Supporting information

Plasmon-Enhanced Fluorescence of PbS Quantum Dots for Remote Near-Infrared Imaging

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1. Experimental procedures

Fabrications of Au seeds and urchin-like Au NPs: 1 ml of 10 mM sodium citrate solution and 1 ml of 10 mM $HAuCl_4$ solution was added to 37 ml nanopure H_2O (18.2 MΩ cm) in a 50 ml beaker. Then, 1 ml of 100 mM sodium borohydride ($NaBH_4$) cooled in an ice-bath for 10 minutes was added to the sodium citrate-$HAuCl_4$ solution. The resulting solution turned reddish-brown immediately, which indicated the formation of Au seeds with a diameter of 5 nm. Au seeds were left undisturbed at 30 ^oC for 3 hours to allow for hydrolysis of any remaining $NaBH_4$ before further use. For secondary growth of Au seeds, 200 ml 50 mM cetyltrimethyl ammonium bromide (CTAB) was stirred at 30 ^oC until dissolved. 4 ml of 25 mM $HAuCl_4$ solution, 2 ml of 100 mM ascorbic acid was added in sequence. After the solution turned colorless, 1.6 ml of 10 mM silver nitrate and 40 μL of NaI was quickly added, respectively. To initiate growth, Au seeds was added, briefly stirred, and allowed to sit for 10 hours at a constant temperature of 30 ^oC. Urchin-like Au NPs with various diameters were tailored by adding different volumes of Au seeds from 40 to 280 ml.

Synthesis of SiO_2 shell and PbS QDs: Prior to synthesis of the silica shell, Au NPs were washed three times by the centrifugation at 14000 rpm for 10 minutes to remove any excess CTAB in the gold colloid. The base-catalyzed condensation of SiO_2 shells onto the Au NPs was accomplished by addition of 600 μL of 100 mM NaOH to the 8 ml Au NPs to adjust pH value to 10. The deposition of silica shell was initiated by addition of various amounts of tetraehtylorthosilicate (TEOS) to Au NPs solution under vigorous stirring. Different volume of TEOS solution for from 20 to 200 μL corresponded to different shell thickness from 5 to 20 nm. After the final TEOS addition, solution is allowed to react overnight while stirring. Au@SiO_2 NPs are

collected by the centrifugation at 14,000 rpm for 10 minutes. For chemical synthesis of PbS QDs, 10 ml distilled water was added to 489.6 mg N-Acetyl-L-Cysteine (NAC) under magnetic stirring, and its PH value is adjusted to 8.0 by adding 100 mM NaOH. After 10 ml of 100 mM lead acetate was introduced into the solution of NAC, 10ml of 50 mM aqueous solution of Na_2S was slowly added. Finally, aqueous solution instantly turned from buff to dark-drown, indicating the formation of PbS QDs.

Acquisitions of fluorescence spectroscopy: In the process of measuring the fluorescence, the laser went through a fold mirror, two mirrors, a beam splitter and then projected onto the sample. The fluorescence spectrum was collected by CCD and the fluorescence lifetime was measured by time correlated single photon counter. To take fluorescence imaging, the sample was set onto the beam splitter and the CCD was placed at the position of trigger diode, we changed the distance between them to obtain the best imaging distance. In the experiment, the distance between the CCD and the sample was changed from 35 to 70 cm, when the distance was 35 cm the image was clearest, as increasing the distance the clarity was decreasing until the image could not be recognized.

Computer simulation: In three-dimensional finite difference time domain (FDTD) simulations, the unit cell was defined as $0.25\times0.25\times0.25$ nm^3. The number of periods of the incident sinusoidal plane wave was set to 10 to guarantee calculation convergence, which could be judged by checking whether near zone electric field values had reached a steady state. The sinusoidal plane wave had an amplitude of 1 V/m, and an irradiation wavelength of 826 nm.

2. Supporting figures.

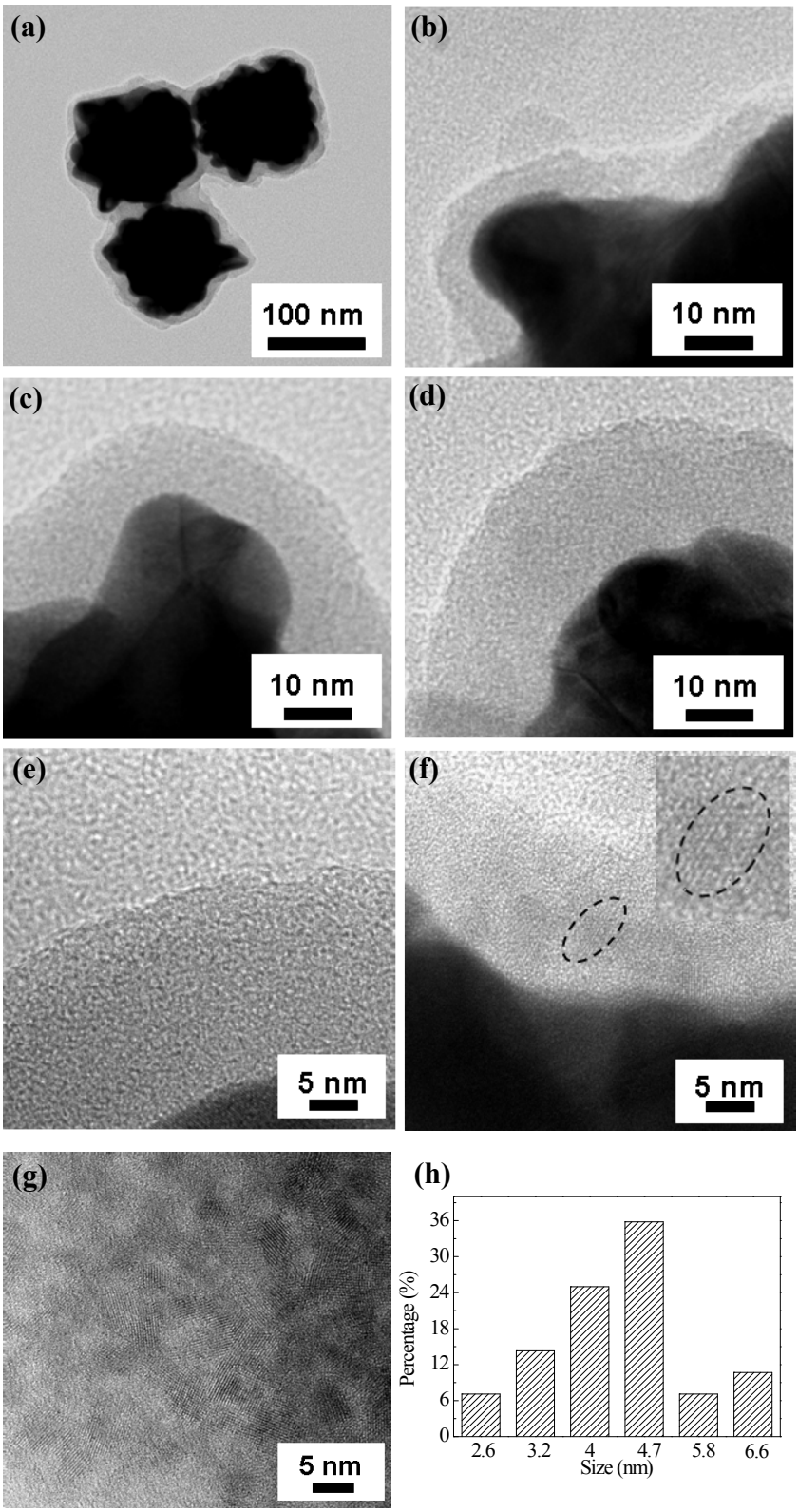

Figure S1. TEM images of Au@SiO_2 NPs with tunable shell thicknesses. (a) Au NP uniformly coated by SiO_2. (b-d) The thicknesses of SiO_2 coated onto the Au NPs are 5, 10 and 20 nm, respectively. (e) High resolution TEM image of pure SiO_2 coated onto Au NPs. (f) High resolution TEM image of PbS QDs hybridized onto Au@SiO_2 NP. The circled regions are PbS QDs. The inset Fig. S1(f) is the magnified image of PbS QDs. (g) HRTEM image of PbS QDs and (h) its size distribution.

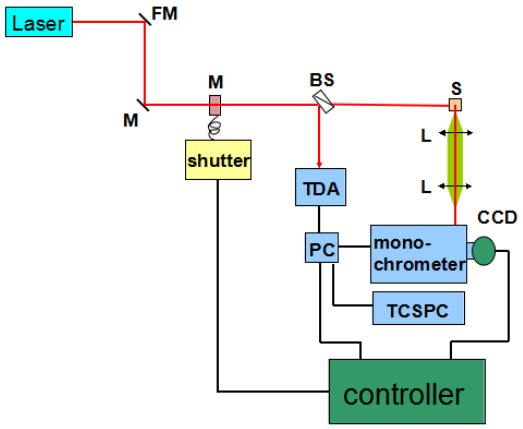

Figure S2. Optical configuration for collecting fluorescence spectroscopy. BS: Beam Splitter; TDA: Trigger Diode; FM: Fold Mirror; M: Mirror; L: Lens; PC: Personal Computer; S: Sample; TCSPC: Time Correlated Single Photon Counter.

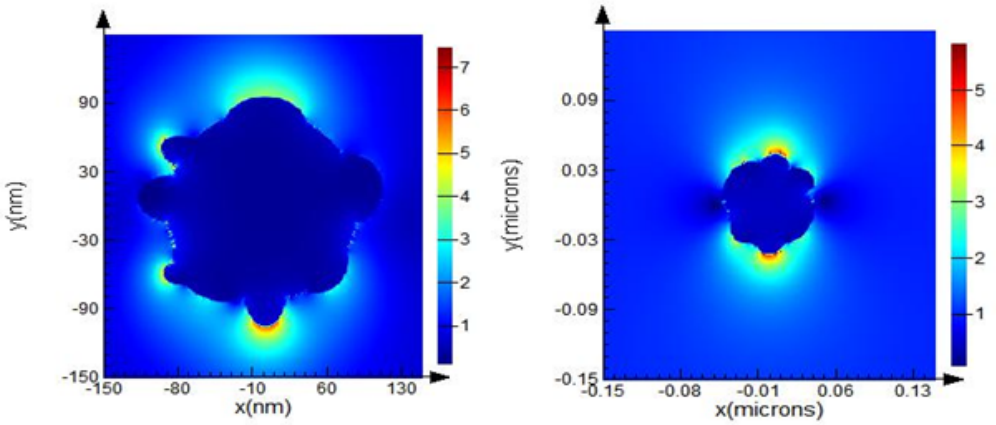

Figure S3. Field distributions of Au NPs with the diameters of 170 and 50 nm calculated by FDTD simulation. The wavelength of the exciting laser is 826 nm. Laser polarization is vertical.

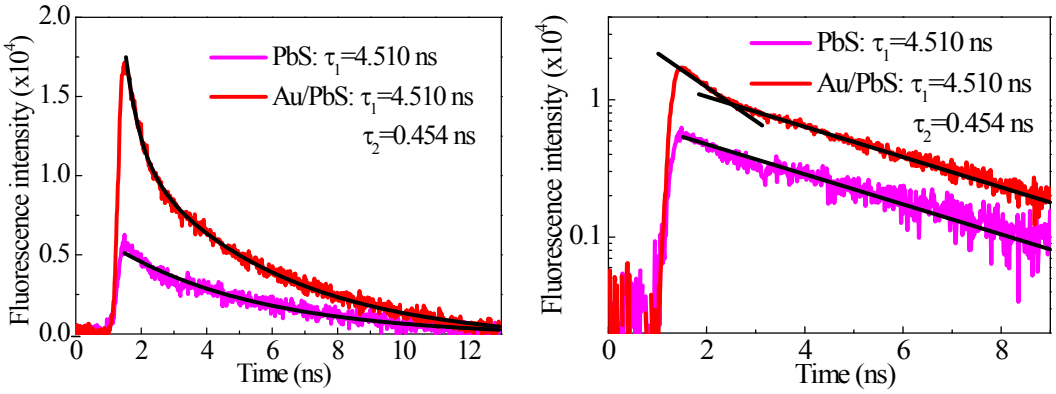

Figure S4. (Left) The experimental data and fitting curve of transient fluorescence spectra of pure PbS QDs and the hybrid consisting of Au@SiO_2 NPs and PbS QDs. The data for pure PbS QDs is fitted following the equation $y = Ae^{-\frac{x}{\tau_1}} + y_0$. The data for the hybrid is fitted following the equation $y = A_1 e^{-\frac{x}{\tau_1}} + A_2 e^{-\frac{x}{\tau_2}} + y_0$. (Right) The vertical axis is log scale in order to facilitate visualizing the single and double exponential decay evidenced by their different slopes. Black lines are plotted only for guarding the eyes.

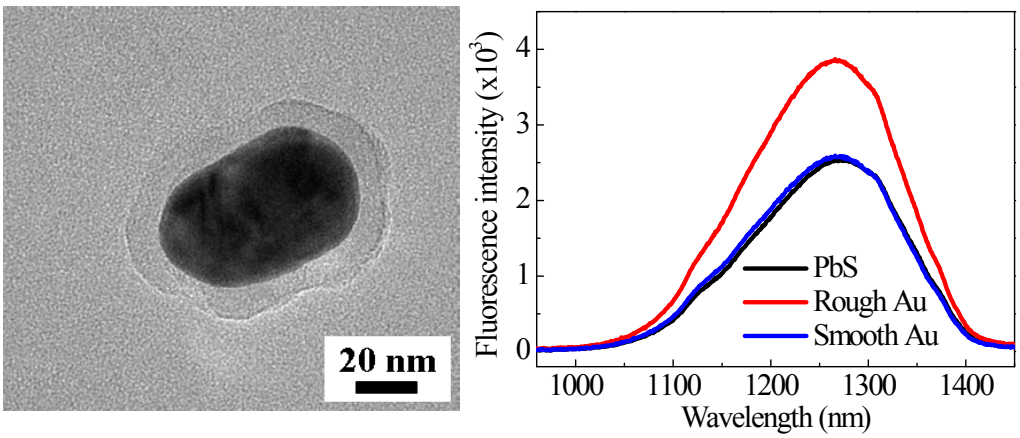

Figure S5. (Left) Gold nanoparticle with smooth surface is coated SiO_2 with a thickness of 10 nm. (Right) fluorescence spectra of the hybrid consisting of PbS QDs and gold nanoparticles with smooth and rough surfaces. The SiO_2 shell is 10 nm in thickness.

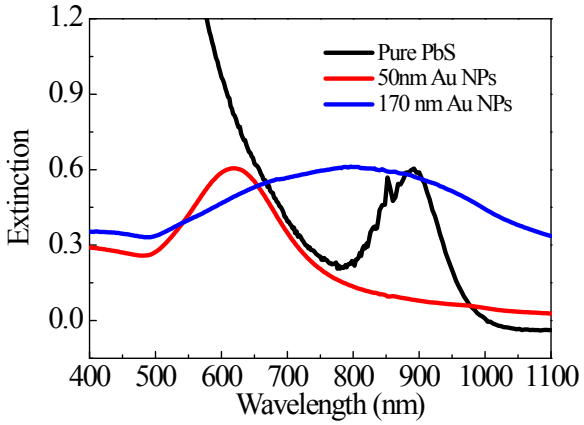

Figure S6. Extinction spectra of pure PbS QDs, and the hybrid consisting of PbS QDs and Au@SiO_2 NPs. A spike at 850 nm results from the switching of light source.