

Supporting Information

Plasmon-Induced Spatial Electron Transfer between Single Au Nanorod and ALD-coated TiO₂: Dependence on TiO₂ Thickness

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METHODS

Preparation of un-coated Au nanorods (NRs). Uncoated Au NRs were synthesized by a seed-mediated method. Briefly, the seed solution was made by adding a freshly prepared, ice-cold aqueous solution of NaBH₄ (Sigma-Aldrich, 0.6 mL, 0.01 M) into a mixture solution composed of HAuCl₄·3H₂O (Sigma-Aldrich, 0.025 mL, 0.1 M) and CTAB (TCI, 10 mL, 0.1 M). The solution was stirred vigorously for 2 min and aged at room temperature for 5 min before use.

The growth solution was prepared by dissolving CTAB (9.0 g) and 5-bromosalicylic acid (Wako Pure Chemical Industries, 1.1 g) in 250 mL of warm water (Millipore, 55 °C). To this solution, 4.8 mL of 0.01 M AgNO₃ (Sigma-Aldrich) was added, and after keeping undisturbed at room temperature for 15 min, 250 mL of 1 mM HAuCl₄·3H₂O solution was added. After gentle mixing of the solution for 15 min, 1.28 mL of 0.1 M ascorbic acid (Nacalai Tesque) was added with vigorously stirring for 30 s until the mixture became colorless. At this point, 0.8 mL seed solution was added to the entire

growth solution. The mixture was stirred for 30 s and left undisturbed at 27 °C for 12 h. The color of the growth solution slowly changed from colorless to violet indicating the growth of Au nanoparticles.

Characterization of Materials. Extinction spectra were taken using quartz cuvettes of 1-cm path length on a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer. Scanning electron microscope (SEM) images were obtained with JSM-6330FT microscope (JEOL). Transmission electron microscopy (TEM) measurements were carried out on JEOL-2100 operated at 200 KV. For TEM measurement, the Au NRs were dispersed on SiO₂-supported TEM grids, and then coated with TiO₂ by ALD under the same conditions as that on quartz cover glass.

FDTD Calculations. The computational simulations were performed by using the finite-difference-time-domain (FDTD) method with perfectly matched layers (PML) boundary condition. A software package, FDTD Solutions 8.11 (Lumerical Solutions, Inc.), was employed to perform FDTD calculations. The Au NR is modeled as a cylinder capped with two half-spheres at the ends, with a length of 49 nm and a diameter of 14 nm. The boundary with NRs inside was divided into meshes of 0.5 nm in size. For NRs dispersed in aqueous solutions, the refractive index of the medium was set to be 1.33.

Sample preparation for single-particle photoluminescence (PL) experiments. The quartz cover glasses were purchased from DAICO MFG CO., Ltd. (Japan) and cleaned by sonication in a 20% detergent solution (As One, Cleanace) for 6 h, followed by repeated washings with warm water for 5 times. Finally, the quartz cover glasses were washed again with Milli-Q ultrapure water (Millipore). The as-synthesized Au NRs suspensions were centrifuged at 12 000 rpm (Hitachi, himac CF16RX) to remove excess surfactant and washed with Milli-Q ultrapure water for 2 times. The Au NRs with a low concentration were spin-coated on the pre-cleaned quartz cover glass, which was subsequently annealed at 100 °C for 0.5 h to immobilize the NRs on the glass surface. Then the quartz cover glass was treated with O₃ for 15 min to remove the

residual surfactant on Au NRs. Finally the surface was deposited with a layer of TiO₂ with thickness of 1 ~ 5 nm by ALD (Savannah S100, Ultratech/CambridgeNanoTech). Tetrakis(dimethylamido)titanium (TDMAT) and H₂O were used as precursors and the deposition temperature was 150 °C. A deposition rate of 0.4 Å/cycle was obtained.

Single-Particle PL Measurements by Confocal Microscopy. Single-particle PL images and spectra were recorded by using an objective scanning confocal fluorescence microscope system (PicoQuant, MicroTime 200). The samples were excited through an oil-immersion objective lens (Olympus, UplanSApochromat, 100×, 1.4 NA) with a circular-polarized 488-nm continuous wave (CW) laser controlled by a PDL-800B driver (PicoQuant). Typical excitation powers for the PL measurements were 300 μW at the sample. The emission from the sample was collected by the same objective and detected by a single-photon avalanche photodiode (Micro Photon Devices, PDM 50CT) through a dichroic beam splitter (Chroma, 405/488rdc) and long pass filter (Chroma, HQ513CP). For the spectroscopy, only the emission that passed through a slit entered the imaging spectrograph (Acton Research, SP-2356) that was equipped with an electron-multiplying charge-coupled device (EMCCD) camera (Princeton Instruments, ProEM). The spectra were typically integrated for 20 s.

Surface plasmon resonance (SPR) is described as the resonant photo-induced collective oscillation of conduction electrons. Surface plasmons can concentrate the light flux in small regions surrounding the nanostructure, and the SPR-enhanced electric fields will permeate into a neighbouring semiconductor, which is known as plasmon resonance energy transfer (PRET) process. Surface plasmons can also decay by the formation of excited (hot) electrons. The SPR-generated electrons can cross the Schottky barrier formed at the interface between metal NPs and semiconductors, or relax by radiative decay to generate plasmon photoluminescence (PL).^{1,2} Specifically for Au NRs, the interband transition was excited initially to produce electron–hole pairs.

A fast interconversion occurs between the electron–hole pairs and the transversal surface plasmon resonance (TSPR) that subsequently decays radiatively, generating the short-wavelength PL. Meanwhile, the hot electrons lose their energy nonradiatively and interconvert to the LSPR mode, which emits a photon via radiative decay (long-wavelength PL).^{1, 2} To maximize charge separation of hot electrons from the Au NRs surface, the Au NRs can be coupled with an efficient electron acceptor, e.g., high-work-function metals,^{3, 4} graphene⁵ or TiO₂. Such a charge transfer from the Au NRs can effectively weaken the intrinsic ultrafast energy relaxation in the Au. Meanwhile, the hot electrons transfer from Au to TiO₂ competes with the plasmon emission, leading to PL damping. Therefore, the hot electrons transfer process can be investigated *via* tracking the PL change of Au NRs. Meanwhile, because the chemical synthesis of Au NRs often yields a broad distribution of sizes and aspect ratios, single-particle spectroscopy enables the exclusion of undesirable effects caused by sample heterogeneity.

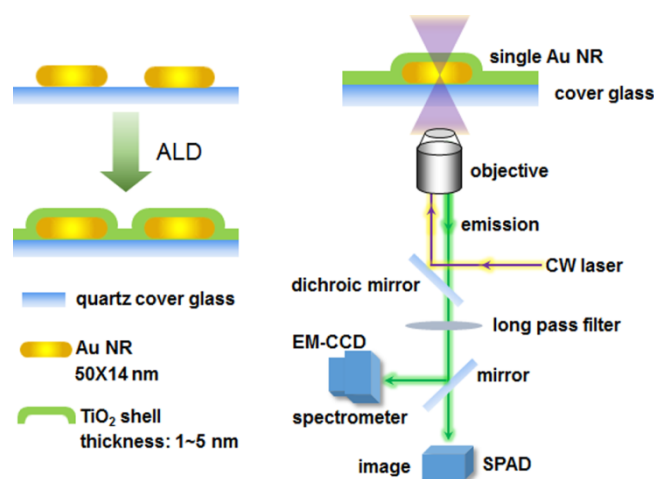


Fig. S1 Illustration of the experimental setup for the sample preparation (left) and single-particle PL spectroscopy based on confocal microscope system (right).

To directly monitor the PL behavior of single Au NR coated with TiO₂, the confocal microscope system was utilized combined with ALD technique (as shown in Fig. S1). Firstly, mono-dispersed Au NRs with a low concentration were spin-coated on the pre-

cleaned quartz cover glass, which was subsequently annealed at 100 °C for 0.5 h to immobilize the NRs on the glass surface. Then the quartz cover glass was treated with O₃ for 15 min to remove the residual surfactant on Au NRs. Finally the surface was deposited by a layer of TiO₂ with thickness of 1 ~ 5 nm *via* ALD. The single-particle PL measurement was carried out with a circular-polarized 485 nm continuous wave (CW) laser to avoid the excitation of TiO₂, while only the interband excitation of Au NRs occurs. For the PL measurement, suitable dichroic mirror and long pass filters were utilized to completely remove the laser excitation light. The PL image was obtained by a single-photon avalanche diode (SPAD). While for the spectroscopy, the emission passed through a slit with width of 150 μm and was collected by an electron-multiplying charge-coupled device (EMCCD) camera.

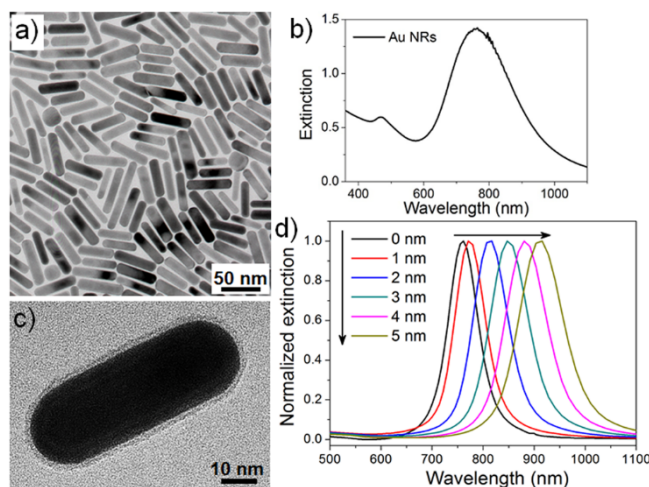


Fig. S2 (a) TEM images and (b) UV-vis-NIR extinction spectra of the as-prepared Au NRs. (c) Representative TEM image of single TiO₂-coated Au NR with thickness of 2 nm. (d) Calculated extinction spectra at the LSPR region for single TiO₂-coated Au NRs with various shell thickness of 0 ~ 5 nm using the FDTD method.

The Au NRs were synthesized by the seed-mediated method.^{6, 7} Fig. S2a shows transmission electron microscopy (TEM) image of the as-synthesized Au NRs. These NRs have an average aspect ratio of 3.7, and they gave rise to an LSPR peak centered at

about 763 nm (Fig. S2b). It is known that the ALD provides uniform, monolayer thickness control of the layer, which is crucial for studying the plasmonic interaction of metal NPs with semiconductor layers.⁸ To confirm the homogeneity of the TiO₂ layer deposited at 150 °C by ALD, the Au NRs were dispersed on SiO₂-supported TEM grids, and then coated with TiO₂ by ALD under the same conditions as those dispersed on quartz cover glass.

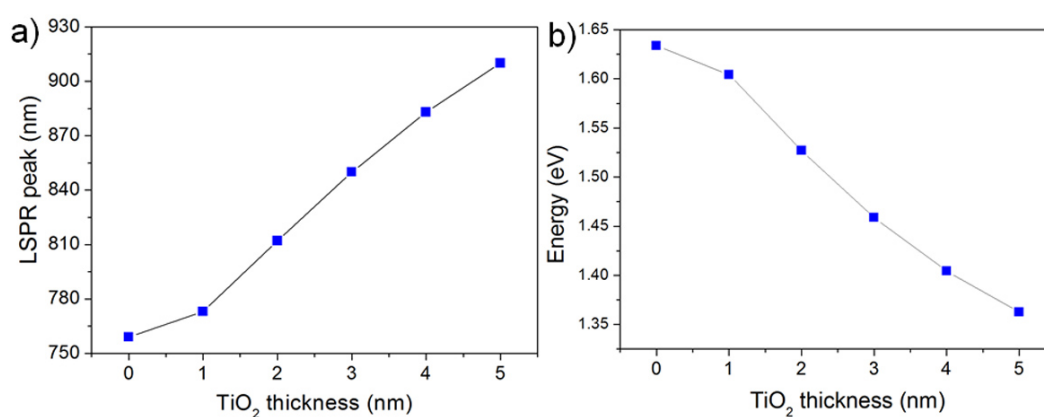


Fig. S3 Calculated LSPR peak position (a) and energy (b) as a function of TiO₂ shell thickness.

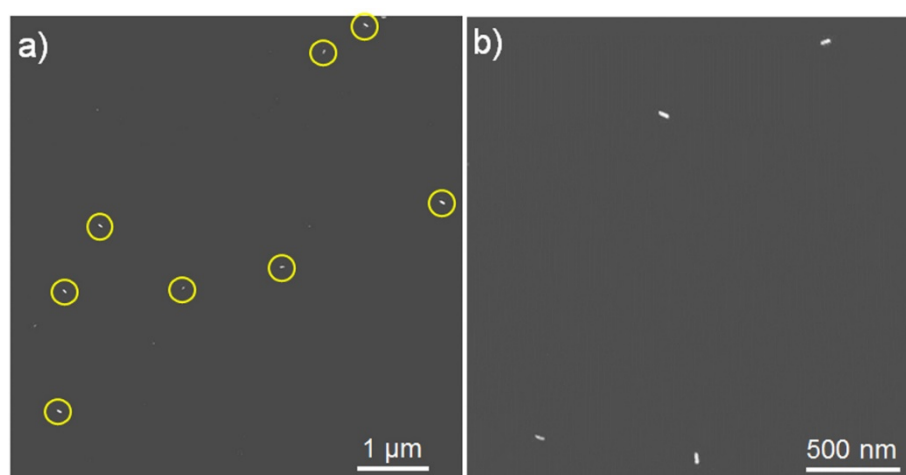


Fig. S4 Large-area (a) and zoomed-in (b) SEM images of mono-dispersed Au NRs deposited on quartz cover glass substrate.

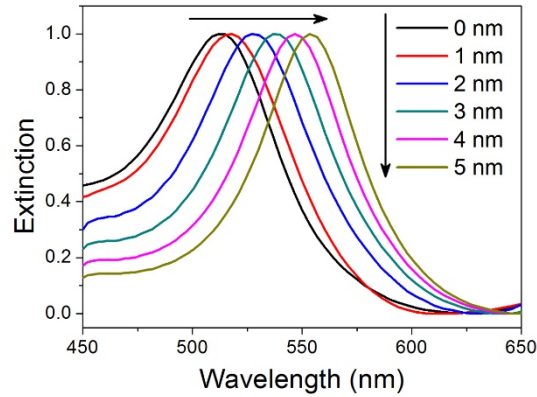


Fig. S5 Calculated normalized extinction spectra for TiO₂-coated Au NRs with various shell thickness of 0 ~ 5 nm using the FDTD method. The refractive index of the surrounding medium was taken to be 1, simulating the conditions in single-particle PL experiment.

To investigate such a red shift of TSPR PL peak, the extinction spectra for TiO₂-coated Au NRs with various shell thicknesses were calculated by the FDTD simulation, while the refractive index of the ambient medium was taken to be 1, simulating the atmospheric conditions in single-particle PL experiment.

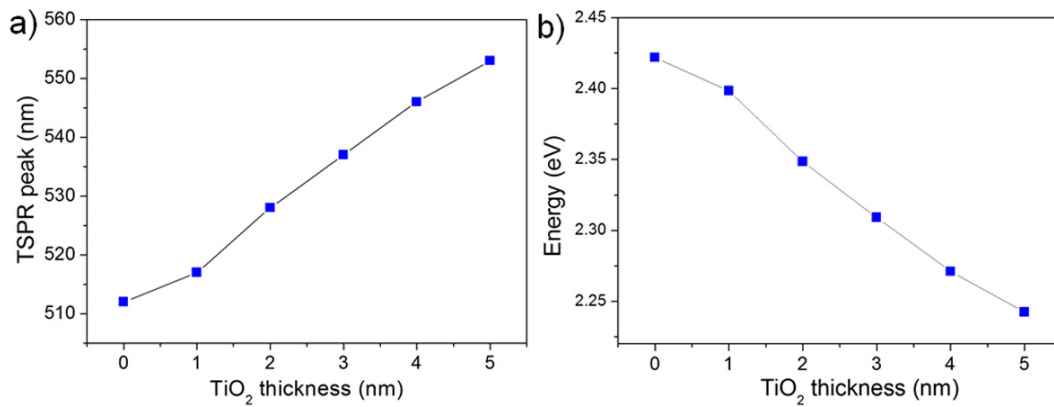


Fig. S6 Calculated TSPR peak position (a) and energy (b) as a function of TiO₂ shell thickness.

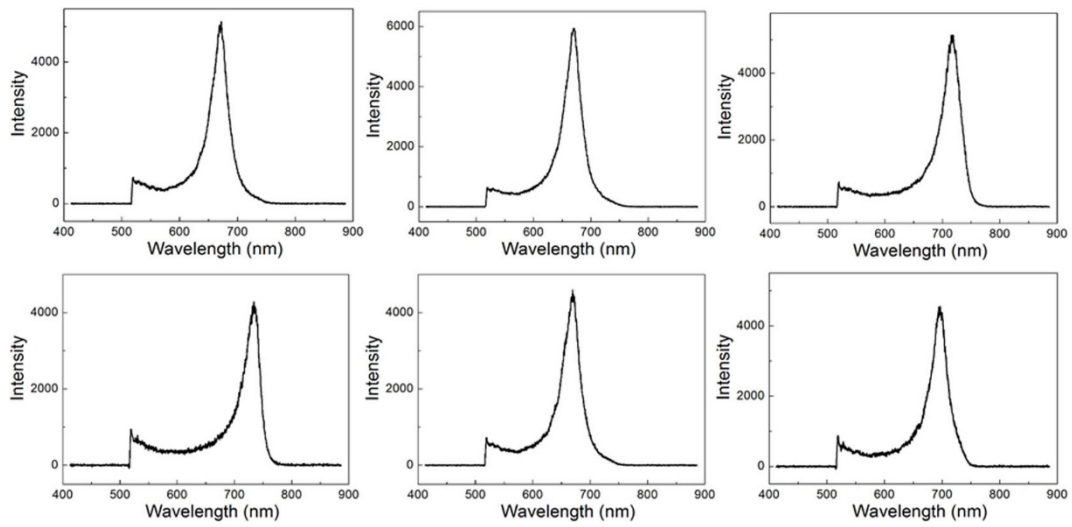


Fig. S7 PL spectra of six representative single naked Au NRs.

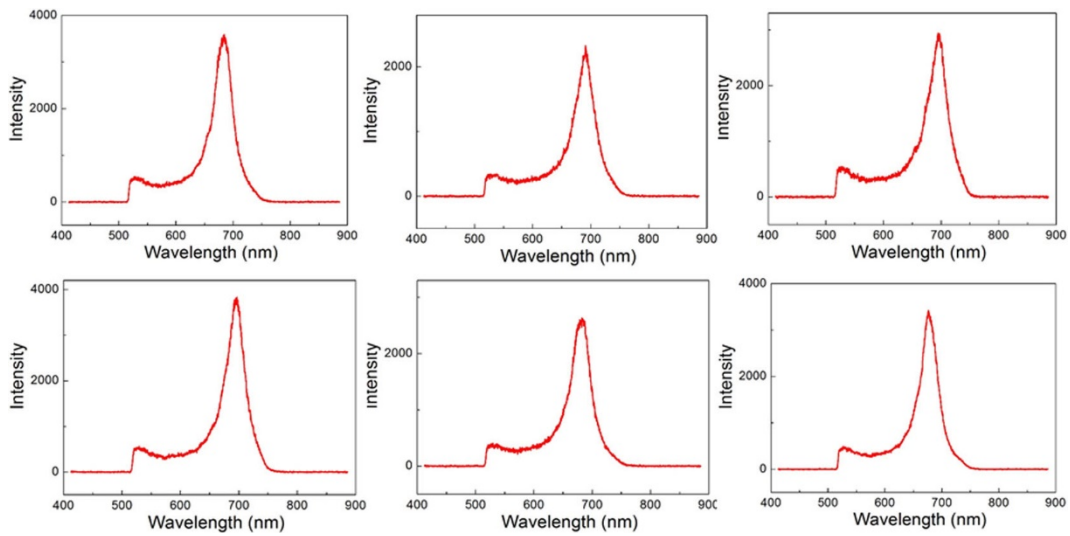


Fig. S8 PL spectra of six representative single TiO₂-coated Au NRs with thickness of 1 nm.

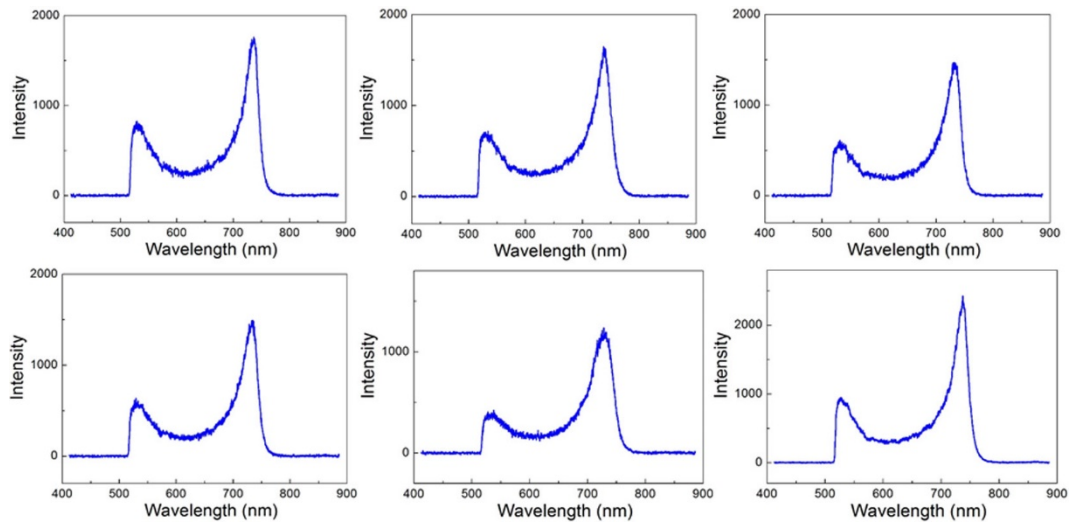


Fig. S9 PL spectra of six representative single TiO_2 -coated Au NRs with thickness of 2 nm.

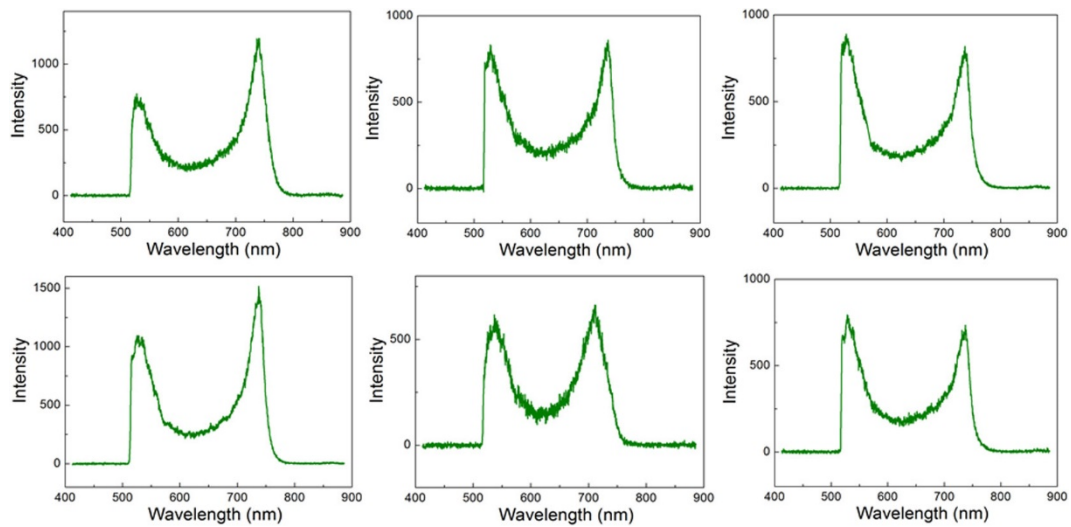


Fig. S10 PL spectra of six representative single TiO_2 -coated Au NRs with thickness of 3 nm.

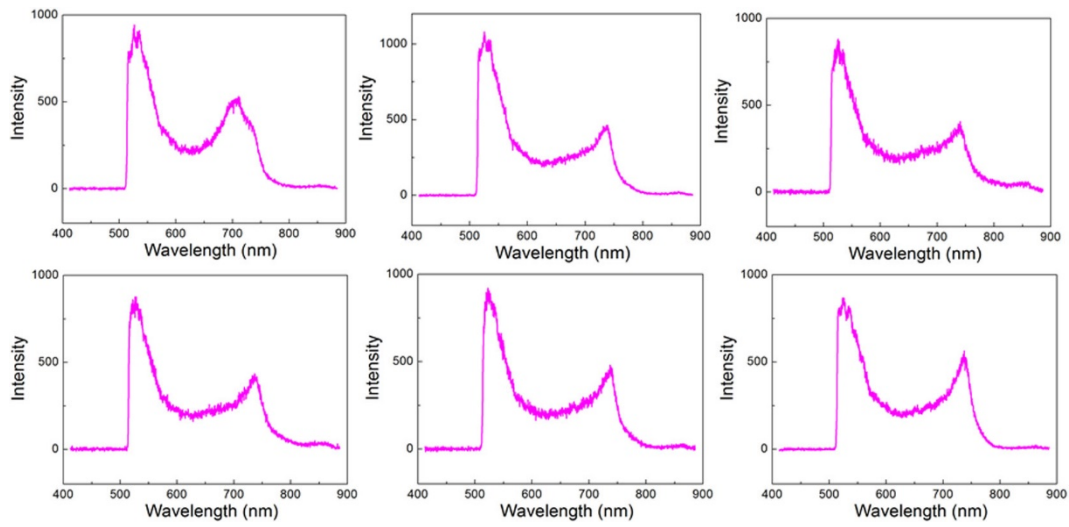


Fig. S11 PL spectra of six representative single TiO₂-coated Au NRs with thickness of 4 nm.

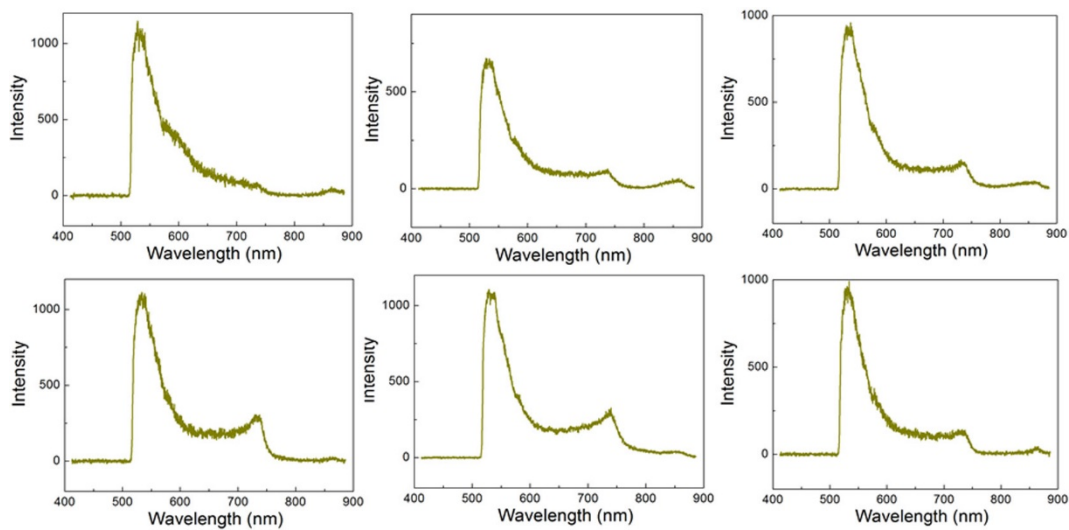


Fig. S12 PL spectra of six representative single TiO₂-coated Au NRs with thickness of 5 nm.

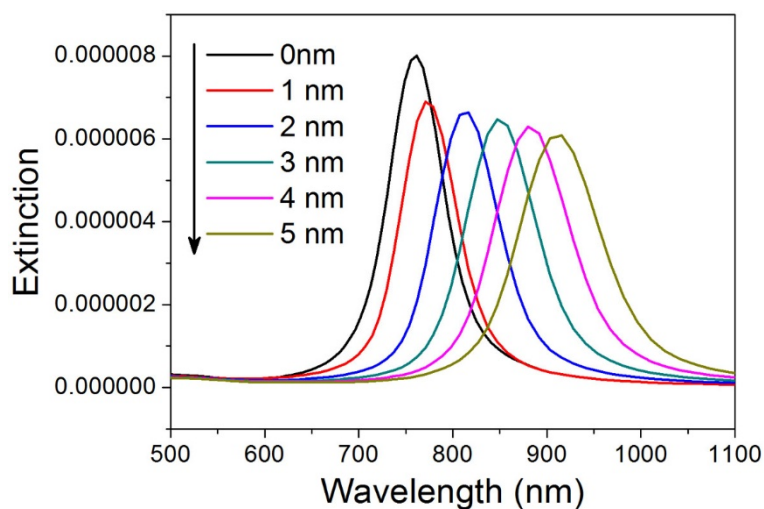


Fig. S13 Calculated extinction spectra at the LSPR region for single TiO₂-coated Au NRs with various shell thickness of 0 ~ 5 nm using the FDTD method.

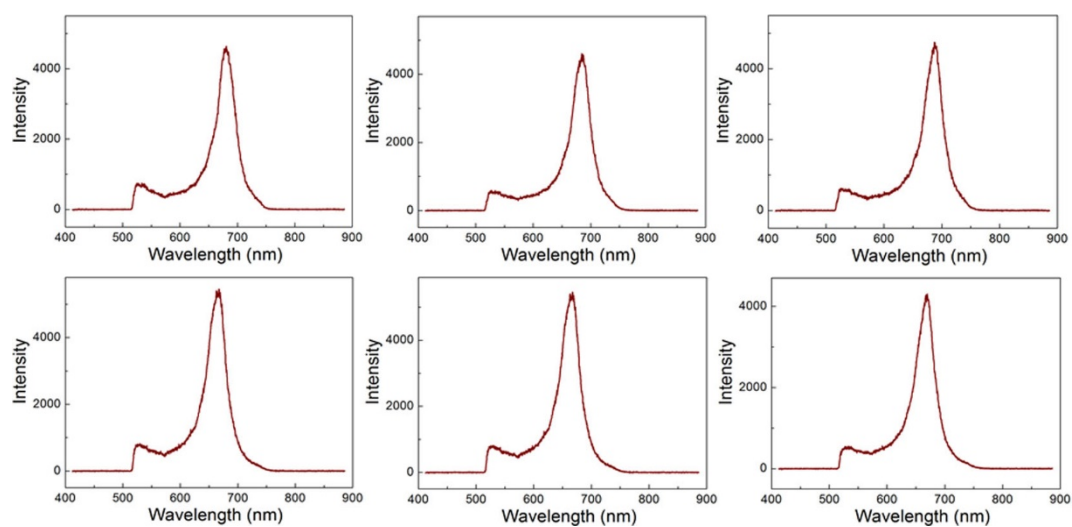


Fig. S14 PL spectra of six representative single Al₂O₃-coated Au NRs with thickness of 5 nm.

Notes and references

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