Research Article

Broadband Frequency-Tunable Whispering-Gallery-Mode Superradiant Light from Quantum Dots in Colloidal Solution

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We examine superradiant (SR) light or amplified spontaneous emission (ASE) from a whispering-gallery-mode (WGM) laser comprising various sized (CdSe) ZnS quantum dots (QDs) in colloidal liquid. Laser-induced fluorescence (LIF) with a full width at half maximum (FWHM) of 40 nm is observed when the colloidal QD system is pumped with 2 mJ of laser light at 355 nm (3rd harmonic of Nd:YAG laser). Under optimal conditions of pump energy and focusing, ASE at 520 nm with a bandwidth of $\Delta \lambda = 8$ nm (FWHM) and divergence of 9 mrad is observed. When the QDs are embedded on a high-Q factor silica microsphere ((functionalized with an amine), SMA), they generate WGMs with random peak distributions. Finally, when all the QDs embedded in SMAs are mixed and placed in a cuvette, we obtain a “WGM laser” that is almost continuously tunable from 520 nm to 630 nm with a spectral width less than 2 nm (FWHM) in the WGM and less than 1.2 nm in the cavity mode. We believe that this is the first report on a frequency tunable laser obtained using (CdSe) ZnS QDs embedded in an SMA, exhibiting an efficiency of 0.06%.

1. Introduction

Quantum dots (QDs) are very small semiconductor particles of the order of few nanometers such that electron and holes are confined in all spatial dimensions [1], and this very small QD size affords optical and electronic properties different from those of larger particles. These sizes of QDs are achieved mostly with the use of chemical synthesis, and at these sizes, the QDs behave more like organic molecules than atoms; thus, their properties can be modified by changing the QD size [2]. The quantum size effect reduces the number of intermediate Fermi bands and enlarges the band gap of the QDs with decrease in their size. If energy (for e.g., photons) that is greater than or equal to the band gap is supplied to such QDs, then an electron-hole pair is created, and this electron-hole pair forms an exciton. Such excitons acts like pseudohydrogen atoms, and for a brief period of time, they move together through a distance that is called the diffusion length [3–5]. These excitons define the photoluminescence properties of the QDs. Excitons can recombine to produce photon or also recombine in nonradiative Auger recombination [6]. In the begging years of QD discovery, researchers faced difficulties in gating laser from QDs, because of its eight-fold degeneracy [7–11]. But due to unique photoluminescence properties of QDs, which enable the design of photonic devices, other aspects of QDs have led to extensive research, because of the broadband spectral tunability, solution processability, low lasing threshold, high-temperature operation, and impressive chemical stability offered by QDs [12–16]. In this context, colloidal QD-based white-light-emitting diodes have been demonstrated [17–19]. Electrically pumped QD lasers were demonstrated, but their power is very low [20, 21]. Optical pumping is a way around to produce high-power laser from QDs. When any exciton recombines to produce spontaneously, emitted photon induces stimulated emission, and if the gain in QD medium is high, then in a single pass produces a highly directional intense cone of light emitted known as...
amplified spontaneous emission (ASE). ASE in QDs was reported in earlier reports [22–24]. Even if quantum dot tunable laser was designed [25], still white-light lasers are difficult to realize and fabricate.

In the last decade, researchers have extensively focused on disordered gain materials to fabricate “random” lasers. While in conventional lasers, beams are emitted from ordinary resonators comprising two reflectors, one 100% reflective and the other a partially reflecting mirror, fluctuating refractive indices or manifold light scattering acts as feedback in the case of random lasers [26–29]. Random lasers have many optical modes that can be in “Anderson confinement” or otherwise confined in space or extended depending on the mean free path of the sample [30, 31]. In this regard, researchers have studied several disordered gain media ranging from organic semiconductor materials such as dye-doped liquid crystals, π-conjugated polymers, oligomers to fluorescing biological tissues, photonic crystals, and rare earth-doped nanopowders [32–34].

In parity-time symmetric system, phase transition can be triggered in a random gain medium by optical scattering [35, 36]. If the scattering is feeble, photon propagation can be explained by an ordinary diffusion process. On the other hand, when the quantity of scattering increases, recirculated light scattering begins to backpropagate, which interferes with forward-propagating waves in a disordered structure, in turn enhancing backscattering (the so-called feeble localization) [37, 38]. Once the flux of the scattering increases beyond a threshold rate, the system exhibits a strong localized state, and light propagation is suppressed due to multiple scattering beams interfering with each other [39]. This phenomenon is called the Anderson localization of light, and it can be considered the spectroscopic equivalent of electronic localization in solids [40].

Such scattering under favorable conditions can be amplified to create whispering-gallery-mode (WGM) lasers. WGM laser QDs comprise CdSe/ZnS core–shell QDs dispersed in hybrid polymers and composed of two types of monomers with different rates of polymerization. When exposed to UV light for curing, due to the different polymerization rates of the two monomers, an inhomogeneous polymer with a range of refractive index fluctuations is formed, which produces spatially localized random resonator gain media. Random lasing is generated in this media when the pump energy is above a threshold of 7 mJ/cm². This type of random laser contains many modes originating from spatially localized resonators. Here, we remark that WGMs with high-Q factors (>10⁷) have been demonstrated in fused silica capillaries filled with efficient dye laser solutions, which are mixtures of donor and acceptor dyes [41].

WGM lasing from blue colloidal liquid has been demonstrated in ternary CdZnS/ZnS alloyed core/shell QDs, and quasi-disk WGM microlasers have been realized via a simple modification of the surface tension of water, which deforms the lasing cavity, and this deformation can be used to modify the lasing peaks [42]. Other studies have also reported the use of a flexible polymeric thin film of CQD/PMMa composite coated atop a second-order grating structure to produce WGM lasers with emission around 600 nm with a threshold less than 10 kW/cm² with 5 ns pulse pumping. Along similar lines, other studies have utilized QDs doped with silica microspheres (5.06 μm in diameter) to achieve WGM lasing. These researches have shown that it is possible to achieve fine tuning of the WGMs [43].

So far, many reports have published the WGM of quantum dot. But there is only a few report on QD@Si. Furthermore, there is no report that a single solution with combination of various QD@Si could produce WGM in a manner that it could be used as a single emitting source that could be tuned over a wide range of wavelength with almost continuous tunability. Also this system produces laser pulse with little variation in energy output. In this backdrop, here, we demonstrate a broadband frequency-tunable WGM laser based on QDs (CdSe/ZnS) embedded in a silica microsphere (QD@Si) with a tunable range from 510 to 640 nm. To the best of our knowledge, ours is the first report on frequency-tunable WGM lasers based on QD@Si. The application of WGM laser ranges from integrated optics, optical sensor [44], energy storage [45], and optical logic gates [46], and in the future, it has potential application as Li-Fi emitters.

2. Materials and Methods

The chemical synthesis of QD CdSe cores has been reported elsewhere. In our study, the core was purified with a procedure comprising successive precipitation and redissolution over several trials. A few layers of ZnS were grown on top of the core with the use of the SILAR method [47].

As regards the microspheres, 100% solid, 0.5 μm diameter amine-functionalized silica microspheres (SMA) purchased from Polysciences, Taipei, Taiwan, were used as received. The average size of the silica microspheres was determined to be 0.3 μm, with the maximum size being 0.7 μm. The QDs were attached to the surface of SMA particles via covalent bonds between QDs to form microresonators, as illustrated in Figure 1.

Optical properties such as fluorescence, absorption, and lasing were recorded for QDs in solutions of different concentrations. The solutions were stored in fused quartz cuvettes with dimensions of 1 × 1 × 4 cm (L × W × H) and an optical path length of 1 cm. A spectrophotometer (PerkinElmer LAMBDA 950) was utilized to measure the absorption spectra over the wavelength range from 330 to 550 nm. Similarly, a spectrofluorometer (PerkinElmer LS-55) was utilized to measure the fluorescence spectra over the range from 400 to 500 nm, and the wavelength of excitation was 355 nm. All experiments were carried out at room temperature (20°C).

For all laser experiments, an Nd:YAG laser’s (Brilliant B, Quantel) 3rd harmonic (355 nm) was used as the pump source to optically excite the samples (QDs in solutions). The pump laser had a repetition rate of 10 Hz and pulse duration of 5 ns, and these laser pulses were made incident on the QD solutions in cuvettes as line of light obtained via a plano-convex (quartz) lens (Edmund Optics). Such a line of light (at focal point) excites the solution along a line that is perpendicular to the excitation source. When the pump energy and solution concentration were optimal, an intense cone of light
was observed to emanate from both sides of the cuvette along the line of excitation. This light, called superradiant (SR) light or amplified spontaneous emission (ASE), was transmitted to a spectrometer (Ocean Optics, USB-4000ES-RX) to monitor and record the ASE spectra. The output ASE was also simultaneously recorded by an ultrafast photodetector (UPD) connected to an oscilloscope to monitor the time evolution of the ASE signal. In our study, the combined time resolution of the UPD and oscilloscope was 180 ps.

3. Results

3.1. Spectral Properties. The absorption spectra (Figure 2) of our samples (QD-1 to QD-5) confirm that our QDs exhibit the regular features of (core) shell ones. The solution used was THF for a QD concentration range of 1 to 70 mg in 5 mL of solution. As reported earlier, the (CdSe) ZnS QDs exhibit two distinct features. (i) There is a primary peak at longer wavelengths (from 510 nm to 615 nm) with a Stokes shift of ~20 nm with respect to the photoluminescence peak. (ii) The absorbance increases steadily in the shorter wavelength region and reaches a maximum in the UV region. The spectral shape remains the same for all dot sizes, and only the absorbance increases as the concentration increases. These observations imply that there is no ground-state aggregation present in the (CdSe) ZnS QDs. Table 1 lists the details of all the QDs used in our study.

Figure 3 shows the PL spectra for different sizes of (CdSe) ZnS QDs at a concentration of 4 mg in 5 mL of THF. The PL spectra exhibit a peak with an FWHM of ~27 nm. The intensity of the photoluminescence spectra at this concentration is approximately equal for samples QD-1 to QD-5.

3.2. Amplified Spontaneous Emission Properties of QDs. Laser-induced fluorescence (LIF) spectra is produced when laser is used as the excitation source; unlike normal lamp used in spectrofluorometer, LIF spectra would have smaller FWHM. Figure 4 shows LIF obtained when a pump energy of 3 mJ was delivered to one of the samples (CdSe/ZnS (560 nm, QD-1) dispersed in THF at a concentration of 26 mg/5 mL). The LIF spectrum exhibits a peak around 559 nm with an FWHM of 27 nm. The LIF is observed to increase with spectral narrowing of the FWHM to around 16 nm with the peak at 566 nm when the pump energy is raised to 9 mJ. In the study, an intense amplified spontaneous emission (ASE) was obtained as a cone of light with a divergence of 5 mrad on the two sides of the cuvette perpendicular to the pump when the pump energy increased to 15 mJ. The peak emission wavelength in this case was 567 nm, the spectral bandwidth was 6 nm (FWHM), and the sum of output energy in both directions was 6 μJ with an efficiency of 0.04%.

In order to monitor the temporal profiles of the LIF and ASE from the 560 nm QD laser pumped by a 3rd harmonic (355 nm, 10 Hz) nanosecond laser, the output emission was transmitted to a UPD connected to an oscilloscope with the trigger signal being acquired from the Q switch out of the pump laser. In Figure 5, curve (i) shows the nearly smooth bell-shaped profile (temporal profile) of the pump pulse with FWHM of 10 ns, while curve (ii) illustrates the pulse shape of the threshold LIF, wherein the pulse width is only 3 ns, with a rise time of 1 ns and a fall time of 2 ns.

Curve (iii) indicates the ASE temporal profile with an 800 ps FWHM, very sharp rise time (200 ps), and longer fall time (600 ps) corresponding to the 20 mg QD concentration in 5 mL solution with the previously specified pulse energy.

Figure 6 shows the normalized ASE spectra for three QD samples that exhibited lasing, and we note that the peaks appear similar. The ASE peaks are located at 521 nm (QD-1), 567 nm (QD-2), and 614 nm (QD-4), and the ASE efficiency of the QDs decreases with the increase in the size of the QDs. The efficiency of QD-1 was maximal, with the highest ASE intensity (78600 a.u.) for a concentration of 30 mg/mL, while QD-2 exhibited an ASE intensity of 63420 a.u. for a concentration of 28 mg/mL, and the ASE intensity of QD-4 was 57890 a.u for a concentration of 32 mg/mL, being the least efficient of the three QDs that lased. As the particle size increases, the scattering of quantum dot also increases, this could contribute to the lower optical gain. Other QD samples exhibited LIF with an FWHM of 17 nm (QD-3) and 18 nm (QD-3) for concentrations of 30 mg/mL. Strictly speaking, these samples did not exhibit ASE, but they were on the verge of exhibiting ASE.
The following aspects of our results are noteworthy: (a) ASE could be achieved by transverse excitation as in the case of standard laser dyes such as coumarin or fluorescein or more recent conductive macromolecules such as PFO-co-pX; (b) the optical gains of these QDs are comparable with those of conventional laser dyes such as rhodamine B or a conjugated polymer like MEH-PPV; further, the quantum yields of the fluorescence are also comparable [48].

3.3. Whispering-Gallery-Mode Laser. Figure 7 shows the observed WGM lasing with the wavelength (nm) represented on the x-axis, the intensity (a.u.) on the y-axis, and pump energy (mJ) on the z-axis. Sample QD-3 (590 nm), dissolved at a concentration of 10 mg in 2 mL THF, was mixed with 3 mg of amine-functionalized silica microspheres (SMA) and sonicated for an hour. The sample was then pumped with a pulse energy of 1 mJ (3rd harmonic of Nd:YAG, 6 ns) to obtain LIF, and when the pump energy was around 1–4 mJ, WGM lasing was observed. Further, when the pump energy was above 4.3 mJ, the WGM intensity reached a maximum, with many random bands with an average FWHM around 1.2 nm. Figure 7 shows the observed WGM lasing with the wavelength (nm) represented on the x-axis, the intensity (a.u.) on the y-axis, and pump energy (mJ) on the z-axis.

Figure 8(a) shows the relationship between the pump power and the average line width. From the figure, we note that when the pump energy is less than 2 mJ, the line width is greater than 16 nm (FWHM). Red circles are line width.

### Table 1: Specifications of quantum dots used in the study.

<table>
<thead>
<tr>
<th>Quantum dot sample</th>
<th>Size of quantum dot (nm)</th>
<th>Size of core (nm)</th>
<th>Peak λf of emission (nm)</th>
<th>Peak λa of absorption (nm)</th>
<th>Stokes shift δλ = λf − λa</th>
</tr>
</thead>
<tbody>
<tr>
<td>QD-1</td>
<td>2.0</td>
<td>5.5</td>
<td>630</td>
<td>611</td>
<td>19</td>
</tr>
<tr>
<td>QD-2</td>
<td>2.0</td>
<td>4.4</td>
<td>609</td>
<td>590</td>
<td>19</td>
</tr>
<tr>
<td>QD-3</td>
<td>2.0</td>
<td>3.6</td>
<td>595</td>
<td>575</td>
<td>20</td>
</tr>
<tr>
<td>QD-4</td>
<td>1.8</td>
<td>3.2</td>
<td>563</td>
<td>541</td>
<td>22</td>
</tr>
<tr>
<td>QD-5</td>
<td>1.4</td>
<td>2.6</td>
<td>521</td>
<td>501</td>
<td>20</td>
</tr>
</tbody>
</table>

The following aspects of our results are noteworthy: (a) ASE could be achieved by transverse excitation as in the case of standard laser dyes such as coumarin or fluorescein or more recent conductive macromolecules such as PFO-co-pX; (b) the optical gains of these QDs are comparable with those of conventional laser dyes such as rhodamine B or a conjugated polymer like MEH-PPV; further, the quantum yields of the fluorescence are also comparable [48].
measured of QD-3 for pump energy 0.5–2 mJ; Figure 8(b) shows the spectra corresponding to (A) of Figure 8(a). When the pump energy is in the range of 2–5.5 mJ, the line width fluctuates between 16 nm and <2 nm represented as blue diamond in Figure 8(a) and obtained spectral profile was depicted in Figure 8(c) as (B), (C), and (D). This fluctuation arises due to the randomness of the gain in the solution, and the gain and scattering are at critical values in the range of the pump energy for this solution mixture concentration. This result could form evidence that “random” WGM also exists for certain pump powers. When the pump power was greater than 5.5 mJ, WGM lasing was observed for all QDs illustrated as green triangle in Figure 8(a) and spectra corresponding to (F) are shown in Figure 8(d).

Similar WGM lasing results were obtained for other QD samples in solution, as shown in Figure 9. For sample QD-1, the concentration was 8 mg/2 mL and the SMA concentration was 1.3 mg in 1 mL.

Next, the WGM solutions (approximately 4 mL each) were taken and mixed together, and the resulting solution mixture was poured into a clean cuvette and pumped with a 355 nm Nd:YAG laser. When the pump energy was 4 mJ, LIF was observed, as shown in Figure 10 (magnified by a factor of 6). When the pump power was increased to 8 mJ, the solution mix yielded a broadband WGM from 510 nm to 630 nm, with a sharp dip around 540 nm. This dip was because of the gap in emission shown in Figure 3 (PL) and Figure 10 (LIF). Nevertheless, we were able to observe continuous WGM laser emission over a wavelength range of 120 nm. Figure 11 shows the external feedback, unlike ordinary cavity, this is just to reflect the ASE that goes to the other side back towards the grating; this process increases the feedback and improves the efficiency by 50%.

Figure 11 shows the broadband LIF with the spectral profile being nearly flat from 510 to 630 nm for the sample without feedback, and when the sample was placed in the cavity, the emitted laser beam exhibited a 1 nm spectral width (the detection limit of the spectrograph was 0.5 nm) with an efficiency of 0.06%.

Figure 11 shows the external feedback set-up, wherein the excitation source was 355 nm (3rd harmonic). The pump pulse from the laser is focused as a line using a planoconvex quartz mirror with focal length 5 cm; at the focal line, the dimension of laser line was 0.1 cm × 1 cm. The quartz cuvette contained the colloidal quantum dot was placed at this focal line, QDs@Si gets excited, and WGM laser was produced due
to the random feedback within the Qds@Si mixed solution. The output power varies randomly due to variations in feedback. The front coated broadband ultrafast mirror (Edmund Optics, USA) fully (100%) reflects the light to the other side of cuvette, where a grating with 1800 lines/mm connected to a stepper motor was placed for tuning and the output wavelength comes out of a slit.

4. Conclusions

In this study, we performed the simultaneous excitation of five QD samples using the third harmonic of an Nd:YAG laser as the optical pump source. With appropriate selection of the pump energy and QD concentration, samples QD-1, QD-3, and QD-4 exhibited ASE; ASE was not observed for the remaining samples (QD-2 and QD-5). However, all samples exhibited WGM lasing when they were embedded into a high-Q factor silica microsphere functionalized with an amine. Finally, with a solution with all five QDs
embedded in an SMA, we obtained WGM lasing that was almost continuously tunable from 520 nm to 630 nm with a spectral width less than 2 nm (FWHM) in the WGM and less than 1.2 nm in the cavity mode. The overall efficiency was 0.06%, corresponding to a pulse energy of 10 μJ and peak power of 1.8 kW.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare no conflict of interest.

Authors’ Contributions

Saradh Prasad, Mamduh J. Aljaafreh, and Ahmad H. S. Othman did the experiments and data collection and wrote the manuscript; Saradh Prasad and Mamduh J. Aljaafreh did the analysis of data and wrote the manuscript; Mohamad S. AlSalhi and Saradh Prasad did the analysis of data and checked the manuscript consistency; and Mohamad S. AlSalhi conceived the experimental idea, designed the experimental set-up, and wrote the manuscript.

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References


