

Supporting information for

Photoluminescence Enhancement by Exciton-Plasmon Coupling in MAPbI₃ Quantum Dots on Gold Nanorods

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EXPERIMENTAL SECTION

Materials

MAI (CH₃NH₃I, >98%), PbI₂ (>99%), oleic acid (OA, >85%), oleyl amine (OAm, >50%), γ -butyrolactone (GBL, >99%) were obtained from TCI Chemicals. Deoxidized toluene (spectroscopic grade), toluene (for spectrochemical analysis), dehydrated *N, N*-dimethylformamide (DMF, spectroscopic grade), acetone (>99%), dehydrated acetonitrile (ACN, 99.8%), and deionized water were obtained from Fujifilm Wako. The Au NR solution (NIR-20-750) was obtained from NanoSeedz, and 3-mercaptopropyl trimethoxysilane (MPTS, >95%) from Sigma-Aldrich.

Au NRs film preparation

Au NR films were prepared by depositing Au NRs on MPTS functionalized glass substrates. First, a 500 μ L MPTS solution (a mixture of 5% MPTS, 85% acetone, and 10% deionized water) was dispersed on 25 $\times$ 50 mm² glass coverslips and left for 30 min. The coverslips were successively washed with acetone, deionized water, and acetone and dried by air blowing. The MPTS got hydrolyzed in water and provided free thiol groups on the coverslips. Next, 500 μ L of an Au NR solution (diluted to 1/10th of the commercial sample) was spread on the coverslip and retained for 2 h, during which Au NRs were tethered on the substrate *via* disulfide bond formation. After 2 h, the Au NR solution was removed using a pipette, and the coverslips were cleaned using deionized water and acetone and then dried using an air duster.

Synthesis of ligand-free (bare) MAPbI₃ PQDs

Ligand-free bare MAPbI₃ PQDs (BQDs) were synthesized by a modified spray method.^{S1} Briefly, 0.25

mmol PbI₂ and MAI were dissolved in 1 mL dehydrated DMF. Then, 1 mL GBL was added to the solution to form the 0.125 M MAPbI₃ precursor solution, which was loaded into a spray bottle and sprayed on a coverslip or an Au NR film attached on 5% MPTS functionalized coverslip in a Fume hood. The sample was retained in air for 2 h to evaporate the solvent.

Synthesis of ligand-capped colloidal MAPbI₃ PQDs

Ligand-capped colloidal MAPbI₃ PQDs (LQDs) were prepared by a modified ligand-assisted reprecipitation (LARP) method.^{S2} Typically, 0.1 mmol PbI₂ (45.9 mg), 0.08 mmol MAI (12.7 mg), 200 μ L OA, and 10 μ L OAm were dissolved in 2 mL ACN by 15 min ultrasonication and 5 min stirring. 1 mL of this mixture was injected into 10 mL of deoxidized toluene under vigorous stirring. The as-synthesized crude solution was centrifugated at 7000 rpm for 10min, collected the residue, redissolved it in 12 mL toluene, centrifuged at 2000 rpm for 5 min, and collected the supernatant for further studies. The obtained LQD sample was to 1/20th the concentration and prepared samples for the PL blinking studies, STEM imaging, and absorption and PL measurements.

Absorption and PL measurements

Absorption spectra of LQDs, an Au NR solution, Au NRs, and Au-PQD films were recorded in an Evolution 220 (ThermoFisher) or a Hitachi UH5210 spectrometer. PL spectra were recorded in a fiber-optical spectrometer (Flame FLMS 144.14, Ocean Optics) connected to a single-particle microscope system.

Single-particle PL measurements

BQDs and BQD-Au single particle samples were prepared by the method. LQDs and LQD-Au single particle samples were prepared by dropping a 10 μ L solution on 25 $\times$ 50 mm² glass coverslips or Au NRs films attached on 5% MPTS functionalized coverslips, overlaying the solution with a lens-cleaning paper, and dragging. The PL intensity trajectories of single PQDs were recorded at 32 ms on a microscope (IX70, Olympus) connected to an EMCCD (iXon, Andor Technology), a 40 $\times$ Olympus objective lens (NA = 0.60), a 1% neutral density (ND) filter and a 600 nm long-pass (LP) filter. The PQDs samples were excited by 532 nm cw laser (Millenia IIs, Spectra Physics, 8.3×10^{-3} W cm⁻²).

TEM and HRSTEM imaging

BQD samples for TEM imaging were prepared by spraying a 0.125 M MAPbI₃ precursor solution on STEM Cu100P grids. LQD and Au NR samples for TEM imaging were prepared by dropping a 10 μ L LQD or Au NR solution on STEM Cu100P grids. BQD-Au samples for TEM imaging were prepared by spraying a 0.125 M MAPbI₃ precursor solution on Au NR-coated STEM Cu100P grids. LQD-Au samples for TEM imaging were prepared by dropping a 10 μ L LQD solution on Au NR-coated STEM Cu100P

grids. All the samples were dried overnight in a vacuum. LQD-Au samples for HRSTEM were prepared on HRC-C10 HRSTEM Cu100P grids, similar to the TEM samples. TEM images were recorded using a Hitachi HD-2000 STEM operated at 200 kV. HRSTEM images were recorded in a JEM-ARM200F High-resolution STEM operated at 200 kV.

Time-resolved PL measurements

PL decays of PQDs were acquired using a TCSPC system composed of an avalanche photodiode (APD-AQR14, PerkinElmer) and a single-photon-counting module (SPCM-830, Becker & Hickl, GmbH). Single PQDs were excited by a 405 nm picosecond laser (PicoQuant, 1 MHz) with a pinhole and 480 nm LP filter.

TA measurements

The LQDs on a blank coverslip or an Au film were excited with femtosecond (fs) laser pulses (400 nm, 200 μ W, 1 kHz) delivered from a Ti: Sapphire laser (Spitfire and Tsunami, Spectra-Physics). The repetition rate for the probe pulses was set at 0.5 kHz using a chopper (Model 3501, New Focus, Inc.). Absorption transients were probed with delayed fs white-light continuum pulses generated by focusing the fundamental fs laser pulses (800 nm) into a D₂O cell. After passing through the sample, the probe pulses were detected using a polychromator-CCD camera combination (Spectra Pro-HRS500 and Spec-10, Acton Research Co., and Princeton Instruments). The optical density variation (ΔOD) is defined as $\Delta OD = \log(I_{OFF}/I_{ON})$, where I_{OFF} and I_{ON} are the intensities of probe pulses in the absence and the presence of the pump pulse, respectively. The time resolution was 100 fs. All measurements were performed at room temperature.

FDTD simulations

Electromagnetic simulations were performed to investigate the near-field spectra and the near-field intensity distributions of Au NRs and Au-PQD samples using FDTD solutions (Lumerical, Inc.). The simulations were performed on a discrete and homogeneously spaced mesh with a mesh size of 0.5 nm. The simulation models were prepared according to the structures, sizes, and absorption spectra of Au NRs and PQDs. For the dielectric function of Au, the values reported by Johnson and Christy were used.^{S3}

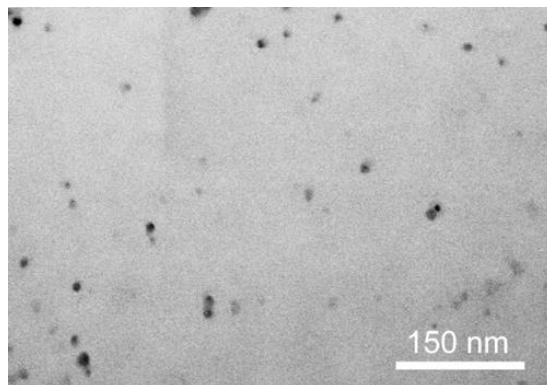


Fig. S1 An enlarged TEM image of a BQD sample in Figure 1C

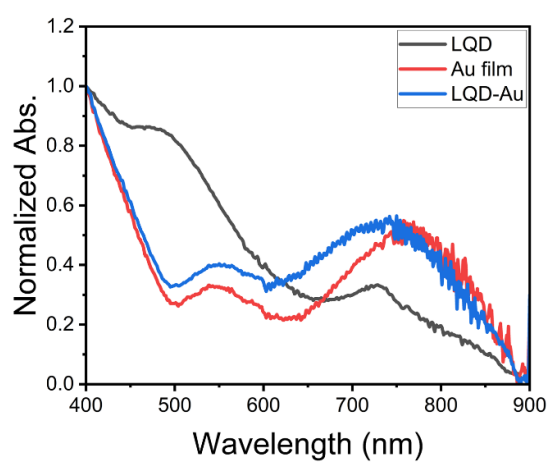


Fig. S2 Absorption spectra of PQD and Au NR samples.

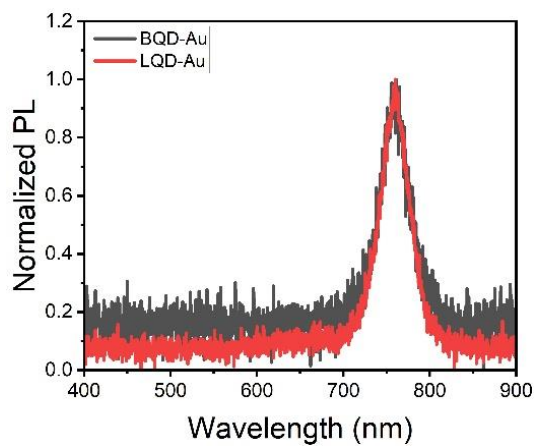


Fig. S3 PL spectra of PQD-Au samples.

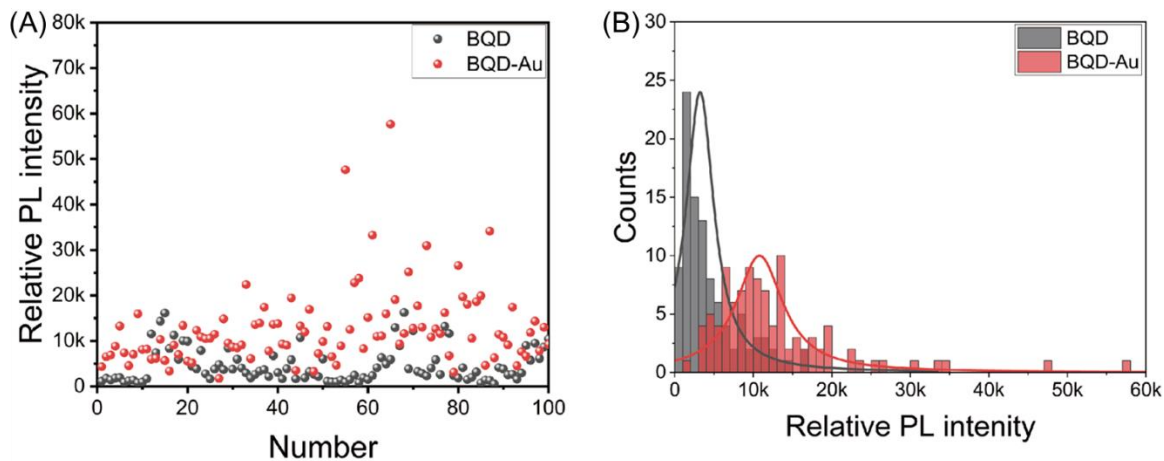


Fig. S4 PL intensity distributions for PQDs: (A) a scatter graph, and (B) a histogram.

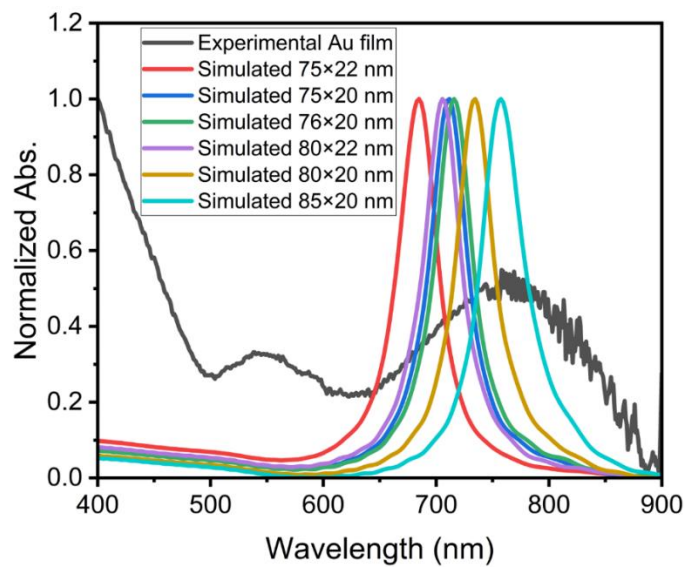


Fig. S5 Simulated and experimental absorption spectra of different size Au NRs.

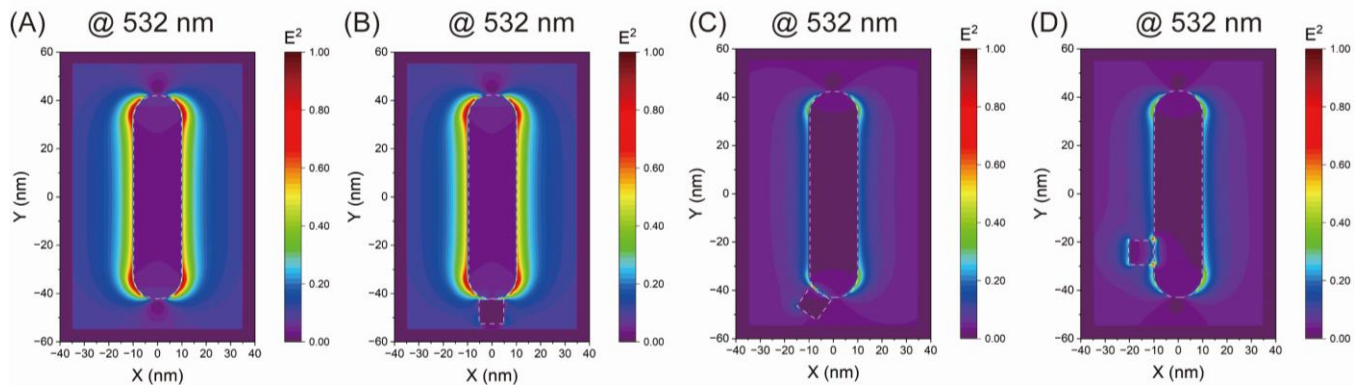


Fig. S6 Simulated electric field distributions for (A) an Au NR, (B), a PQD on an Au NR tip, (C) a PQD on an Au NR tip side, and (D) a PQD on an Au NR side for transverse polarized laser excitations.

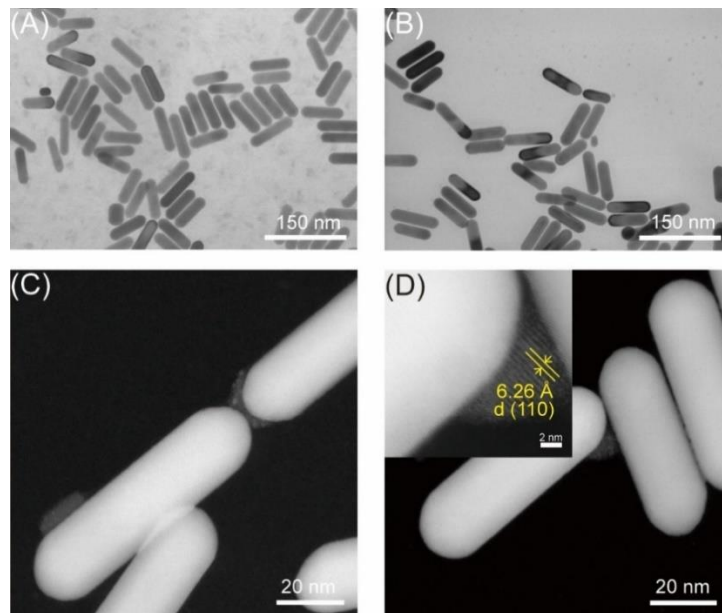


Fig. S7 TEM and HRSTEM images of BQD-Au and LQD-Au samples. (A, B) TEM images of (A) BQD-Au and (B) LQD-Au. (C, D) HRSTEM images of (C) LQD on an Au NR tip and side and (D) LQD on an Au NR tip and side junction. The inset image (D) shows the MAPbI₃ LQD lattice distance of 6.26 Å (110) interplanar spacing.

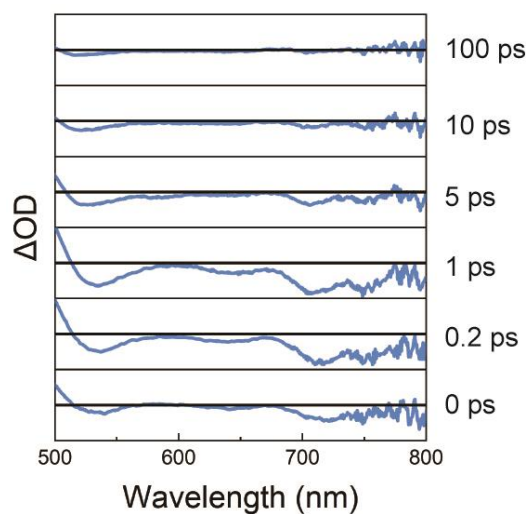


Fig. S8 TA spectra of an Au NR film sample.

Table S1. GSB bleach-recovery fitting parameters and the average recovery times (τ_{av}).

Au	B_1 -0.001	B_2 -0.956	B_3 -0.257		B_4 -0.0067	τ_{av} 2.2 ps
	τ_1 400 fs	τ_2 1.2 ps	τ_3 6.7 ps		τ_4 100.0 ps	
LQD	B_1 -0.001	B_2 -0.75	B_3 -0.292		B_4 -0.003	τ_{av} 1131.7 ps
	τ_1 400 fs	τ_2 66.8 ps	τ_3 3886.8 ps		τ_4 4000.0 ps	
LQD-Au	B_1 -0.001	B_2 -0.807	B_3 -0.179		B_4 -0.001	τ_{av} 46.4 ps
	τ_1 400 fs	τ_2 8.0 ps	τ_3 220.0 ps		τ_4 787.7 ps	

Reference

- S1. Pushkarev, A. P., Korolev, V. I., Markina, D. I., Komissarenko, F. E., Naujokaitis, A., Drabavicius, A., et al. A few-minute synthesis of CsPbBr₃ nanolasers with a high quality factor by spraying at ambient conditions. *ACS Appl. Mater. Interfaces* **11**, 1040–1048 (2019).
- S2. Zhang, F., Huang, S., Wang, P., Chen, X., Zhao, S., Dong, Y., et al. Colloidal synthesis of air-stable CH₃NH₃PbI₃ quantum dots by gaining chemical insight into the solvent effects. *Chem. Mater.* **29**, 3793–3799 (2017).
- S3. Johnson, P. B., Christy, R. W. Optical constants of the noble metals, *Phys. Rev. B* **6**, 4370–4379 (1972).