# *Articles*

## Effect of Pressure on the Photoluminescence of Polynucleotide-Stabilized Cadmium Sulfide Nanocrystals

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This work describes the effects of pressure on the photoluminescence of Q-CdS (quantum-confined cadmium sulfide) nanoparticles stabilized by hexametaphosphate, calf thymus DNA, polyadenylic acid, polyuridylic acid, and polyadenylic−uridylic acid in the pressure range from atmospheric pressure to 4 kbar. A marked difference is observed between Q-CdS/polyadenylic acid and that of Q-CdS/polyuridylic acid in terms of pressure-induced changes in the luminescence; coating the surface of each type of Q-CdS with cadmium hydroxide results in a leveling effect whereby only a steady diminution of emission intensity is observed in each case. A model involving pressure-induced perturbation of anionic sulfide hole traps at the semiconductor nanocrystal surface is proposed to explain these observations.

### Introduction

Quantum-confined semiconductor nanocrystals (Q-NCs) exhibit interesting optical and electronic properties due to quantum size effects.[1] These properties depend not only on the particle size but also on surface states, since Q-NCs are characterized by a large ratio of surface to interior atoms. Compared to the preparation of monodispersed nanocrystals, a fundamental understanding and the subsequent control of surface states is a more complex problem.[2] For real nanocrystals with rough surfaces, atoms at the interface may not be fully coordinated; i.e., dangling bonds and other defects (vacancies, etc.) are common. Thus the surface is chemically active and can strongly interact with stabilizer and solvent molecules in the surrounding medium.[3] These surface states produce traps within the band gap of nanocrystals from which photogenerated charge carriers can recombine radiatively or nonradiatively. As a consequence, photoluminescence (PL) spectroscopy is a very useful and sensitive method to investigate the surface states of Q-NCs. While several surface modification approaches [such as covering the surface of Q-CdS (quantum-confined cadmium sulfide) with cadmium hydroxide][2a] have been developed to remove surface defect sites or reduce nonradiative pathways, more information is desired in order to develop a fuller understanding of the surface states of Q-NCs in general.

In our laboratories, we have spent an extensive effort analyzing the properties of Q-CdS stabilized by polynucleotides.[4−7] Polynucleotides are employed not only for their ordered polyphosphate backbone but also for the structural and compositional diversity of polynucleotides such as DNA in general. In principle, polynucleotide stabilizers (such as DNA) permit an evaluation of how sensitive changes in stabilizer structure perturb the photophysical properties of the semiconductor, thereby allowing for a more detailed analysis of the role of the interface in semiconductor photophysical properties. For nucleotide-stabilized Q-CdS, cadmium ions at the nanoparticle surface can bind to nucleic acids at three possible locations: the anionic oxygen atoms of the phosphate groups, the hydroxyl groups of the ribose sugar moieties, and the nitrogen atoms of the purine and pyrimidine bases. Surface sulfide sites can presumably interact with accessible amine protons of the bases as well. For cadmium hydroxide passivated Q-CdS (so-called "activated" Q-CdS), surface Cd−OH groups can form hydrogen bonds with the anionic oxygen atoms of the phosphate group or with the oxygen and nitrogen

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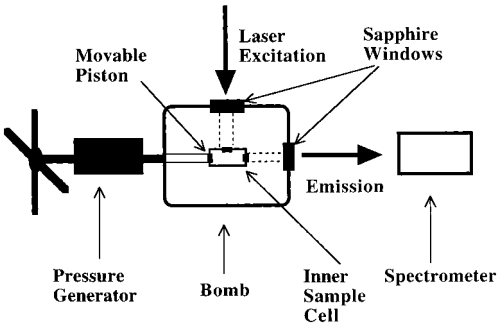


**Figure 1.** Schematic drawing of the apparatus used for pressurizing the Q-CdS/polynucleotide samples in the 1−4 kbar regime.

atoms of the bases.

In this work, we report the effects of modest pressure on the photoluminescence of nonactivated and cadmium hydroxide-activated Q-CdS nanoparticles stabilized by hexametaphosphate (HMP), calf thymus DNA (CT DNA), polyadenylic acid (poly[A]), polyuridylic acid (poly[U]), and the single-stranded random copolymer of polyadenylic−uridylic acid (poly[A,U]) in the pressure regime ranging from atmospheric pressure to 4 kbar. It is expected that in this regime, the main effect of pressure will be with respect to changes in nanoparticle-stabilizer interactions, nanoparticle−nanoparticle interactions, conformation of the polynucleotide stabilizer, and solvent dielectric effects; all of these in principle can impact defect-related luminescence. This is in contrast to the previous high-pressure studies of II−VI semiconductor nanoparticles, which have emphasized the size-dependent nature of the solid−solid-phase transitions at much higher pressures ($\sim 10^2$ kbar).[8,9]

## Experimental Section

**Reagents.** All the following polynucleotides were purchased from Sigma: CT DNA (sodium salt), poly[A], poly[U], and poly-[A,U]. The relative molar concentrations of all aqueous polynucleotide solutions were determined spectrophotometrically by employing the following molar extinction coefficients ($M^{-1}$ $cm^{-1}$) at 260 nm: CT DNA, 6600; poly[A], 15 400; poly[U], 9900, poly[A,U], 11 400.[6] Solutions of 0.1M $Cd(ClO_4)_2 \cdot 6H_2O$ (Aesar, electronic grade) and 0.1 M $Na_2S \cdot 9H_2O$ (98%, Aldrich) were freshly prepared immediately prior to the experiments. Mallinckrodt HPLC-grade $H_2O$ was used exclusively as the solvent in each case.

**Apparatus.** Absorption spectra were recorded on a HP 8452A diode array spectrophotometer using quartz cells. Photoluminescence spectra were recorded with a Spex 0.22 m double spectrometer. Excitation was provided by a Linconix 325 nm HeCd laser. High-pressure experiments were carried out in a custom designed apparatus (Figure 1) whereby a given Q-CdS/polynucleotide solution is placed into a 0.6 mL stainless steel cell which has two sapphire windows perpendicular to each other and a stainless steel piston which is sealed by a Teflon O-ring. The cell was loaded in the chamber of a steel bomb which also has two perpendicular sapphire windows. Isobutyl alcohol was used as a pressure transmitting medium. Pressure was generated by a High-Pressure Equipment Co. piston-type screw pump capable of reaching 60 000 psi. At each pressure interval, the sample was allowed to equilibrate for ~1 h prior to recording the PL spectrum. The pressure was measured directly by a calibrated Manganin-type gauge.

**Q-CdS/Polynucleotide Preparation.** Typically, 1−5 mg of a given polynucleotide was dissolved in 1 mL of distilled deionized water, and the concentration was determined spectrophotometrically. The polynucleotide solution was then diluted to either $1 \times 10^{-3}$ M (for activated samples) or $2.5 \times 10^{-3}$ M (for nonactivated samples). In general, the volume of these solutions was ~2 mL after dilution. Then 2 $\mu$L of a 0.1 M $Cd(ClO_4)_2$ solution (5 $\mu$L for the nonactivated samples) was added to the polynucleotide solution, resulting in a final $Cd^{2+}$ concentration of $1 \times 10^{-4}$ M (activated samples) or $2.5 \times 10^{-4}$ M (nonactivated samples). The solutions were transferred into a flask which was fitted with a septum and purged with nitrogen for ~30 min. Immediately, an equimolar amount of $Na_2S$ stock solution (Cd:S) was added into the flask via syringe. The flask was vigorously shaken for 2 min and allowed to stabilize for several minutes before further characterization.

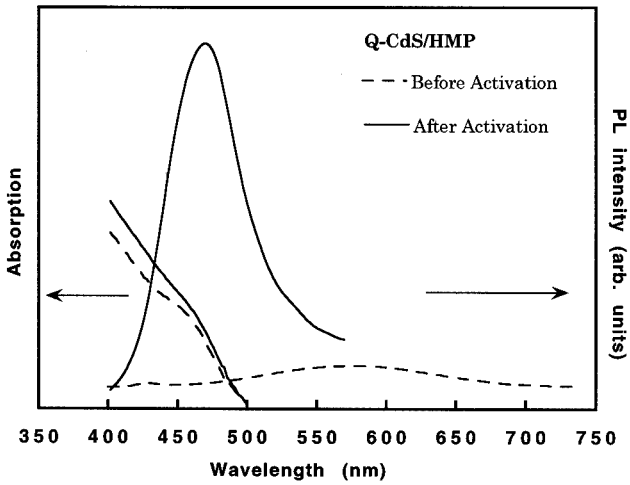


**Figure 2.** Absorption and photoluminescence spectra of nonactivated and activated Q-CdS stabilized by hexametaphosphate (HMP).

Activation of Q-CdS particles by cadmium hydroxide was achieved by adjusting the pH of a given nonactivated Q-CdS solution to 10.5 with 1.0 M NaOH, followed by dropwise addition of the stock $Cd(ClO_4)_2$ solution until the maximum PL intensity was reached.

Photoluminescence quantum yields ($\Phi$) of the Q-CdS nanoparticles were determined by employing $[Ru(bpy)_3]Cl_2$ (Alfa Aesar) as a reference and calculated from the expression:

$$Q_u = Q_s(A_s/A_u)(D_u/D_s)$$

where $Q_s$ is the $\Phi$ of $[Ru(bpy)_3]Cl_2$, known to be 0.042% at a concentration of 1 mM;[2b] $A_s$ and $A_u$ are the absorbance values of the $[Ru(bpy)_3]Cl_2$ solution and Q-CdS colloids, respectively, at 325 nm; $D_s$ and $D_u$ are their corresponding integrated PL intensities at this 325 nm excitation wavelength.

## Results

**Q-CdS/HMP.** As a control group, Q-CdS nanoparticles stabilized by the relatively simple polymer hexametaphosphate (HMP) were prepared by known routes,[2a] and the effect of increasing pressure on the observed luminescence was evaluated. Under the preparative conditions employed, Q-CdS with an absorption onset of 490 nm and corresponding average particle size of ~50 Å is obtained. Activation of photoluminescence of this type of sample by layering the surface with cadmium hydroxide results in shifting the relatively weak red emission (ranging from 550 to 700 nm) to a strong PL feature at 470 nm; a negligible red-shift from the corresponding absorption spectrum is observed (Figure 2). This observation is consistent with previous observa-

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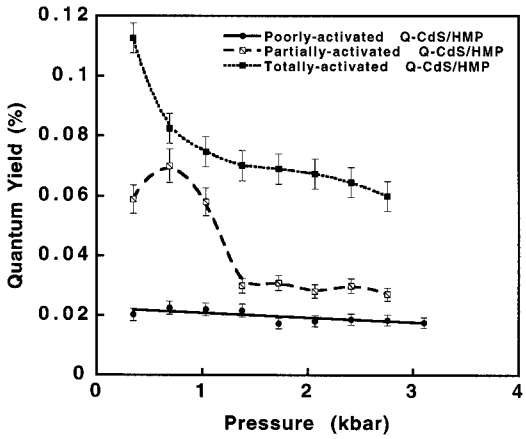


**Figure 3.** Effect of increasing pressure on the observed emission intensities for Q-CdS/HMP with different initial quantum yields (Φ). Relative Φ values were controlled in these samples by adding different amounts of 0.1 M $Cd^{2+}$ stock solution during the activation process.

tions suggesting that this layering process results in the efficient blocking of defect sites and that band gap or near band gap fluorescence becomes the predominant process of recombination.[2a]

Figure 3 illustrates the effect of increasing pressure on the PL of three activated Q-CdS/HMP samples with different initial quantum yields (Φ). It is possible to alter Φ values in these samples by adding different amounts of 0.1 M $Cd^{2+}$ stock solution during the activation process; these variations in the activation process produce no significant differences in absorption or emission line shape between samples, however. Sample a had the highest initial Φ, which exhibited a steady decrease with increasing pressure. Sample b was "partially activated" with a slightly lower initial Φ; this type of sample abruptly loses appreciable emission intensity between 1 and 1.4 kbar. At pressures beyond 1.4 kbar, no significant changes were observed. Sample c was poorly activated and thus had the lowest initial Φ; there is a negligible effect of high pressure on the PL intensity in this case.

Nonactivated Q-CdS/HMP nanoclusters were investigated, but the emission spectra of these samples constantly change with time at room temperature and it was not possible to analyze pressure effects in these samples.

**CdS/calf thymus DNA, CdS/poly[A], CdS/poly[A,U], CdS/poly[U].** Use of the polynucleotides poly[A], poly[A,U], poly[U] as stabilizers according to the procedure described above results in the formation of Q-CdS with an average diameter of 35 Å, consistent with previous work.[6] Q-CdS prepared in the presence of calf thymus DNA is slightly larger in size, approximately 50 Å, once again comparable to these previously characterized nanoclusters.[4] Figure 4 illustrates the effect of surface Cd hydroxide formation on the absorption and emission spectra of Q-CdS stabilized by these polynucleotides.

In the PL spectra of Q-CdS/calf thymus DNA (see Figure 4a), both activated and nonactivated solutions exhibit a broad trap emission band with a maximum near 550 nm. Activation through hydroxide layering results in an enhancement of PL intensity, with no shift in the observed emission maximum. This observation

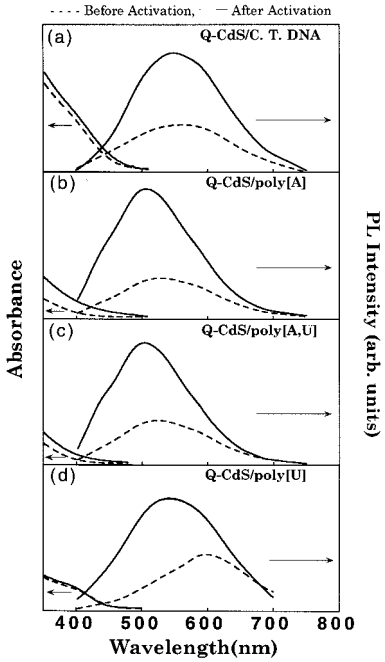


**Figure 4.** Absorption and photoluminescence spectra of nonactivated and activated Q-CdS stabilized by (a) CT DNA, (b) poly[A], (c) poly[A,U], and (d) poly[U].

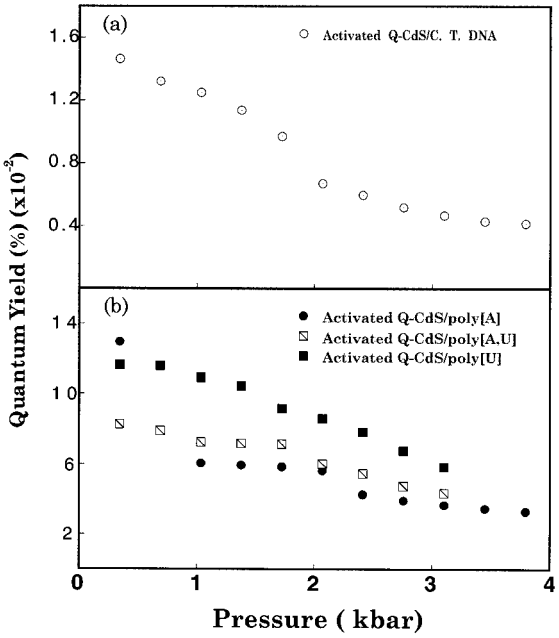


**Figure 5.** Effect of increasing pressure on the observed emission intensities of activated Q-CdS stabilized by (a) CT DNA, (b) poly[A], (c) poly[A,U], and (d) poly[U].

suggests that the activation process in Q-CdS/calf thymus DNA does not block the surface traps as in the case of Q-CdS/HMP. Nonradiative pathways are presumably reduced, but trap emission is still the dominant pathway for electron−hole recombination.

A similar effect of activation was observed for the case of Q-CdS/poly[A] and Q-CdS/poly[A,U] (see Figure 4b,c). However, activation in Q-CdS/poly[U] shifts the emission peak from 600 to 540 nm with no change in the corresponding absorption spectrum (see Figure 4d).

As shown in Figure 5, the effect of high pressure on the photoluminescence of activated Q-CdS stabilized by these polynucleotides is similar to that of the "totally"

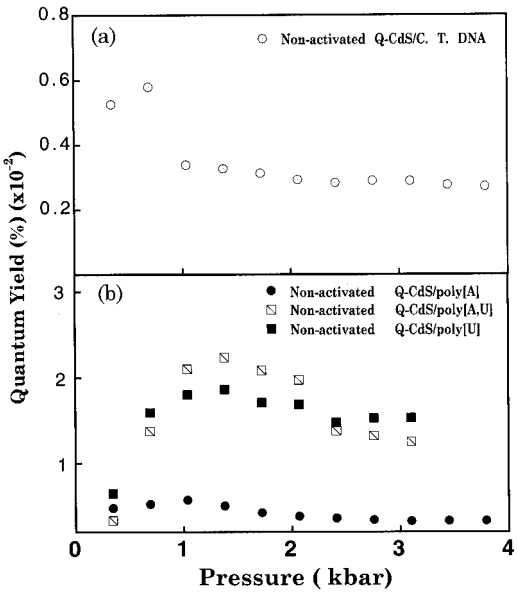


**Figure 6.** Effect of increasing pressure on the observed emission intensities of nonactivated Q-CdS stabilized by (a) CT DNA, (b) poly[A], (c) poly[A,U], and (d) poly[U].

activated Q-CdS/HMP sample a; i.e., all samples experience a steady diminution of PL intensity with the application of increasing pressure.

For the case of nonactivated Q-CdS /poly[A,U] and Q-CdS/poly[U], the PL intensities of these two materials were enhanced with increasing pressure up to a value of 1.4 kbar (Figure 6). Increasing the pressure beyond that value (up to 3.1 kbar) did not result in any further significant changes in Q-CdS emission intensity. Thus the net effect of high pressure on nonactivated Q-CdS/poly[A,U] and Q-CdS/poly[U] is the enhancement of PL. It is anticipated a priori that defect emission, even with appreciable intensity, should demonstrate different pressure-induced changes than for excitonic-type luminescence. Interestingly, nonactivated Q-CdS/poly[A] displays a trivial increase in emission intensity with increasing pressure, acting in a manner very similar to poorly activated Q-CdS/HMP sample c.

During the high-pressure experiments, there were no measurable shifts in emission maxima, and after the high pressure was released, the absorption spectra remained identical to that of the starting Q-CdS/polynucleotide solution. Therefore, the possibility of photocorrosion of Q-CdS particles under illumination was excluded.[10]

## Discussion

The application of increasing pressure (up to 3.5 kbar) to all *activated* Q-CdS solutions resulted in the diminution of PL intensity. This observation can be explained in part by hydrogen-bonding interactions between the S···Cd···OH structures on the particle surface and with the anionic oxygen atoms of the phosphate groups which exist in HMP and all the polynucleotide moeities. For Q-CdS in aqueous solution, the hole traps are most likely localized at the sulfur anions at the particle surface.[2a,3] Capping the sulfur anions with cadmium hydroxide leads to enhancement in PL intensity by blocking these hole traps.[2a] When the stabilizer and/or solvent molecules interact with the S···Cd···OH structure(s) at the particle surface, S−Cd bond(s) would be perturbed and the hole traps exposed. Increasing the pressure of the system presumably increases the extent of these interactions through an enhanced hydrogen bonding with the surface hydroxyl groups, resulting in a diminution of the trap PL. Another possibility is that an increase in solvent static dielectric constant (with pressure) is responsible for diminution of the trap PL intensity. Such a conclusion is based on previous measurements of Q-CdS trap PL in different solvents and noting that the solvent's dielectric constant is inversely proportional to PL intensity; it must be stressed, however, that this trend was established for Q-CdS in aprotic solvents.[3]

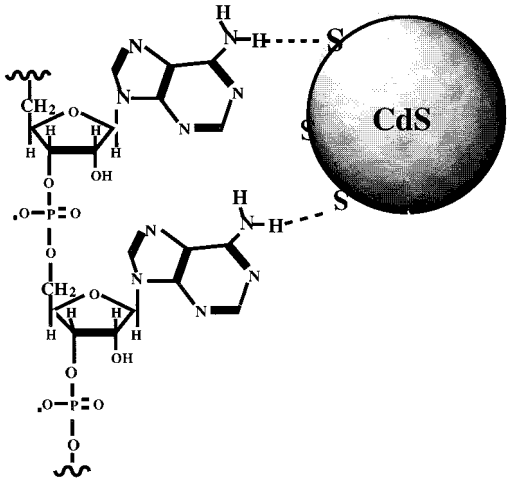


**Figure 7.** Cartoon representation of the possible modes of interaction of anionic surface sulfide sites of nonpassivated Q-CdS with amino moeities of the pyrimidine bases of poly-[A].

For these hydroxide-capped CdS surfaces, one can speculate that the oxygen and nitrogen atoms of the bases of the polynucleotides do not seem to be strongly involved in this hydrogen-bonding interaction, since variation of base composition of the single-stranded polynucleotides did not lead to different high pressure dependent behaviors. This is not surprising, since the presence of surface OH moieties presumably disrupts any extensive interaction between the Q-CdS surface and the polynucleotide.

For the *nonactivated* Q-CdS/polynucleotide solutions, there are two issues to consider. The first is the lower initial quantum yield of the CdS nanoparticles relative to the cadmium hydroxide-treated Q-CdS; the second is the slight enhancement of PL at the initial application of pressure (∼1 kbar) with little change induced by further pressure increases. From a chemical perspective, the relatively lower initial quantum yields of the nucleotide-coated CdS surface(s) likely arises from the ineffective ability of the N−H moeities present in the nucleotides to passivate the anionic sulfide hole traps at the nanocluster surface. Such a conclusion is consistent with the previous observations demonstrating that protic solvents in general depassivate such sites at the

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CdS surface through hydrogen bonding with sulfur anion sites.[3] It is also consistent with our previous studies involving the quenching of the PL of cadmium hydroxide-layered Q-CdS upon exposure to polynucleotides.[5]

This interaction between N−H groups and sulfide traps also explains the effects of increasing pressure on these nonactivated nucleotide-stabilized CdS surface(s) (Figure 7). For poly[U]- and poly[A,U]-stabilized Q-CdS (and to a lesser extent, poly[A]-stablized Q-CdS), the initial application of pressure apparently disrupts this interaction, resulting in a slight enhancement of the luminescence. However, beyond a certain pressure (∼1 kbar) the emission intensity remains essentially unchanged. The fact that poly [U]/Q-CdS and poly[A,U]/Q-CdS are affected more strongly (i.e., a significantly larger percent enhancement) by the application of intial pressure suggests that it is easier for pressure to disrupt $N-H-S^{2-}$ interactions in the case of a uracil moeity than for adenine. This is consistent with the greater basicity of adenine-containing nucleotides, as the primary amino group of this base makes the lone pair electrons far more accessible than those of the ring nitrogen of uracil.

## Conclusion

This work has demonstrated that the application of modest pressure (1−4 kbar) on the photoluminescence of Q-CdS nanoparticles can be employed to usefully discern between different types of surface stablizers, most specfically between hydroxide-capped CdS and polynucleotide-stabilized nanoparticles. The pressure-induced changes (or lack therof) in the Q-CdS emission are most easily understood in terms of perturbation of anionic sulfide hole traps at the semiconductor nanocrystal surface. Further studies exploring the general utility of this approach to other types of modified semiconductor surfaces are under investigation.

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