

Surface Transformation and Photoinduced Recovery in CdSe Nanocrystals

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CdSe nanocrystals in solution and films can enter a metastable state in which the highly luminescent nanocrystals become dark. This change, which we attribute to a surface transformation, can be caused by heating or by changing the environment of the nanocrystals at room temperature. The metastable transformation is reversed upon illumination of above-band-gap light, at which point the nanocrystals are again highly luminescent.

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Semiconductor nanocrystals, or quantum dots, are attractive physical systems because the strong confinement of excited electrons and holes leads to dramatically different optical and electronic properties compared to the bulk semiconductor [1]. Besides the blueshift of optical transitions due to the kinetic energy of the confinement, the concentration of oscillator strength in narrow transitions between “zero-dimensional” exciton states results in a large resonant nonlinear optical response; and there is the possibility of increased luminescence efficiency as the electron and hole may be confined together in a region away from nonradiative recombination centers.

As the size of the nanocrystal is reduced, the role of the surface increases. The promise of high luminescence efficiency was realized in II-VI nanocrystals such as CdSe when surface passivation was achieved by organic ligands used in the hot solution growth method [2]. The passivation was further improved by growing a layer of a higher band gap capping material (ZnS) between the CdSe core and organic ligand layer, giving photoluminescence efficiencies above 50% [3].

Few details are known about the surface itself. X-ray photoelectron spectroscopy (XPS) studies [4] revealed that oxygen in the presence of light attacks the selenium or sulfur atoms, forming oxides that evaporate. Nuclear magnetic resonance (NMR) studies [5] of the organic ligand layer [tri-octylphosphine (TOPO) is the most common] show that, because of the size of the conical TOPO molecule, they bind to less than half of the surface Cd atoms in most nanocrystals. Most of the organic ligand molecules can be exchanged with other weakly binding ligands such as pyridine. But about 30% of the native ligands are tightly bound to the surface, and are not replaced in the exchange [5]. CdSe nanocrystal surfaces exhibit structural disorder as observed by x-ray absorption near-edge spectroscopy [6], but no model for the complex surface has yet been given.

Even in CdSe nanocrystal samples with high quality passivation, surface effects are prominent. After an initial relaxation of less than 1 ps to intrinsic nanocrystal states, some electrons are trapped in “deep” surface traps on a

scale of tens of picoseconds [7]. The holes thermalize in 1 to 2 ps, with rates that are insensitive to surface passivation, but which could still involve intrinsic delocalized surface states [7]. These traps emit a broad defect luminescence at an energy of about 70% of the nanocrystal band gap. The band edge photoluminescence (PL), sensitive to the overlap of hole and electron wave functions, decays at an intermediate rate. The state from which the band edge PL is emitted is not fully understood. The earliest work assigned it to a surface localized state, but the magnetic field effect on the PL lifetime and very long lifetime at low temperatures suggest an emitting state with definite angular momentum intrinsic to the nanocrystal [8]. Low temperature studies of single nanocrystals show time dependent wandering in the PL spectrum, attributed to reversible photoinduced surface changes, until eventually the nanocrystal is damaged irreversibly and no longer luminesces [9]. Persistent spectral hole burning and a photoinduced reduction in the band gap have been observed in CdSe and other nanocrystals embedded in a crystal or glass, and is explained by photoinduced modifications in the nanocrystal surface-host interface [10].

In this Letter, we report transformations of CdSe nanocrystals to a metastable “dark” state in which the PL efficiency is strongly reduced. Exposure of these dark nanocrystals to light reverses the transformation, after which the nanocrystals again have high PL efficiency, or become “bright” again. We attribute these transformations to a surface transformation, by which we mean some change in the surface structure. Our studies include PL and ultrafast PL up-conversion.

Continuous-wave PL was excited at 488 nm by an Ar laser. Films and powders were heated or cooled under vacuum; solutions were heated in sealed tubes. Up-conversion measurements of PL dynamics used the second harmonic of an amplified Ti:sapphire laser at 400 nm to excite the nanocrystals; the PL was summed in a beta-barium borate crystal with delayed 800 nm pulses to generate the gated up-converted signal.

CdSe capped with TOPO (CdSe:TOPO) and CdSe/ZnS:TOPO nanocrystals were synthesized by a hot chemical

method [2]. The diameter of the CdSe nanocrystal core was estimated by comparing the PL peak wavelength with the published relation for the blueshift with size [2]. The CdSe core diameters ranged from about 3 to 4 nm, with typically a 5% distribution in size. The ZnS capping layer thickness was similarly found by observing the small redshift [3] of the PL after adding the ZnS capped layer, and found to be about one monolayer. The TOPO-capped CdSe/ZnS nanocrystals in solution show very high PL efficiencies typical of the best reported [4,5], above 50% compared to a laser dye. The pyridine-capped nanocrystals have slightly lower efficiency, and the nanocrystals without the ZnS layer have efficiencies of about 5% in solution.

We first discovered a large decrease in the band edge PL efficiency upon heating films of nanocrystals to temperatures as low as 200 °C in vacuum. In laser experiments using blue light, we found that the PL recovered in the illuminated spot, leaving the rest of the sample dark. In addition, the *defect* PL (around 1.8 eV) is also quenched in the dark state (though not as strongly), and likewise recovers under illumination. Without illumination, samples can remain dark for at least months. We observed this PL loss and photoinduced recovery effect for films with both nanocrystal surface compositions (CdSe or ZnS) and both organic ligands (TOPO or pyridine).

We have also seen this PL darkening and photoinduced recovery effect upon heating dilute *solutions* of each class of samples, again for both surface compositions and ligand types. Figure 1(a) shows a heating-cooling-illumination cycle in a CdSe:TOPO sample in solution in alkanes in a sealed tube. As the sample is heated to 120 °C, the PL drops as might be expected in a model of thermally activated trapping to surface defects. But when it is cooled to room temperature, only about half of the originally bright nanocrystals have recovered their PL efficiency. The squares in Fig. 1(a) show the restoration of the PL after doses of more intense laser illumination. The room temperature PL loss depends on the maximum temperature to which the sample is heated and the rate of cooling, and can be essentially 100%, as seen in Fig. 1(b), which shows the remaining PL after heating to various temperatures for CdSe and CdSe/ZnSe samples derived from the same CdSe core. The broad transition from 50 to 200 °C indicates that there is a broad distribution of characteristic temperatures for the transition from bright to dark states. These results with solutions and films show that the effect is inherent to individual nanocrystals, and the effect can occur regardless of whether the nanocrystal has a CdSe or a ZnS surface.

The dynamics of the photoinduced recovery are shown in Fig. 2 for the CdSe:TOPO sample in Fig. 1, for illumination at 488 nm. The curve is a stretched exponential form $1 - \exp[(t - t_0)/\tau]^\beta$, where t is the time of illumination, proportional to the number of photons absorbed. All samples show the same recovery form, but with different parameters. Samples in solution show ex-

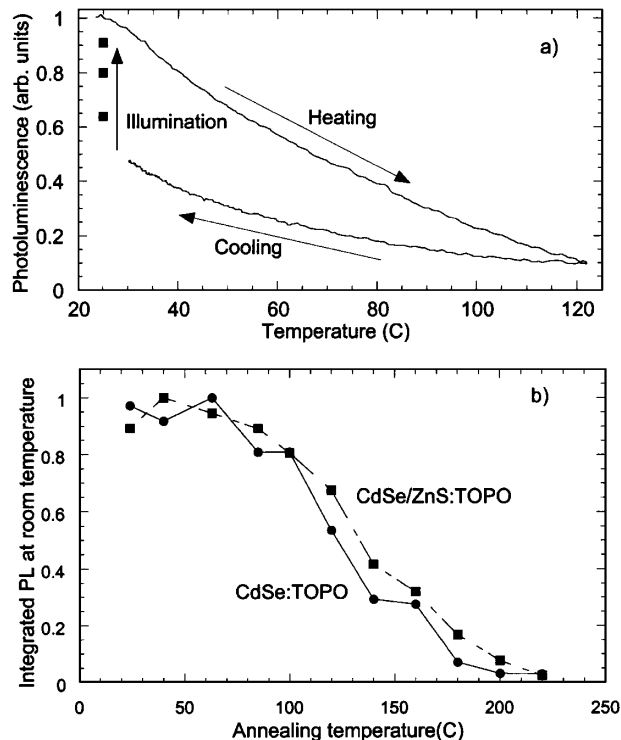


FIG. 1. Photoluminescence (PL) loss and photoinduced recovery in 4 nm nanocrystals in solution, normalized to room temperature PL. (a) PL vs T curves for heating and cooling of CdSe:TOPO nanocrystals in hexanes, showing a loss of PL efficiency upon cooling. The squares represent PL recovery steps caused by periods of laser illumination. (b) Relative PL efficiency at room temperature vs the annealing temperature in an annealing-cooling step. Samples were heated in a furnace for 10 min at the annealing temperature, and cooled to room temperature prior to measuring the PL.

ponents β near 0.8, while in films the exponents β are much lower, from 0.2 to 0.4. The parameter τ can be especially sample- and environment-dependent. In most films, the presence of a vapor of a polar molecule such as water or methanol is needed to catalyze the photorecovery. This catalysis proves that the dark state represents a change in the surface of the nanocrystals. Short photorecovery times are seen in very dilute solutions as well as in concentrated solutions and films, which argues against a model of ligand molecules simply leaving the surface as the nanocrystal is heated.

Up-conversion measurements of band edge PL dynamics in a film sample in the bright, dark, and recovered states is shown in Fig. 3. In the bright state, the sample PL has a double-exponential decay with times of about 25 ps and 1 ns. After heating to 220 °C (dark state), these times shorten to 14 and 350 ps. This faster decay, together with our observation that the usual *defect* PL around 1.8 eV is also quenched in the dark state, suggests that a *new* surface defect is active after the transformation. When in the photorecovered state, the sample has the same dynamics as in the original bright state, suggesting that the original surface state has been recovered.

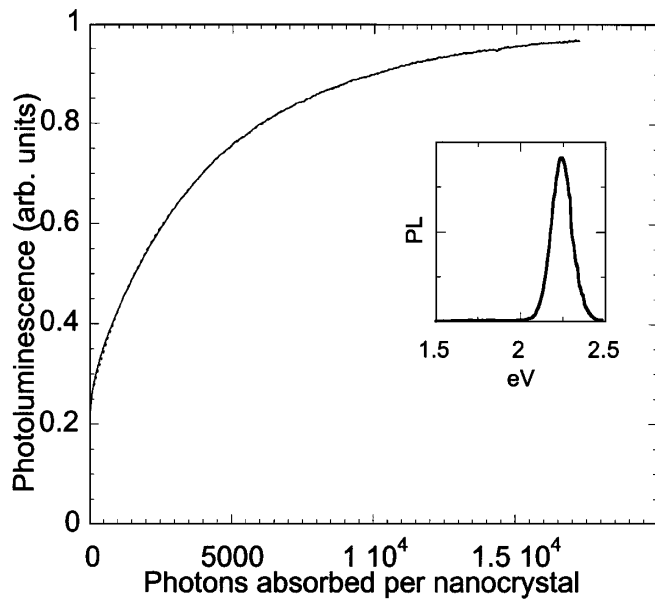


FIG. 2. Photoinduced recovery of photoluminescence (PL) efficiency of the CdSe:TOPO sample in Fig. 1(a), darkened by heating to 240 °C. The dashed line (obscured by data) is a fit to stretched exponential dynamics. Normalized to fully recovered PL. Inset: PL spectrum.

We thus attribute the PL loss upon annealing to trapping to a new or altered surface defect due to a transformation of the surface at temperatures between 100 and 300 °C. Surface reconstruction to symmetries different from bulk symmetry is common in extended planar II-VI surfaces [11], as well as other semiconductors. The surface structure can depend sensitively upon annealing temperature and excess

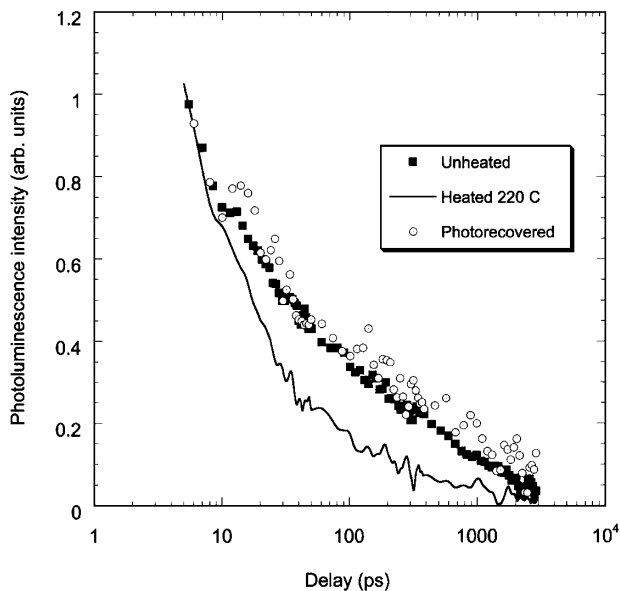


FIG. 3. Photoluminescence decay in a film of CdSe/ZnS nanocrystals in the bright, dark, and recovered states. The decay is faster in the dark state for both ps and ns ranges, but the dynamics in the recovered state are identical to those of the original bright state.

fluxes of either atomic species. For spheroidal nanocrystals, the surface structure can be very complicated, as many distinct surface planes will be exposed on the curved and faceted surface. As the sample is cooled, the surface remains in the metastable transformed state, and the coupling to the new defect continues to keep the nanocrystal dark at room temperature.

This photoreversible loss of PL efficiency can also be seen without heating, by changing the environment of the ligand layer. For example, when films are cast from solution, the PL efficiency is lower than in solution; in some cases, illumination of films can reverse this, improving the efficiency. Upon freezing and thawing solutions of nanocrystals, the PL efficiency drops, and it also shows photoinduced recovery. This loss of PL efficiency without heating in disordered films and in the frozen-thawed solutions probably arises from disordering the ligand layer. We expect films to lose PL efficiency from long-range radiative transfer of excitations [12] from PL-efficient nanocrystals to defective nanocrystals, which occurs only at high concentration. But probably just as important is that, when the nanocrystals form a film, the long TOPO molecules from neighboring nanocrystals disturb the normal spherical ligand arrangement, destabilizing the surface and making a transformation more likely. Up-conversion measurements of PL dynamics show that nanocrystals in films have a faster PL decay than in solution. This is expected in the nanosecond range for radiative coupling to defective nanocrystals. But the decay is also faster in the picosecond range, showing that trapping to surface defects on the initially excited nanocrystal is faster in films than in solution, probably caused by a surface transformation in at least some nanocrystals when going into the film.

We now discuss the illumination-induced recovery of the surface transformation, which we have observed in nanocrystals darkened in a variety of ways. One possible mechanism for the photoinduced recovery is that electrons may be trapped in the antibonding (or holes in the bonding) orbitals of strained surface bonds, weakening them further, and allowing the surface to return to the original bright state. In films, which have the highest disorder and barriers to recovery, an absorbed polar molecule apparently lowers the barrier to photorecovery. Disordered semiconductors show photoinduced bond switching and other photoinduced structural transformations, some of which are reversible [13]; however, they almost universally decrease the PL efficiency rather than enhance it as we observe. We note that the photoinduced PL recovery cannot be directly related to the intermittent on/off switching [14] seen in the studies of single CdSe nanocrystals attributed to Auger ionization of the nanocrystal. They are unrelated first because light turns the nanocrystal bright in our case, and second because the charging is seen to recover in a few seconds, while the darkening we report can last for at least many months.

The initial (presaturation) PL photoinduced recovery rate depends on the laser intensity, as seen in Fig. 4. The recovery rate $(1/PL)(dPL/dt)$ is equal to the rate of photoinduced increase in the fraction of bright particles (the luminescence is linear in I). We show in Fig. 4 that the initial recovery rate $(1/PL)(dPL/dt) \sim I^{1/2}$ over a large range of laser intensities. From simple rate models, the low power of $\frac{1}{2}$ suggests that the rate-limiting step of the photo-recovery of the surface depends *linearly* on the concentration of trapped electrons or holes on dark nanocrystals, which in turn depends on intensity as $I^{1/2}$ due to bimolecular recombination of the long-lived trapped species.

The stretched exponential form observed (Fig. 2) in the photoinduced recovery is seen in the relaxation of a wide variety of systems with strongly coupled hierarchical degrees of freedom [15], and in disordered systems [16]. The dynamics are consistent with a model of the surface photo-transforming in hierarchical steps, in which slow steps depend upon the completion of the previous faster step [15]. The stretched exponential dynamics could also result from a wide distribution [16] in energy barriers to phonon-assisted phototransformation, due to a disordered surface. The lower value of β for films compared to solutions suggests that the hierarchical constraints are stronger in films or that the barrier distributions are broader.

In summary, we have found evidence for surface transformation in organically capped CdSe nanocrystals under a variety of circumstances, resulting in the loss of PL efficiency. The transformation is metastable, and illumination of the nanocrystals with above-band-gap light reverses the transformation, with stretched exponential dynamics. While the complex surface of CdSe nanocrystals cannot yet be modeled, the transformation and

photorecovery shows that the barriers to surface transformations are rather small, probably due to the many competing surface planes on the spheroidal nanocrystals. A knowledge of these transformations may be useful in attempts to grow extended structures with nanocrystals using surface- or photochemistry. Since apparently small changes in surface structure can have a dramatic effect on the coupling of photoexcitations to surface states, we might also envision modulating the coupling of the interior or surface states of two neighboring nanocrystals which share a portion of their surfaces. Such a controlled coupling could be useful for quantum or classical computing schemes involving nanocrystals.

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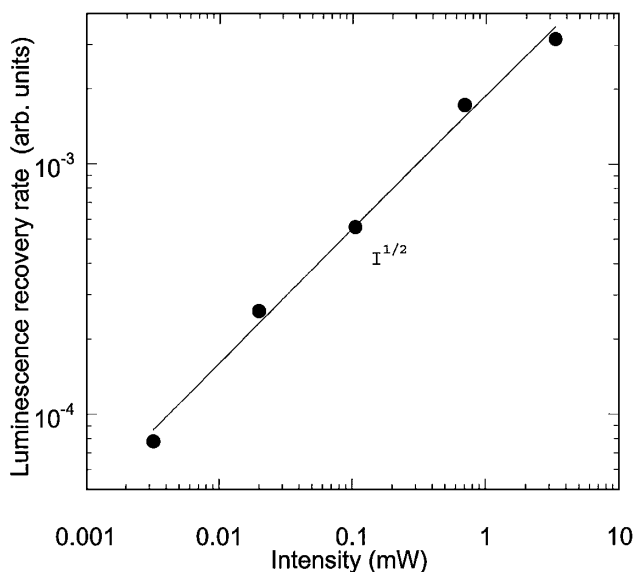


FIG. 4. Rate of initial luminescence recovery, $(1/PL)(dPL/dt)$, as a function of laser intensity, in a CdSe/ZnS nanocrystal powder which was darkened by heating to 250 °C. The line is a fit to a power law with exponent of 0.5.

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