Lasing from colloidal InP/ZnS quantum dots

Shuai Gao,[1,2] Chunfeng Zhang,[2] Yanjun Liu,[2] Huaipeng Su,[1,2] Lai Wei,[2] Tony Huang,[2] Nicholas Dellas,[3] Shuzhen Shang,[4] Suzanne E. Mohney,[3] Jingkang Wang,[1,5] and Jian Xu[2,4,*]

[1] *School of Chemical Engineering and Technology, State Key Laboratory of Chemical Engineering, Tianjin University, Tianjin 300072, China*

[2] *Department of Engineering Science and Mechanics, The Pennsylvania State University, University Park, PA 16802, USA*

[3] *Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA*

[4] *Optical & Electronic information Engineering College, University of Shanghai for Science and Technology, No. 516, JunGong Road, Shanghai, China*

[5] *wangjkch@tju.edu.cn*

**jianxu@engr.psu.edu;*

Abstract: High-quality InP/ZnS core-shell nanocrystal quantum dots (NQDs) were synthesized as a heavy-metal-free alternative to the gain media of cadmium-based colloidal nanoparticles. Upon UV excitation, amplified spontaneous emission (ASE) and optical gain were observed, for the first time, in close-packed InP/ZnS core-shell NQDs. The ASE wavelength can be selected by tailoring the nanocrystal size over a broad range of the spectrum. Moreover, the optical gain profile of InP/ZnS NQDs was matched to the second order feedback of holographic polymer-dispersed liquid crystal gratings, leading to the very first demonstration of an optically-pumped, nanocrystal laser based on InP/ZnS core-shell NQDs.

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Zero-dimensional colloidal semiconductors, or nanocrystal quantum dots (NQDs), have been a unique family of optical gain media that holds several potential advantages, including temperature insensitivity, low lasing threshold, high efficiency and broad wavelength coverage [1–4]. Amplified spontaneous emission (ASE) and lasing of Cd(S,Se,Te) and Pb(S,Se) NQDs have been achieved at room temperature with a variety of photonic structures including microrings, microspheres, photonic crystals, and distributed feedback resonators [5–10]. Nevertheless, the toxicity of cadmium and lead constituents in those NQDs poses a barrier to their practical applications due to environmental concerns. Among many II-VI and III-V colloidal compounds, InP NQDs are emerging as a promising type of photostable fluorophores that offer comparable or even broader emission wavelength coverage than cadmium-based nanoparticles, and, at the same time, eliminate the intrinsic toxicity. The distinctive properties of InP NQDs have motivated us to investigate the possibility of achieving ASE and lasing in this type of heavy-metal-free colloidal nanostructures.

Colloidal InP NQDs has only been studied with photoluminescence (PL) and time-resolved PL characterization to date [11,12]. While there have been a few reports of lasing emission from self-assembled InP quantum dots that were epitaxially grown and embedded in (In,Ga,Al)(As,P) layers [13–15], ASE and lasing phenomena in colloidal InP NQDs have yet to be observed. In comparison with the epitaxially-grown, pyramid-shaped InP quantum dots of hundred of nanometers in dimensions, the chemically synthesized colloidal InP NQDs exhibit spherical shapes with much smaller dimensions (2-10nm in diameters), which renders them highly efficient for excitonic emission and broader tunability of bandgap energy and emission wavelengths. The missing stimulated emission in InP NQDs to date can be largely attributed to the poor surface passivation of the III-V colloidal compound, which leads to the high rates of surface trapping and, consequently, to the high nonradiative carrier losses [16].

Toward this end, we have modified the existing synthetic technique for the nanoparticle growth such that the InP cores can be more effectively passivated by ZnS shells, which is manifested by the high luminescence efficiency, size-tunable color, as well as the negligible degradation of NQDs upon their long-time exposure in the ambient environment. Furthermore, we report in this communication the very first observation of room-temperature ASE and lasing behavior of InP-based colloidal quantum dots as a heavy-metal-free alternative to cadmium-based NQDs. InP/ZnS core/shell NQDs of variable sizes were fabricated into slab waveguides to produce ASE in green-, red-, and near-infrared (IR)-wavelengths. Time-resolved photoluminescence (TRPL) of the slab waveguide sample was recorded, suggesting a fast radiative recombination of tens of picoseconds for the stimulated emission. Finally, the optical gain profile of InP/ZnS NQDs was matched to the second order feedback wavelengths of the gratings that were holographically formed in polymer-dispersed

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liquid crystals (HPDLC), leading to the demonstration of an optically-pumped InP colloidal nanocrystal laser.

The NQDs employed in the present study have core-shell structures consisting of InP crystalline cores and ZnS shells, which were synthesized with an approach modified from a previously reported technique [17]. Nucleation of InP cores were accomplished in a non-coordinating solvent by injecting $P(TMS)_3$ to the $In(Ac)_3$ in the presence of fatty acid precursors at an elevated temperature (~178°C). The reaction temperature was lowered to ~168°C subsequently to allow the nuclei to grow into highly crystalline nanoparticles. By employing fatty amine precursors in the present work, the nucleation temperature of InP cores has been substantially augmented from early reported values, which allows for the growth of high-quality, nearly monodisperse InP nanoparticles under favorable growth conditions. For shell formation, the technique of successive ion layer adhesion and reaction (SILAR) method [18] was applied to overcoating InP cores: purified cores were dispersed in octadecene (ODE) and heated to ~150°C under nitrogen, wherein zinc and sulfur precursors, of precisely determined doses, were consecutively injected at the temperature of 150°C and 210°C, respectively. The reaction solution was then kept at ~150°C for 30 minutes to complete the growth of monolayer-thickness ZnS shells over InP cores, and the above procedure was cycled to grow, layer by layer, thicker shells in the core-shell nanocrystal structure. The NQDs synthesized in the present work were overcoated with two monolayers of shells.

During the nanocrystal synthesis, the diameter of the NQDs was tailored between 3~7 nm by varying the amount of the fatty acid in the reaction solution, which, in turn, leads to the capability of tuning NQD emission and excitonic absorption over the wavelength range of 530-700nm, as illustrated in Fig. 1(a). The quantum yield (QY) of the as-prepared core-shell InP/ZnS NQDs was measured to be ≥40% for all the nanocrystal sizes achieved in our work. The epitaxial growth of the core–shell structures was verified by transmission electron microscopy as shown in Fig. 1(b). Well-resolved lattice fringes were continuous throughout the entire quantum dot, indicative of the epitaxial nature of the ZnS shell growth over the InP cores in spite of the lattice mismatch between the respective lattices (~7%) . Measurements of the NQD size by high-angle annular dark field scanning TEM (HAADF STEM) was also performed to verify the sizes measured by regular bright field TEM. In this case, the NQD diameter measured by HAADF STEM were the same as the diameter measured from the lattice fringes in the bright field TEM images. This indicates the entire NQD is single crystalline with the shell grown epitaxially, because image contrast in the HAADF STEM technique is primarily determined by atomic number. Therefore, any amorphous shell that may be present would show up by this technique as opposed to blending in with the amorphous C film the QDs are imaged on, which can occur in high-resolution bright field TEM images where phase contrast can dominate.

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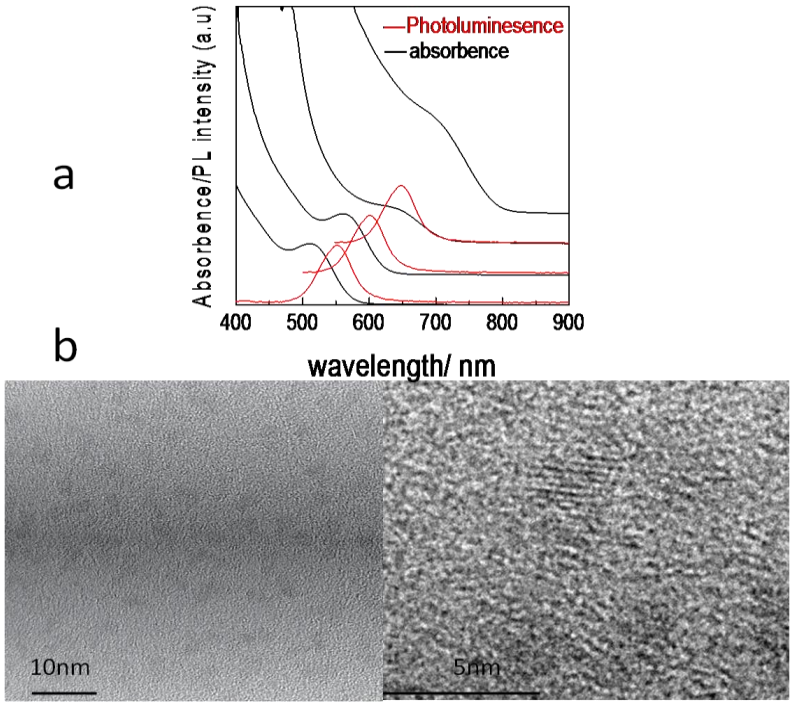

Fig. 1. (a) Absorption and PL Characterization of InP/ZnS core/shell NQDs of different size and (b) low (left) and high (right) magnification transmission electron microscopic images of the red-emitting NQDs

ASE was observed in the close-packed, solid-state films of the InP/ZnS core/shell NQDs that were spin-cast deposited over glass substrates from the hexane solution. By controlling the spin speed, the thickness of the NQD film can be precisely adjusted to ~500nm, yielding the slab waveguide structure that is necessary for ASE generation. These films were surface-excited with femtosecond laser pulses at $\lambda \approx 400$nm (Libra, 1 kHz, 80 fs, Coherent, Inc.) via a cylindrical lens. Light emission from the NQD slab waveguides was collected with a spectrometer equipped with photomultiplier tubes (PMT) (SpectroPro 500i, ~ 0.05 nm spectral resolution).

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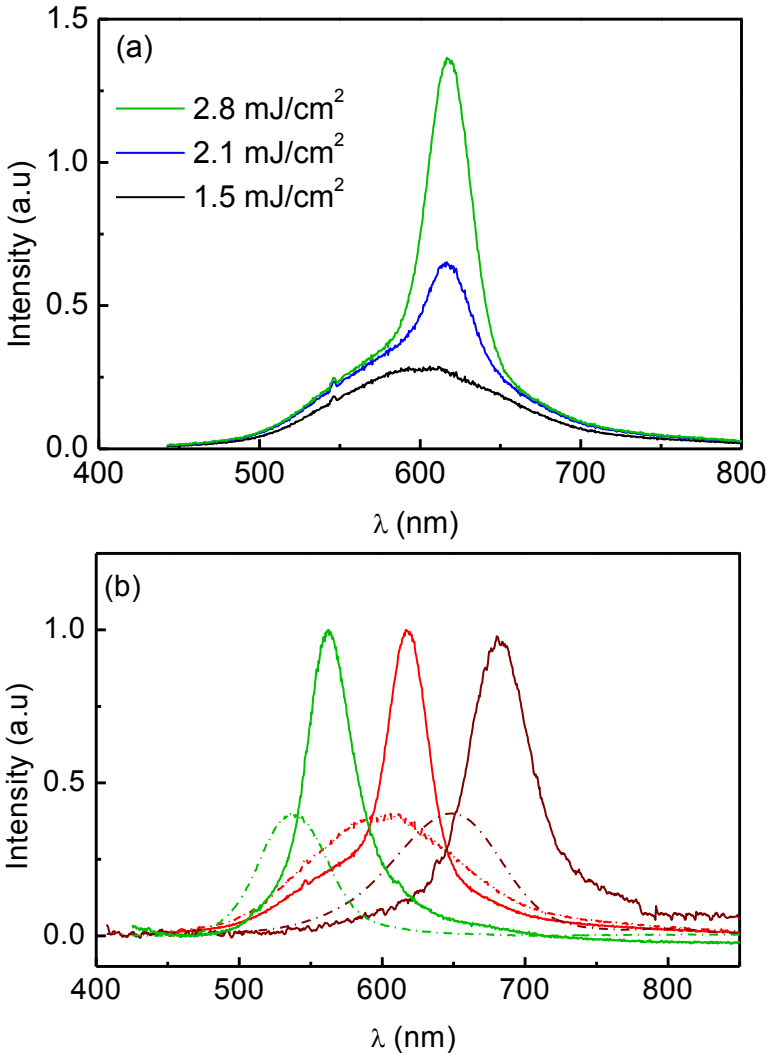

Fig. 2. (a) Emission spectra of InP/ZnS core/shell NQDs at different excitation fluence; (b) spontaneous emission and ASE from the NQDs emitting at green, red, and near-IR wavelengths.

Figure 2(a) shows the room-temperature ASE spectra of a NQD waveguide pumped at different energy densities. The size of the InP/ZnS core/shell NQDs comprising the waveguide is ~4.5nm. At a relatively low excitation energy (~1.5 mJ/cm^2), spontaneous emission of the NQDs dominates the waveguide output with a maximum at ~610 nm and a full-width-at-half-maximum (FWHM) bandwidth of ~70 nm. When the excitation fluence reaches the threshold value of ~2mJ/cm^2, there is a dramatic collapse of the emission bandwidth down to less than 20 nm, with a red-shift of the peak emission to ~616 nm. The observed threshold behavior provides unambiguous evidence of the presence of stimulated emission in the optically-pumped InP/ZnS core/shell NQDs, suggesting that net optical gain can be achieved for potential lasing action with these cadmium-free colloidal NQDs. In addition, size-tunable ASE emission has been demonstrated with InP/ZnS core/shell NQDs of different diameters. The spectra in Fig. 2(b) plot the spontaneous emission and ASE from NQDs with 3nm, 4nm, and 6nm diameters, and reveal the broad coverage of lasing wavelengths with the novel gain media of InP/ZnS NQDs.

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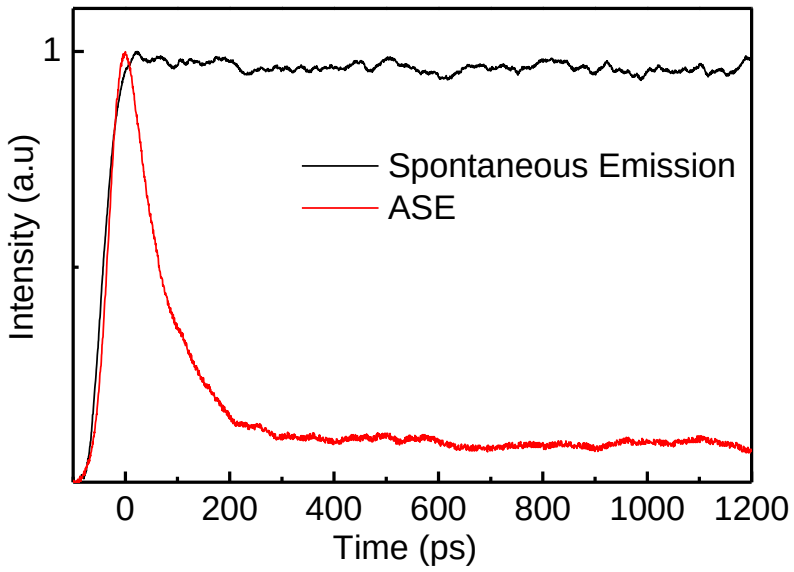

Fig. 3. Time-resolved PL traces with excitation fluence below (spontaneous emission) and above (ASE) the lasing threshold.

In the present work, the presence of stimulated emission in InP/ZnS core-shell NQDs was further confirmed with TRPL characterization of the nanocrystals in the slab waveguide sample. In the transient lifetime measurement, femtosecond laser pulses, 80fs in pulse duration, and centered at λ≈400nm-wavelength, were used for excitation. The fast decays of the NQD stimulated emission were characterized with the Kerr shutter technique. A CS_2 liquid cell was used as the Kerr medium with a temporal resolution of ~1 picosecond (ps). The measurement result (Fig. 3) uncovers a much faster recombination for the stimulated emission than that for the spontaneous emission in InP/ZnS core-shell NQDs: while the long fluorescence lifetime of the NQDs is far beyond the picosecond-time scale, a faster decay process, with an exponential fitting lifetime of ~70 ps, dominates the transient profile when the excitation energy rises above the ASE threshold. Previous studies of CdSe NQDs by us and groups elsewhere have suggested that a fast nonradiative Auger recombination is present in the NQDs with a lifetime ranging from tens to hundreds of picoseconds. When stimulated emission takes place in the quantum dots, the radiative biexciton recombination is sufficiently fast to compete with the Auger relaxation to produce efficient radiation in the nanoparticles [4,8,9]. We have therefore postulated that a similar ultrafast recombination mechanism underlies the ASE process in the InP/ZnS core-shell NQDs under study. This speculation is also consistent with the observed red shift of the peak ASE wavelengths of the NQDs with respect to the maximum of the NQD spontaneous emission due to single-exciton recombination (Fig. 2(b)) [20,21].

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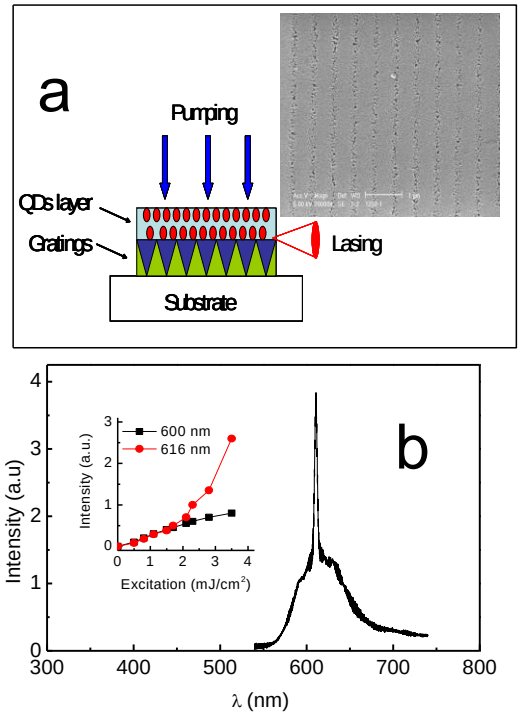

Fig. 4. (a) Schematic diagram of the nanocrystal DFB laser structure containing InP/ZnS core-shell NQDs and an underlying HPDLC grating. The inset shows the SEM image of the grating; (b) emission spectrum of the nanocrystal lasing peaked at λ≈616nm. The inset shows the emission intensities of NQDs as functions of the excitation fluence energy.

Finally, in order to demonstrate the lasing action in the cadmium-free nanocrystals, InP NQD-based distributed-feedback (DFB) laser structures were fabricated by spin-depositing NQD waveguides over HPDLC gratings, as illustrated in Fig. 4 (a). The gratings were holographically formed in polymer-dispersed liquid crystals through photo-initiated polymerization-induced phase separation, the details of which have been described elsewhere [19]. In brief, prepolymer syrup was sandwiched between two pieces of ITO glass and subject to the holographic exposure by placing the sample behind the base of a right angle prism. The exposure laser wavelength was 514.5 nm from an Ar^+ laser. The exposure intensity and time were 20 mW/cm^2 and 2 minutes, respectively. After exposure, the samples were further cured for 5 min by a mercury lamp. All the grating samples were 7 μm thick. The theoretical grating spacing was 0.57μm, which could be calculated from the geometry of the recording setup. This grating spacing was in good agreement with the SEM images as shown in inset of Fig. 4(a). The alternating polymer-rich and LC-rich lamella in the grating provides a high index modulation of 0.06, facilitating the lasing action with low threshold if a gain material is involved [19]. During the grating design, the refractive index of the NQD films was taken into account in order to match the Bragg condition of the gratings to the gain profile of the NQD waveguide.

For the lasing characterization, pulsed laser excitation (λ≈400nm, 80fs, 1KHz repetition rate) was focused to a stripe, 50μm in width, on the top surface of the grating-coupled waveguide of the NQD DFB laser using a cylindrical lens. The edge emission from the

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waveguide was coupled into a spectrometer and recorded with the PMT. Figure 4(b) shows the spectrum of the NQD lasing emission (λ = 616nm) when the excitation energy was greater than the threshold value. The inset in Fig. 4(b) plots the integrated emission intensities as functions of the excitation energy for two NQD DFB lasers containing InP/ZnS core-shell nanocrystals with 616nm and 600nm diameters, respectively. The threshold behavior of the optically pumped NQD lasing is clearly revealed in the plot with a threshold energy fluence ~2.0 mJ/cm^2.

In summary, we have observed, for the first time, amplified spontaneous emission and optical gain in close-packed InP/ZnS core-shell NQDs upon UV excitation. Moreover, the optical gain profile of InP/ZnS NQDs was matched to the second order feedback of holographic polymer-dispersed liquid crystal (H-PDLC) gratings, leading to the very first demonstration of an optically-pumped, nanocrystal laser based on these cadmium-free NQDs. The output color can be selected by tailoring the size of the InP-based nanocrystals as well as the corresponding grating periodicity.

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