Supplementary documents

Low Threshold Amplified Spontaneous Emission from Tin Oxide Quantum Dots: A Instantiation of Dipole Transition Silence Semiconductors

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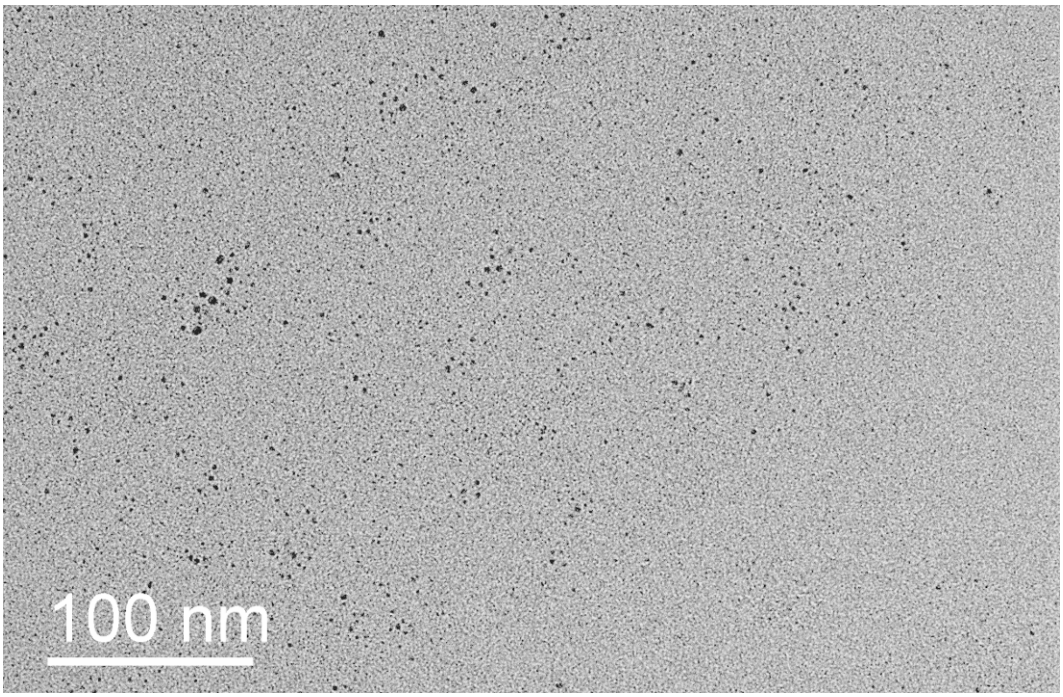

Figure S1. TEM image of SnO_2 QDs grown by PLAL. It is observed that there is no aggregation of the SnO_2 QDs.

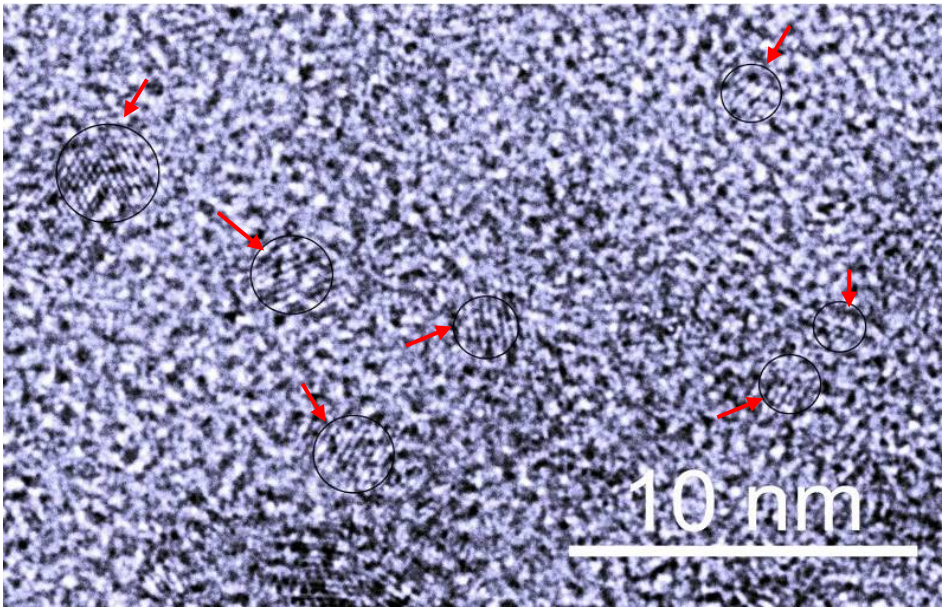

Figure S2. High-resolution TEM image of SnO_2 QDs grown by PLAL. The black circles indicated that the location of the SnO_2 QDs.

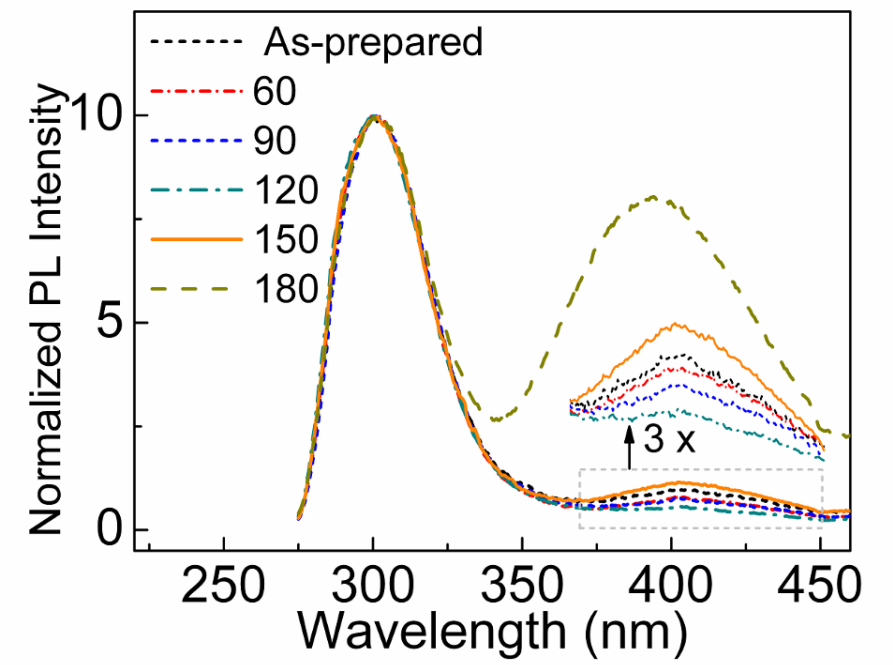

Figure S3. Normalized PL spectra of SnO_2 QDs in water annealed at different temperature. The FWHM of the PL spectra for the annealing temperature of SnO_2 QDs below 150 ^oC remained unchanged as the relative intensity of defects level decreases with the increase of annealing temperature. However, the resultant PL spectrum is broadened for the annealed temperature of SnO_2 QDs reaches 180 ^oC. This is because the relative intensity of defects level increases with the annealing temperature higher than 150 ^oC.

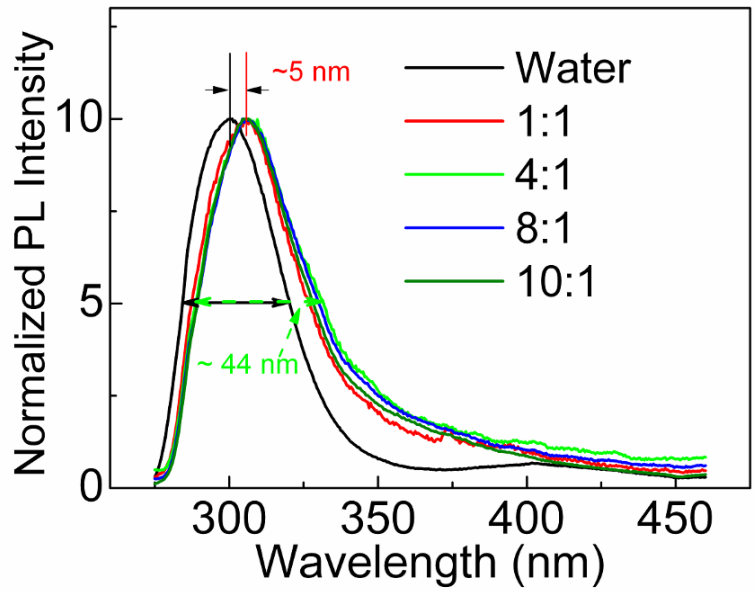

Figure S4. Normalized PL spectra of SnO_2 QDs dispersed inside host solution with different ratio between water and PEG_{400} where the volume of water was kept unchanged in the

experiment. The volume ratios (water: PEG_{400}) used in the experiment are 1:1, 4:1, 8:1, and 10:1. The emission peaks redshift by ~5nm and the corresponding linewidths broaden by ~6 nm after the SnO_2 QDs had transferred from water to PEG_{400} with lesser volume.

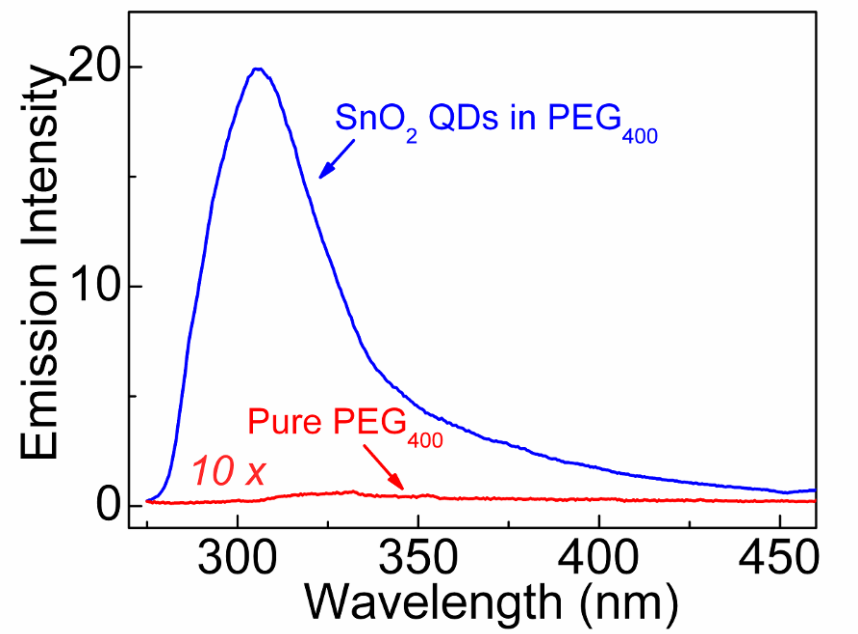

Figure S5. Emission spectra of PEG_{400} and SnO_2 QDs-PEG_{400} under 260 nm UV light (Xe lamp) excitation. These emission spectra were measured by UK Edinburgh Instruments FLS900 fluorescence spectrometer at room temperature.

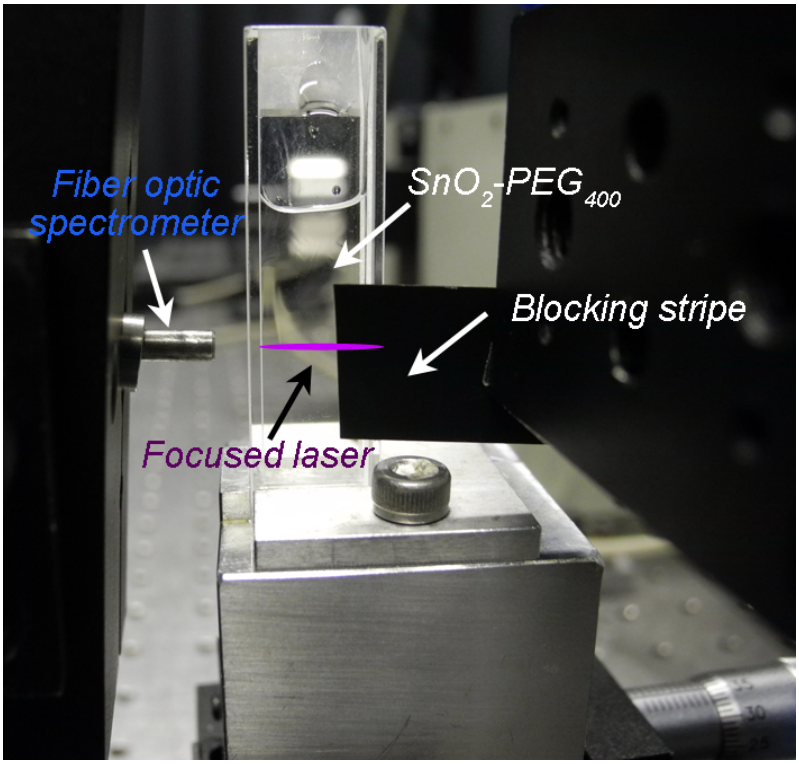

Figure S6. Photo explains the use of variable stripe length (VSL) method for the optical gain measurement. SnO_2 QDs dispersed in PEG_{400} was poured into a quartz micro-cell. A pump stripe (260 nm laser pulse) was focused onto the side of the quartz micro-cell (i.e., the purple line) to excite the SnO_2 QDs. The length of the pump strip was controlled by the blocking stripe. By changing the length of the blocking stripe, the intensity of amplified spontaneous emission from SnO_2 QDs can then be altered. The light emission was then being coupled to a spectral analyzer via an optical fiber.

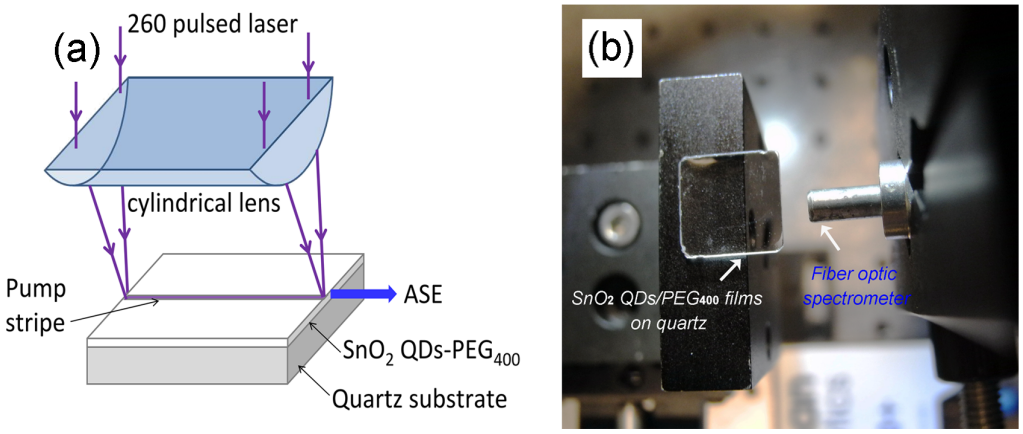

Figure S7. (a) Schematic diagram of ASE measurement. (b) Photo of the SnO_2 QDs-PEG_{400} thin film deposited on quartz substrate.

As the refractive index of SnO_2 QDs-PEG_{400} film (~1.6005) is larger than that of the quartz substrate (~1.5765) and the surrounding air at 305 nm, transverse optical confinement should be obtained. For a pump stripe is excited on the surface of the SnO_2 QDs-PEG_{400} film, lateral confinement of light can also achieved through the gain guiding effect. Hence, it is expected that ASE can be obtained from the light travelling along the length of the pump stripe provided that the corresponding net optical gain is sufficiently high.

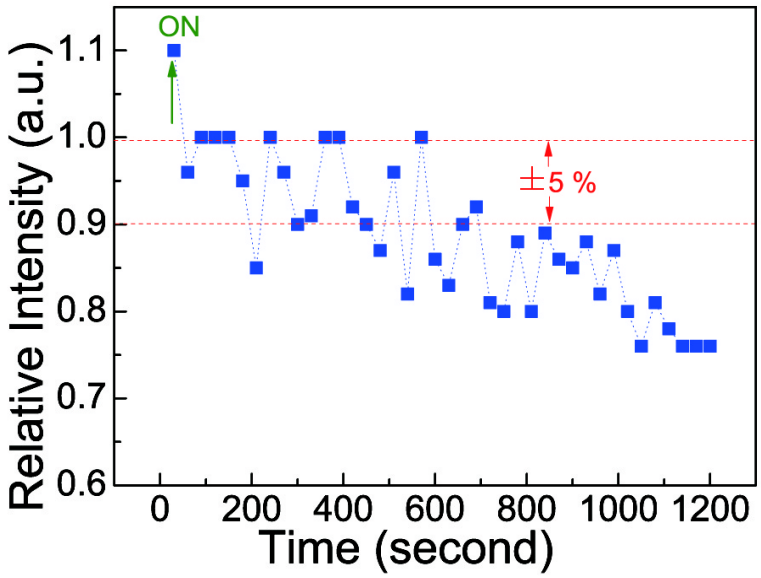

Figure S8. Time-dependent emission intensity of SnO_2 QDs in PEG (excitation: 260 nm laser, average power: ~2 mW)

Refractive indices of PEG_{400} and quartz and the formation of thin film waveguide

The refractive index of PEG_{400} was measured by a Leica Abbe Mark II Plus Refractometer at wavelength and temperature of 589 nm and around 22 °C, respectively and was found to be ~1.461. It is expected that the refractive index of PEG_{400} will be increased with the reduction of wavelength. If we assumed that the change of refractive index of PEG_{400} with wavelength is similar to that of the organic liquid (such as Ethylene Glycol), it can be estimated that the refractive index of PEG_{400} at around 305 nm should be larger than 1.6. The corresponding refractive index of quartz (SiO_2, silica) is about 1.576 at 305 nm. See the link: http://refractiveindex.info/?group=CRYSTALS&material=SiO2.

For SnO_2 QDs dispersed inside PEG_{400}, the corresponding refractive index should be similar to that of the PEG_{400} as the volume of SnO_2 QDs is relatively small. Hence, by depositing a layer of SnO_2 QDs mixture with PEG_{400} on quartz substrate, waveguide guiding effect should be obtained from the transverse direction of the thin film. If a pump stripe is excited on the surface of the SnO_2 QDs-PEG_{400}/quartz substrate, there will be a lateral confinement of light via the gain guiding mechanism. Hence, light will then be guided along the lateral and transverse directions and can be propagated along the longitudinal direction to establish amplified spontaneous emission.

Calculation of exciton binding energy from optical absorption spectroscopy

Consider an electron-hole pair bound by Coulomb interaction in a quantum dots having a dielectric constant ε. The wave-function of relative electron-hole motion, $\psi(r)$, can be found from the Schrödinger equation analogous to one describing the electron state in a hydrogen atom:

$$[-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{\varepsilon r}]\psi(r) = E\psi(r) \qquad \text{(S-1)}$$

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is the Laplacian operator, $\mu = \frac{m_e m_h}{m_e + m_h}$ is the reduced mass, r is the distance between electron and hole. The eigen-energy of Eq. (S-1) is:

$$E_n = -\frac{\mu R}{n^2 \varepsilon^2 m_0} \tag{S-2}$$

where n (=1, 2, 3, ….,) is an integer and $R = m_0 e^4 / 2\hbar^2 = 13.6eV$. The binding energy E_b of the ground exciton state is well known as

$$E_b = \frac{\mu e^4}{2\hbar^2 \varepsilon^2} = |E_1| \tag{S-3}$$

From (S-2), it can be shown that $E_2 = ¼E_1$. Hence,

$$|E_1 - E_2| = \left|E_1 - \frac{1}{4}E_1\right| = \frac{3}{4}|E_1| \tag{S-4}$$

From (S-3) and (S-4), the exciton binding energy can then be expressed as

$$E_b = |E_1| = \frac{4}{3}|E_1 - E_2| \cdot \tag{S-5}$$

Reference: (a) Watanabe *et al, Nat. Mater.* **2004,** 3, p. 406, **(b)** p. 279 in Peter Y. Yu, Manuel Cardona, Fundamentals of semiconductors: physics and materials properties (3rd edition), Springer-Berlin; New York.

Estimation of the polarization term $P = \frac{e^2}{4\pi\varepsilon_0 R}\overline{\sum_{n=1}^{\infty}\alpha_n (\frac{S}{R})^{2n}}$ in equation (3-1)

The P/E_{ex} ~3 is empirically estimated according to the reference[R2]. From the available experimental results of semiconductor nanocrystals, we observed that it is possible to approximate the value of polarization term, P, to a range between ~2 and ~4 of the value of the exciton binding energy, E_{ex} dependent on the material of the nanocrystals. **Figure R1** shows the plots of P/E_{ex} ratio versus the radius of CdS nanocrystals where the solid red circles are the measured data and the dash-dot line is the fitted line [R2]. It is noted that the ratio P/E_{ex} is roughly proportional to its radius. Other semiconductors are also shown in Figure R1. Hence, we assumed that the value of P/E_{ex} is in between ~2 and ~4 so that we set it to ~3.

[R2] Brus, L. E., Electron-Electron and Electron-Hole Interactions in Small Semiconductor Crystallites - the Size Dependence of the Lowest Excited Electronic State. *J. Chem. Phys.* **1984,** 80, 4403-4409.

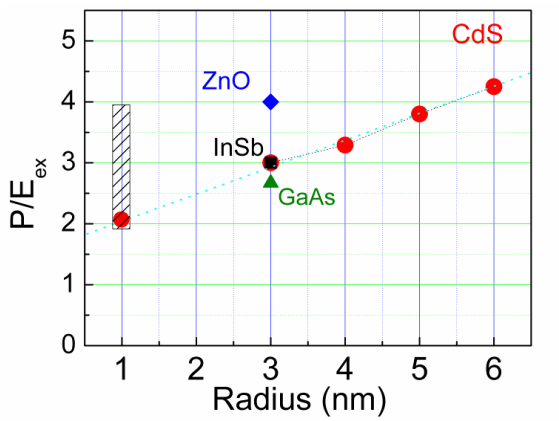

Figure R1. P/E_{ex} versus the radius of different nanocrystals.