Gain Control in Semiconductor Quantum Dots via State-Resolved Optical Pumping

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Excitonic state-resolved optical pumping experiments were performed on strongly confined semiconductor quantum dots. We demonstrate for the first time that optical gain is dependent upon the initial excitonic state. By prescribing the specific multiexcitonic states which can create, block, and ultimately control optical gain spectra, we recover the theoretically predicted size independence, even in systems which previously showed zero gain. In addition, we show for the first time that stimulated emission in quantum dots can be controlled via specific multiexcitonic interactions.

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One-dimensional confinement of charge carriers in semiconductor quantum wells is now a well-established method to enable efficient optical gain and lasing with improved performance metrics such as carrier threshold, gain coefficients, differential gain, temperature stability, and operating temperature. Strongly confined quantum dots are particularly appealing, in principle, as the particle's size would enable spectral tuning [1]. It was expected that the three-dimensional carrier confinement in semiconductor quantum dots would further improve the performance of gain materials. Despite their initial promise, the results from nearly two decades of work suggests that strongly confined semiconductor quantum dots do not universally yield optical gain.

Perhaps the first demonstration of optical gain in strongly confined semiconductor quantum dots was work by Klimov and Bawendi [2]. It was argued that a thin film geometry with high loading fractions was essential to produce optical gain in these CdSe quantum dots. In subsequent years, optical gain was observed in CdSe quantum dots in their native solution but only for the largest sizes [3]. In solution, optical gain could not be demonstrated in particles with radii smaller than 2.3 nm, thereby removing much of the expected value of confinement-based tunability, furthermore suggesting potentially fundamental barriers related to quantum size effects.

A key result from prior works is that enhanced multiexcitonic interactions may fundamentally impede the development of optical gain [2,3]. The presence of more than one exciton per quantum dot results in a shifting of the level structure [1]. In particular, the interaction of the two excitons necessary for population inversion yields a biexciton. Rather than generate optical gain under intense pumping, the complex interplay of many-body interactions in the quantum dot yields absorption at precisely the emitting wavelength, thereby blocking optical gain.

The early experiments on strongly confined quantum dots suggested that, while optical gain is possible in some cases, it is neither size universal nor efficient in the canonical strongly confined CdSe quantum dot. Similar results have been obtained in related materials such as CdS, PbS, and PbSe, generally accompanied by even larger thresholds and smaller differential gains [4–6].

In addition to the multiexcitonic interactions which were believed to result in gain blocking, it was believed that the gain lifetime in these quantum dots would be too short, due to enhanced Auger recombination rates [7]. In order to bypass the perceived limitations of quantum dots, alternative materials such as quantum rods were investigated. The underlying premise was that the rods may have more favorable gain characteristics due to weaker multiexciton interactions and/or slower Auger recombination times [8–10].

In order to avoid the influence of multiexcitons, a dramatic demonstration of low gain thresholds at the single exciton level was recently provided by Klimov and coworkers [11]. In this case, a type II core or shell structure was engineered to produce negative biexciton binding energies which lowered the theoretical threshold for the development of optical gain into the single exciton regime. The last decade of work on strongly confined colloidal quantum dots suggests that the pathway to a universal, size tunable nanocrystalline gain material lies not with strongly confined quantum dots but with development of new materials [8–11] and new host media [2].

Here we show for the first time that optical gain is indeed a size-independent, spectrally controllable property of strongly confined colloidal CdSe quantum dots. By exploiting the discrete level structure intrinsic to quantum confinement, we can spectroscopically prescribe specific single and multiexcitonic states. Doing so reveals that these materials generate large optical gain, even for the smallest particles in solution. The differential gains and occupation thresholds are shown to be essentially independent of particle size and exhibit near-universal behavior when maintaining a constant initial excitonic state. Furthermore, we show that the capacity to specify the precise nature of the multiexciton allows for the tailoring of the gain and amplified spontaneous emission (ASE) spectra.

These results were obtained using a state-resolved optical pumping scheme, where the pump pulse is tuned into resonance with specific initial excitonic states. Experimental details are noted in our prior works [12–14] and in the supplementary information [15].

It is well known that the photoinduced absorption (PA) due to multiexcitons can prevent optical gain [1,3,11,16]. In our prior works [12,14], we have shown that the magnitude and dynamics of this PA are dramatically dependent upon the initial excitonic state [15]. Broadly, higher excitonic states and surface trapped carriers yield larger PA. In the absence of state-resolved pumping, we find that prior works were done under conditions which were optimal for masking the true optical gain, which we show here is intrinsic to strongly confined quantum dots.

Figure 1(a) shows the linear absorption spectrum (OD_0) and the spontaneous photoluminescence spectrum (PL) of a typical CdSe quantum dot in toluene solution. The transitions in the spectra are denoted by atomiclike term symbols based upon prior works by Efros [17] and Bawendi [18,19]. Figure 1(b) shows the nonlinear absorption spectrum ($OD_{NL} = \Delta OD + OD_0$) resulting from a pump pulse tuned to each of the lowest four transitions. The presence of optical gain is demonstrated by negative absorption (i.e., stimulated emission) in the nonlinear spectra.

The position of the stimulated emission (SE) is strongly a function of the initial excitonic state. Following excitation of the band-edge transition ($1S_e - 1S_{3/2}$) at 619 nm, the SE maximum is at 636 nm. When exciting the particle at 510 nm, resonant with the $1S_e - 2S_{1/2}$ transition, the SE maximum redshifts to approximately 653 nm. In general, as the excitonic energy is increased, the SE spectrum progressively redshifts. These spectra were taken at a time delay of 1 ps, at which point hot exciton relaxation should be complete [12,13,20]. The same results were obtained at much later time delays, ensuring these results were not due to timing.

Figure 1(c) quantifies the influence of the initial excitonic state upon the gain performance. Here we have reported the occupancy $\langle N \rangle$ dependence of the stimulated emission cross section at the maximum of the measured SE spectra ($-\sigma_{SE}$) for each excitonic state. The cross section $-\sigma_{SE}$ is reported relative to the known absorption cross section of the band-edge transition (σ_{1S}) [21] [i.e., $OD_0(1S_e - 1S_{3/2}) = 1$]. The threshold for the development of optical gain is surpassed when $-\sigma_{SE}/\sigma_{1S} > 0$. The gain threshold ($\langle N \rangle_{th}$), differential gain, and σ_{SE} are strongly a function of the initial excitonic state, even after completion of intraband relaxation. One sees that the threshold increases and the differential gains decrease as the pump pulse is resonant with higher-lying excitons. The progressive decrease in the ratio $-\sigma_{SE}/\sigma_{1S}$ at $\langle N \rangle = 0$ reflects the redshifting in the maximum of the SE spectra when pumping with higher-lying excitons. These results are a direct reflection of interference from the state-dependent photoinduced absorption [12,14,15].

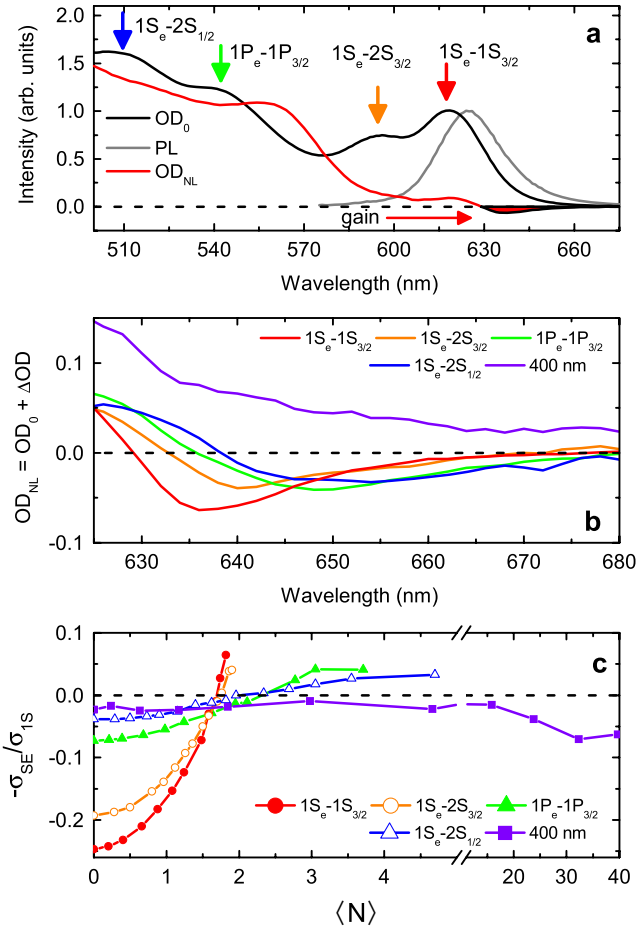

FIG. 1 (color online). State-resolved optical pumping of quantum dots. Absorption, emission, and nonlinear absorption spectra (band-edge excitation) of CdSe quantum dots ($R = 2.8$ nm) in toluene solution (a). The nonlinear spectra were measured following excitation of the transitions denoted by the arrows. The negative region (red) corresponds to optical gain. Nonlinear absorption spectra as a function of the initial excitonic state. The maximum of the stimulated emission redshifts as excitonic energy is increased (b). Stimulated emission cross sections normalized to the band-edge exciton absorption cross section as a function of exciton concentration ($\langle N \rangle$) for the different initial excitonic states (c).

These experiments were also performed with excitation at 400 nm in order to make correspondence with prior works that do not use state-resolved pumping. Pumping at 400 nm was completely unable to generate optical gain in these material conditions despite an $\sim 10\times$ larger excited state population [Fig. 1(c)]. The results here with 400 nm excitation are completely consistent with prior works which showed that the particle size, passivating ligands, and surrounding matrix all have a profound influence on the efficiency and even the presence of gain [3].

This state-resolved approach to optically pumping quantum dots has a clear result: One can prescribe the optimal initial excitonic state to yield gain. In this implementation of the approach, material conditions which generate zero

gain using 400 nm pumping can be state-selectively driven such that they generate efficient gain, thereby overcoming the extrinsic materials issues.

In order to test the universality of this approach, three different sizes of CdSe quantum dots were pumped, directly into the band-edge exciton. Figure 2(a) shows the normalized absorption bleaching spectra ($-\Delta\mathrm{OD}/\mathrm{OD}_0$) as a function of exciton occupancy ($\langle N\rangle$) for $R = 2.1$ nm. The onset of gain is represented by $-\Delta\mathrm{OD}/\mathrm{OD}_0 > 1$. The upper panel shows that the SE is redshifted with respect to the PL, due to the well-known biexciton interaction [1,11,12,14,16,22,23]. The approach used here can generate strong optical gain at very low thresholds. Perhaps most notably, this result was achieved under conditions which were previously believed to generate zero gain—small CdSe quantum dots, in solution, with ligands that were believed to prevent the development of optical gain.

These data show that $\langle N\rangle_{\mathrm{th}}$ as well as $(-\Delta\mathrm{OD}/\mathrm{OD}_0)_{\mathrm{max}}$ show variance across the stimulated emission spectrum. Perhaps not surprisingly, these numbers are most ideal at the red edge of the SE spectrum, where there is minimal absorption. In order to show size independence of gain, we have chosen to monitor the onset gain at the peak of the SE spectrum for each size [Fig. 2(b)]. Here one sees that the onset of gain and the differential gain, as well as its maximum value, shows no size dependence, in stark contrast to prior works which did not use state-resolved pumping schemes. The size-independent threshold for gain of $\langle N\rangle_{\mathrm{th}} \approx 1.6$ is consistent with the simple modeling provided here [15] and elsewhere [16]. The anticipated universality of gain in quantum dots can be recovered upon direct excitation into the band-edge exciton.

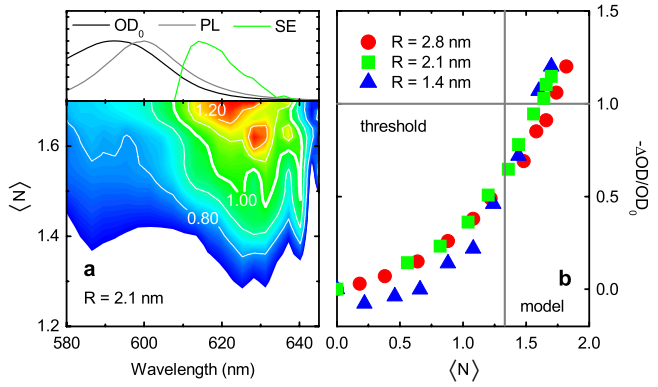

FIG. 2 (color online). Size-independent gain thresholds obtained under conditions of band-edge excitation. The normalized absorption bleaching ($-\Delta\mathrm{OD}/\mathrm{OD}_0$) as a function of the average number of excitations per particle $\langle N\rangle$ for one size of dot (a). Gain is achieved when this ratio is greater than one. The upper panel displays the normalized linear absorption, photoluminescence, and stimulated emission spectra. The differential gains and thresholds for three sizes of quantum dots ($R = 2.8$, 2.1, and 1.4 nm) (b). The development of optical gain is independent of particle size, recovering the universal behavior predicted by theory.

Broadly, the initial state dependence of gain metrics such as thresholds and bandwidths will arise from specific multiexciton interactions associated with a given state. We focus on the initial state dependence of the stimulated emission spectra of CdSe/ZnS in Fig. 3. Here the SE spectra are plotted as a function of the mean exciton occupancy ($\langle N\rangle$), upon pumping directly into the states denoted in each panel. The SE spectra are normalized to a band edge $\mathrm{OD}_0 = 1$ in order to report on the stimulated emission cross section $\sigma_{\mathrm{SE}}(\lambda)$ relative to the known absorption cross sections [21] for the band-edge exciton $\sigma_A(1S_e - 1S_{3/2})$. The contours shown correspond to $\sigma_{\mathrm{SE}}/\sigma_A$. In all cases, this ratio approaches 0.11, among the largest values ever measured in a quantum dot system.

Perhaps the most meaningful metric is the differential gain $d\sigma_{\mathrm{SE}}/d\langle N\rangle$. The differential gain can be obtained from the contours in Fig. 3. A practical laser should be driven under conditions which generate significant gain, well above the threshold. The differential gains reported here are approximately an order of magnitude larger than in experiments on quantum dots that do not use state-resolved pumping [3,6,11,24] and even larger than in the recent type II materials that yielded single exciton gain [11,24]. Notably, these gain metrics were obtained under conditions specifically chosen to generate zero gain in the absence of this state-resolved approach.

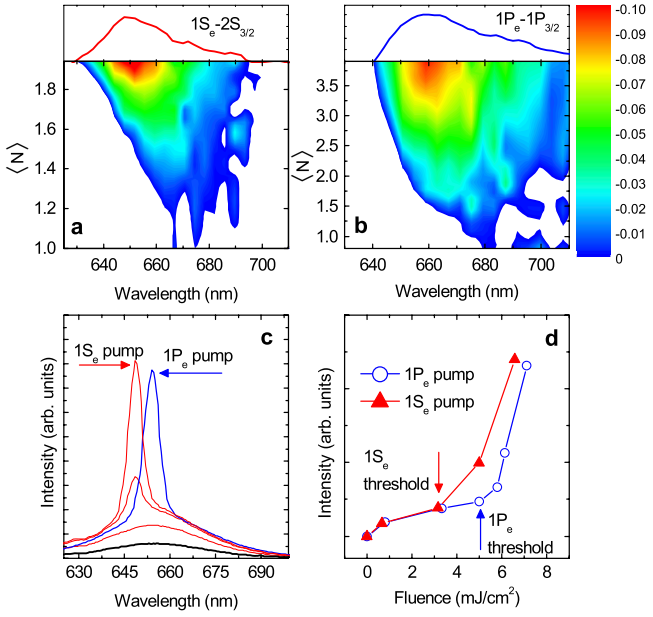

FIG. 3 (color online). Gain tailoring via the initial excitonic state. The stimulated emission spectra as a function of $\langle N\rangle$ for colloidal CdSe/ZnS ($R = 2.8$ nm) in toluene, scaled to the absorption cross section of the band-edge exciton for two initial excitonic states (a),(b). The upper panels show the stimulated emission spectra for each pump at the maximum fluence. Development and spectral tuning of amplified spontaneous emission based upon the initial state (c). State-dependent ASE thresholds (d).

The clear observation is that the SE spectra are strongly a function of the initial excitonic state. In particular, the higher-lying states have enhanced red-edge stimulated emission resulting in a much larger gain bandwidth. Under resonance with the lowest two excitonic states, the mean occupancies saturate at $\langle N \rangle = 2$, due to the degeneracy for the $1S_e$ state [1,2]. In contrast, the higher two states can have more excitons due to larger degeneracy in the $1P$ states [1,2,16]. When estimating $\langle N \rangle$, we employ the Poissonian approach to carrier populations for the higher two states [1,11,16] and a non-Poissonian approach to the lower two states [15]. We note that the upper two states have overlapping $1S$ and $1P$ electronic states under the envelope approximation [17,18]. In an atomistic picture, these higher-lying states are further removed from this simple picture [25]. The experimental observation of bandwidth tailoring suggests the presence of specific multiexcitonic transitions and potentially higher order multiexcitonic interactions. Recent theory has demonstrated that emission from biexcitons and triexcitons is distinct [26]. The spectral tuning of the stimulated emission based upon the initial excitonic state is due to the larger degeneracy of the higher excitons. We propose that stimulated emission from a $1S$ pump arises only from biexcitons, whereas emission from a $1P$ pump arises from a statistical distribution of bi-, tri-, and possibly higher multiexcitons.

Prior work has discussed that the presence of stimulated emission in a pump or probe experiment does not guarantee that ASE will be observed [2]. Essentially, the number density of the excited particles should be large enough to allow spontaneous emission to be amplified within the stimulated emission lifetime. We report on ASE in drop cast films of CdSe/ZnS with a band-edge exciton at 624 nm in Fig. 3(c). A thin film geometry was used due to its high loading fraction [2]. Figure 3(c) clearly shows the line narrowing and threshold conditions characteristic of ASE [1,2,11]. With a $1S_e$ pump at 600 nm, ASE was generated at 649 nm. Remarkably, the higher-lying $1P_e$ pump at 500 nm generates redshifted ASE at 654 nm [Fig. 3(c)]. This effect is not due to heating since neither the spontaneous PL nor the ASE signals spectrally move based upon fluence [15].

Figure 3(d) shows that the ASE threshold also is state-dependent, confirming the stimulated emission results in Fig. 1(c). The difference in the ASE wavelength confirms the ability to gain tailor quantum dots based upon the initial excitonic state and suggests the importance of understanding the specific multiexcitonic interactions [14] responsible for these effects.

The spectral bandwidth, tunability, and initial state-dependent thresholds of the SE and ASE spectra suggest that the simplest models of optical gain in quantum dots [1,11,16] (two- or three-level systems) may be missing many of the salient details. The underlying physics of multiexciton-based level shiftings [1,11,14] is certainly the key issue in optical gain in quantum dots. This broad point has been well discussed in the literature, but the specific details of which multiexciton is responsible for these gain phenomena remains an open topic. Experiments are currently underway [12] which aim to report on state-resolved studies of multiexcitons in order to identify the specific many-body interactions underlying these results.

In conclusion, we have demonstrated that optical gain in strongly confined CdSe quantum dots is both universal and efficient. A state-resolved optical pumping scheme was employed to find the states which yielded the largest gain cross sections. Under these conditions, optical gain is size-independent. In contrast, different initial excitonic states were populated which yielded enhanced gain bandwidth, suggesting the ability to tune gain spectra via tailored multiexciton interactions. This approach yielded universal and efficient optical gain in strongly confined semiconductor quantum dots, even in material conditions that were believed to show zero gain. This state-resolved approach should be useful for gain studies in any quantized nanostructure.

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[1] V. I. Klimov, Annu. Rev. Phys. Chem. **58**, 635 (2007).
[2] V. I. Klimov *et al.*, Science **290**, 314 (2000).
[3] A. V. Malko *et al.*, J. Phys. Chem. B **108**, 5250 (2004).
[4] Q. Darugar *et al.*, Appl. Phys. Lett. **88**, 261108 (2006).
[5] V. Sukhovatkin *et al.*, Opt. Lett. **30**, 171 (2005).
[6] R. D. Schaller *et al.*, J. Phys. Chem. B **107**, 13 765 (2003).
[7] V. I. Klimov *et al.*, Science **287**, 1011 (2000).
[8] S. Link *et al.*, J. Appl. Phys. **92**, 6799 (2002).
[9] M. Kazes *et al.*, J. Phys. Chem. C **111**, 7898 (2007).
[10] H. Htoon *et al.*, Appl. Phys. Lett. **82**, 4776 (2003).
[11] V. I. Klimov *et al.*, Nature (London) **447**, 441 (2007).
[12] S. L. Sewall *et al.*, Phys. Rev. B **74**, 235328 (2006).
[13] R. R. Cooney *et al.*, Phys. Rev. Lett. **98**, 177403 (2007).
[14] S. L. Sewall *et al.*, J. Chem. Phys. **129**, 084701 (2008).
[15] See EPAPS Document No. E-PRLTAO-102-068915 for supplementary information and analysis. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
[16] V. I. Klimov, *Semiconductor and Metal Nanocrystals: Synthesis and Electronic and Optical Properties* (Marcel Dekker, New York, 2004), p. 484.
[17] A. L. Efros *et al.*, Annu. Rev. Mater. Sci. **30**, 475 (2000).
[18] D. J. Norris *et al.*, Phys. Rev. B **53**, 16 338 (1996).
[19] D. J. Norris *et al.*, Phys. Rev. B **53**, 16 347 (1996).
[20] R. R. Cooney *et al.*, Phys. Rev. B **75**, 245311 (2007).
[21] W. W. Yu *et al.*, Chem. Mater. **15**, 2854 (2003).
[22] J. M. Caruge *et al.*, Phys. Rev. B **70**, 085316 (2004).
[23] C. Bonati *et al.*, Phys. Rev. B **71**, 205317 (2005).
[24] S. A. Ivanov *et al.*, J. Phys. Chem. B **108**, 10 625 (2004).
[25] L.-W. Wang *et al.*, J. Phys. Chem. B **102**, 6449 (1998).
[26] A. Franceschetti *et al.*, J. Phys. Chem. C **111**, 6154 (2007).