

Nanocrystal Quantum Dots

From fundamental photophysics to multicolor lasing

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Semiconductor lasers are ubiquitous in modern society and play a key role in technologies ranging from CD players to optical telecommunications. Current-generation lasers have high power output and low lasing thresholds, are stable over a wide range of temperatures, and are cheap and easy to produce. Still, there is room for improvement. We are developing a new type of laser based on ultrasmall bits of semiconductor material called quantum dots (QDs). Consisting of only a few hundred to a few hundred thousand atoms, QDs bridge the gap between the solid state and single atoms, and hence these specks of matter exhibit a mix of solid-state and atomic properties. In our work, we concentrate on nanoparticles that are synthesized by colloidal chemistry, and therefore, they are often called colloidal or nanocrystal QDs (NQDs). Interestingly, the emission wavelength (that is, the emission color) of QDs depends on the dot size, and in the case of semiconductor nanocrystals, color can be controlled precisely through simple chemistry. We are therefore developing an altogether new type of color-selectable lasing medium.

Although this paper focuses on our NQD laser work, quantum dots are “bigger” than lasers. Because of their small dimensions and size-controlled electronic spectra, NQDs can be viewed as tunable artificial atoms with

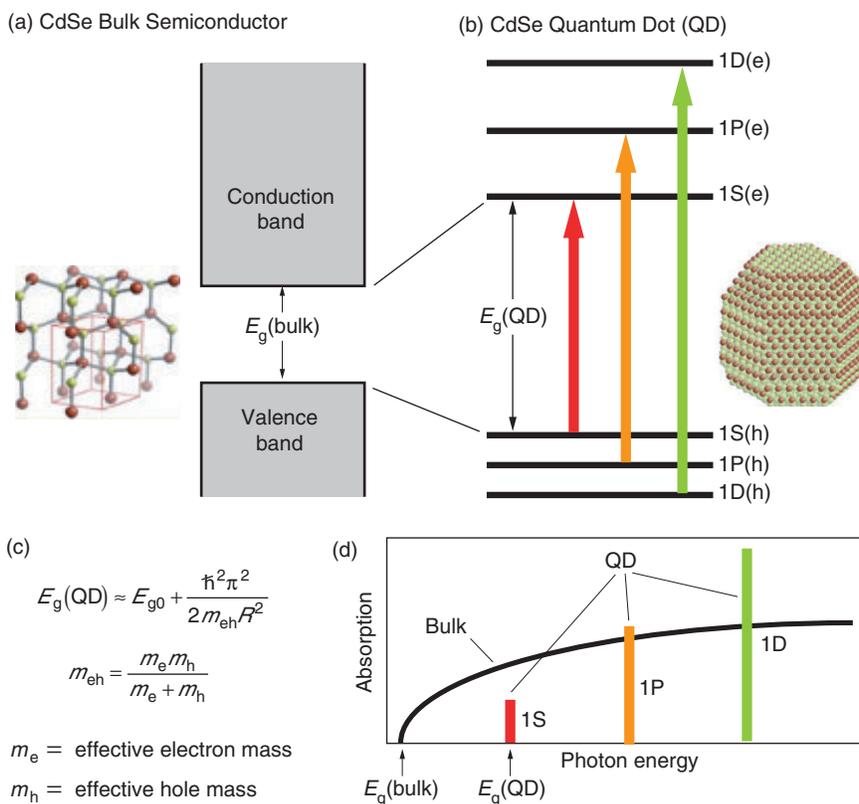


Figure 1. Quantum Dots (QDs)

(a) A bulk semiconductor such as CdSe has continuous conduction and valence energy bands separated by a “fixed” energy gap, $E_g(\text{bulk})$. Electrons normally occupy all states up to the edge of the valence band, whereas states in the conduction band are empty. (b) A QD is characterized by discrete atomic-like states with energies that are determined by the QD radius R . These well-separated QD states can be labeled with atomic-like notations, such as 1S, 1P, and 1D. (c) The expression for the size-dependence separation between the lowest electron and hole QD states— $E_g(\text{QD})$, the QD energy gap—was obtained with the spherical “quantum box” model. (d) This schematic represents the continuous absorption spectrum of a bulk semiconductor (black line) compared with a discrete absorption spectrum of a QD (colored bars).

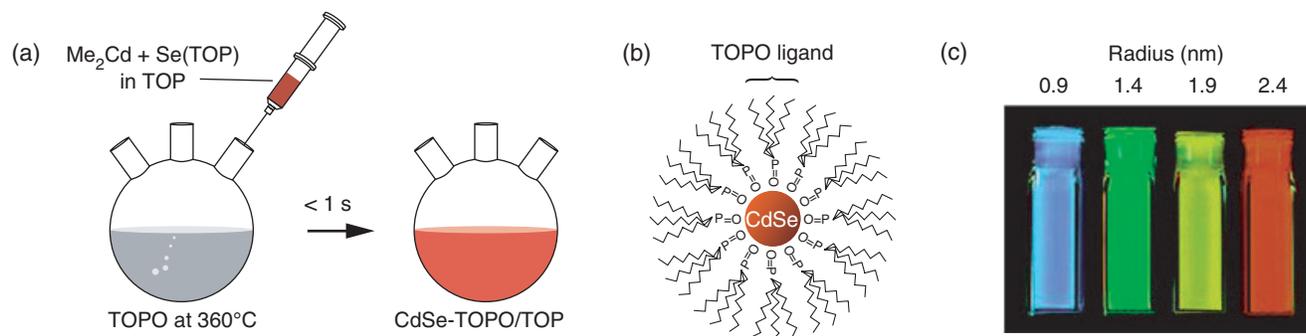


Figure 2. Nanocrystal Quantum Dots (NQDs)

(a) An organometallic method is used for the fabrication of highly monodisperse CdSe NQDs. Nucleation and subsequent growth of NQDs occurs after a quick injection of metal and chalcogenide precursors into the hot, strongly coordinating solvent—a mixture of trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO) in the case shown. After a fixed period, removing the heat source stops the reaction. As a result, NQDs of a particular size form. (b) The colloidal NQDs obtained by the method illustrated in (a) consist of an inorganic CdSe core capped with a layer of TOPO/TOP molecules. (c) Solutions of CdSe NQDs of different radii, under ultraviolet illumination, emit different colors because of the quantum size effect. A 2.4-nm-radius dot has an energy gap of about 2 eV and emits in the orange, whereas a dot of radius 0.9 nm has a gap of about 2.7 eV and emits a blue color.

properties that can be engineered to suit either the needs of a certain experiment or a specific technological application. When coated with a suitable, chemically active surface layer, NQDs can be coupled to each other or to different inorganic or organic entities and thus serve as useful optical tags. We can now chemically manipulate NQDs almost as well as standard molecules, and can assemble them into close-packed ordered or disordered arrays that mimic naturally occurring solids. Furthermore, because their dimensions, shapes, and surface properties can be manipulated with ease, NQDs are ideally suited to serve as nanoscale laboratories for studies of fundamental quantum mechanical effects.

The Quantum Size Effect and QDs

One of the defining features of a semiconductor is the energy gap separating the conduction and valence energy bands. The color of light emitted by the semiconductor material is determined by the width of the gap. In semiconductors of macroscopic sizes—bulk semiconductors—the gap

width is a fixed parameter determined by the material's identity.

The situation changes, however, in the case of nanoscale semiconductor particles with sizes smaller than about 10 nanometers. This size range corresponds to the regime of quantum confinement, for which the spatial extent of the electronic wave function is comparable with the dot size. As a result of these “geometrical” constraints, electrons “feel” the presence of the particle boundaries and respond to changes in particle size by adjusting their energy. This phenomenon is known as the quantum-size effect, and it plays a very important role in QDs.

In the first approximation, the quantum-size effect can be described by a simple “quantum box” model (Efros and Efros 1982), in which the electron motion is restricted in all three dimensions by impenetrable walls. For a spherical QD with radius R , this model predicts that a size-dependent contribution to the energy gap is simply proportional to $1/R^2$, implying that the gap increases as the QD size decreases. In addition, quantum confinement leads to a collapse of the continuous energy bands of a bulk material into discrete, atomic-like energy levels. The discrete structure

of energy states leads to a discrete absorption spectrum of QDs, which is in contrast to the continuous absorption spectrum of a bulk semiconductor (see Figure 1).

The NQDs discussed earlier are small quantum dots that are made by organometallic chemical methods and are composed of a semiconductor core capped with a layer of organic molecules (Murray et al. 1993). (See Figure 2.) The organic capping prevents uncontrolled growth and agglomeration of the nanoparticles. It also allows NQDs to be chemically manipulated as if they were large molecules, with solubility and chemical reactivity determined by the identity of the organic molecules. The capping also provides “electronic” passivation of NQDs; that is, it terminates dangling bonds that remain on the semiconductor's surface. As discussed below, the unterminated dangling bonds can affect the NQD's emission efficiency because they lead to a loss mechanism wherein electrons are rapidly trapped at the surface before they have a chance to emit a photon. Using colloidal chemical syntheses, one can prepare NQDs with nearly atomic precision; their diameters range from nanometers to tens of nanometers and

size dispersions as narrow as 5 percent. Because of the quantum-size effect, this ability to tune the NQD size translates into a means of controlling various NQD properties, such as emission and absorption wavelengths. The emission of cadmium-selenium (CdSe) NQDs, for example, can be tuned from deep red to blue by a reduction in the dot radius from 5 nanometers to 0.7 nanometer.

Nanocrystal Lasers: Advantages and Problems

Lasers made from bulk semiconductor materials have been used for several decades. (Laser fundamentals are described in Figure 3.) Although numerous advances were made throughout those years, laser performance improved dramatically with the introduction of so-called quantum well lasers, in which charge carriers—electrons and holes—were confined to move in a plane—that is, they were free to move in a two-dimensional (2-D) quantum well. Compared with bulk semiconductors, the quantum well has a higher density of electronic states near the edges of the conduction and valence bands, and therefore a higher concentration of carriers can contribute to the band-edge emission. Consequently, it takes less intense “pumping” of energy into a quantum-well laser to get it to lase (the lasing threshold is lower). Additionally, quantum-well lasers show improved temperature stability and a narrower emission line.

In QDs, the charge carriers are confined in all three dimensions, with the result that the electrons exhibit a discrete atomic-like energy spectrum. In very small QDs, the spacing between these atomic-like states is greater than the available thermal energy, so thermal depopulation of the lowest electronic states is inhibited. It was therefore anticipated that a

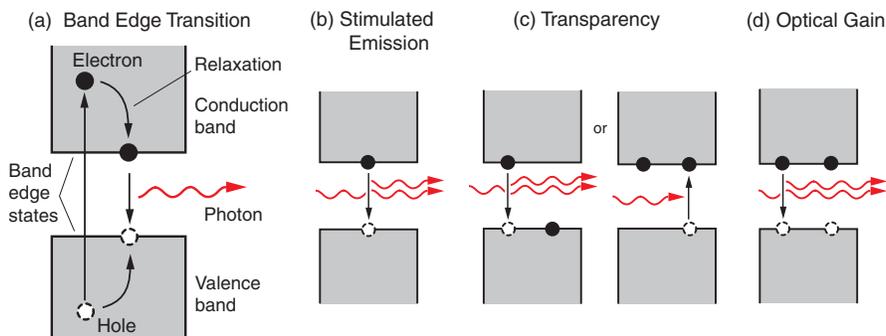


Figure 3. Laser Basics

(a) “Pumping” energy into a semiconductor can excite an electron, e , into the conduction band. That electron leaves behind a hole, h , in the normally filled valence band, and thus an e - h pair is created. The electron and hole each relax to the respective band-edge states by nonradiative processes. During the band-edge transition, a photon is emitted as the excited electron spontaneously recombines with the hole. (b) Stimulated emission occurs when a photon induces the excited electron to decay. The emitted photon has the exact frequency, phase, and polarization of the initial photon. (c) For a ground state that contains two electrons (population equality) can lead to two equally probable outcomes: The incoming photon stimulates the excited electron to decay, producing an extra photon (left), or the photon excites the ground-state electron and is absorbed (right). There is no net gain or loss of photons. In this case, the medium is in the transparency regime. (d) Optical gain can occur if there are more electrons in the excited state than in the ground state (population inversion) because photon absorptions inhibited. If a population inversion is established in a bulk system and if the gain from stimulated emission is larger than losses that absorb or scatter photons, the system will exhibit amplified spontaneous emission (ASE). In a laser, an ASE-capable medium is placed in a reflecting cavity, and thus the photon field builds on itself.

QD laser would have a temperature-insensitive lasing threshold at an excitation level of only one electron-hole (e - h) pair per dot.

Lasing in QDs was first reported in 1991 (Vandyshv et al. 1991) and was achieved in an optically pumped device with relatively large (approximately 10-nanometer) CdSe nanoparticles. The QDs were fabricated by high-temperature precipitation in molten glass. Later, lasing was also observed for QDs grown by epitaxial techniques (Ledentsov et al. 1994). As expected, the QD lasers showed an improved performance and featured a lower lasing threshold and enhanced temperature stability by comparison with quantum-well lasers.

These successes provided us with strong motivation for the development of lasers based on NQDs less than

10 nanometers in diameter. In this size range, spacing between electronic levels can exceed hundreds of milli-electron-volts (meV), a much larger value than the room temperature energy scale of about 24 meV. Size-controlled spectral tunability over an energy range of 1 electron volt was expected. However, after a decade of research that provided some tantalizing hints of optical gain, NQDs failed to demonstrate lasing action.

The failures were often attributed to material defects or dangling bonds on the surface of the NQDs, which were a natural consequence of the large surface-to-volume ratio of the sub-10-nanometer particles. The defects lead to electronic states that lie within the material’s energy gap. Electrons can relax into those states, whereupon they typically undergo

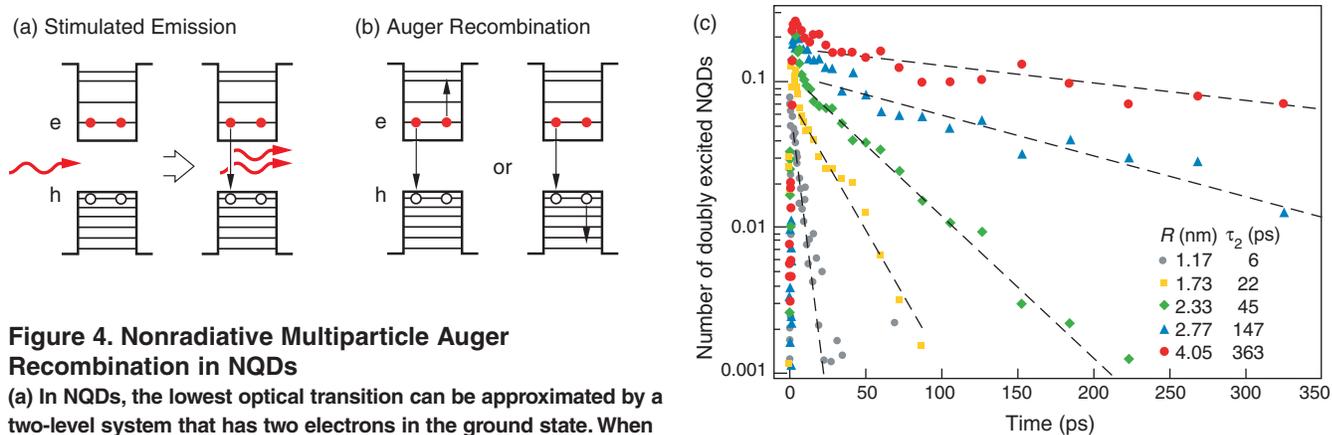


Figure 4. Nonradiative Multiparticle Auger Recombination in NQDs

(a) In NQDs, the lowest optical transition can be approximated by a two-level system that has two electrons in the ground state. When both electrons are excited, a population inversion occurs, and the NQD can exhibit optical gain. An incoming photon stimulates one electron to decay, producing an extra photon. (b) The two-electron excited state also allows for a loss mechanism called nonradiative Auger recombination, whereby the energy from e-h recombination is not released as a photon but is transferred to either an electron or a hole. (c) Experiments show that the smaller the dot, the shorter the Auger recombination time (τ_2). Even the largest dot has a significantly shorter τ_2 than the radiative decay time.

either nonradiative or radiative (in-gap “deep-trap” emission) decay to the ground state. Thus the surface defects introduce carrier losses that inhibit the optical gain. Another concern raised in several theoretical papers was the reduced efficiency of electron-phonon interactions that results from the discrete, atomic-like energy structures, an effect that reduces the ability of carriers to enter into the band-edge states and hence reduces luminescence efficiencies. However, our research team eventually realized that the main difficulty in getting our ultrasmall NQDs to lase stemmed from a largely unforeseen problem known as multiparticle Auger recombination (Klimov et al. 2000).

Multiparticle Auger Recombination vs Optical Gain

As in the case of other lasing media, QDs require a population inversion in order to produce optical gain (refer to Figure 3). The population inversion corresponds to the situation in which the number of electrons in a high-energy excited state is greater than that in the low-energy

ground state. In small dots, the lowest “emitting” transition can be treated as a two-level system that contains two electrons in its ground state. To invert such a system, one has to promote both electrons from the ground to the excited state, meaning that optical gain in QDs originate from nanoparticles that contain two e-h pairs (doubly excited nanoparticles).

Paradoxically, whereas the intrinsic decay of singly excited QDs is due to the e-h recombination and the emission of a photon, the deactivation of two e-h pair states is dominated by nonradiative Auger recombination (Klimov et al. 2000a). In the latter case, the e-h recombination energy is not released as a photon but is transferred to a third particle (an electron or a hole) that is re-excited to a higher energy state (see Figure 4). Auger recombination has a relatively low efficiency in bulk semiconductors because of restrictions imposed by energy and momentum conservation. But linear, or translational, momentum conservation is a consequence of the translation symmetry of bulk crystals, and this symmetry is broken in QDs (the electrons feel the dot’s boundaries). Therefore, translational-momentum conservation does not

apply to QDs, so the probability of Auger effects is greatly enhanced.

Since Auger recombination and optical gain develop from the same initial state (that is, two e-h pairs in a dot), the Auger decay is unavoidable in the regime of optical amplification and will always impose an intrinsic limit on optical gain lifetimes. In CdSe NQDs, for example, Auger recombination leads to the deactivation of doubly excited nanoparticles on time scales from approximately 400 picoseconds to approximately 10 picoseconds, depending on the dot size (the smaller the dot, the faster the recombination). These time scales are significantly shorter than the time of the radiative decay (approximately 20 to 30 nanoseconds), which obviously should hinder the development of lasing.

QD Solids: A New Type of Lasing Medium

We realized the hindering role of Auger recombination only toward the end of 1999, after we had conducted detailed studies of multiparticle dynamics in CdSe NQDs (Klimov et al. 2000a). Soon after, we also realized how to overcome this problem. Optical

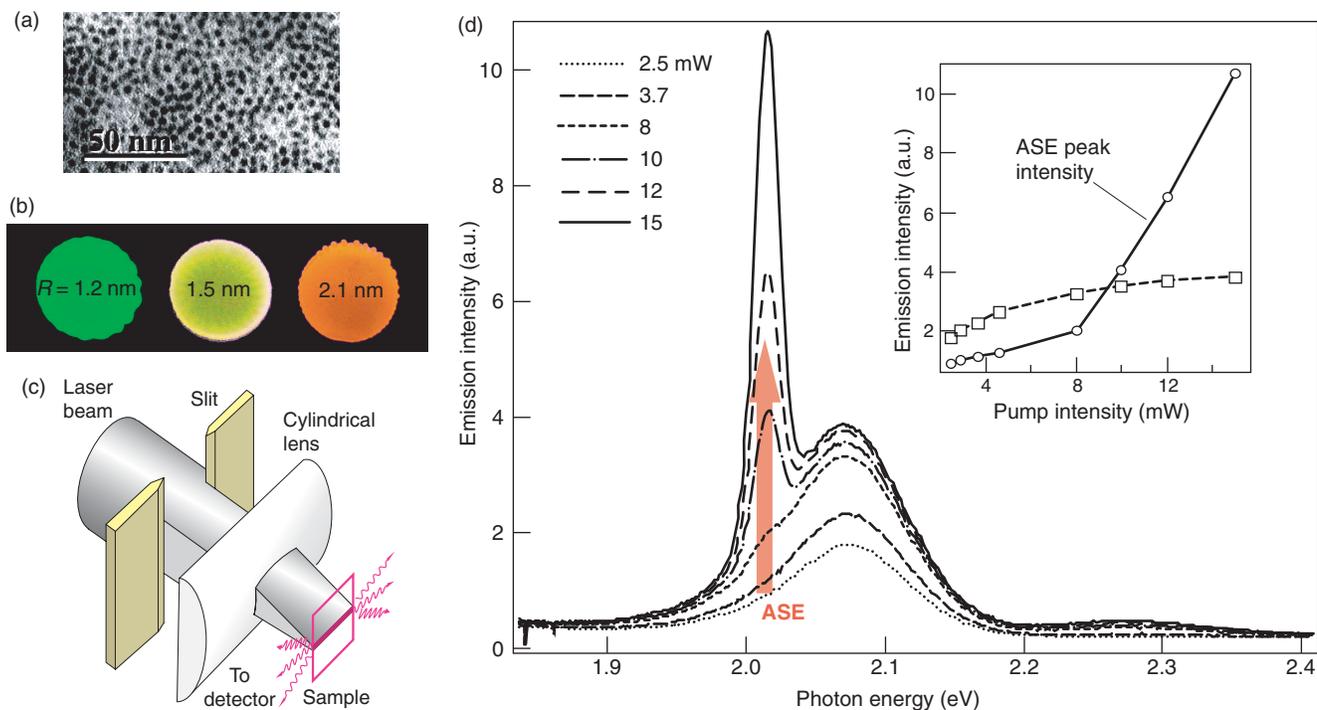


Figure 5. Observation of Amplified Spontaneous Emission

(a) This is a typical transmission electron microscopy (TEM) image of a matrix-free NQD solid film. The black dots are the semiconductor cores, whereas the space between the dots is taken up by the capping molecules. (b) The figure shows images of three CdSe NQD solid films taken under ultraviolet illumination. The films are fabricated from dots whose radii are 1.2, 1.5, and 2.1 nm. If the TOPO has a 1.1-nm length, these films have filling factors ranging from ~17% to ~26%. (c) This illustration shows our experimental setup. The cylindrical lens focuses the pump beam into a stripe on the NQD film. The ASE was detected at the edge of the film, which acted as an optical waveguide. (d) As the intensity of the pump beam increased, a sharp ASE band developed in the emission spectra of the NQD film. (Inset) The intensity of the ASE peak (circles) rose sharply once a pump laser intensity of 8 mW was reached, indicating the start of stimulated emission and optical gain (the NQD radius was 2.1 nm, and the sample temperature, $T = 80$ K). The open squares show the sublinear dependence of the emission intensity outside the sharp ASE peak.

gain relies on the effect of stimulated emission, the rate of which can be enhanced by simply increasing the concentration of NQDs in the sample.

We estimated that the stimulated emission rate would exceed the Auger decay rate in a medium with NQD filling factors of 0.2 to 1 percent (Klimov et al. 2000b). Such densities are readily achieved in close-packed NQD films (also known as NQD solids). For example, NQDs capped with trioctylphosphine oxide (TOPO) will self-assemble into a thin film that can have filling factors as high as 20 percent, well above the estimated critical loading required for the development of stimulated emission.¹

We demonstrated optical gain for the first time by using close-packed,

matrix-free films of CdSe NQDs (Klimov et al. 2000b). In these experiments, the NQD samples were optically excited by the output of an amplified titanium:sapphire pump laser (see Figure 5). At pump intensities of approximately 8 milliwatts, we observed the development of a sharp, amplified spontaneous emission (ASE) peak situated on the low-energy side of the spontaneous emission band. The dependence of this peak on the pump-laser intensity showed a threshold behavior that was a clear signature of the transition to the optical-amplification regime. We also confirmed that the frequency of the ASE peak changed with the size of the dot. Because of strong quantum

confinement, the peak in the smallest dots was blue-shifted with respect to that in bulk CdSe by more than 0.5 electron volt.

In order to slow down the NQD degradation that results when the sample heats up, we performed initial experiments at cryogenic temperatures. More recently, after improving the optical quality of our NQD solids, we were also able to demonstrate optical gain in NQDs at room temperature (Mikhailovsky et al. 2002).

Interestingly, the same pump flu-

¹Another approach to achieving high-density NQD materials is to incorporate the NQDs into transparent sol-gel matrices. See Sundar et al. 2002 and Petruska et al. 2003 for details.

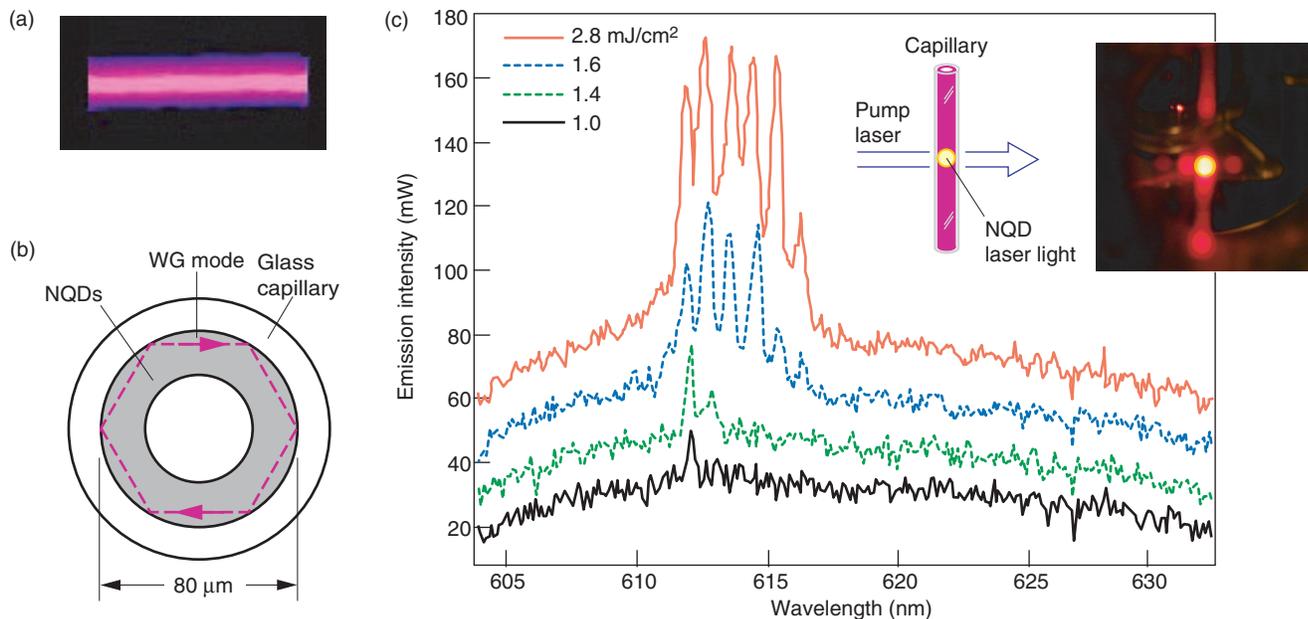


Figure 6. NQD Lasing

(a) This microphotograph of an NQD microcavity fabricated by incorporation of an NQD solid layer into a microcapillary tube was taken under ultraviolet illumination (the NQD layer on the inner side of the tube appears pink). (b) A cross-sectional view of the NQD microcavity illustrates an optical path of a WG mode. (c) This plot shows the development of lasing into sharp WG modes. The spectra are taken at higher and higher pump fluences. Lasing into a single, sharp WG mode develops at $\sim 1 \text{ mJ cm}^{-2}$. The position of this mode (612.0 nm) corresponds to the optical gain maximum (Malko et al. 2002). As the pump fluence is further increased, additional WG modes develop on the low-energy side of the 612.0-nm mode. The insets show a schematic and photo of the laser setup.

ences (number of photons per pulse per centimeter squared) that were used to excite room temperature ASE in CdSe NQDs were not sufficient to produce light amplification in bulk CdSe samples. The reason is that light amplification in bulk CdSe can be due to both low-threshold excitonic and high-threshold e-h plasma mechanisms. Excitons are bound states of e-h pairs that are “naturally” confined in space because of the Coulomb attraction between opposite charges. The e-h interaction energy in the exciton (approximately 16 meV in bulk CdSe) provides a barrier for the re-excitation of electrons and holes into the “dense” continuum of unbound e-h pair states. The existence of this “natural” barrier reduces the threshold for the “excitonic” optical gain compared to that for unbound charge carriers. However, at room temperature, excitons dissociate because of large electron thermal energies (approximately 24 meV). This

process quenches the exciton-related gain and results in a significantly increased ASE threshold. Because of the large interlevel spacing in NQDs, “quantum-confined” excitons are more robust than bulk excitons, allowing one to excite room temperature ASE at pump levels comparable to those at cryogenic temperatures. This is an illustrative example of enhanced temperature stability in lasing applications expected for strongly confined dots.

In order to demonstrate true lasing action, the NQD gain medium must be combined with an optical cavity that provides efficient positive feedback. Figure 6 shows one example of a “laser fabricated in a beaker” that we made by incorporating NQD solids (Klimov et al. 2001, Malko et al. 2002) into a microcapillary tube. The cylindrical microcavity can support two types of optical modes: planar waveguide-like modes that develop along the tube length, and whispering gallery (WG)

modes that develop (because of total internal reflection) around the inner circumference of the tube. The modes propagating along the tube can only achieve the ASE regime because no optical feedback is present. The WG modes can support a true lasing action (microring lasing). After several attempts, we were able to uniformly fill the interior of the tube with the NQDs and achieved the first occurrence of NQD lasing (Klimov et al. 2001, Malko et al. 2002). Several types of cavities have since been utilized to demonstrate NQD lasing, including polystyrene microspheres (Klimov and Bawendi 2001), and distributed-feedback resonators (Eisler et al. 2002).

Outlook

The first demonstrations of NQD lasing devices indicate a high potential for NQD materials to be new

types of lasing media, characterized by wide-ranging color tunability, high temperature stability, and chemical flexibility. Thus far, we have only achieved lasing action by using a pump laser to create the population inversion in NQDs. An important conceptual challenge, however, awaits us in the area of electrical injection pumping. Currently, our lasing media consist of NQDs suspended in a non-conducting matrix, and it is not possible to excite the dots electrically.

One possible strategy to achieve electrical injection is by combining “soft” colloidal fabrication methods with traditional, epitaxial crystal-growing techniques and incorporate dots into high-quality injection layers of wide gap semiconductors. A possible technique that is “gentle” enough to be compatible with colloidal dots is energetic neutral-atom-beam epitaxy. This method utilizes a beam of neutral atoms carrying significant kinetic energy of several electron volts. The beam energy is sufficient for the activation of nonthermal surface chemical reactions, eliminating the need to heat the substrate in order to grow high-quality films for NQD encapsulation.

Because of Auger recombination, however, electrical pumping of NQD lasing devices would still be significantly more difficult than pumping of simple, “nonlasing” light emitters. Interestingly, there is a possible approach to completely eliminate Auger recombination from NQDs. It stems from the realization that the optical-gain requirement of two e-h pairs (the same initial state that allows Auger recombination to occur) is a consequence of the electron-spin degeneracy of the lowest emitting transition. Two electrons occupy the same ground state; therefore, both must be excited to achieve a population inversion. If the ground-state degeneracy could be broken (perhaps through interactions with magnetic impurities) the gain can, in principle,

be realized with a single e-h pair, and Auger decay would no longer be a problem for either optically or electrically pumped NQDs. ■

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