

Tunable Near-Infrared Optical Gain and Amplified Spontaneous Emission Using PbSe Nanocrystals

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Here, for the first time, we demonstrate amplified spontaneous emission (ASE) from PbSe nanocrystals (NCs) with emission energies tunable in the near-infrared (IR). We show that despite complications associated with a high, 8-fold degeneracy of the lowest quantized states and fast, nonradiative Auger recombination, optical gain parameters of PbSe NCs are comparable to those of CdSe NCs used for light amplification in the visible. These results indicate that previous unsuccessful attempts to realize the lasing regime in NCs of lead salts were not due to intrinsic physical reasons but likely resulted from material quality issues. By using a novel sol–gel procedure that provides both good quality surface passivation and high NC filling factors ($> 15\%$), we fabricate PbSe NC/sol–gel nanocomposites that produce ASE, which is tunable via NC size, in the near-IR. This finding indicates the feasibility of NC-based amplifiers and lasers tunable in the near-IR range and, in particular, in the range of telecommunication windows.

Chemically synthesized nanocrystals (NCs) exhibit wide-range size-controlled tunability of the emission color and high photoluminescence (PL) quantum yields (QYs). These characteristics make NCs attractive materials for light-emitting applications ranging from bio-labeling¹ and solid-state lighting² to optical amplification and lasing.^{3,4} Similar to such “soft” light emitters as organic dyes and conjugated polymers, colloidal NCs offer chemical flexibility and processability and can be easily incorporated into photonic structures or optical waveguides.^{5,6} However, while organic molecules are poor infrared (IR) light emitters, III–V⁷ and IV–VI⁸ NCs show efficient IR emission with high, up to near-unity QYs.⁹ Here, we analyze the fundamental physics of light amplification in PbSe NCs with emission energies in the near-IR. We experimentally verify that the lowest quantized states of PbSe NCs exhibit a high, 8-fold degeneracy. We find that despite this high degeneracy and fast, nonradiative Auger recombination,^{10,11} PbSe NCs exhibit optical gain parameters that are similar to those of CdSe NCs, which have been shown to produce light amplification at visible wavelengths.³ Using a novel sol–gel procedure that maintains good surface passivation and high NC filling factors, we demonstrate size-tunable ASE from PbSe NC/sol–gel nanocomposites prepared in the form of “active” planar waveguides.

To date, light amplification and lasing have only been demonstrated for II–VI CdSe NCs.^{3–6} However, because of the large energy gap (> 1.75 eV), these NCs cannot be used for light amplification in the IR spectral range. On the other hand, tunable NC-based media capable of producing emission (see Figure 1a) and optical gain at a specific near- or mid-IR wavelength (within, e.g., telecommunication and atmospheric transparency windows) are highly desirable for a number of applications ranging from optical communications and remote sensing to a recent proposal of coherent plasmon generation.¹² Lead salts such as PbSe have been used as IR gain media in quantum-well-based devices.¹³ Although previous studies of lead-salt NCs (PbS) dispersed in glass matrixes provided some indications of optical gain,¹⁴ no evidence for the ASE regime

was obtained. The existence of optical gain, however, does not ensure the development of ASE and laser action because of potentially hindering factors such as short gain lifetimes and/or strong optical losses that could lead to negative modal (i.e., net) gain despite the fact that the material gain (as measured, e.g., in ref 14) is positive.³ The failure of all previous attempts to produce ASE using lead-based NCs resulted in the perception that fundamental physical issues prevent ASE and lasing regimes in these materials.

A review of PbSe properties may indeed lead to discouraging conclusions regarding the use of these materials for optical gain applications. One possible obstacle to the development of optical gain is associated with a multivalley character of the PbSe band structure [4 equivalent band minima at the L points of the Brillouin zone (Figure 1b)], which together with a 2-fold spin degeneracy, can lead to the 8-fold total degeneracy of NC quantized states involved in the “emitting” transition.¹⁵ This high degeneracy, which we experimentally confirm below, directly impacts the optical gain threshold (i.e., the condition for the population inversion) by increasing it up to 4 electron–hole (e–h) pairs per NC on average instead of just 1 e–h pair in the case of 2-fold degeneracy.

Another potential complication is associated with highly efficient Auger recombination in which the e–h recombination energy is not released as a photon but is instead transferred to a third particle (an electron or a hole).¹¹ In bulk semiconductors, the Auger recombination rate increases exponentially as the energy gap is decreased.¹⁶ Therefore, this process is much more efficient in narrow-band PbSe¹⁷ than, e.g., in wide-gap CdSe, leading to a fast, subnanosecond carrier decay at excitation densities greater than 10^{18} cm⁻³. In sub-10 nm PbSe NCs, the effective carrier densities are $> 10^{19}$ cm⁻³ in the case of just a few e–h pairs per NC, and hence Auger recombination can severely limit lifetimes of multi-e–h pair states that are responsible for producing optical gain.¹⁸

However, the above qualitative analysis is based upon properties of bulk PbSe and can only be indirectly related to PbSe NCs. To experimentally study optical gain properties of PbSe NCs, we use high-quality colloidal samples fabricated via

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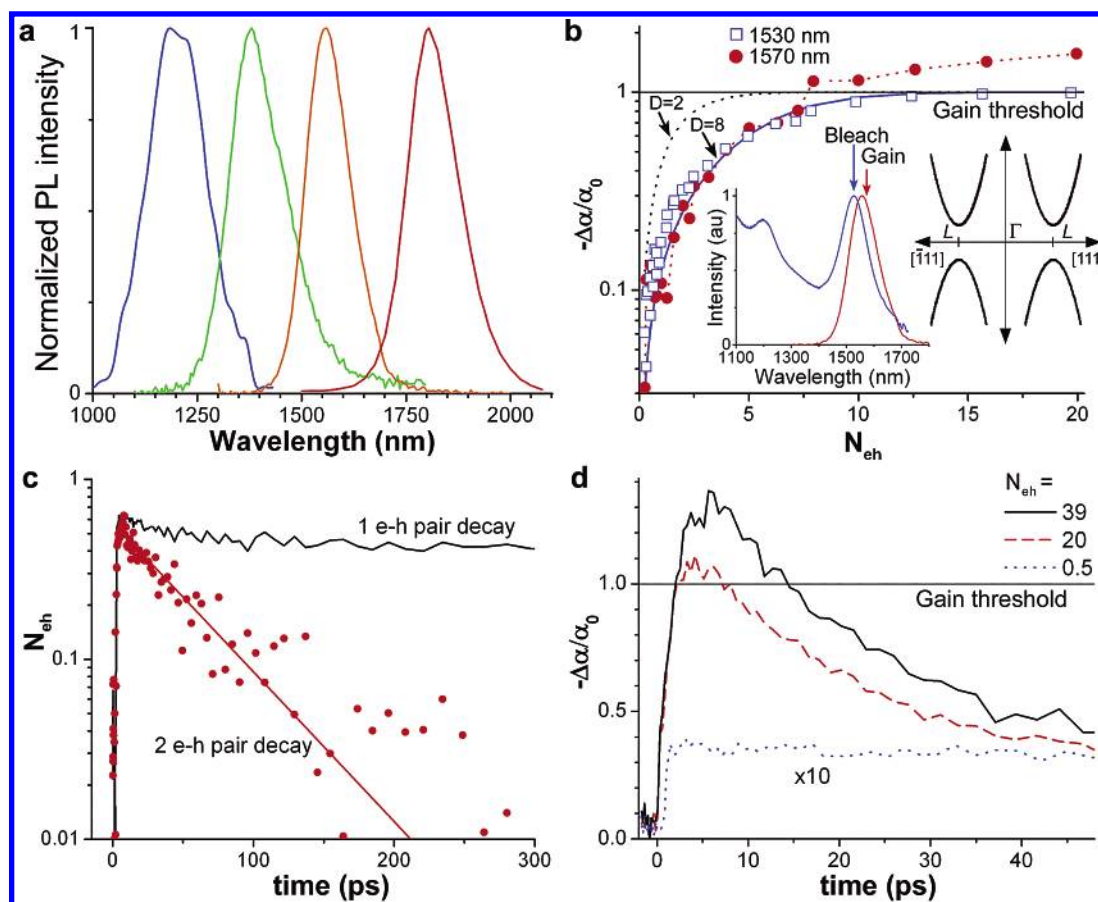


Figure 1. Optical properties of PbSe NC/hexane solutions. (a) The emission energies of PbSe NCs are size-tunable through the near-infrared with emission QYs of 70% (when compared to the IR laser dye IR26 and corrected for detector and diffraction grating efficiencies). (b) The pump-power dependent bleaching behavior of the A_1 band-edge absorption maximum (1530 nm) of PbSe NCs in hexane (squares) is closely reproduced by the Poisson distribution for NC populations in the case of the 8-fold degeneracy ($D = 8$) of states involved in the A_1 transition (solid line); this behavior differs significantly from that observed in the case of the 2-fold degeneracy ($D = 2$) (black dotted line) typical, e.g., for CdSe NCs.¹⁹ The 4 equivalent band minima at L points of the Brillouin zone, which give rise to this 8-fold degeneracy, are shown schematically (inset). The pump-dependent bleaching at 1570 nm (circles) (~ 15 nm red-shifted from the PL band maximum) indicates a transition to optical gain ($-\Delta\alpha/\alpha > 1$) for excitation densities > 8 e-h pairs/NC. (c) The high efficiency of Auger recombination is indicated by a direct comparison of the biexciton (circles) and single exciton (black line) decays. The biexciton decay is characterized by ~ 50 ps time constant, which is orders of magnitude faster than that for single excitons. (d) Highly efficient Auger recombination leads to the acceleration of the bleaching/gain decay (measured at 1570 nm) with increasing pump level. The gain lifetime measured at excitation densities corresponding to gain saturation (solid line) is ~ 10 ps.

an organometallic route⁸ that show $\sim 5\%$ size dispersion and $\sim 70\%$ PL QY in hexane solutions. To detect optical gain and to monitor its dynamics, we use a transient absorption (TA) experiment in which the sample is excited by 50 fs, 1.55 eV pulses from an amplified Ti-sapphire laser, and the absorption change, $\Delta\alpha$, within the photoexcited spot is probed by variably delayed, 100 fs pulses from a tunable IR optical parametric amplifier. Optical gain corresponds to the situation for which the absorption bleaching is greater than the ground-state absorption, α_0 , and hence that the absorption of the excited sample ($\alpha = \alpha_0 - |\Delta\alpha|$) is negative. As a measure of excitation densities, we use an average number of e-h pairs per NC, N_{eh} , generated by the pump pulse.

To evaluate the degeneracy of the lowest quantized levels in PbSe NCs and to estimate the “theoretical” gain threshold, we perform pump-induced absorption saturation measurements at the position of the band-edge absorption maximum (A_1). In Figure 1b, we compare the results of these measurements with saturation curves calculated for 2- and 8-fold degenerate states assuming the Poisson distribution of NC populations.¹⁹ This comparison indicates that the degeneracy of the lowest NC levels is indeed 8 (as expected from the analysis above), suggesting that the gain threshold is 4 e-h pairs per NC. Further, this result shows that optical gain in PbSe NCs originates from high-order

multiexcitonic states ($N_{eh} \geq 5$), which is in sharp contrast to CdSe NCs, for which the band-edge optical gain is dominated by well-defined biexcitonic ($N_{eh} = 2$) states (as a result of the 2-fold degeneracy of the lowest quantized levels).¹⁸ Therefore, exciton-exciton interactions are expected to have a much stronger effect on the lasing performance of PbSe NCs in comparison with CdSe NCs via a strong influence on gain spectral and dynamical characteristics.

By monitoring TA signals below the A_1 absorption peak, we observe a gradual increase in $|\Delta\alpha|/\alpha_0$ with decreasing probe photon energy until it crosses unity, indicating a transition to optical gain (Figure 1b). Pump-dependent measurements of $|\Delta\alpha|$ (circles) at the gain spectral maximum (1570 nm) indicate that the gain threshold occurs at $N_{eh} \sim 8$, which is twice as high as the theoretical threshold, likely because of a competing contribution from excited state absorption as was previously observed for solutions of CdSe NCs.²⁰ However, despite being high in terms of the number of e-h pairs per NC, because of relatively large absorption cross sections, the “practical” threshold pump fluences for PbSe NCs are comparable to those for CdSe NCs and are ~ 0.1 – 1 mJ cm⁻² per pulse. Furthermore, from the saturated gain magnitude (Figure 1b), we estimate that the gain cross section is $\sim 2 \times 10^{-15}$ cm², which is more than an order of magnitude greater than in CdSe NCs.³

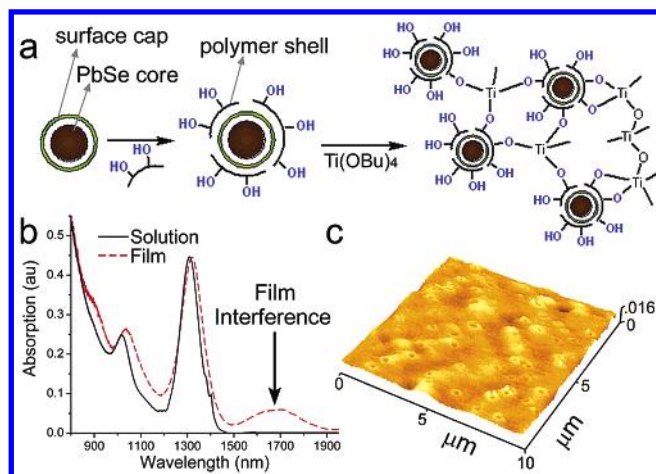


Figure 2. Sol-gel/NC synthetic route. (a) NCs are mixed with an amphiphilic polymer, which interacts with the NC surface and its capping ligands, forming a complex. The hydrophilic COOH groups (for clarity, only the OH reactive site of the COOH functionality is shown schematically) found on the exterior of this complex serve as the reactive sites through which the NCs are incorporated into the titania sol-gel matrix. (b) This chemistry, which can be generalized to other materials, allows the desirable optical properties of the NCs to be maintained when cast as high quality optical films, as can be seen in the reproducible absorption spectra of NCs before and after incorporation into the sol-gel film. (c) An atomic force microscopy image shows the high quality of the PbSe NC/sol-gel film with a height nonuniformity of <6 nm (much less than λ_{PL}).

To evaluate the role of multiexciton Auger recombination, we monitor pump-intensity dependent TA dynamics at both the A_1 absorption maximum (Figure 1c) and the gain band maximum (Figure 1d). Comparison of single e-h pair (exciton) and two e-h pair (biexciton) decays extracted from the A_1 bleaching dynamics¹¹ indicates that multiparticle interactions lead to a dramatic shortening of the biexciton lifetime ($\tau_2 \approx 50$ ps) compared to the single exciton lifetime. Strong multiparticle interactions directly affect optical gain dynamics (Figure 1d). At a low pump fluence ($N_{eh} < 1$), the $\Delta\alpha$ decay within the gain band is slow (consistent with single-exciton dynamics in Figure 1c), but it accelerates dramatically at pump fluences above the gain threshold for which nonradiative Auger recombination governs the decay of photoexcited carriers. The gain lifetime is ~ 10 ps at pump powers corresponding to gain saturation. Although quite short, this time is comparable to that observed in CdSe NCs.

The above results indicate that despite the fact that the physics of PbSe NCs seems to be unfavorable for optical gain applications, the measured optical gain parameters (gain threshold, cross section, and lifetime) are comparable or even superior to those in CdSe NCs. This observation indicates that previous failures in achieving ASE in lead-salt NCs have not been due to intrinsic “physical” reasons but were likely a result of insufficient material quality.

Two material parameters important for ASE performance are the quality of NC surface passivation and the concentration of NCs in the matrix/solvent. A sufficiently high degree of surface passivation is required to keep photoexcited carriers in the “gain-active” quantized states without being trapped at the surface for at least as long as the intrinsic, Auger-recombination-limited optical gain lifetime.¹⁸ On the other hand, high NC volume fractions (practical threshold is a few percent⁶) are required to produce a fast buildup of the stimulated emission that “beats” the Auger decay. One approach that satisfies both conditions is the self-assembly of NCs into close packed solids.³ Such solids maintain the high QYs achieved in solutions and also provide

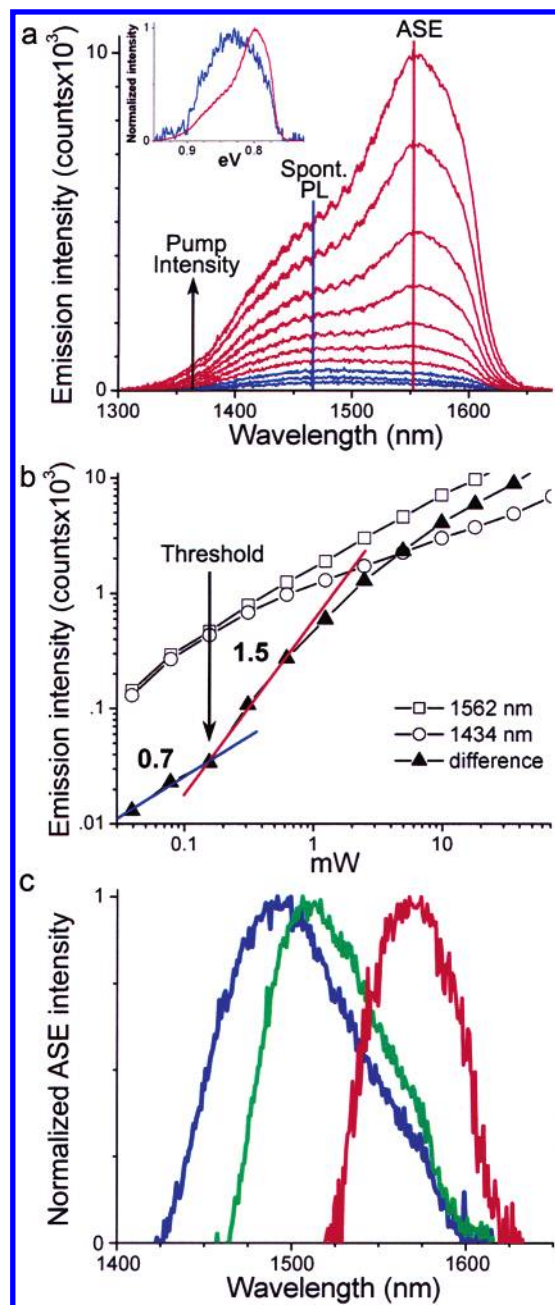


Figure 3. Amplified spontaneous emission in PbSe NCs. (a) Development of a spectrally narrowed ASE band at 1555 nm is observed as a function of pump power (100 Hz pump laser repetition rate) for a NC/sol-gel composite at $T = 80$ K. Comparison of normalized emission spectra produced using low (blue) and high (red) pump intensities (inset), which are dominated by spontaneous PL and ASE, respectively, shows the ASE as a spectrally narrowed, red-shifted band. The high-frequency modulation present in the spectra is an etalon artifact associated with the array detector. (b) Growth of the ASE band is observed to be superlinear following subtraction of the strong spontaneous PL background with a clear threshold of ~ 0.2 mW (linear fit slopes below and above threshold on the log-log plot are indicated). Growth of the spontaneous PL band exhibits sublinear power dependence due to the saturation of the population of the lowest quantized states as indicated by absorption saturation results in Figure 1b. (c) Extracted ASE bands (spontaneous PL subtracted) from multiple samples exhibit size tunability over a range of ~ 1425 – 1625 nm.

very high NC densities ($>20\%$ volume fractions), well above what is required to produce ASE.

However, our experiments with self-assembled PbSe NC films indicate that because of a relatively weak binding of capping molecules to the PbSe NC surfaces, these films rapidly degrade

under the intense laser illumination and do not allow realization of the ASE regime. To improve the stability of PbSe NCs in the solid-state form, we have developed a new procedure for incorporating NCs into transparent titania sol–gel matrixes. Because the surface chemistry of the PbSe NCs is different from the behavior of CdSe NCs, the previously reported routes to CdSe–titania nanocomposites^{5,6} that involved ligand surface exchange are not directly applicable to the PbSe NCs. Here, we use an amphiphilic polymer to complex the PbSe NCs that bypasses the surface exchange and renders the NCs alcohol-soluble.²¹ Though some of the hydrophilic COOH moieties on the polymer can bind to the NC surface, others will be found along the periphery of the NC–polymer complex, providing the reactive sites that allow the NCs to be directly tethered to the titania network (Figure 2a). As illustrated in Figure 2b, the absorption spectrum of PbSe NCs after incorporation into the titania matrix maintains the same sharp features as the original solution, indicating a high monodispersity of NCs in the solid-state form. Further, via combined optical and profilometry measurements, we infer very high NC filling factors ($\sim 15\%$), which are well above the critical density required for the development of ASE.

For ASE studies, we fabricate high optical quality sol–gel/NC films ($\sim 1\text{--}2\ \mu\text{m}$ thickness) on quartz slides by spin-coating (planar waveguide configuration). The films are pumped with a laser beam focused into a narrow stripe of approximately 1 cm length. To facilitate the development of ASE we use uncompressed, 200 ps pulses from an amplified Ti-sapphire laser, which allow us to extend the duration of the optical gain beyond its “natural” Auger-recombination-limited lifetime. As the pump level is gradually increased, we first observe a spectrally uniform growth of the spontaneous PL band (maximum at 1490 nm) with an initial linear increase followed by saturation due to the transition to the Auger recombination regime. At higher pump levels, a new band rapidly grows on the red side of the spontaneous PL (1555 nm). Following the subtraction of the background resulting from the “saturated” spontaneous emission, this new band shows a well-defined threshold ($\sim 0.2\ \text{mW}$) and a clear superlinear growth; both of these observations are signatures of the ASE regime. The spectral width of the extracted ASE band (Figure 3) is significantly narrower (by a factor of 3.2) than the width of the spontaneous emission band and does not show significant changes with increasing pump level (similar behavior is observed in CdSe NCs²²), which is likely due to NC heterogeneity in the sample. Control experiments performed on both dilute solutions and low-filling factor ($< 3\text{--}5\%$) films do not show the 1555 nm band, indicating that it is not due to “intra-NC” nonlinear effects, such as multiexciton recombination.²³ Further, the ASE mechanism is confirmed by the fact that in pump dependent measurements on high-filling factor samples, the 1555 nm emission only develops at sufficiently long stripe lengths, which is consistent with a strong (exponential) dependence of the emission intensity on the amplification length expected for the ASE regime. We have observed ASE for multiple sol–gel/NC films at both liquid nitrogen and room temperatures; the room-temperature threshold is a factor of 2 higher than at cryogenic temperatures because of a decrease in film optical quality due to thermal effects.

“Active” solid-state PbSe NC nanocomposites demonstrated in this Letter have significant technological potential. The gain spectrum of sol–gel glasses activated with 4.8 nm diameter NCs

extends from 1450 to 1550 nm, which covers the $1.5\ \mu\text{m}$ telecommunications window. Compared to Er-doped fibers that are typically used for light amplification in this spectral range (20–30 nm bandwidth and $0.01\ \text{cm}^{-1}$ gain), these new NC-activated glasses, for just a single size, offer significantly greater bandwidth and higher gain magnitude (100–150 nm and $\sim 100\ \text{cm}^{-1}$). The large refractive index (1.8–1.9) and high optical quality of sol–gel films allow one to directly use them as planar optical waveguides. The NC nanocomposites can also be easily processed into structures of other geometries (e.g., uniform cylindrical or structured photonic fibers) or combined with feedback elements (e.g., distributed feedback gratings) to enter the lasing regime.

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