and emission spectra of CdSe NCs were shown comparing dilute solutions with ordered arrays (SLs) that indicated interdot coupling in the arrays.[1] More recently, energy transfer studies have been conducted on NC glassy solids[14,15] and Langmuir–Blodgett monolayers and bilayers.[16] Also, photoconductivity was studied in close-packed NCs layers,[17] and while the investigated structural forms in many cases included areas of two- and three-dimensional ordered assemblies, more selective studies and comparative characterization of crystallographically organized and amorphous NC solids are still not easy to conduct. This fact is due primarily to the difficulty of applying most characterization techniques to microscopic structures without their isolation or, at least, visual identification.

The goal of this work was to obtain three-dimensional SLs of CdSe of a shape and size that would enable direct optical characterization. Our studies were concentrated on SLs with faceted shapes, which could be easily identified and distinguished in surrounding amorphous solids of NCs. Here, we report the preparation of faceted SLs from CdSe nanocrystal solutions in nonanoic acid and present the first results of photoluminescence (PL) measurements made directly in single, faceted SL crystals. Results are compared with the same

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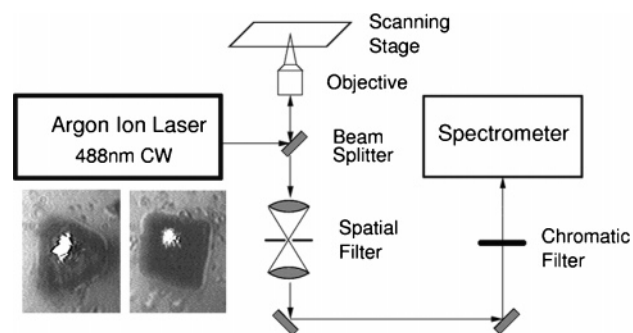
Figure 1. Schematic of the experimental setup used for photoluminescence measurements. Micrographs show faceted superlattices with 10 μm aperture bright spots from the focused laser beam.

measurements made in amorphous solid layers and solution dispersions.

Experimental Section

CdSe NCs were synthesized using standard air-free techniques.[18-20] Precursor prepared from 0.37 g of dimethylcadmium Cd(CH$_3$)$_2$ (STREM Chemicals) and 0.148 g of Se powder (Aldrich) codissolved in 9.481 g of tri-*n*-butylphosphine TBP (STREM) was stored in a refrigerator prior to the experiment. The mixture of trioctylphosphine oxide (TOPO, 99% purity, Aldrich) and tetradecylphosphonic acid (TDPA, 99%, Alfa Aesar) in the mole ratio of 98:2 was evacuated at 110 °C and heated under Ar to 360 °C. Three milliliters of the precursor mixture was quickly injected into the TOPO−TDPA solution, and the reaction was allowed to continue until the desired size of NCs, monitored by measurements of UV−visible absorption, was reached. The amount of TOPO−TDPA mixture was 6−8 g, and the time of the reaction varied from 5 to 50 min depending on the size of the final crystals. Reactions were terminated by removing heat. Methanol was added at approximately 50 °C to precipitate NCs, which were further separated by centrifuging, then washed several times by methanol, dried under Ar flow, and stored in the Ar glovebox, where all solutions were made. Test samples of toluene solutions with moderate concentration of NCs (0.15−0.20 mg/mL) were prepared from all synthesized batches. Batches that exhibited narrow size distribution in their absorption and PL spectra were selected for further experiments. NC size was also estimated from TEM images, by measuring 300−400 NCs in each sample. Only samples with size distribution less than ±10% were used (NCs are identified below by their initial average size without showing the deviation). In addition, samples of NCs that showed a tendency to form organized assemblies as observed in TEM were selected for further crystal growth experiments. To prepare saturated solutions for growth of SLs, dry powder of NCs was added to nonanoic acid (NA) in excess such that the solid did not dissolve completely after intensive stirring. Saturated solutions were separated from the solid by centrifuging and deposited as liquid drops on optical microscope glass slides and on gold TEM grids. The liquid was allowed to evaporate slowly. Sometimes evaporation of the NA was accelerated by short-term exposure of the slides to vacuum. After complete evaporation of the solvent, which could continue from a few days to few weeks, the slides were examined in optical and fluorescence Olympus microscopes with maximum magnification of 2500. The absorption of solutions and thin solid layers was measured using a Shimadzu UV−visible spectrophotometer. PL spectra were obtained using the confocal laser setup shown in Figure 1.

A collimated Ar+ 488 nm excitation beam was filtered using a narrowband excitation filter and focused through an air objective to a

spot diameter on the order of 10 μm. The emitted fluorescence was collected using the same microscope objective. After passing through a spatial filter, the light was chromatically filtered using a 498 nm long-pass filter, then sent into a spectrometer equipped with a CCD multichannel detector. The spectrometer grating had a groove spacing of 300 lines/mm. The acquisition time per spectrum was 0.5 s. In some cases, a Fluoromax-2 spectrometer was used for PL measurements in solutions. TEM analyses of the grids were made at UC Berkeley and at Lawrence Livermore National Lab using a TEM Tecnai-12 and a high-resolution TEM (HRTEM) Philips CM300FEG with accelerating voltage of 100 and 300 kV, respectively. All measurements and observations were made at room temperature.

Results and Discussion

Growth of faceted crystals is the formation of a crystallographic lattice by the attachment of building units of uniform size and shape. The absence of sharp fluctuations in the rate of this attachment, or crystal growth rate, is one of the most essential conditions for formation of large homogeneous crystals.[21] The major factor influencing growth rate is supersaturation, which, in the case of solution growth, can be expressed as

$$\sigma = (C - C_0)/C_0 \qquad (1)$$

where C is the real concentration, and C_0 is the equilibrium concentration (solubility) of the solute in the solution at the temperature of growth.[22] Unfortunately, in the case of NCs, it is difficult to operate by the quantitative values of solubility because it depends on the size of NCs and the composition of colloidal surface layers. Precise measurements are still to be made. However, some qualitative estimates can be drawn from general considerations. From eq 1, the gradual increase of σ, required for growth of homogeneous faceted crystals, can be achieved by either increasing concentration of the solute or decreasing its solubility. Increasing concentration at constant solubility results typically from evaporation of solvents, while decreasing solubility can be achieved by the use of temperature reduction methods or double-solvent techniques reported so far for growth of CdSe SLs.[1,12] A classical pair in such techniques is the combination of toluene and methanol. Addition of methanol to toluene solutions, in which NCs are highly soluble, sharply decreases solubility and, therefore, is successfully used for precipitation of NC powders. However, in the process of SL formation, the fact that CdSe NCs are completely insoluble in methanol may be considered as an additional reason for instability at the solid−liquid interface. In addition, in open systems, faster evaporation of methanol will lead not to increase but decrease and fluctuations of σ preventing formation of the fully faceted SLs.[23] More careful choice of solvent pairs can provide homogeneous conditions for size-selective precipitation and slow formation of uniform clusters, as done in a less volatile octane−octanol system.[1] CdSe NCs have relatively high solubility in octane, being still soluble in octanol, although at much lower level. The preferential evaporation of lower boiling octane over the alcohol leads to the gradual increase of σ by both increasing the concentration of NCs and decreasing solubility, resulting in successful formation of faceted SLs.[1]

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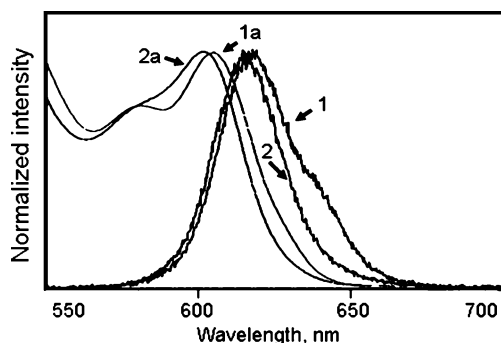
Figure 2. Absorption and photoluminescence spectra of a 5.1 nm CdSe NC sample dissolved in toluene (1 and 1a) and nonanoic acid (2 and 2a).

An alternative to multisolvent techniques is simple growth from a single solvent used in this work. Since the concentrations of solutes in supersaturated solutions can be significantly higher than those of the diluted solutions typically used in experiments with NC dispersions, easily evaporated solvents in which NCs have high solubility are not the best choice to obtain faceted assemblies by solvent evaporation. Fast evaporation of the solvent from highly concentrated solutions is more likely to result in uncontrollable precipitation of aggregates containing different size NCs and the formation of continuous, mixed, solid layers rather than separate crystals with selective sizes. The choice of NA was made for the reason of its extremely low volatility and relatively small solubility of CdSe NCs. In addition to meeting these conditions, the use of NA provided a noticeable size-selective effect. Figure 2 compares the absorption and PL spectra of diluted solutions of the same NC sample in toluene, which is traditionally used as a solvent for CdSe NCs and NA. The wide asymmetric shape of the spectrum (1) indicates that the initial NCs dissolved in toluene had a relatively wide size distribution. In the NA, due to lower solubility, only a portion of the smaller NCs dissolves, producing a blue-shifted, more symmetric spectrum (2) corresponding to a narrower size

distribution. High viscosity and extremely low evaporation rate of NA may introduce certain inconvenience slowing down experiments. At the same time, the same properties could promote slow diffusion and size-selective precipitation needed for formation of SLs.

Figure 3 presents optical micrographs and TEM images of the three-dimensional, faceted microcrystals obtained from NA solutions. Formation of such crystals reproducibly occurred in all analyzed samples (seven samples of NCs with size from 3 to 5.5 nm), with numbers from a few to several tens observed on each slide. Relatively large size (up to 100 micron) enables easy observation of the SLs in optical transmission (Figure 3a) and fluorescence microscopes (Figure 3b,c). Rectangular, triangular, and sometimes hexagonal shapes of the crystals, as determined by the characteristic angles between the edges (60, 90, and 120°) are consistent with cubic symmetry, as previously reported for CdSe SLs.[1,2] It should be noted that formation of these crystals directly correlated with the size distribution of the initial NCs. Larger numbers and more perfect faceted shapes were typical for samples with narrower size distribution and larger size of NCs. With NCs smaller than 2.5 nm, formation of faceted crystals in our experiments has not been observed, even when the initial NCs had a narrow size distribution.

The main optical feature that directly relates these three-dimensional crystals to SLs is their bright luminescence, with the same colors as the initial NCs (Figure 3b,c). These colors do not disappear or change during easy dissolution of the crystals in the initial or any other solvent used for CdSe NCs. Examination of the crystals in a fluorescence microscope under the UV light did not reveal any signs of photobleaching or decomposition, and stored in a glovebox, crystals preserved their shape and bright PL during several months of observations. No quantitative measurements of the quantum yield were done, but PL in the faceted crystals was always brighter than in the background amorphous layers of NCs. More detailed TEM
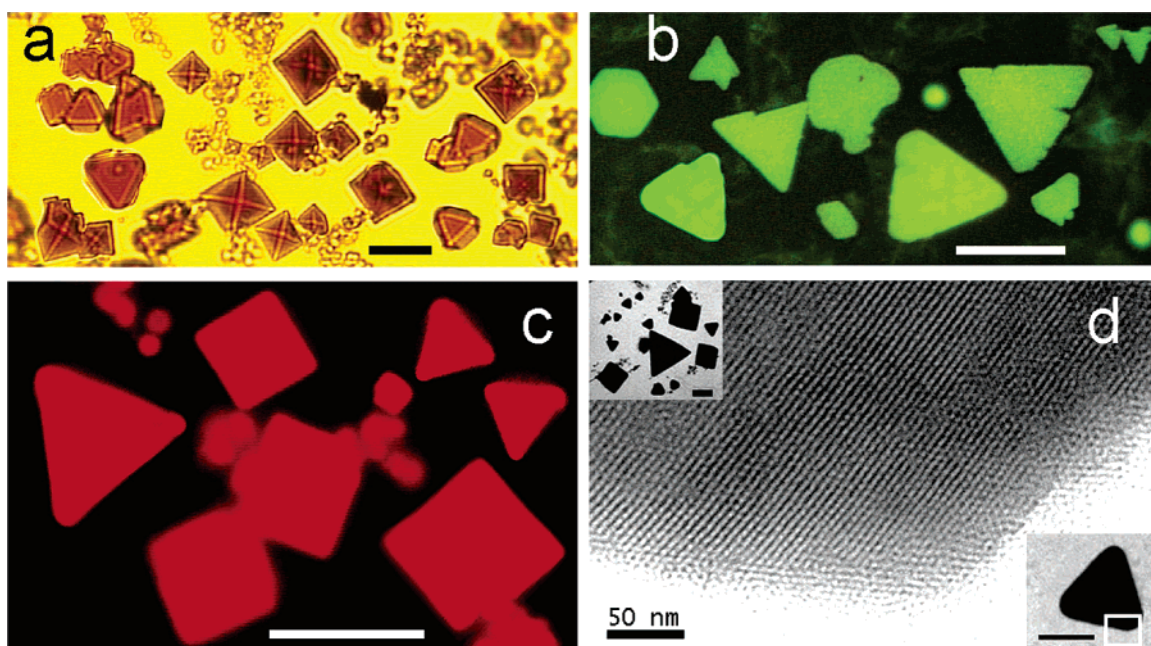

Figure 3. Faceted, colloidal crystals grown from CdSe NC solutions in nonanoic acid: (a) optical transmission micrograph of three-dimensional, faceted SLs formed from 5.3 nm NC solution; (b) and (c) fluorescence microscope images of crystals obtained, respectively, from 3.5 and 5.3 nm NCs; (d) TEM image taken from the edge of a colloidal crystal formed from 5.3 nm CdSe NCs. Inserts show low magnification TEM images of crystals with similar structure: (a) and (c) bars are 100 μm, (b) bar is 50 μm; (d) inserts bars are 1 μm.
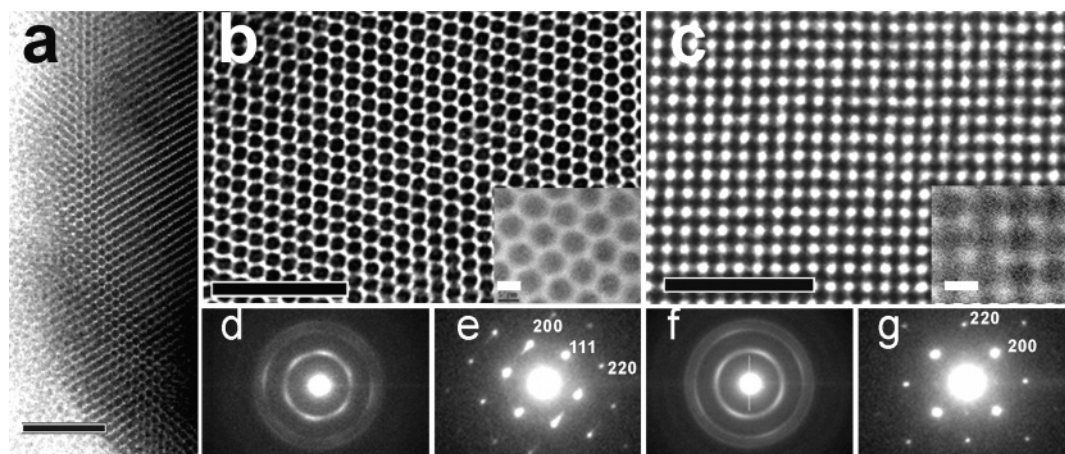
Figure 4. TEM images obtained from CdSe faceted superlattices formed from 5.3 nm NCs: (a) typical image of a crystal edge; (b and c) ⟨110⟩ and ⟨100⟩ projections obtained in the thin areas close to the edges; inserts are respective HRTEM images; segmented rings of the corresponding wide-angle electron diffraction patterns (d and f) show partial alignment of NCs within an fcc superlattice identified by the small-angle electron diffraction (e and g). Bars are 50 nm in (a), (b), and (c), and 5 nm in the inserts.

analysis of the same crystals obtained on the corresponding TEM grids (Figure 3d) provided direct evidence of their nanoscale structure. Distinctive superstructure, consistent with the size of the initial NCs found in all crystals on the edges or other areas available for transmission of the electron beam, shows that the crystals in Figure 3 are faceted SLs of CdSe. There is, however, a feature that makes them slightly different from regular, bulk, faceted crystals. Rounded corners and not straight edges are seen in some crystals in the optical and low magnification TEM images of Figure 3. At higher magnification, all facets lose their sharpness, revealing thin layers and gradual slopes (Figure 4a) instead of abrupt edges, which are typical for single crystals of bulk materials. One of the reasons for imperfect faceting could be a variation in size of the constituent NCs. At the same time, detailed TEM analysis showed remarkably uniform size of NCs in an individual SL. Images similar to those presented in Figure 4b,c revealed no difference in NC size, neither in one limited spot nor in several areas of the same faceted SL. Considering the absence of measurable size distribution, the dominant reason for the imperfect faceting is probably associated with the absence of complete alignment of individual wurtzite-structure NCs within a SL. Wide-angle electron diffraction patterns (Figure 4d,f) show only a partial alignment of NCs indicated by the segmented deflection features observed previously and explained by the van der Waals interaction between neighboring dots and with the substrate.[1,2] The weak interaction between NCs bound internally by considerably stronger intramolecular forces allows for the definition of the SLs as molecular crystals.[24] The lack of the alignment should introduce distortion into the precisely directed anisotropy that is required to form perfect crystal facets. More analyses are required to understand what determines the degree of the NCs alignment, as well as to answer a question about the possibility of completely aligned SL formation. Our experiments indicate a possible connection between the degree of the alignment and NC size. The segmented structure of wide-angle electron diffraction patterns was observed only for SLs of NCs larger than 4.5 nm. The same diffraction patterns

obtained with NCs smaller than 3.5 nm contained uniform diffraction rings showing isotropic orientation of NCs within SLs.

Small-angle electron diffraction patterns obtained from all faceted SLs (Figure 4e,g) correspond to well-defined fcc structures, which indicates nearly a single size of the NCs within an individual SL. In different SLs, the size of NCs and corresponding lattice parameters could be different. The size range of NCs measured from HRTEM images in various individual SLs of the two NC batches presented in Figure 3b,c was 3.0−3.5 nm (±7.7% deviation) and 4.9−5.3 nm (±3.9% deviation), respectively. These ranges, which are close to the size distribution in the initial batches, show that not only one size but also the majority of NCs took part in the crystal formation process. However, only NCs of the same size tend to self-assemble into a faceted SL with a certain lattice parameter. The SLs of different lattice parameters could form from the initial NCs either simultaneously or, most likely, successively due to the size-selective solubility promoted by slow evaporation of the solvent. The thickness of the surface layers separating individual NCs in different SLs was found to be 1−1.3 nm, which would be close to the length of a TOPO molecule, although without specific measurements, the composition of the surface layer is difficult to define more precisely.

The reproducible formation and easy optical visualization of the SLs made it possible to perform the first selective characterization of their optical properties. A scanning confocal microscope (Figure 1) allowed for the acquisition of PL spectra from specific points on a microscope slide, which included drops of liquid, clearly distinguished faceted SLs (photos in Figure 1), and amorphous layers. The results of the measurements made with the same samples of 5.3 and 3.5 nm NCs are presented in Figure 5. Absorption and PL spectra measured in the initial, diluted solutions with a concentration of about 0.05 mg/mL (spectra 1 and 2 in Figure 5a,d) have shapes and widths typical for CdSe NC samples with narrow size distribution. Absorption remained unchanged in all measurements made with the same sample of NCs, while the situation with photoluminescence was different. PL spectra measured in concentrated saturated solutions (spectra 3 in Figure 5a,d) and in random

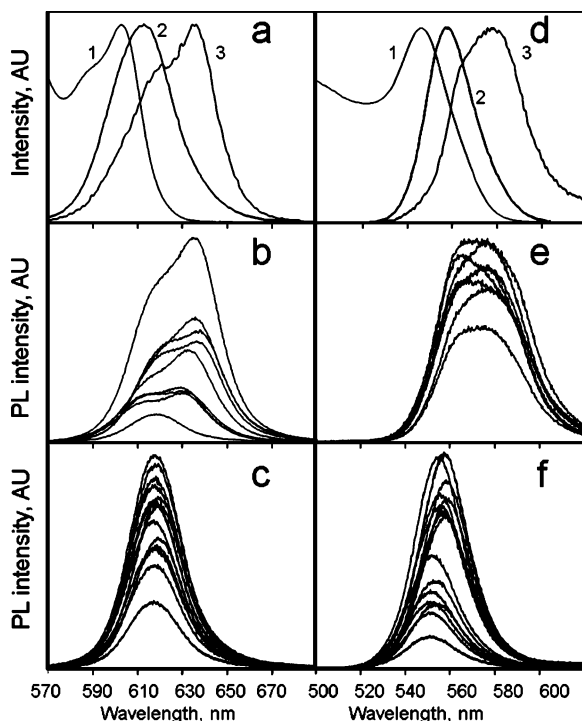(24) Wright, J. W. *Molecular Crystals*; Cambridge University Press: New York, 1995.

Figure 5. Optical spectra of 5.3 (a−c) and 3.5 nm (d−f) CdSe NC: (a and d) normalized spectra of the initial solutions in NA; 1 and 2, absorption and PL spectra of diluted solutions; 3, PL of saturated solutions; (b and e) PL spectra measured at random spots in the solid amorphous layers deposited on a glass slide from saturated solutions; (c and f) PL spectra measured in individual faceted superlattices.

Figure 6. Transformation of PL spectra of CdSe NC dispersions in toluene due to energy transfer between NCs of different size: (a) solution mixture of two samples, 1 and 2, initial PL spectra of 2.9 and 5.1 nm NC solutions, respectively; 3, spectrum of the mixture prepared from equal volumes of the initial solutions shows relative increase of the long-wave PL intensity due to the re-absorption of PL from the smaller NCs; (b) spectra of solutions prepared from the same 5.1 nm NC sample at gradually increasing concentration from 0.033 to 2.7 mg/mL; aggregation and decreasing distances between NCs result in the red shift and irregularity of the spectra shape.

spots of corresponding solid layers (Figure 5b,e), which did not have any faceted shapes, always revealed broad, inconsistent structure with fluctuating peak positions. This inconsistency completely disappears in spectra of the faceted SLs (Figure 5c,f), which return to a narrow, symmetric shape substantially different from the spectra of the neighboring, solid, amorphous layers. It should be noted that spectra measured at different points of any individual SL were identical, and therefore, each spectrum in Figure 5c,f corresponds to a separate faceted crystal.

The most probable explanation of the difference in the optical properties of the amorphous and organized solids presented in Figure 5 is connected with the phenomenon of energy transfer (ET)[25] between NCs of different size considered in detail in a number of recent works.[2,14−16] The process of radiationless ET arises from coupling between the electromagnetic fields generated by the transition dipoles of resonant transitions in the excited donor and ground state acceptor. In systems of two dissimilar dots, one smaller (the donor) and the other larger (the acceptor), ET leads to quenching of the luminescence quantum yield (QY) of the donor and enhancement of the luminescence QY of the acceptor.[14] This domination of the larger NCs in PL phenomena leads to a red shift in the spectra of amorphous solid layers compared to the initial solutions. It appears that the same phenomenon of energy transfer takes place also in concentrated solutions of NCs. Figure 6a (1 and 2) shows individual spectra of moderately diluted solutions prepared from CdSe NCs of two different sizes with initially equal PL intensity measured in a standard quartz cuvette. The third solution was prepared by mixing both solutions in equal volume ratio. If PL
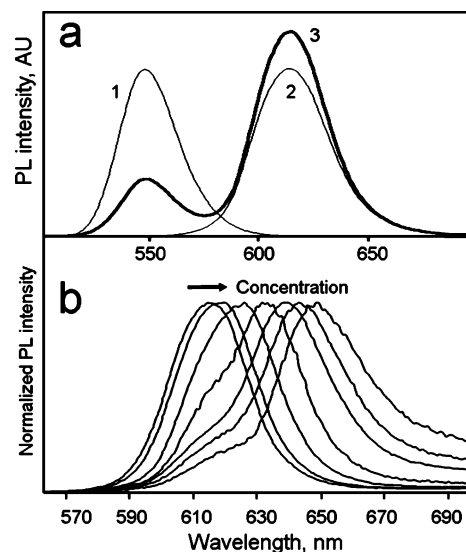
of the NCs was completely independent, equal intensity would be expected from both samples in the solution mixture. Instead, similar to measurements made previously for solid mixtures,[2] the long wavelength intensity increases and the short wavelength intensity decreases due to ET from the smaller dots to the larger NCs.

The phenomenon of the ET can explain the red shift and irregularity in the shape of spectra at increasing concentrations of NCs within the same sample with a size distribution (Figure 6b). The fact that the process is fully reversible, and spectra return to their initial, narrow, symmetric shape upon dilution of the concentrated solutions, indicates that most likely the transformation of the PL spectra occurs as a result of aggregation.[26,27] Within the aggregates, the distance between NCs should be close to that between particles in solids, thus allowing for the same ET to occur in solutions. In addition, since the ET occurs only partially,[2] the combination of the initial wavelengths of nonaggregated NCs with the red-shifted wavelengths of the clusters results in broader spectra with irregular shapes.

Higher concentration and aggregation of NCs may explain the red shift and distortion of the shape of PL spectra of saturated solutions in comparison with the initial diluted solutions in Figure 5a,d. It is natural to expect that amorphous layers precipitating from saturated solutions inherit the structure of aggregates with random size and interparticle distances formed in the concentrated solutions needed for growth of faceted crystals. This occurrence can explain the irregular shapes and broad widths of the final spectra of the amorphous layers (Figure 5b,c) and their similarity to the spectra of the corresponding saturated solutions. Similar to the case of concentrated solutions,

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the dissolution of the amorphous solids leads reversibly to the initial narrow-shaped spectra in the diluted state.[2]

In the case of SLs, the uniform size and constant distances between NCs in a crystal lattice produce a narrow symmetric shape of the PL spectra. Identical spectra measured in different spots of one SL reflect its structural uniformity, while variations of the peak position in spectra of different SLs correspond to the difference in NC size and lattice parameters. As follows from Figure 5, the positions of SL spectra peaks can be red-shifted, coincide with, or (some spectra in Figure 5f) even blue-shifted relative to the spectrum of the initial diluted solutions. This result can be understood taking into the account different factors affecting spectral lines of solutions and SLs. Solution spectra, even in the diluted state, result from the collective luminescence of NCs with different sizes,[28] which could be, in addition, affected by a certain level of energy transfer due to the existing size distribution. The SLs contain only selective sizes, and depending on whether these sizes are bigger or smaller in comparison with the majority of NC sizes in initial solutions, PL spectra of SLs can be shifted into longer or shorter wavelengths compared to the diluted solutions. The fact that PL spectra of all SLs are blue-shifted relative to the spectra of the concentrated solutions, from which they were grown, as well as the higher PL intensity observed in SLs in comparison to the amorphous solid layers may indicate a lower degree of ET resulted from more homogeneous sizes of NCs. However, more specific analyses are needed to quantitatively determine to what level both size distribution and ET are decreased in the faceted SLs compared to solutions and amorphous solid layers. The widths of PL spectra in Figure 5c,f may be considered too large in comparison to almost discrete lines obtained in single-dot measurements at cryogenic temperatures.[28,29] At the same time, even in single-dot measurements made at ambient conditions,[30] the line can broaden under the effect of temperature. Additional broadening can be introduced by structural changes, as evidenced by the fact that line widths of conventional molecular crystals at room temperature are always broader than those of individual molecules in gas phase or solutions.[24] Considering all these effects, neither the position nor the width of the solution

and SL spectra can be compared directly. More systematic search for better solvents combined with the additional advances in narrow size distribution syntheses and size-selective procedures may result in growth of larger faceted SLs sufficient for their separation from amorphous solids. Redissolution of such crystals can open further opportunities for comparative studies of single-size NC systems in liquid and solid state.

Conclusions

Faceted superlattices were obtained from CdSe nanocrystal solutions in nonanoic acid at sizes sufficient for optical characterization. Reproducible crystal growth was promoted by low solubility, slow solvent evaporation, and a size-selective effect. Structural TEM analyses, which included direct imaging, wide-angle and small-angle electron diffraction, showed that each individual superlattice is composed of nanocrystals of uniform size assembled into an fcc lattice. Direct optical measurements were made in faceted superlattices, NC solutions, and amorphous solid layers. The results showed that photoluminescence spectra of faceted superlattices had narrow-width symmetric shapes with a peak position which could coincide with or be red- or even blue-shifted relative to the initial diluted solution. In comparison, photoluminescence spectra of concentrated solutions and corresponding amorphous solids exhibited irregular asymmetric shapes and increasing red-shifts and widths with increasing concentration of NCs. The results were explained by energy transfer due to the size distribution and presence of nonuniform aggregates in concentrated solutions and amorphous solids and the absence of these factors in single-size nanocrystal superlattices.

Supporting Information Available: Comparison of super-lattices to other faceted shapes commonly forming in CdSe nanocrystal solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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