Electronic Supplementary Information

Visualizing the bi-directional electron transfer in a Schottky junction consisted of single CdS nanoparticles and a planar gold film

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Experimental Procedures

Materials. The CdS nanoparticles were prepared as follows: 0.14 M 400 mL Na_2S was slowly added to 0.14 M 500 mL $Cd(OAc)_2$ under stirring. The yellow suspension was stirred for 24 h and kept for an additional 24 h. Yellow-colored precipitate was filtered and dispersed in 60 mL pure water. The as-prepared suspension was transferred to a Teflon-lined stainless steel autoclave, which was heated at the temperature of 473 K for 72 h. The yellow slurry was washed three times with pure water and ethanol, respectively. The yellow precipitate was dried for another 24 h in vacuum at 368 K.

Characterizations. As-prepared CdS nanoparticles was characterized by dynamic light scattering spectroscopy (DLS, Malvern Nanosizer) and diffuse reflection UV-vis spectrum (UV-3600, Shimadzu). Raman spectrum was collected with a Raman microscope (InVia-Reflex, UK). A 25 mW, 785 nm laser was adopted, and the exposure time was 10 s.

SPRM apparatus. The plasmonic imaging of CdS nanoparticles was carried out on a home-built SPRM microscope. SPRM was consisted of an inverted optical microscope (Nikon, Ti-E), coupled with a super-luminescent diode (Qphotonics Inc., wavelength = 680 nm, output power = 0.2 mW), a linear polarizer (Edmund Optics, Catalog No. 54-926), a beam splitter (Thorlabs, Catalog No. BSW10R), and a CCD camera (Pike F-032B, Allied Vision Technology). A high numerical aperture objective (CFI Apochromat TIRF 60XH N.A. 1.49) was required to excite SPPs in aqueous solution. A PDMS chamber with a volume of 600 μL (flexPERM slide, SARSTEDT) was adhered onto a gold-coated coverslip (BK-7 No. 1 glass, Fisher Scientific, Catalog No. 12-541-B), which was placed on the microscope stage, acting as a reaction well. The gold-coated coverslip was fabricated by sequentially covering a coverslip with a 2 nm Cr layer, and a 47 nm Au layer with high-power impulse magnetron sputtering (HIPIMS, MSI50x6-L, GCEMarket).

A 150W fiber-coupled mercury lamp was adopted as the light source for blue and green light illumination, by placing a blue (500 nm low-pass) and green (530-580 nm band-pass) filter between the lamp and condenser (N.A. = 0.52). The illumination density of blue/green light (for photo-excitation) and red light (for SPRM) was measured by a power-meter (PM100D, Thorlabs). Another 620 nm high-pass filter was placed between the beam splitter and the camera to keep the light from the condenser from entering the camera. For capturing the SPRM images under blue/green light illumination, a Qphotonics superluminescent diode (SLD) was adopted as the SPRM light source, as it exhibited much better stability. However, its maximum output power is ~ 2 mW. In order to excite SPPs for hot electron injection, a laser diode (Coherent OBIS, wavelength = 660 nm, output power adjustable from 0.5 to 70 mW) was adopted as the SPRM light source instead. Note that the effective power of red light for generating SPPs was ~35 mW because only 50% of the incident light reached objective after passing through a 50/50 beam splitter. OBIS laser diode exhibited larger noise due to the worse output stability compared with the Qphotonics SLD.

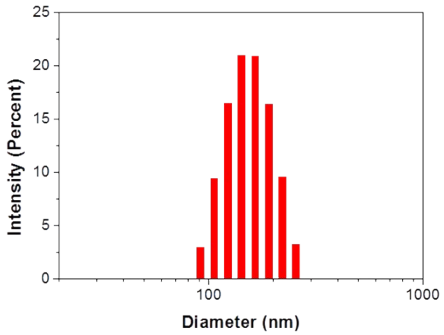
The CdS NPs powder was dispersed in deionized (DI) water with a concentration of 0.05 mg/mL under the vigorous sonication for ca. 6 minutes. The size of the CdS NPs was ca. 160 nm after the sonication as indicated in Fig. S1. The yellow suspension was added onto the gold chip for 3 seconds and then rinsed quickly with DI water. The CdS NPs modified gold chip was then transferred to the SPRM with the addition of reaction solution for further experiments.

Results and Discussion

S1. Size-distribution of as-prepared CdS nanoparticles

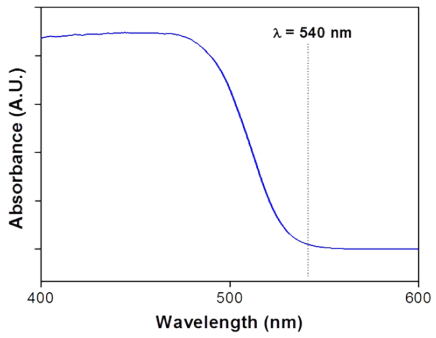
Fig. S1 displays the size distribution of as-prepared CdS nanoparticles characterized by dynamic light scattering (Malvern Nanosizer), revealing an average diameter of 160 ± 20 nm.

Fig. S1. Size distribution of as-prepared CdS nanoparticles.



S2. Diffuse reflection UV-Vis absorption spectrum of as-prepared CdS nanoparticles

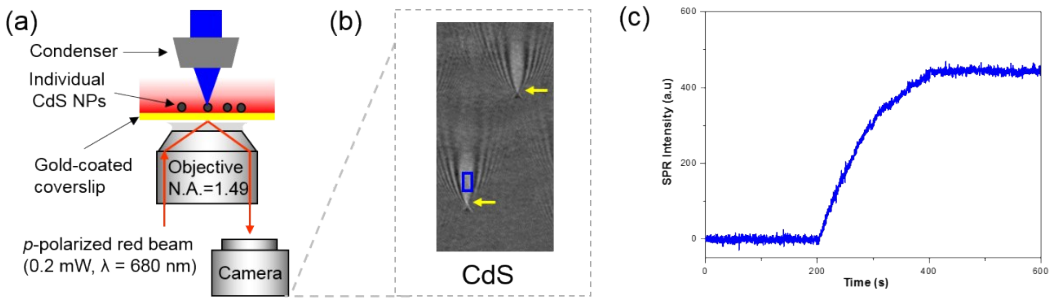
Fig. S2. Diffuse reflection UV-Vis absorption spectrum of as-prepared CdS nanoparticles.



S3. SPRM imaging of CdS nanoparticles

The SPRM setup (Fig. S3a) was built on an inverted optical microscopy (Nikon, Ti-E). 47nm-thick gold film coated on a glass coverslip was used as the SPR sensor chip. The SPR image of CdS nanoparticles is displayed in Fig. S3b. When illuminating the interface with blue light (λ<500 nm), photo-induced electron injection from CdS nanoparticles to gold film resulted in a hole-rich CdS, which oxidized S^{2-} in the solution to deposit sulfur at the nanoparticle surface, increasing the SPR intensity (Fig. S3c).

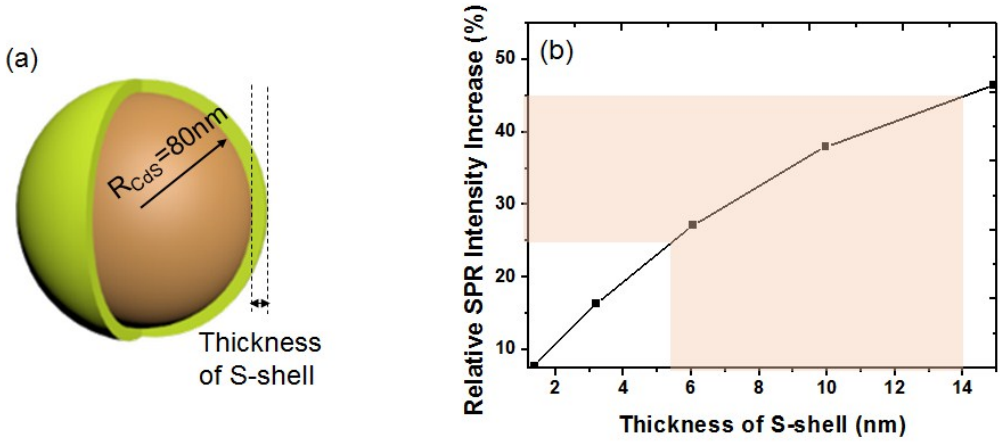
Fig. S3. (a) Schematic illustration of the home-built SPRM setup. (b) Representative SPRM image of two CdS nanoparticles, in which yellow arrows indicate the locations of the nanoparticles, and blue rectangle indicates the region-of-interest we typically select to quantify the contrast. Image intensity within the blue rectangle is averaged to be used as the SPRM intensity. (c) The SPRM intensity curve of a CdS nanoparticles when illuminated with blue light (200^{th} – 400^{th} second). The blue light power density is 14 mW/mm^2.



S4. Estimation of deposited sulfur shell thickness with COMSOL simulation

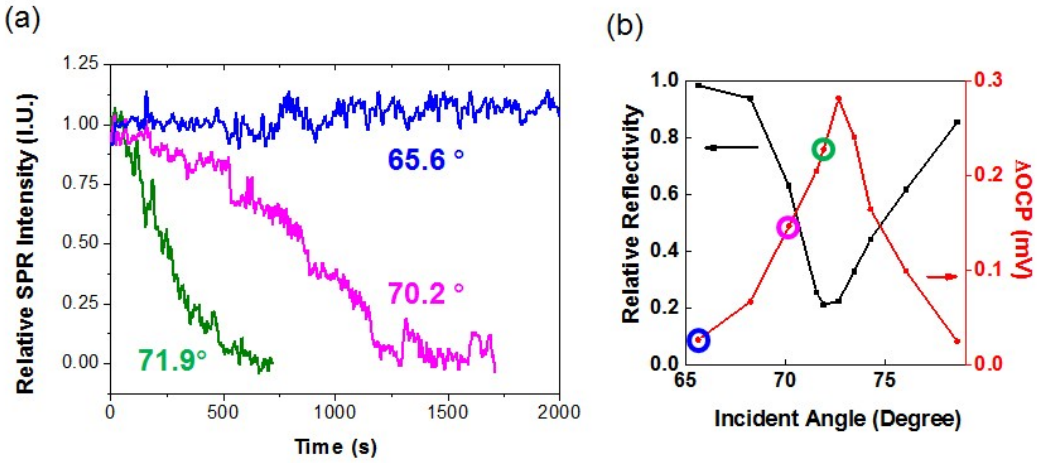
The sulfur-induced SPR intensity increase of a single CdS nanoparticle was calculated by a COMSOL software with a previously-established 3-dimensional model. Please refer to our previous publication Anal. Chem., 2016, 88, 2380-2385 for details regarding the COMSOL simulation and model. The model is consisted of a spherical CdS nanoparticle with a radius of 80 nm (refractive index = 2.5) surrounded by a sulfur shell with different thickness ranging from 1 to 15 nm (refractive index of sulfur was set to 2.1). Experimental results often revealed a relative SPR intensity change between 25 – 45%, corresponding to a thickness of 5 to 14 nm.

Fig. S4. (a) 3-Dimensional model of CdS@S used for COMSOL simulation. (b) Calculated dependence of relative SPR intensity increase (percentage) on the thickness of sulfur shell.



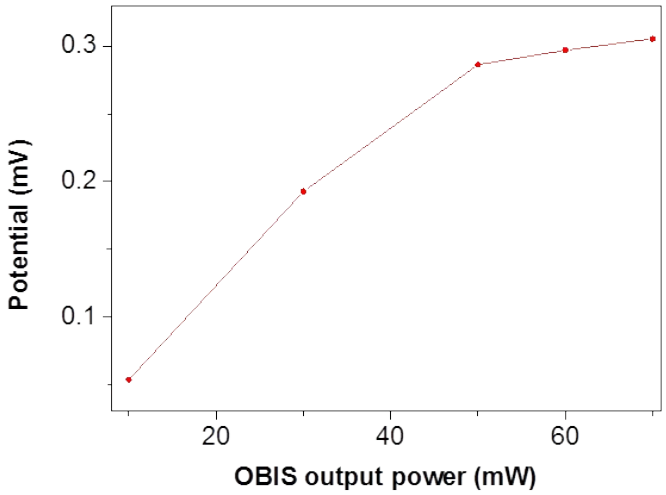
S5. Dissolution rate of sulfur under different incident angles

Fig. S5. (a) Representative SPRM intensity curves of single CdS nanoparticles under different red light incident angle (OBIS laser, output power = 70 mW). Faster dissolution rate is observed when the incident angle is close to the surface plasmon resonance angle (72.6° in this case). (b) The locations of above-mentioned three angles are marked by green, magenta, and blue circles, respectively.



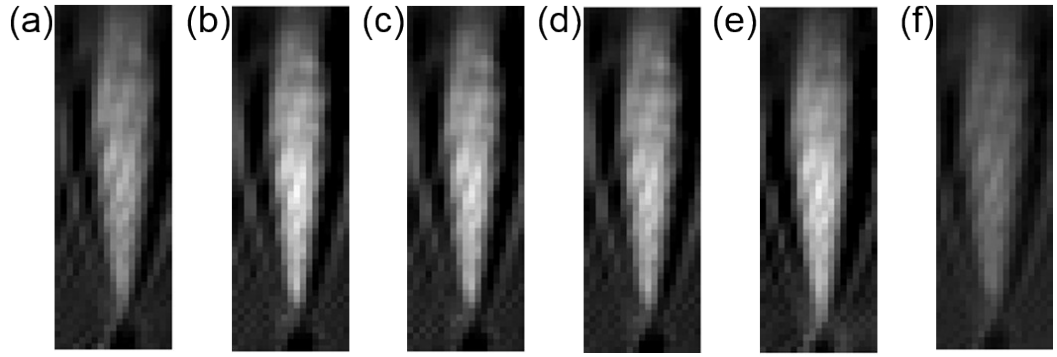
S6. The relationship of OCP change and the power of incident red light

Fig. S6. Δ OCP increases with increasing power of red light (660-nm OBIS laser diode).



S7. Control experiments on thermal effect

Fig. S7. SPRM image of a single CdS nanoparticle: (a) before and (b) after the illumination of blue light of 200 seconds, (c) another 200 seconds after the withdrawal of blue light in the presence of 0.05 mM Na_2S, (d) after the incubation with 35 °C 0.05 mM Na_2S solution for 200 seconds (room temperature is 20 °C), after the illumination of 70 mW red light at (e) non-SPR angle (0 deg) and (f) SPR angle (71.5 deg) sequentially.



S8. Descriptions of movie S1

Movie S1 shows the SPRM images of two individual CdS nanoparticles during the entire experiment. The first SPRM image has been subtracted from the video to emphasize the SPRM changes due to deposition and dissolution of sulfur. The experimental procedure is described below:

0-200 s, baseline recording. No blue light. OBIS power = 0.5 mW for SPRM imaging.

200-400 s, sulfur deposition. Apply blue light. OBIS power = 0.5 mW.

400-700 s, sulfur is stable in the presence of 0.05 mM Na_2S. No blue light.

700-1400 s, sulfur dissolution. Change the OBIS power to be 70 mW. Note that the effective power of red light for generating SPPs was ~35 mW because only 50% of the incident light reached objective after passing through a 50/50 beam splitter.