

Room-temperature amplified spontaneous emission at 1300 nm in solution-processed PbS quantum-dot films

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We report room-temperature amplified spontaneous emission and spectral narrowing at infrared wavelengths in solution-processed films made up of PbS quantum-dot nanocrystals. The results are relevant to optical amplification and lasing integrated upon a variety of substrates. The active optical medium operates at room temperature without any additional matrix material, providing an optical gain of 260 cm^{-1} and a pump threshold of 1 mJ/cm^{-2} . Nanocrystals synthesized in an aqueous solution and stabilized by use of short ligands result in high quantum-dot volume fractions in solid films and in a redshift emission relative to absorption.

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Integration of light emitters, detectors, modulators, and signal-processing elements on a single chip would combine electronic-based computing with optical- and radio-frequency-based communications, as follows. An integration-enabling material should be readily deposited onto a range of substrates through processing out of solution rather than by high-temperature epitaxy, will produce light efficiently, and will provide optical gain for lasing at communications wavelengths (1300–1600 nm). It will perform at and above room temperature at which such chips will necessarily operate.

Recent related progress includes electroluminescence in PbS nanocrystals (NCs) in a polymer matrix,¹ low-temperature (80 K) spectral narrowing and optical gain in PbSe NCs in an inorganic sol-gel titania matrix,² and room-temperature optical gain in PbS NCs in a glass matrix.³ Although optical gain in PbS quantum-dot-doped glasses has been reported,³ amplified spontaneous emission (ASE) was not demonstrated: Low quantum-dot volume fraction, poor surface passivation, and a large size distribution are the major impediments. An approach based instead on solution-processed NCs is highly desirable: It will permit the combination of quantum size-effect tunability, offer control over surfaces and their resultant electronic and chemical interactions, and facilitate processing onto a diversity of substrates—rigid or flexible; smooth

or rough; flat or curved; inorganic; organic, including biological; crystalline or amorphous; and conducting, semiconducting, or insulating. In summary, a widely integrable lasing material requires the full combination of infrared amplification, solution-based fabrication, and room-temperature operation.

We demonstrate herein room-temperature observation of infrared ASE and spectral narrowing in solution-processed quantum-dot NC films.

Achieving room-temperature infrared ASE is challenging because of the major parasitic effect of fast nonradiative Auger recombination, which increases exponentially with emission wavelength and temperature. Population inversion for optical gain is particularly difficult to achieve when absorption and photoluminescence peaks overlap, as in uncoupled quantum dots passivated by long insulating organic (tri-*n*-octylphosphine oxide) and oleate⁴ ligands.

We separated absorption and luminescence by using short ligands for interdot coupling and redshifting emission relative to absorption. We prepared PbS NCs⁵ in aqueous solutions, using thiols as stabilizing agents. The combination of thioglycerol and dithioglycerol as capping agents resulted in NCs of the best quality. A solution containing $\text{Pb}(\text{CH}_3\text{COO})_2$, thioglycerol, and dithioglycerol was adjusted to pH 11 by the addition of triethylamine. The synthesis was performed at room temperature without NC

aggregation. A solution of sodium sulfide was then added. The molar ratio Pb:S was varied from 1:0.3 to 1:0.7. The typical concentration of NCs in solution was 3.5 mg/ml. The system was purified by dialysis against an aqueous triethylamine solution at pH 10. Figures 1(a) and 1(b) show x-ray diffraction patterns and a high-resolution TEM image of PbS NCs, respectively, revealing high crystal quality. The x-ray diffraction pattern matches the reference powder diffraction pattern of PbS. The crystal structure derived from the positions of the wide-range diffraction peaks points to cubic PbS. The average NC size was measured with a direct convolution profile fitting program to be 3–4 nm, confirmed by image analysis of multiple-transmission electron micrographs. Quantum-size-effect tuning is manifest in photoluminescence (PL) spectra of NCs in aqueous solution [Fig. 1(c)].

We prepared pure 2- μm -thick NC films by drop casting a NC solution onto a quartz substrate. No host material was employed. The solid volume fraction of PbS NCs stabilized by use of the short (0.45-nm-long) ligand molecules is 28–35%. As optical gain g^m is proportional to the concentration of nanocrystals N_{NC} , as $g^m \sim N_{\text{NC}}/[\tau_{\text{NC}}(\Delta E)_{\text{inhom}}]$, where $(\Delta E)_{\text{inhom}}$ is the inhomogeneous spectral breadth and τ_{NC} is the spontaneous lifetime, a high volume fraction is desired for ASE.⁶

Figure 1(d) presents absorption and luminescence spectra of a PbS NC film. The redshift of luminescence relative to absorption results from the merging of NC energy levels, given close packing aided by short ligands. This three-dimensional superlattice effect is also responsible for the less-pronounced excitonic peak, manifested as a defined shoulder in the absorption spectrum.

We present in Fig. 2 evidence of room-temperature optical gain through the observation of ASE. We used the variable stripe length (VSL) technique⁷ depicted in Fig. 2(a). The thin-film sample was optically excited by an amplified Ti:sapphire laser (~ 1.7 ps; $\lambda_{\text{exc}} = 800$ nm; pump fluence, 0.06–20 mJ/cm^2). The laser beam was focused by a cylindrical lens to form a narrow (~ 25 - μm) stripe on the sample's surface. Length l of the stripe was controlled with a variable slit. Emission from the sample was collected from the edge into a Peltier-cooled PbS detector. A grating monochromator and a liquid-nitrogen-cooled Ge detector were used for spectral measurements. Thus the VSL method is based on measurement of the emission intensity I_{ASE} from the sample edge as a function of length l of the excited region and can be described by a one-dimensional amplifier model⁶:

$$I_{\text{ASE}} = \frac{I_S}{g} (e^{gl} - 1), \quad (1)$$

where I_S is a constant that is proportional to the spontaneous emission intensity and g is the modal (i.e., net) optical gain.

Particular care was applied to extract accurate optical gain values from VSL measurements. The central part of the Gaussian laser beam with 8-mm-diameter

full width at half-maximum was focused by a cylindrical lens and used for excitation. A knife scan was performed to ensure uniform intensity distribution. The excitation fluence was constant over the entire l range. To prevent Fresnel diffraction of the pump

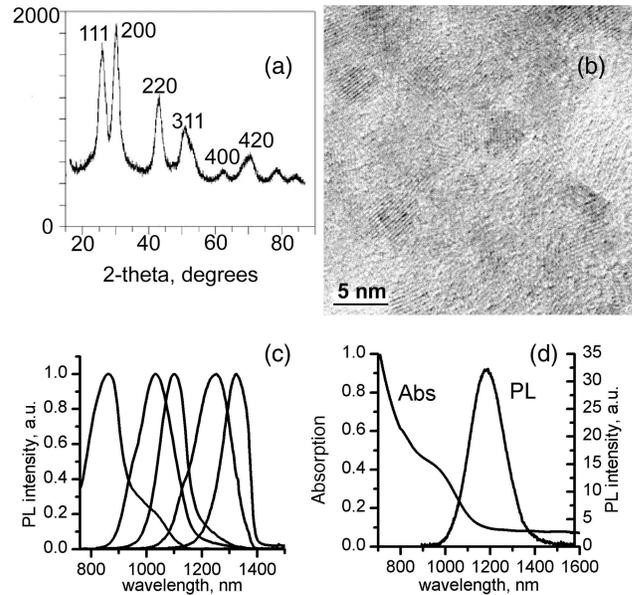


Fig. 1. (a) X-ray diffraction patterns of PbS NCs, (b) high-resolution TEM image of PbS nanoparticles, (c) PL spectra of PbS in an aqueous solution with various NC diameters from 3 to 5 nm, (d) absorption and PL spectra of a pure PbS NC film.

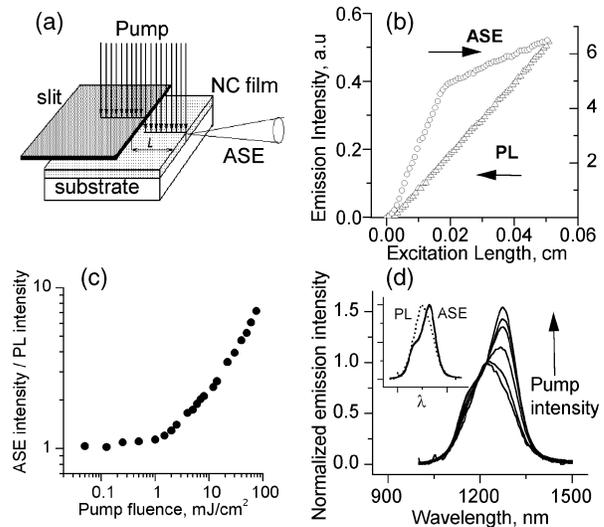


Fig. 2. (a) Experimental configuration for the VSL method. (b) Emission intensity as a function of stripe length for low (triangles) and high (circles) pump intensities. (c) Growth of ASE compared with growth of spontaneous PL intensity with a threshold of ~ 1 mJ/cm^2 . (d) Evolution of the emission spectra as a function of pump intensity normalized at the point of the PL peak position for 150- μm excitation length. Inset, Normalized emission spectra for low and high pump intensities (PL and ASE, respectively). The threshold behavior and spectral narrowing of (c) and (d) were obtained for a stripe length of 150 μm , corresponding to the maximum gain length observed in the sample.

beam at the slit edge we positioned the variable slit directly upon the sample's surface. The collection optics was carefully chosen to provide constant coupling efficiency over excitation length l . Experimental difficulties and the applicability of the VSL method to optical gain measurements in planar waveguides are reviewed in detail elsewhere.⁸ All possible experimental artifacts have one distinct feature: Their artificial VSL pseudosignature is independent of excitation intensity. We therefore performed our measurements over a wide range of pump intensities: Emission intensity versus stripe length l for low (triangles) and high (circles) pump intensities is presented in Fig. 2(b). The ASE length is limited by the optical gain lifetime. Growth of ASE has a defined threshold of 1 mJ/cm^2 [Fig. 2(c)]. We estimate⁷ an optical net modal gain coefficient g of $260 \pm 20 \text{ cm}^{-1}$.

Figure 1(d) shows the spectrum of light emission from the side of the NC film as pump power is increased. Beyond a pump power of 1 mJ/cm^2 , a new, narrower spectral band emerges that is redshifted relative to the PL peak. The threshold behavior [Fig. 2(c)] of the intensity in this band is observed for the $150\text{-}\mu\text{m}$ stripe length and is characteristic of ASE. Partial overlap of absorption and luminescence bands is responsible for the red shift of the optical gain band relative to the PL peak.

We have shown what is to our knowledge the first evidence of room-temperature amplified spontaneous emission and spectral narrowing at infrared wavelengths in aqueous-solution-processed quantum-dot NC films. These NCs are prepared at room temperature by a one-stage process with no need for organic solvents, encapsulation, or size-selective precipitation. The results are relevant to optical amplification and lasing integrated upon a variety of substrates. The

active optical medium operates at room temperature without any additional matrix material, providing an optical gain of 260 cm^{-1} and a pump threshold of 1 mJ/cm^2 . NCs synthesized in aqueous solution and stabilized by use of short ligands result in high quantum-dot volume fractions in solid films and in a three-dimensional superlattice effect that redshifts emission relative to absorption.

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