Low threshold amplified spontaneous emission from tin oxide quantum dots: a instantiation of dipole transition silence semiconductors†

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Direct bandgap semiconductors, such as In2O3, Cu2O, and SnO2, have enormous applications in photochemistry, photovoltaics, and optoelectronics. Due to the same parity of conduction and valence bands, the dipole transition is silent in these direct bandgap semiconductors. The low band-to-band transition efficiency prevents them from high intensity light emission or absorption. Here, we report the fabrication of SnO2 quantum dots (QDs) with sizes less than the exciton Bohr radius by a facile “top-down” strategy based on laser fragmentation of SnO in water. The SnO2 QDs shows exciton emission at ~300 nm with a high quantum yield of ~17%. Amplified spontaneous exciton emission is also achieved from a thin layer of SnO2 QDs dispersed in PEG400 on a quartz substrate. Therefore, we have shown that SnO2 QDs can be a potential luminescent material suitable for the realization of ultraviolet B lasing devices.

The direct bandgap oxide semiconductors, rutile SnO2, GeO2, In2O3, and cuprite Cu2O, are widely used in photochemistry, photovoltaics, and optoelectronics, in applications such as photocatalysis, solar cells, photodetectors and light emitting devices etc.1-10 The uppermost valence band and the lowest conduction band of the above semiconductors have same parity symmetry11,12 and the dipole transition between the conduction and valence band is silent (or so called “dipole forbidden”) due to the optical selection rule. As a result, those dipole silence semiconductors suffer from low efficiency of band-to-band absorption or emission, which limit their applications. For example, SnO2 has supreme physical and chemical properties suitable for a wide range of applications in Li-ion batteries, solar cells, and gas sensors.11-15 In addition, a wide direct bandgap (3.6 eV), high exciton binding energy (130 meV), and good electrical characteristics (e.g. electron mobility: ~250 cm2 V−1 s−1) make SnO2 a promising host material for the next generation of non-polar ultraviolet LEDs and photodetectors.7-10,16 which has been demonstrated by Li et al., Brovelli et al., Yang et al., Min et al., and Chen et al. Unfortunately, the efficiency of exciton emission is suppressed in the mostly-reported SnO2 due to the same even parity of the conduction and valence bands.17

The electronic band structures of low dimensional semiconductors will be altered due to the quantum confinement effect.18 There have been, however, few reports on the realization of quantum confined SnO2 nanocrystals that could support high-intensity exciton radiative recombination.19-21 The use of a “bottom-up” colloidal chemistry method was developed for the fabrication SnO2 QDs and quantum wires with good control of the corresponding dimension and shape.19-21 Hitherto, neither amplified spontaneous emission (ASE) nor stimulated emission, which is the Lydian stone for lasing materials, had been demonstrated at the excitonic wavelength from SnO2.

Pulsed laser fragmentation in liquid (PLAL) is a clean, facile and versatile “top-down” method to synthesize high quality nanomaterials.22-24 Early attempts to fabricate SnO2 nanoparticles by laser fragmentation use metal Sn as target, however, the exciton emission is still in the dark state.25-27 Materials with a low boiling point are usually preferred as the source materials in the laser fragmentation process to generate tiny nanoparticles.28 SnO has a boiling point (i.e., 1527 °C) lower than that of Sn and SnO2 (i.e., 2602 °C for Sn and 2500 °C for SnO2). In this paper, we report on the synthesis of SnO2 QDs in water by using laser fragmentation of SnO powder as the source material. It can be shown that the SnO2 QDs have uniform diameter of 1.8 ± 0.3 nm and support photoluminescence with a peak wavelength and bandwidth of ~300 and ~38 nm with quantum yield of 17%, respectively. Furthermore, optical gain and ASE at the exciton wavelength can also be obtained from the SnO2 QDs. To
best of our knowledge, this is the first report on optical gain and ASE at the exciton wavelength from SnO2 QDs. Our strategy can also be applied to solve the problem of limited absorption or emission efficiency in dipole transition silence semiconductors, such as GeO2, In2O3, and Cu2O.

The formation of SnO2 QDs can be explained as follows: SnO powder, which has a dark-blue color, favors the absorption of 1064 nm laser power and breaks down into smaller pieces of SnO QDs. Simultaneously, the SnO QDs react with water at a high temperature to form SnO2 QDs via the reaction SnO + H2O $\rightarrow$ SnO2 + H2. This reaction had been verified by measuring the generation of H2 gas during the laser fragmentation process, as shown in Fig. 1. The concentration of SnO2 QDs is about 0.05–0.08 mg mL$^{-1}$. The weight conversion efficiency from SnO to SnO2 QDs is 1.5%. Fig. 2(a) shows the transmission electron microscopy (TEM) image of the SnO2 QDs. The size distribution of the SnO2 QDs is also shown in Fig. 2(b). A statistical analysis (for more than 300 QDs in the study) had indicated that the QDs are polydisperse with diameters of 1.8 $\pm$ 0.3 nm (i.e., polydispersity $\delta$ = 16.7%), which can be seen also in the high-resolution TEM (HRTEM) in Fig. S1.$^\dagger$ Hence, the use of SnO powder can produce SnO2 QDs with better size uniformity and smaller particle size than widely employed Sn powder.$^{32}$ The HRTEM image given in Fig. 2(c) shows that the lattice spacing of the SnO2 QDs is 0.212 nm (see also Fig. S2†). This lattice spacing is related to the (210) crystal plane and is consistent with the rutile SnO2 phase data.$^{33}$

Fig. 1  (a) Schematic illustration of the formation of the SnO2 QDs. The mass density of SnO and SnO2 is 6.45 and 6.99 g cm$^{-3}$, the change of the QDs’ size due to oxidization is small. (b) The generation of H2 gas during the process of pulsed laser fragmentation. The corresponding chemical reaction is given by SnO + H2O $\rightarrow$ SnO2 + H2.$^{29,30}$

As plotted in the inset of Fig. 3(a), two absorption peaks at 4.49 eV (~276.2 nm) and 4.6 eV (~269.6 nm), which are due to the s-like exciton absorption structures,$^{34,35}$ are observed from the absorption spectrum of the SnO2 QDs (black dotted line). The corresponding exciton binding energy, $E_b$, can be estimated from an atomic-hydrogen-like orbital model from eqn (1)

$$E_n = -\frac{\mu R_y}{n^2 \varepsilon m_0}$$  

(1)

where $R_y$ is Rydberg constant, and $n (=1, 2, 3\ldots)$ is the quantum number.$^{12}$ For bulk SnO2, electron and hole effective masses $m_e$ and $m_h$ are 0.277 $m_0$ and 2.95 $m_0$, respectively.$^{36}$ As shown in the inset in Fig. 3(a), the energy difference between the 1s and 2s exciton absorption peaks, $|E_1 - E_2|$, is 0.11 eV, the value of exciton binding energy $E_b = |E_1| = \frac{4}{3} |E_1 - E_2|$ is 0.147 eV (see

Fig. 2  (a) TEM image, (b) histogram of diameter distribution, and (c) HRTEM of the SnO2 QDs in water. (d) Photos of the mixture of SnO powder and H2O (left), the mixture after laser fragmentation (middle) and the mixture of SnO2 QDs and water after centrifugation (right).
the ESI‡ for the calculation of $E_b$, which is larger than that of its bulk counterpart (i.e., 0.13 eV [ref. 37 and 38]). This increase in the value of $E_b$ can be explained by the influence of the quantum confinement effect arising from the small size of the SnO$_2$ QDs. Therefore, this first observation of 1s and 2s exciton absorption peaks is another evidence of dipole transition in the SnO$_2$ QDs.

Fig. 3(b) indicates that there are two emission peaks observed from the photoluminescence (PL) spectrum of the SnO$_2$ QDs (black dotted line). The PL from water-dispersed SnO$_2$ microparticles (purity: 99.9%) with average size $\sim$45 µm is also plotted as a reference. The dominant peak (i.e., exciton peak) with a peak wavelength of $\sim$300 nm (i.e., 4.13 eV) with a bandwidth below 40 nm is due to the radiative recombination of exciton Stokes shifting from the 1s absorption peak at 4.49 eV. The weak peak (i.e., defect peak) with a peak wavelength of $\sim$404 nm (i.e., 3.07 eV) originates from the surface defects, such as oxygen vacancies.9,33,37

The weak peak ($\sim$404 nm) originates from the surface defects. The PL stability of the SnO$_2$ QDs in water can be maintained for more than 12 months of storage under a normal office environment.

For a Wannier exciton,12 the Bohr radius $a_B$ can be calculated by adopting eqn (2):

$$a_B = a_B^H \frac{m_0}{\mu}$$

The Bohr radius of a hydrogen atom $a_B^H$ is 0.053 nm, $\mu = m_0m_e/m_e + m_0$ is the effective reduced mass and $m_0$ is the electron mass; the optical frequency dielectric constant $\varepsilon$ of SnO$_2$ is 9.9. The exciton Bohr radius $a_B$ of SnO$_2$ is estimated to be 2.1 nm.

The PL spectra of the SnO$_2$ QDs in water can be found to be less than 40 nm. The PL spectra of the SnO$_2$ QDs synthesized by other methods (i.e., see also Table 1)9,21 have a resultant peak with FWHM larger than $\sim1.5$ to 4 times that of the SnO$_2$ QDs. This is because their defect peak (i.e., arisen from the surface defects) has an intensity compatible with that of the exciton peak, and the exciton and defect peaks cannot be distinguished from the emission spectra. The large amount of surface defects observed from the SnO$_2$ QDs fabricated by chemical syntheses may be due to (1) the relatively low fabrication temperature, and (2) the presence of chloride impurities within the precursor (i.e., which may form non-radiative recombination centers). On the other hand, the instant temperature and pressure rise to a few thousands °C and tens GPa (ref. 40) respectively due to the laser pulses used to realize SnO$_2$ QDs by our PLAL allow the recovery of surface defects and the improvement of crystal quality. The narrow resultant peak has verified that PLAL using SnO powder as the source material can obtain high-quality SnO$_2$ QDs with fewer surface defects.

The radius of SnO$_2$ QDs is below the Bohr radius of exciton $a_B$, the optical bandgap $E_g$ calculated by the variational method given by Brus can be written as:19,29

$$E_g = E_g^{bulk} + \frac{\hbar^2n^2}{2\mu R^2} - \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon R} + \frac{e^2}{4\pi\varepsilon_0\varepsilon R} \sum_{n=1}^{\infty} \frac{\alpha_n(S/R)^{2n}}{\mu}$$

where $E_g^{bulk}$ is the bulk bandgap energy of SnO$_2$ (3.6 eV), $R$ is the quantum dot’s radius, and $\hbar$ is the Planck constant divided by $2\pi$. The polarization term $P = \frac{e^2}{4\pi\varepsilon_0\varepsilon R} \sum_{n=1}^{\infty} \frac{\alpha_n(S/R)^{2n}}{\mu}$ originates from the Coulomb interaction of the polarization charges at the QDs’ surfaces. The bar means the spatial average over a electron wavefunction, $S$ and $\varepsilon$ are the dielectric constant of solution.29 If the average diameter of the QDs is assumed to be 2.0 nm, the value of $E_g$ is found to be 4.79 eV. The calculated value of is 0.261 eV, which is larger than the bulk binding energy of SnO$_2$ (i.e., 0.13 eV [ref. 37 and 38]). This value is consistent with the peak wavelength of the exciton peak of the SnO$_2$ QDs as shown in Fig. 3(b). Hence the PL emission peak at 4.13 eV can be related to the exciton recombination.

The full-width at half-maximum (FWHM) of the resultant exciton peak of SnO$_2$ QDs in water is found to be less than 40 nm. The PL spectra of the SnO$_2$ QDs synthesized by other methods (i.e., see also Table 1)9,21 have a resultant peak with FWHM larger than $\sim1.5$ to 4 times that of the SnO$_2$ QDs. This is because their defect peak (i.e., arisen from the surface defects) has an intensity compatible with that of the exciton peak, and the exciton and defect peaks cannot be distinguished from the emission spectra. The large amount of surface defects observed from the SnO$_2$ QDs fabricated by chemical syntheses may be due to (1) the relatively low fabrication temperature, and (2) the presence of chloride impurities within the precursor (i.e., which may form non-radiative recombination centers). On the other hand, the instant temperature and pressure rise to a few thousands °C and tens GPa (ref. 40) respectively due to the laser pulses used to realize SnO$_2$ QDs by our PLAL allow the recovery of surface defects and the improvement of crystal quality. The narrow resultant peak has verified that PLAL using SnO powder as the source material can obtain high-quality SnO$_2$ QDs with fewer surface defects.

Table 1 Comparison of the peak emission wavelength and linewidth of the SnO$_2$ QDs obtained from different methods. (All the experiments were carried out in the fluorometer under the excitation of Xe lamp)

<table>
<thead>
<tr>
<th>Method</th>
<th>Emission wavelength</th>
<th>FWHM</th>
<th>Quantum yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis of tin salt in ethanol</td>
<td>~302 to 307 nm</td>
<td>~59 nm</td>
<td>—</td>
</tr>
<tr>
<td>Chemical solution system method PLAL</td>
<td>~330 nm</td>
<td>~150 nm</td>
<td>—</td>
</tr>
<tr>
<td>PLAL</td>
<td>~300 nm</td>
<td>38 nm</td>
<td>12–17%</td>
</tr>
</tbody>
</table>
The exciton intensity of SnO₂ QDs can be improved by more than 3 times after hydrothermal annealing, as shown in Fig. 3(a) and (b). The intensity of the exciton peak increases with the annealing temperature and has a peak value at 150 °C. The quantum yield of excitons can be enhanced from 12% (i.e., before annealing) to 17% (i.e., annealed at 150 °C). This value of quantum yield of our SnO₂ QDs is comparable to that of the ZnO nanorods (i.e., 2%~33%), and is higher than the SnO₂ nanocrystalline films grown by sputtering (~0.3 to 0.5%). Furthermore, the intensity of defect peak reduces with an increase of the annealing temperature to 120 °C (see also Fig. S3†). This indicates that there is a reduction of surface defects after hydrothermal annealing in this range of temperature. The intensity ratio between exciton and defect peaks versus annealing temperature is also shown in the inset of Fig. 3(b). It is noted that there is a peak value of ~14 (i.e., exciton peak has intensity 14 times the value of defect peak) at an annealing temperature equal to ~120 °C. These results indicated that the optimized annealing temperature is between 120 and 150 °C.

Recently, Xu et al. have investigated the effect of cross section size on the ASE in CdS nanoribbons. Due to the small size of the SnO₂ QDs, increasing the packing density is a facile and effective route to enhance the cross section of the SnO₂ QDs. The volume reduction of SnO₂ QDs in water by evaporation will lead to the aggregation of SnO₂ QDs. As a result, the solution will become turbid and the exciton peak intensity will be significantly reduced. The high viscosity of PEG400 (101.5 cP for PEG400, 0.89 cP for water) can minimize the aggregation of QDs. Hence, the annealed SnO₂ QDs (i.e., at 120 °C for 10 hours and has minimum surface defects) were transferred into water soluble PEG400 with a lesser volume. As the boiling point of PEG400 (~250 °C) is higher than that of water, water can be evaporated from the mixture to achieve the transfer process. The concentration of SnO₂ QDs can be adjusted by controlling the volume ratio between PEG400 and water. As shown in Fig. 3(d), the exciton peak intensity can be enhanced by more than 10 times after the transfer of SnO₂ QDs into PEG400. The PEG400 solutions with SnO₂ QDs still remain clear and transparent, and the loading fraction of QDs in PEG is ~0.06 to 0.5 mg mL⁻¹.

It was observed that the exciton peak of the SnO₂ QDs in PEG400 exhibits a redshift of when compared to that in water (see also Fig. S4†). At room temperature, optical dielectric constant, εsol, of water and PEG400 is 1.7 and 2.1, respectively. From the polarization term $P = \frac{e^2}{4\pi\varepsilon_0 R} \sum_{n=1}^{N} \alpha_f \left( \frac{S}{R} \right)^{2n}$ in eqn (3), the $P_{eff}$ decreases with the decrease of $\varepsilon_{sol}$ as observed from Fig. 3(d) and S4† which is consistent with the PL results. The corresponding emission peak wavelength remained unchanged for different concentrations of SnO₂ QDs in PEG400 (see also Fig. S4†). Thus, the possibility of the reduction of the energy bandgap of SnO₂ QDs due to the increase of its size at high concentrations can be excluded from consideration. The variation of exciton emission is mainly due to the change in the dielectric constant of the host solution. At the same time, the presence of PEG400 has negligible contribution on the exciton emission of the SnO₂ QDs in PEG400 (see Fig. S5†).

In order to examine the exciton emission performance of the laser fragmented-SnO₂ QDs, the net optical gain, G, of the SnO₂ QDs (i.e., using sample given in Fig. 3(d) with ratio 10 : 1 for water : PEG400) was measured by the variable stripe length (VSL) method (see Fig. S6† for the experimental setup). Fig. 4(a) shows the exciton emission intensity (at λ ~ 305 nm) of SnO₂ QDs in PEG400 versus stripe length. The deduced net optical gain G is 24, 27, 35, and 41 cm⁻¹ for input powers equal to 150, 250, 317 and 433 kW cm⁻², respectively. The net optical gain per power of the SnO₂ QDs in PEG400 is ~0.08 cm⁻¹ kW⁻¹ cm². Net optical gain spectra of the SnO₂ QDs in the PEG400 under various excitation powers are also plotted in Fig. 4(b). At a pump power of 433 kW cm⁻², the gain bandwidth is around 70 nm. Absorption can be observed at wavelengths shorter than ~270 nm even for higher pump powers due to the exciton absorption of the SnO₂ QDs. For wavelengths longer than 390 nm, the minimum optical gain is roughly equal to zero due to the large energy bandgap of the SnO₂ QDs.

The realization of ASE is unambiguous evidence of a material having high-optical quality suitable for optoelectronics applications. Hence, the demonstration of ASE from the proposed SnO₂ QDs can verify that the problem of dipole transition silence has been overcome. Fig. 5(a) illustrates the room-temperature PL spectra of the SnO₂ QDs in a PEG400 film waveguide at different excitation powers. A narrowing of the emission linewidth from ~48 to ~23 nm is observed for excitation power increases from ~0.57 to ~1.97 MW cm⁻².

![Fig. 4](image)

**Fig. 4** (a) Optical gain at the wavelength of exciton peak and (b) optical gain spectra of the SnO₂ QDs in PEG400 (fabricated by using 10 : 1 of water : PEG400 ratio for the transfer process). The error bars are due to the relative systematic errors (5%) from the fiber optic spectrometer.

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respectively. In addition, the wavelength of the emission peak slightly redshifts with the increase of excitation power. Fig. 5(b) shows the plot of the peak intensity and FWHM of the emission spectra versus the pump power. It is observed that a kink (or threshold) appears on the plot of peak intensity versus pump power with the narrowing of spectral linewidth. The threshold of the waveguide is found to be about 0.8 MW cm\(^{-2}\). According to the previous investigations on ASE in other materials,\(^{45,46}\) there are two main factors that can be used to verify the presence of ASE: (1) an intensity superlinear kink, and (2) the narrowing of emission peaks for excitation power above the threshold value. As both of these two factors were observed from our SnO\(_2\) QDs, such optical behavior of the SnO\(_2\) QDs-PEG\(_{400}\) film can be described as ASE. Hence, we verified that the SnO\(_2\) QDs fabricated by the proposed method have sufficient optical gain to support lasing emission at the excitonic emission wavelength (~300 nm). It should be pointed out that there is a FWHM difference between the Table 1 and Fig. 5(b). The difference is due to the use of different excitation sources.

In summary, SnO\(_2\) QDs with exciton emission at ~300 nm with a high quantum yield (~17\%) were fabricated by laser fragmentation of SnO powder dispersed in water. Both exciton absorption and emission is observed from the SnO\(_2\) QDs. An optical gain with a value of ~0.08 cm\(^{-1}\) kW\(^{-1}\) cm\(^2\) was observed in the annealed SnO\(_2\) QDs dispersed in PEG\(_{400}\). ASE at the exciton wavelength with a low threshold power (0.8 MW cm\(^{-2}\)) is also demonstrated from the film of SnO\(_2\) QDs in PEG\(_{400}\) on quartz. These results show that the exciton emission from SnO\(_2\) QDs is strong enough for UVB laser applications. The methodology demonstrated in quantum confined SnO\(_2\) potentially provides a universal strategy for other important dipole silence semiconductors, such as In\(_2\)O\(_3\), Cu\(_2\)O, for photochemistry, photovoltaic, and optoelectronic applications.

**Experimental details**

1. Fabrication process of the SnO\(_2\) QDs

**Fabrication of the SnO\(_2\) QDs.** 60 mg of blue-black tin(II) oxide (SnO, 10 micron, >99\%, Sigma-Aldrich Co.) was first poured into a glass bottle containing 20 mL DI water (or absolute ethanol purchased from Sigma-Aldrich Co.). A pulsed operation (6 ns, 10 Hz) laser beam, which has a wavelength of 1064 nm, a diameter of ~10 mm, and a peak power density of ~200 MW cm\(^{-2}\), was then irradiated onto the mixture of SnO and water (CAUTION: High-powered laser can cause severe skin burns and permanent eye damage!). The mixture was stirred simultaneously during the irradiation process. The laser irradiation lasted for 30 minutes and a yellow precipitate was observed from the glass bottle, as shown in Fig. 2(d). Centrifugation (6000 rpm, 20 min) was applied to separate the SnO\(_2\) QDs from the precipitate (i.e. the large size SnO\(_2\) nanoparticles and residual SnO powder). The retrieved solution with SnO\(_2\) QDs was transparent, as shown in Fig. 2(d). The high temperature and pressure caused by laser fragmentation may be responsible for the decrease of the surface defects in the SnO\(_2\) QDs.

2. **Hydrothermal annealing of the SnO\(_2\) QDs.** The SnO\(_2\) QDs solution was poured into a sealed glass bottle protected by an autoclave, and placed inside a temperature regulated oven for 10 hours. In order to study the optical performance of the annealed SnO\(_2\) QDs, the annealing temperature was varied between room-temperature and 180°C.

3. **Condensation of the SnO\(_2\) QDs in solution.** The concentration of the SnO\(_2\) QDs was controlled by mixing the water solution with different volumes of PEG\(_{400}\) (Sigma-Aldrich Co.). Then, the mixture was heated at 80°C for 6 hours to evaporate the water.

2. **TEM and UV-vis spectroscopy**

The morphology of the SnO\(_2\) QDs was investigated by using a JEM-2100F transmission electron microscope (TEM) with an accelerating voltage of 200 kV. The UV-vis absorption spectrum of the SnO\(_2\) QDs in water was measured using a SHIMADZU UV-2550 spectrometer.

3. **Optical measurements**

**PL measurements.** The photoluminescence (PL) spectra were collected using a UK Edinburgh Instruments FLS900 fluorescence spectrometer excited at a wavelength of 260 nm using a 450 W xenon lamp. A quartz microcell filled with DI water (or PEG\(_{400}\)) was used as a reference to measure the PL spectra of the SnO\(_2\) QDs.

**Quantum yield measurements.** The fluorescence quantum yield (QY) was measured by using the Edinburgh Instruments integrating sphere with 150 mm in diameter and coated with a layer of BaSO\(_4\) on its inner surface. The QY, \(\eta\), can be calculated by

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**Fig. 5** (a) Illustration of the room-temperature PL spectra of the film excited at different pump powers. The inset shows the PL spectra of the film under 0.57 (below threshold) and 1.97 MW cm\(^{-2}\) (above threshold) of excitation. (b) The peak intensity and linewidth of the emission spectra versus pump power.
the following formula: \( \eta = p/\sigma = (E_{\text{emission}} - E_{\text{solvent}})/(E_{\text{sample}}) \), where \( p \) is the photons emitted by the sample, \( \sigma \) is the photons absorbed by the sample. \( E_{\text{emission}}, E_{\text{sample}} \) and \( E_{\text{solvent}} \) are the sample emission spectrum, excitation light spectrum, and emission spectrum of solvent in the sphere, respectively. The emission and excitation wavelength are selected from 275 to 370 nm and 260 to 270 nm, respectively. The excitation bandwidth was set to 3 nm and the emission bandwidth was found to be 0.5 nm.

**Laser excitation technique.** 260 nm nanosecond pulses with a repetition rate of 10 Hz and linewidth <6 cm

- **Optical gain and amplified spontaneous emission (ASE) measurements.** The optical gain was measured using a variable stripe length (VSL) method. If 1 is the length of the pumping stripe and \( I_{\text{total}} \) is the total intensity detected from the side of the quartz microcell with an internal width of 2 mm, the corresponding net optical gain, \( G \), can be obtained from the classical VSL equation as follows:

\[
I_{\text{total}}(L, \lambda) = \frac{I_{\text{sp}}(\lambda)}{G(\lambda)} \exp(G(\lambda) L) - 1
\]

where \( I_{\text{sp}} \) is the spontaneous emission intensity and \( \lambda \) is the wavelength of the net optical gain to be selected. The optical gain measurement can be done by using a cylindrical lens to focus a variable pumping stripe of maximum length and width equal to 10 and <0.1 mm respectively onto the side of the microcell with an internal width of 10 mm. The light emitted from the SnO2 QDs was then analyzed using a miniature fiber optic spectrometer (USB2000+, Ocean Optics Co.).

For the ASE measurements, the PEG400 films containing SnO2 QDs were spin-coated onto a quartz substrate. In order to remove the adsorbed organic substance and enhance the surface wettability, the quartz substrate was pre-cleaned through an ultrasonic bath using acetone–ethanol and HCl–H2O2 mixtures for 20 minutes. The ASE experiment is excited by the 260 nm pulsed laser, and the spectra were recorded using a miniature fiber optic spectrometer (USB2000+, Ocean Optics Co.) in pulse triggering mode.

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**References**


