Interplay between Optical Gain and Photoinduced Absorption in CdSe Nanocrystals

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A potential complication associated with the realization of the optical-gain regime in semiconductor nanocrystals (NCs) arises from the competing phenomenon of excited-state absorption. Here, we apply an ultrafast transient absorption technique to study the competition between optical gain and excited-state (photoinduced) absorption in CdSe NCs as a function of NC size, surface passivation, and solvent/matrix identity. We observe that for NCs prepared in such a commonly used solvent as hexane, the contribution from photoinduced absorption rapidly increases with decreasing NC radius, and it completely suppresses optical gain in NCs of small sizes. Further, the magnitude of photoinduced absorption is sensitive both to the type and the quality of surface passivation, as well as to the identity of the solvent/matrix material. These observations, along with a strong size dependence, indicate that photoinduced absorption interfering with optical gain is not intrinsic to CdSe NCs but, instead, results from the involvement of NC interface states/processes.

I. Introduction

Chemical syntheses allow the fabrication of nanosized semiconductor crystals [nanocrystals, (NCs)] with nearly atomic precision.[1,2] These NCs can be prepared in a variety of compositions as nearly spherical particles,[1,2] elongated nanorods,[3] or nanostructures of other complex shapes such as, e.g., tetrapods.[4] The ability to precisely control both size and shape provides a means for engineering the electronic properties of NCs by directly controlling the spatial distribution (e.g., the spatial extent) of electron and hole wave functions. By changing NC size, for example, one can continuously tune the energy gap from that of the bulk material to values that exceed the bulk energy gap by more than 1 eV. The size-dependent energy gap translates into tunable emission and absorption spectra. In the case of CdSe NCs, using this quantum-size effect, one can tune the emission color across the entire visible spectrum from deep red to blue. The tunability of the emission spectra, the high photoluminescence (PL) quantum yields (QYs), and the chemical flexibility/processability of NCs make them attractive for various light emitting applications including color-selectable phosphors for displays and solid-state lighting, light emitting diodes,[5] and biolabeling.[6] Recent work has also demonstrated the feasibility of tunable optical amplification and lasing using nanocrystalline materials.[7−10]

Optical amplification requires a population inversion. In CdSe NCs, the condition for inversion is satisfied if the average number of electron−hole (e−h) pairs excited per NC is greater than one,[7,11] which represents a criterion general for zero-dimensional (i.e., quantum dot) semiconductors.[12,13] Optical gain occurs from the stimulated emission of light. In the process of light amplification, stimulated emission competes with the absorption arising from electrons in both ground and excited states. Under the condition of population inversion, stimulated emission is more efficient than the absorption associated with carriers remaining in the ground state. However, the "parasitic" absorption induced by carriers in the excited state [excited-state

absorption or photoinduced absorption (PA)] can still prevent the development of optical gain, even in the case of the inverted system.[14,15]

In CdSe NCs, intrinsic excited-state absorption features associated with intraband transitions within the manifolds of electron[16] and hole[17] quantized states are located in the near-infrared/midinfrared spectral ranges and do not interfere with optical gain, which occurs as a result of interband transitions (the range of visible spectral energies). However, as we show in this article, CdSe NCs can exhibit intense "extrinsic" PA features in the visible spectral range that show strong dependence on the NC size, the surface conditions, and the matrix/solvent identity. We also observe that this excited-state absorption can completely suppress optical gain in NCs of small sizes.

II. Experimental Section

High-quality CdSe NCs were synthesized via the well-established organometallic routes described by Murray, Norris, and Bawendi [trioctylphosphine oxide (TOPO)/trioctylphosphine (TOP)−capped CdSe NCs][1] and Qu and Peng (amine-capped CdSe NCs).[2] Overcoating of the TOPO/TOP-capped CdSe NCs with a few monolayers of ZnS was accomplished as described previously.[18] To study the effects of reduced surface passivation, the amine-capped CdSe NCs were precipitated from their growth solution using methanol. The precipitated NCs were dissolved in chloroform, and the process was repeated until the desired surface passivation was achieved. The changes in the surface passivation were monitored using PL QY measurements.

To study the competition between optical gain and PA in NC samples, we use high-sensitivity femtosecond transient absorption (TA) measurements.[19] In our experimental configuration, the sample was excited with 100 fs frequency doubled pulses (3 eV photon energy) from an amplified Ti−sapphire laser ($f_r \approx 1$ kHz repetition rate). Broad-band pulses of a femtosecond white-light continuum were generated in a 2 mm-thick sapphire plate in a single-filament regime, which provided a high stability of both the intensity and the spectral shape of the femtosecond white light. A portion of the probe beam was split into a reference channel and directed through an unexcited

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CdSe Nanocrystals

J. Phys. Chem. B, Vol. 108, No. 17, 2004 **5251**

part of the sample; the remaining beam was focused with reflecting optics (to minimize additional dispersion) through the center of the photoexcited spot on the sample. The reference and the signal pulses were sent through a scanning imaging monochromator and detected with matched large-area p−i−n Si photodiodes coupled to current preamplifiers. The signals from the preamplifiers were sent to a differential amplifier and then to a digital lock-in amplifier synchronized to a pump beam chopped at $f_r/2$. Spectrally resolved TA dynamics were measured by changing the pump−probe delay (Δt). Instant TA spectra were detected in the chirp-free configuration by scanning a monochromator (i.e., the probe spectral energy, $\hbar\omega_{pr}$) and simultaneously adjusting the pump−probe delay to compensate for the temporal dispersion of different spectral components within the continuum.[19] This experimental configuration provides accuracy up to 10^4-10^5 in differential transmission.

A TA experiment allowed us to directly compare the absorption of the sample with (α) and without (α_0) pump (nonlinear and linear absorption, respectively). In absorption spectra, optical gain corresponds to $\alpha < 0$, i.e., to pump-induced absorption bleaching ($\Delta\alpha = \alpha - \alpha_0 < 0$) that is greater than α_0 ($-\Delta\alpha/\alpha_0 > 1$). PA corresponds to $\Delta\alpha > 0$, i.e., to the situation for which the absorption of the excited sample is greater than its ground-state absorption.

In ultrafast, pump-dependent studies of NCs, it is convenient to characterize carrier densities in terms of NC average populations, i.e., in terms of the number of e−h pairs per NC averaged over an ensemble. The initial NC average population, N_{eh}, generated by a short pump pulse can be calculated using the expression $N_{eh} = \sigma_a(\hbar\omega_p)J_p$, in which J_p is the per-pulse pump fluence measured in photons per cm^2 and $\sigma_a(\hbar\omega_p)$ is the NC absorption cross section at the pump spectral energy, $\hbar\omega_p$. For the case of optical excitation well above the NC energy gap, the NC absorption cross section can be estimated from the expression[20]

$$\sigma_a(\hbar\omega) = \frac{4\pi}{3}R^3\frac{n_b}{n}|f(\hbar\omega)|^2\alpha_b(\hbar\omega)$$

in which R is the NC radius, α_b and n_b are the absorption coefficient and the refractive index of the bulk semiconductor, respectively, n is the index of the NC sample, and f is the local-field factor that accounts for the difference in the field inside and outside the NC.[21]

All measurements reported below were performed at room temperature.

III. Results

Nanocrystal Size and Interplay between Optical Gain and Photoinduced Absorption. In our analysis of the experimental results described below, we use the simplified model of band-edge optical transitions shown schematically in Figure 1a. In this model we assume that band-edge optical properties of NCs are dominated by transitions involving the lowest electron 1S state and fine-structure hole states derived from the $1S_{3/2}$ hole level (Figure 1a).[22] The band-edge hole states form two groups of closely spaced levels separated by a gap that can be as large as tens of meV in small NCs. The high-energy manifold of hole states is coupled to the 1S electron state by a strong optical transition that is observed in absorption spectra as the lowest, 1S absorption maximum (solid line in Figure 1b). The low energy hole states are coupled to the 1S(e) state by a much weaker transition that gives rise to a band-edge PL band (dashed line in Figure 1b). The large, size-dependent gap between the
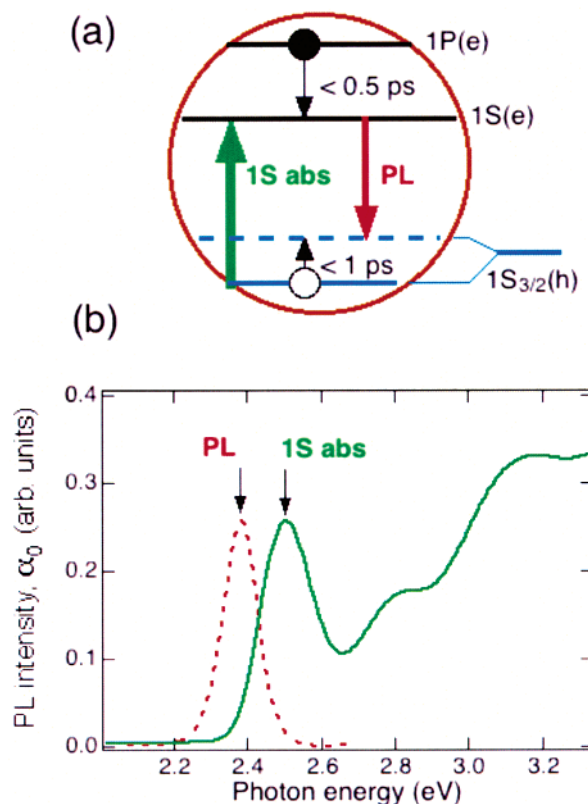

Figure 1. (a) Schematics of "absorbing" (labeled as "1S abs") and "emitting" (labeled as "PL") transitions in CdSe NCs along with intraband relaxation processes leading to a population buildup of the "emitting" transition (these processes are discussed, e.g., in refs 11 and 20. (b) Absorption and PL spectra of CdSe NCs with $R = 1.2$ nm ($T = 300$ K) illustrating a large, "global" Stokes shift between the 1S absorption peak and the PL maximum.

high- and low-energy manifolds of hole states (manifolds of "absorbing" and "emitting" states, respectively) is observed in optical spectra as a large Stokes shift between the lowest 1S absorption maximum and a band-edge PL detected under nonresonant excitation (Figure 1b). This shift is often referred to as the "global" Stokes shift in contrast to the "resonant" Stokes shift[23] observed under quasi-resonant excitation in fluorescence line narrowing experiments.

Figure 2a displays nonlinear absorption spectra of a hexane solution of small, TOPO/TOP-capped CdSe NCs with $R = 1.2$ nm recorded at $\Delta t = 2$ ps after excitation for progressively higher pump intensities. These spectra do not show any evidence for gain ($\alpha < 0$) even at the highest pump density ($N_{eh} = 6$). Instead, the 1S absorption bleaching saturates slightly below a level $|\Delta\alpha|/\alpha_0 \approx 1$, i.e., right before a crossover to optical gain (Figure 2b, squares). Such behavior indicates that the 1S transition is bleached primarily by only one type of carrier, namely electrons.[17] The contribution of holes to the 1S bleaching is insignificant because of the extremely fast relaxation of holes from the "absorbing" (responsible for the 1S absorption) to the lower energy "emitting" (involved in the PL transition) fine-structure state[24] (see schematics of band-edge energy states in Figure 1a).

However, for this NC size, optical gain is not detected at the position of the lowest "emitting" transition either. In the region of this transition, the sample shows increased absorption (i.e., PA). In contrast to 1S bleaching, which saturates at high pump intensities, PA does not show saturation (circles in Figure 2b) and, therefore, cannot be circumvented by simply increasing the excitation density.
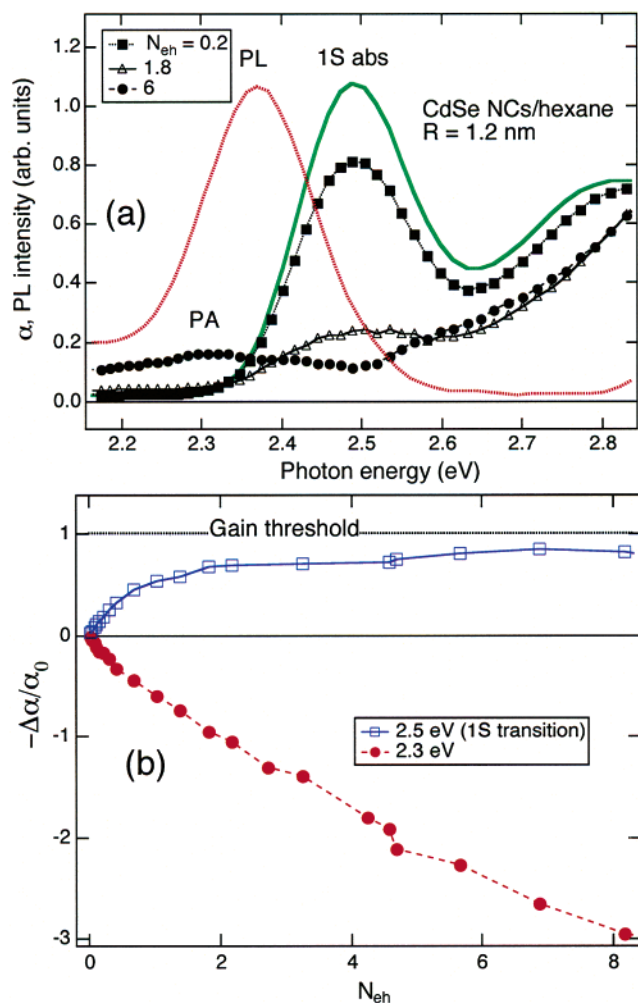
Figure 2. (a) Linear absorption (solid line) and pump-intensity-dependent nonlinear absorption spectra (symbols) of TOPO/TOP-capped CdSe NCs ($R = 1.2$ nm) in hexane that show development of a PA band overlapping with a PL spectrum (dotted line); nonlinear absorption is measured at $\Delta t = 2$ ps. (b) Pump-intensity dependence of normalized absorption changes at the positions of the 1S bleaching (squares) and the PL band (circles).
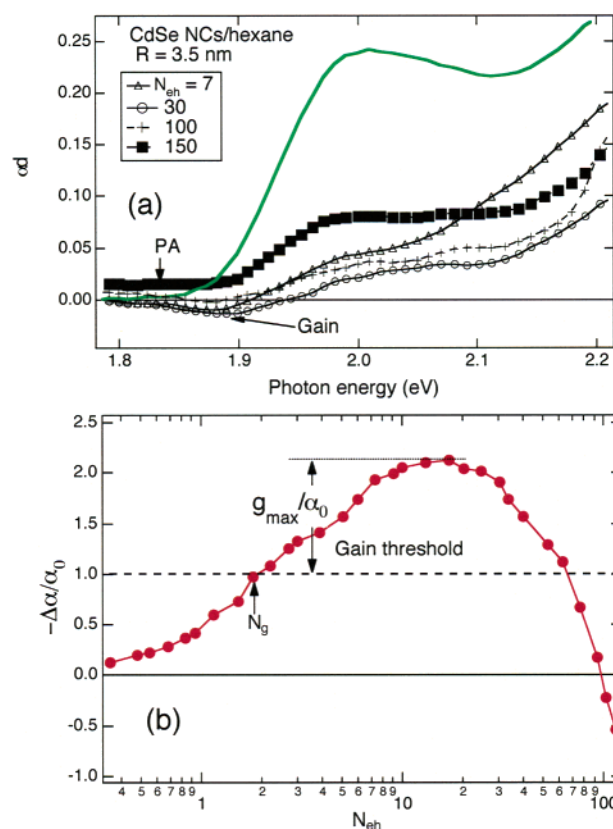

Figure 3. (a) Linear absorption (solid line) and pump-intensity-dependent nonlinear absorption spectra (symbols; measured at $\Delta t = 3$ ps) of TOPO/TOP-capped CdSe NCs ($R = 3.5$ nm) in hexane that show the development of gain ($\alpha < 0$) followed by a gradual transition to PA ($\alpha > \alpha_0$) at very high pump levels (d is the sample thickness). (b) Pump dependence of normalized absorption changes in the spectral region of optical gain ($\hbar\omega_{pr} = 1.89$ eV).

Despite the fact that PA is a general feature of hexane solutions of CdSe NCs, its relative contribution to band-edge TA signals is reduced for larger NC sizes. This effect is illustrated in Figure 3a, which displays the pump-dependent TA spectra for TOPO/TOP-capped CdSe NCs of 3.5 nm radius. These spectra clearly show the development of negative absorption (i.e., optical gain) at the position of the "emitting" transition. As indicated by the TA pump dependence in Figure 3b, optical gain develops between 1 and 2 e−h pairs per dot on average (gain threshold $N_g \approx 1.8$), and at $N_{eh} \approx 17$, it reaches its maximum. Gain decreases at higher excitation densities, which is due to the increase in the relative contribution from excited-state absorption. At very high excitation powers ($N_{eh} > 60$), the band-edge nonlinear optical response is dominated by PA.

Interestingly, the gain magnitude [$g = -(\alpha_0 + \Delta\alpha)$] at the maximum of the pump dependence exceeds the magnitude of the ground-state absorption ($g_{max} \approx 1.1\alpha_0$), i.e., is greater than the value expected for a complete population inversion (α_0) in a simple two-level system. This result indicates that in addition to state filling, optical gain in NCs is significantly affected by Coulomb multiparticle interactions,[25] leading to a shift of the optical transitions in occupied NCs. For CdSe NCs, this effect

was studied experimentally using both TA[26,27] and time-resolved PL measurements,[28] while its influence on the optical gain properties of NCs was analyzed in refs 11 and 29.

Figure 4a compares pump-dependent TA signals recorded at an early time after photoexcitation ($\Delta t = 3$ ps) at the position of the emitting transition for a series of TOPO/TOP-capped NCs of different radii prepared as solutions in hexane. These data clearly illustrate the competition between optical gain and PA as a function of NC size. For small NCs ($R = 1.2$ and 1.5 nm), excited-states absorption overwhelms bleaching before the crossover to optical gain. The critical NC radius above which optical gain is observed is approximately 2.3 nm. Excitation densities for which the crossover to gain occurs (gain threshold) decrease as the NC size is increased. For CdSe NCs of the "critical" 2.3 nm radius, the gain threshold is approached (but not crossed) at approximately $N_{eh} = 8.5$, while it is close to the theoretical limit of ~1 e−h pair per NC for the larger 3.5 nm nanoparticles ($N_g = 1.8$). The strong size dependence of the gain threshold for CdSe NC-hexane solutions is a direct result of the size-dependent interplay between gain and PA, and it specifically arises from the increasing relative contribution of PA with decreasing NC size.

The competition between PA and gain can be formally characterized by introducing a PA threshold (N_{PA}) that we define as the average NC population corresponding to a maximum of the pump-induced absorption bleaching. Above N_{PA}, PA overwhelms the contribution from bleaching/gain, and $-\Delta\alpha$ shows a monotonic decrease as a function of pump fluence. For large NCs ($R = 3.5$ nm), $N_{PA} = 17$, which is above the optical gain
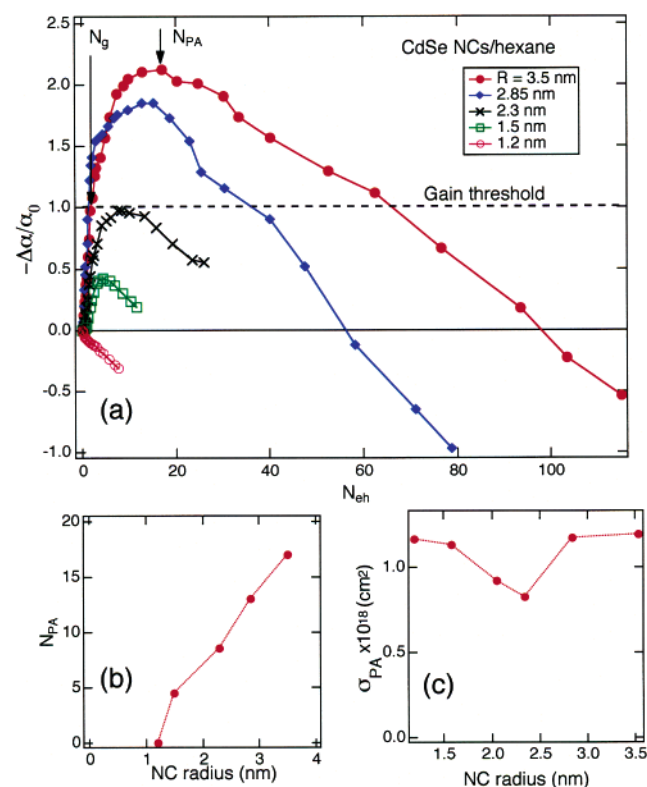
CdSe Nanocrystals

J. Phys. Chem. B, Vol. 108, No. 17, 2004 **5253**

Figure 4. (a) Comparison of pump dependences of normalized absorption changes in the spectral region of optical gain (or "potential" gain) for TOPO/TOP-capped CdSe NCs of different radii prepared in hexane ($\Delta t = 3$ ps). Probe photon energies are 2.384 eV ($R = 1.2$ nm), 2.233 eV ($R = 1.5$ nm), 2.049 eV ($R = 2.3$ nm), 1.878 eV ($R = 2.85$ nm), and 1.872 eV ($R = 3.5$ nm). (b) NC size dependence of the PA threshold (N_{PA}). (c) NC size dependence of the PA cross section (σ_{PA}); the PA cross section is derived from a linear slope of the TA pump dependence in the region $N_{eh} > N_{PA}$.

threshold. The value of N_{PA} rapidly decreases with decreasing NC size (Figure 4b). For the "critical" radius of 2.3 nm, $N_{PA} \approx N_g$, and for radii smaller than 1.2 nm, the PA threshold becomes zero, indicating that excited-state absorption dominates bleaching, even at the lowest fluences used in the experiment.

It is interesting that while TA signals show a complex nonlinear behavior at pump fluences before the PA threshold, the pump dependence of $\Delta\alpha$ above this threshold is close to linear. Since bleaching/optical gain saturates at high pump levels,[25] the observed linear change in TA is almost entirely due to pump-dependent variations in PA, which can be characterized in terms of the effective PA cross section (σ_{PA}) defined as the excited-state absorption per single NC per one absorbed photon. The values of σ_{PA} derived from linear slopes in TA pump dependences are displayed in Figure 4c as a function of NC radius. These data indicate that, at pump fluences above N_{PA}, the PA cross section is remarkably insensitive to the NC size and is around 10^{-18} cm^2. This value is orders of magnitude smaller than typical NC linear absorption cross sections observed for the lowest 1S transition.[20] The statement regarding a weak sensitivity of PA cross section with respect to NC sizes may not be valid in the region below N_{PA}, for which we cannot reliably separate the contributions from bleaching and exited state absorption. In particular, a strong dependence of N_{PA} on the NC size implies that either the PA cross section or at least the ratio between PA and bleaching/gain cross sections should be size-dependent in the regime $N < N_{PA}$.

Effects of Surface Passivation and Matrix Material. In addition to the effects of NC size, we also studied the influence
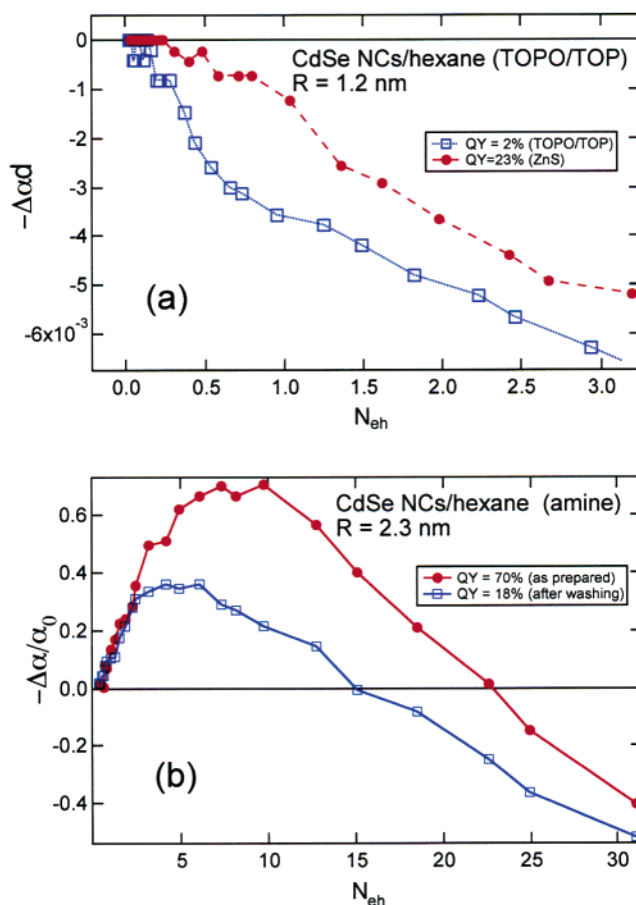

Figure 5. (a) Comparison of TA pump dependences ($\Delta t = 3$ ps, $\hbar\omega_{pr} = 2.295$ eV) for TOPO/TOP-capped CdSe NCs ($R = 1.2$ nm) with (circles) and without (squares) an overcoating layer of ZnS; overcoating with ZnS leads to a significant increase in PL QY (from 2% to 23%). (b) Pump dependence of normalized absorption changes ($\Delta t = 3$ ps, $\hbar\omega_{pr} = 2.032$ eV) for amine-capped CdSe NCs ($R = 2.3$ nm) for the cases of an as-prepared sample (circles) and the same sample but after a partial removal of surface passivation (squares); the reduction in the surface coverage leads to a decrease in the PL QY from 70 to 18%.

of NC surface passivation on the PA strength. In one set of experiments, we compared TA pump dependences measured for NCs of a 1.1 nm radius prepared with and without an overcoating shell of ZnS (Figure 5a). The addition of the outer layer of ZnS significantly improves the passivation of the surface dangling bonds and typically leads to a large increase in PL QY.[30] For samples in Figure 5a, this increase is from ~2% to ~23%. While it improves QY, overcoating with ZnS also affects the TA signals, namely leading to the reduction of PA for a given excitation fluence (Figure 5a). However, the effect of the surface passivation on PA is not as dramatic as the influence of the NC size. In particular, it does not qualitatively modify the TA pump dependence, which remains dominated by PA at all pump fluences.

To further evaluate the effect of the NC surface properties on the strength of excited-state absorption, we used NC samples fabricated by the route described in ref 2. This route provides a surface passivation that is rich in amine groups, making it distinctly different from the TOPO/TOP passivation characteristic of samples discussed earlier. In Figure 5b, we display the TA pump dependences obtained for two amine-passivated samples. The first sample is as-prepared NCs in their growth solution. While the second sample uses the same NCs, in this case the surface cap has been partially removed using methanol. Washing in methanol leads to a reduction in the PL QY from
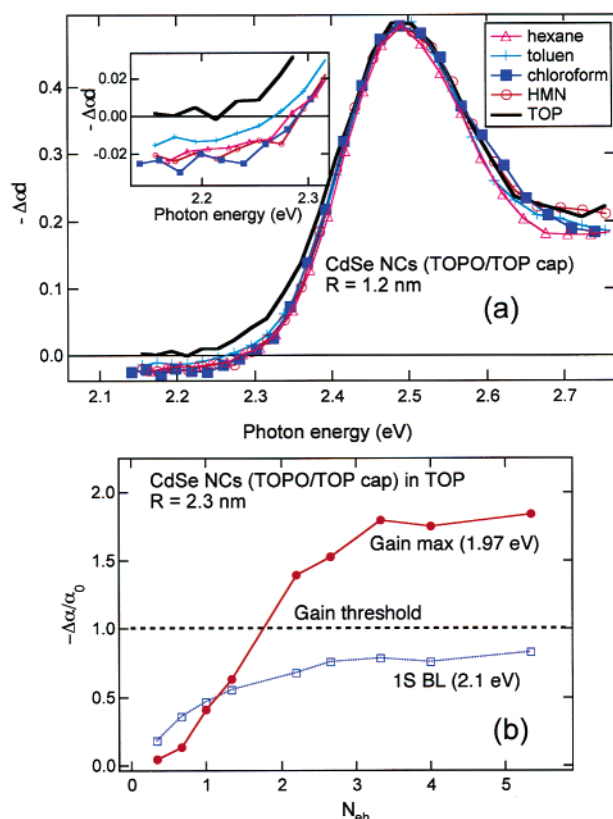
Figure 6. (a) TA spectra recorded for TOPO/TOP-capped CdSe NCs ($R = 1.2$ nm) dissolved in different solvents (indicated in the figure). $N_{eh} = 3$; $\Delta t = 3$ ps. All solvents except for TOP show the development of PA at the position of the "emitting" transition. Inset: expanded view of the PA region. (b) Development of optical gain (circles) in TOPO/TOP-capped CdSe NCs dissolved in TOP ($R = 2.3$; note a difference in radius compared to frame a); $\Delta t = 3$ ps. The pump dependence shown by squares describes the saturation of the 1S absorption feature.

70 to 18%. Both samples show the development of PA as was previously observed for TOPO/TOP-passivated samples. Furthermore, as for the TOPO/TOP-capped NCs, the PA growth is almost linear with pump fluence at $N > N_{PA}$. This linear region can be characterized by $\sigma_{PA} \approx 5 \times 10^{-19}$ cm², which is approximately twice as small as for TOPO/TOP-capped NCs, indicating the sensitivity of PA to the type of surface capping groups. We also observe that PA is sensitive to the density of surface passivation, which has a distinct effect on the PA threshold. For an as-prepared sample, N_{PA} is around 8 e−h pairs per NC, but it is reduced to ∼5 for the sample with the partially removed surface cap (Figure 5b).

In addition to its sensitivity to the identity and quality of the surface passivation, excited-state absorption is also dependent on the type of the solvent/matrix material. We observe that such commonly used solvents as toluene, chloroform, and heptamethylnonane (HMN) show PA with a magnitude that is comparable to the PA magnitude in hexane solutions (symbols in Figure 6a). However, the PA is almost completely suppressed in TOP, one of the NC growth solvents (solid line in Figure 6a). Figure 6b displays pump-dependent TA signals for CdSe NCs ($R = 2.3$ nm) dissolved in TOP and measured at the positions of the 1S absorption maximum (squares) and the PL band (circles). In hexane solutions, pump-dependent $\Delta\alpha$ for these NCs approaches the gain threshold but does not cross it (Figure 4a, crosses). However, in the case of TOP, these NCs clearly show optical gain at the position of the PL band. The transition from absorption to gain occurs at $N_g = 1.8$ (circles
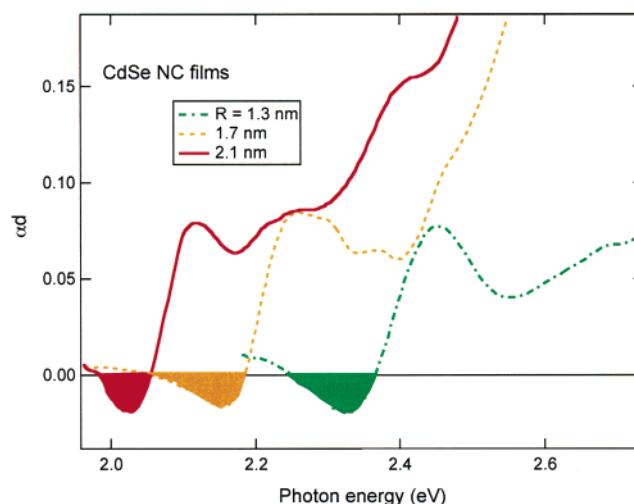

Figure 7. Nonlinear absorption/gain spectra of matrix-free CdSe NCs films fabricated from dots with $R = 1.3$, 1.7, and 2.1 nm. All films show optical gain (filled areas) which corresponds to $\alpha < 0$.

in Figure 6b), which is much lower than the gain threshold observed in hexane (∼8.5). This difference provides an additional piece of evidence that the gain threshold in NC solutions is strongly affected by the competition between optical gain and PA.

We also observe that PA is completely suppressed in matrix-free solid-state films fabricated by drop casting from hexane/octane solutions of TOPO/TOP-capped NCs. In Figure 7, we display normalized nonlinear absorption spectra ($\Delta t = 2$ ps) for three film samples fabricated from NCs with radii 2.1, 1.7, and 1.3 nm. For all samples, NC radii are smaller than the "critical" radius of 2.3 nm, and in the case of hexane solutions, these NCs do not show optical gain. In contrast to hexane-based samples, all solid-state samples show optical gain at the position of the emitting transition, clearly indicating suppression of PA. Our previous studies of another class of solid-state NC samples, fabricated by incorporating NCs into sol−gel matrices,[31] also indicate the suppression of PA.

IV. Discussion

First we would like to discuss the issue of the thermal vs electronic origin of the observed PA. The high intensity pumping used in our experiments can, in principle, lead to significant heating of NCs. Estimations based on bulk CdSe parameters indicate that the absorption of 100 photons by an isolated (thermally decoupled from the environment) NC can lead to an increase in its temperature of more than 100 K. Such an increase in the temperature can produce a low energy shift of electronic levels (in bulk CdSe this shift is approximately 0.36 meV/K), which will be manifested in TA as increased absorption below the lowest 1S absorption maximum. These estimations, however, assume that heat does not dissipate from the NCs. In contrast, our experimental results strongly argue against significant transient overheating of NCs, indicating the existence of efficient heat exchange with the environment.

Strong evidence against the thermal origin of PA is derived from the comparison of TA data for solution and film samples. Because of the efficient "thermal bath" provided by the solvent molecules, overheating is expected to be weaker in solutions than in films. In the case of the thermal origin of PA, stronger overheating should produce more intense PA, which, however, contradicts our results. We always observe strong suppression of PA as we go from solution to film samples.

CdSe Nanocrystals

J. Phys. Chem. B, Vol. 108, No. 17, 2004 **5255**

Another piece of evidence against strong transient heating of NCs is provided by the analysis of pump dependent PL data. Our measurements on both solutions and films do not show any significant PL red shift with increasing pump level, indicating that the NC temperature is not significantly raised upon pumping. This conclusion is valid not only for the spontaneous but also for the stimulated emission [amplified spontaneous emission (ASE)] regimes. Since ASE develops on very short time scales (comparable with Auger recombination times), the latter result indicates that dissipation of heat from the NCs occurs on ultrashort (likely picosecond) time scales.

All of the considerations above strongly show that the observed PA is not of thermal but rather electronic origin. The next question is whether this PA is due to electronic transitions involving "interior" (i.e., quantized) NC states or the states at the NC surface/interface (intrinsic vs extrinsic origin of PA). The strong effect of the identity of the surface ligand and solvent/matrix material on the PA magnitude points toward the "interfacial" origin of PA. The fact that PA is completely eliminated in close-packed solid-state films strongly suggests that the final state involved in the transition leading to the generation of PA is directly related to the solvent/matrix surrounding the NC. Since the wave function of such a state is not expected to penetrate deep into the "bulk" of the NC, the initial state is likely associated with the NC surface and can be due, e.g., to surface dangling bonds. The fact that the PA threshold is reduced by a decreasing degree of surface passivation supports this explanation. The reduction in the PA threshold (N_{PA}) along with a simultaneous increase in the relative contribution of PA to TA signals observed with decreasing NC size is consistent with the "interfacial" origin of PA (smaller NCs have larger surface-to-volume ratios). Furthermore, the fact that the PA cross-section is nearly insensitive to the NC size provides another indirect indication that PA arises not from the transitions involving quantized states (for which both the probabilities and energies are expected to be size dependent) but from the "interface" transitions that are either independent or only weakly dependent on quantum confinement.

Of course with this purely optical study, we cannot identify the exact mechanism for the development of "parasitic" PA that competes with optical gain in CdSe NCs. While we observe that this PA occurs most likely through the involvement of interface states, the exact nature of these states remains unclear. Our suggestion regarding a possible involvement of surface dangling bonds can be verified by conducting, for example, optical studies in conjunction with studies of paramagnetic species at the NC surfaces (via, e.g., optically detected magnetic resonance[32]). More work is also required to clarify the energy positions of states involved in PA. There have been some indications that PA signals are sensitive to the pump wavelength and can, e.g., be reduced by exciting NCs within the lowest 1S absorption resonance.[14,15] These results provide indications that energy levels involved in PA can be more easily reached from the NC high-energy, excited states than from the band-edge states. Our preliminary data on TA as a function of excitation wavelength indicate that the PA "excitation spectra" exhibit a complex dependence on both NC size and interface conditions, and we expect to clarify this dependence in our followup work.

V. Conclusions

In this paper, we have described studies on the competition between optical gain and PA in CdSe NCs as a function of NC size and NC surface properties for both solution- and solid-state samples. We observe that for commonly used hexane solutions, the relative contribution from PA rapidly increases with decreasing NC size. This increase leads to the increase of the optical gain threshold well above the theoretical limit of 1 e−h pair per dot on average. Furthermore, for small NCs ($R <$ 2.3 nm), PA overwhelms optical gain, which prevents the regime of optical amplification. While we observe PA of comparable magnitudes for hexane, toluene, chloroform, and HMN solutions, it is completely suppressed in TOP, which is one of the NC growth solvents. PA is also not observed in matrix-free, close-packed films or in NC/sol−gel titania-based nanocomposites. Our experimental observations of strong PA size dependence, as well as its dependence on the surface cap and the solvent/matrix identity, strongly suggest that PA is not intrinsic to NCs but is rather the property of the NC interface.

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