Electronic Supplementary Material (ESI) for *Journal of Materials Chemistry C.*

Low-threshold stimulated emission in perovskite quantum dots: single-exciton optical gain induced by surface plasmon polaritons at room temperature

Litao Zhao,[1] Yu Chen,[1] Xiantong Yu,[1] Xiao Xing,[2] Jinquan Chen,[3]* Jun Song[1]* and Junle Qu[1]

Materials：

All chemicals were analytical grade and used without further purification. Hexadecyl trimethyl ammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), lead bromide ($PbBr_2$) and cesium bromide (CsBr) were purchased from Sigma. Gold chloride, ammonium nitrate and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd. Dimethyl Formamide (DMF) and formaldehyde were purchased from Aladdin. Ultrapure water (18.25 $M\Omega\ cm^{-1}$) was obtained using a Nanopure system from Aquapro International Company LLC.

Synthesis of the porous silicon encapsulates the gold core. In a typical synthesis, 0.05 g CTAB was dissolved in ultrapure water (25 mL) containing NaOH (0.02g). After a period of gentle stirring at 80 °C, a formaldehyde solution (1.0 M, 0.1 mL) and an aqueous chloroauric acid solution. (77.6 mM, 1 mL) were separately added. Ten minutes later, tetraethyl orthosilicate (TEOS) (0.15 mL) was added with vigorous stirring. To remove the surfactant, the as-synthesized products were dispersed in a solution of ethanol (100 mL) and ammonium nitrate (0.05g), and the mixture was heated at 80 °C for 6 h.

Synthesis of $CsPbBr_3$ perovskite QDs load on the porous silicon encapsulates the gold core. The porous silicon encapsulates gold core powders were dried overnight under vacuum at 80 °C before use. Then, 1.0 mg of porous silicon encapsulates the gold core powder was impregnated with 1 mL of a solution of 0.25 M CsBr and 0.25 M $PbBr_2$ in DMF. After put the mixture solution in a vacuum environment (< 0.01 Pa), the excess solution was removed by centrifugation, and the as-obtained powder was heated to 120 °C in a vacuum oven for 6 h.

Afterwards, the powder cooled to room temperature under vacuum.

Synthesis of $CsPbBr_3$ perovskite QDs load on the porous silicon without the gold core. The porous silicon encapsulates gold core powders was rinse with aqua regia, the white solid product was washed with DI to a PH value of about 7. Then the CsPbBr3 perovskite QDs was loaded on the as mentioned above.

Femtosecond Transient absorption spectroscopy system

Transient absorption measurements were conducted by means of a Helios spectrometer (Ultrafast Systems LLC), with pump and probe beams derived from a regeneratively amplified *Ti:sapphire* laser system (Coherent Legend, 800 nm, 150 fs, 3 mJ/pulse, and 1 kHz repetition rate). A 400 nm pump beam was generated by frequency-doubling of an 800 nm beam in a BBO crystal. A series of neutral-density filter wheels was used to adjust the power of the pump beam. The pump beam was focused on the sample with a beam waist of about 300 μm. A white-light continuum (WLC) from 450 to 750 nm was generated by attenuating and focusing ca. 10 μJ of the 800 nm pulse onto a sapphire window. The WLC was split into probe and reference beams. The probe beam was focused onto the sample (with a beam waist of 250 μm at the sample) by means of a reflector. The intensities of the pump and probe beams were set at the correct ratio for pulse-to-pulse fluctuation of the WLC. The delay between the pump and probe pulses was controlled by a motorized delay stage. The pump beam was chopped by a synchronized chopper to 500 Hz. The change in absorbances for the pumped and unpumped samples was calculated from data obtained by a phase-locking amplifier. The instrument response function (IRF) of this system was measured as around 150 fs by measuring blank solvent (n-hexane) in a 1 mm pathlength cuvette under the same experimental conditions. The core principle of the femtosecond transient absorption system is to measure the absorption signal ΔA (Δ mOD or Δ OD) at every delay time after excitation of the sample by changing the pump/probe optical path. The optical chopper is placed in the pump path to realize calculating the intensity difference (ΔI) by the detection intensity with (I_{pumped}) or without pump ($I_{unpumped}$) pulses, the final recorded transient absorption signal can be written as: $\Delta A = -\log_{10}(1+\Delta I / I_{unpumped})$.

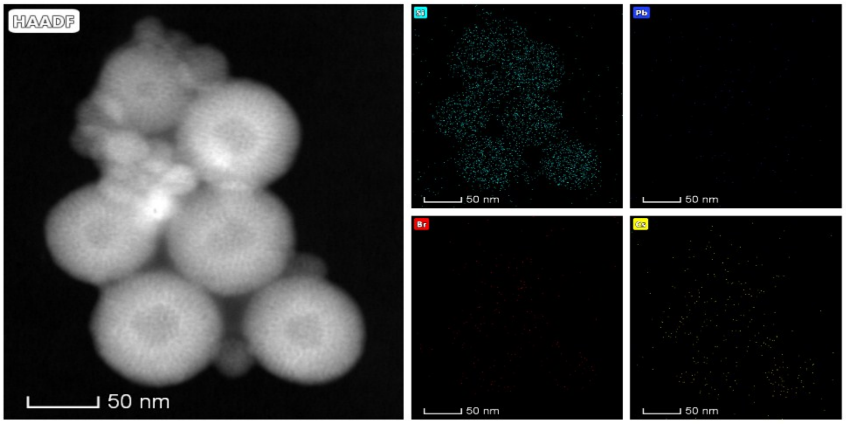

Fig. S1. HAADF-STEM image and corresponding nanoscale elemental mapping of Si, Cs, Pb, and Br of $CsPbBr_3$ QDs loaded in porous silicon shell.

Figure S1 shows the HAADF-STEM image and corresponding nanoscale elemental mapping of Si, Cs, Pb, and Br of $CsPbBr_3$ QDs loaded in porous silicon shell, compared with $CsPbBr_3$ QDs loaded in Au-porous silicon core-shell, the Au core has been removed totally.

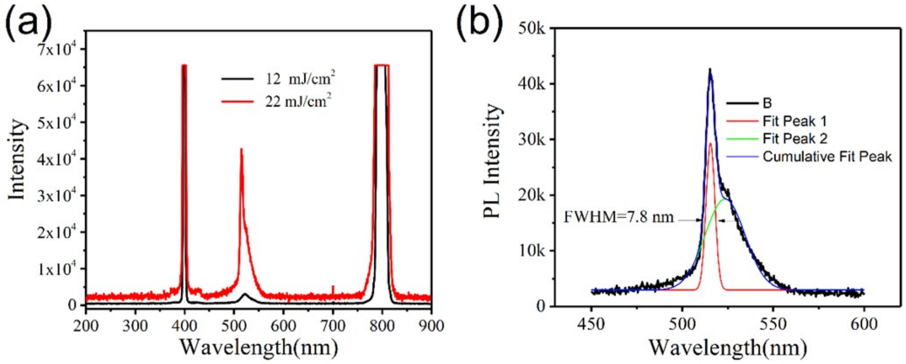

Fig. S2. (a). Pump intensity dependent PL spectra of CsPbBr3 QDs without Au dispersed in n-hexane. (b) Fitting curve of the photoluminescence of $CsPbBr_3$ QDs without Au.

A powdered sample was evenly sandwiched between two pieces of quartz at a thickness of 1 mm and pumped by femtosecond pulses at a wavelength of 400 nm. The repetition rate was 1000 Hz, the pulse width was less than 120 fs, and the focal spot diameter of the excitation beam was about 4 mm. An optical fiber spectrometer (Ocean Optics) was used to collect spectral signals. As shown in Figure S2a, when the emission spectral signals excited by low pump energy were collected, a wide peak appeared at a center wavelength of 522 nm. The power threshold is about 22 mJ/cm^2. Figure S2b shows the multi-peak fitting curve of its emission spectral signals, when the emission spectral signals excited by high pump energy were collected, a narrow plasmonic nano-lasers peak appeared at a center wavelength of 515 nm, and an amplified spontaneous emission (ASE) peak at a center wavelength of 524 nm.

The energies of lowest energy electron (E$_e$) and hole (E$_h$) states can be estimated by:

$$E_e = E_{CB} + \frac{m_h}{m_e + m_h}\left[E_g(QD) + \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon(L/2)} - E_g(bulk)\right] \tag{S1}$$

$$E_h = E_{VB} - \frac{m_e}{m_e + m_h}\left[E_g(QD) + \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon(L/2)} - E_g(bulk)\right] \tag{S2}$$

Where E$_{CB}$,E$_{VB}$, and E_g(bulk) are the conduction band (CB) edge, valence band (VB) edge and band gap of bulk crystals, E_g (QD) the lowest excitonic state energy in QDs, L the QD size, e the electron charge, ε (ε_0) the dielectric constants of bulk crystals (vacuum), and m_h (m_e) the hole (electron) effective mass. Our estimation is basically consistent with the data reported in one of the very recent literature. And the reported value of E_e and E_h are 3.6 and 6.3.[1, 2]

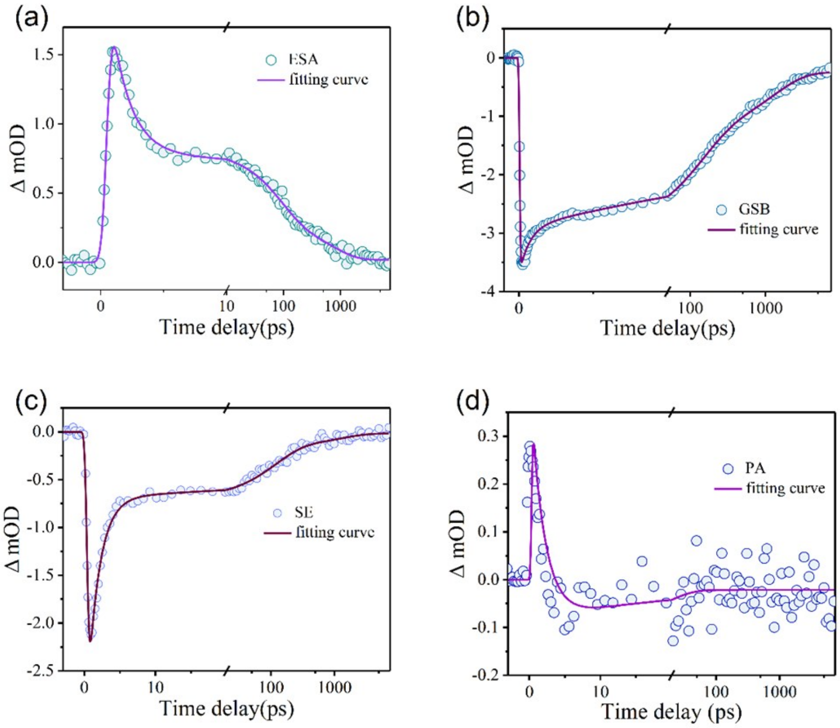

Fig. S3. Time-resolved TAS of $CsPbBr_3$ QDs-Au nanoparticles under low-power pump energy: (a) probed at 480 nm, (b) probed at 520 nm, (c) probed at 545 nm, (d) probed at 610 nm.

Figure S3(a) shows the first section, the selected ESA kinetic curve (480 nm probed) can be fitted with multi-exponential functions, and yields three decay time constants: τ_1=1.5 ps (60%), τ_2= 88 ps (26%), τ_3= 711 ps (14%), the kinetics signals return back to zero. The τ_1 (on the time scale of ten picoseconds) belongs to the interaction between phonons and carriers in the conduction band. The much slower τ_2 and τ_3 (on the time scale of tens of picoseconds and hundreds of picoseconds) can be assigned with the charge transfer from the semiconductor valence band to Au core, the different lifetime scale can be ascribed to the detrapping of the trapped electrons in different trap depths.

Figure S3(b) shows the second section, the selected GSB kinetic curve (520 nm probed) can be fitted with multi-exponential functions, and yields three decay time constants: τ_1=3.5 ps (22%), τ_2= 132 ps (46%), τ_3= 1272 ps (32%), the kinetics signals return back to zero. the second lifetime component τ_2 is associated with the plasmon induced carriers transfer from Au core to the conduction band carriers of QDs, the third lifetime component τ_3 is associated with the radial transition of valence band carriers, and the fastest lifetime component τ_1 can be regard as the hole filling conduction band.

Figure 3(c) shows the third section, the selected SE kinetic curve (545 nm probed) can be fitted with multi-exponential functions, and yields two decay time constants: τ_1=1.6 ps (76%), τ_2= 115 ps (19%) and τ_3= 1215 ps (5%). The fast one component (τ_1) can be regard as *e-h* NR is the abbreviations of electron-hole non-radiative transition between conduction band and valence band, this have been confirmed in the analysis of GSB kinetic curve**.** The time components of τ_2 can be regard as the exciton radiative recombination between conduction band and valence band, and τ_3 can be regard as the radiative recombination of the photogenerated carriers.

Figure S3(d) shows the fourth section, the selected PA kinetic curve (610 nm probed) can be fitted with a multi-exponential decay with a τ_1=1.5 ps (44%) time constant, plus an offset (56%). The fast one (τ_1) can be regard as the final arrival of the equilibrium carriers via carrier-(optical) phonon scattering. The offset in this case is probably due to thermal expansion of the lattice after the electrons and phonons have equilibrated.[3]

Table S1. Best-fit parameters for transient absorption kinetic traces of $CsPbBr_3$ QDs-Au solid powder excited at low pumping power density. Amplitude percentage φ_i was calculated according to $\varphi_i = \alpha_i/\sum|\alpha_i|$. λ_{probe} denotes the probe wavelength.

λ_{probe}	α_1	τ_1	φ_1	α_2	τ_2	φ_2	α_3	τ_3	φ_3
480 nm	0.0012	1.5	60%	0.00051	88	26%	0.00027	711	14%

520 nm	-0.00075	3.5	22%	-0.00158	132	46%	-0.00108	1272	32%
545 nm	-0.00213	1.6	76%	-0.00053	115	19%	-0.00015	1215	5%
610 nm	0.00075	1.5	44%	-0.00095	offset	56%	/	/	/

Figure.4(c) and Figure S3(c) shows a typical kinetic trace recorded with the pump wavelength of 400nm and a probe wavelength of 540 nm. The selected probe photon was right at the position of ASE wavelength in this work.

Both average decay lifetime of stimulated emission of the samples were calculated, and the average lifetime is given by:

$$\bar{\tau} = \frac{\sum_i \alpha_i \tau_i^2}{\sum_i \alpha_i \tau_i} \tag{S3}$$

In this expression τ_i is the decay time, α_i represents the amplitude at t=0 and i stands for the number of decay times. The calculated average lifetimes are 1.2 ns and 127 ps, respectively. The lifetime of 1.2 ns is very consistent with a fluorescence time scale. We can infer that in the sample which excited by low power pumped, the domain relaxation process of the excited state is fluorescence. In this work, the much faster lifetime of 127 ps is associated with the ASE in the sample excited by high power pumped. These conclusions are quite similar with the TRF date of other groups.

Furthermore, the excited state decay rate can be given by its decay lifetime, the function was given by：

$$K_{EXC} = \frac{1}{\bar{\tau}_{EXC}} \tag{S4}$$

the calculated excited state radiative transition rate was $8.3\times10^{8}s^{-1}$ and $7.8\times10^{9}s^{-1}$. This means that, by increasing the excitation power by 7 times, the probability of radiation transition in the excited state increases by 9.3 times, which proves that the number of radiation transition excitons in the excited state is supplemented. This confirms our inference that existence of population inversion distribution in the excited state under high-power pump energy.

References

1. K. Wu, G. Liang, Q. Shang, Y. Ren, D. Kong and T. Lian, *J. Am. Chem. Soc.*, 2015, **137**, 12792-12795.
2. L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, *Nano Lett.*, 2015, **15**, 3692-3696.

3. W. S. Fann, R. Storz, H. W. K. Tom and J. Bokor, *PhRvB*, 1992, **46**, 13592-13595.