Electronic Supplementary Information

In-situ SERS study of surface plasmon resonance enhanced photocatalytic reaction using bifunctional Au@CdS core-shell nanocomposite

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Experimental details

Chemicals and reagents

Tetrachloroauric (III) acid hydrate (AR), sodium citrate (AR), ammonium (AR), thiourea (AR), and MB were purchased from Sinopharm Chemical Reagent (Shanghai) Co., Ltd. p-nitrophenol (pNTP) and cadmium chloride ($CdCl_2 \cdot 2.5H_2O$) was purchased from Alfa Aesar. All reagents were used as received without further purification. Milli-Q water (18.2 MΩ·cm) was used for the preparation of aqueous solutions in the whole study.

Preparation of Au@CdS NPs

Typically, 1.5 mL sodium citrate aqueous solution (1 wt%) was rapidly added into 200 mL boiling $HAuCl_4$ (0.01 wt%) solution to obtain the 55 nm Au NPs. After cooling down to room temperature, 100 mL of the as-prepared 55 nm Au NPs solution, 3 mL cadmium chloride solution (0.1 M) and 5 mL sodium citrate (0.05 M) were added into a round-bottom flask and stirred. Then, the pH value of the solution was tuned to 10 using $NH_3 \cdot H_2O$, after which 1.3 mL thiourea (0.2 M) was added. After stirring at room temperature for another 10 min, the mixture was heated to 70 ^{o}C for 3 h, 5 h, and 8 h to generate Au@CdS NPs with shell thickness of 3 nm, 5 nm, and 10 nm, respectively.

Characterization

The morphology of the Au@CdS NPs was characterized by scanning electron microscope (SEM, HITACHI S-4800) and transmission electron microscope (TEM, JEOL JEM 1400; HR-TEM, JEOL JEM 2100). The UV-Vis absorption spectra were collected on a UV-vis spectrophotometer (UNICO, UV2012C/PC/PCS). EDS mapping analysis was performed on field-emission transmission electron microscope (TEM, Philips TECNAI F30).

Photocatalytic measurements

The photocatalytic activity of samples was evaluated by the degradation of a MB aqueous solution with an initial concentration of 5 ppm in a quartz glass reactor with a water jacket controlling the reaction temperature. A xenon lamp (PerfectLight, MICROSOLAR300) with 500 nm longpass filter ($\lambda > 500$ nm) was used as visible light source to provide a light intensity of 150 $mW \cdot cm^{-2}$, and its distance to the reactor was fixed to about 10 cm. Before the photocatalytic degradation, the samples were soaked in 30 ml of 5 ppm MB aqueous solution and the solution was bubbled with air for 1 h to reach adsorption equilibrium. A thermostatic water cycle system was applied to keep the reaction temperature at 30 ℃ with continuous stirring. After visible light irradiation started, the solution was periodically taken out from the reactor and analyzed with a UV-Vis spectrophotometer.

In-situ SERS study of the photocatalyic reaction on Au@CdS-film

Au film with a thickness of 200 nm was fabricated by electron beam evaporation with Temescal FC2000 on silicon wafer. The Au film was immersed in concentrated sulfuric acid for 15 min, then rinsed by water and dried at room temperature, in order to remove any contaminants. The clean Au film was immersed in 10 mM MB or pNTP ethanol solution for 1 h, and then rinsed with ethanol, to generate MB- or pNTP-assembled Au film, respectively.

A simple procedure was adopted to prepare uniform monolayer substrate from the as-synthesized Au@CdS NPs.[27]. Typically, 5 mL of cyclohexane was added in 20 mL of Au@CdS sol. The mixtures were stirred for 30 s. Then 5 mL of ethanol was added into the mixture dropwise. Finally, a large and uniform monolayer film of Au@CdS appeared, which was then transferred to the as-prepared MB- or pNTP-assembled Au film. By this way, the MB or pNTP molecules were located in the gap between Au@CdS and Au film, so that their Raman signals can be greatly enhanced.

A confocal Raman spectrometer (HORIBA, X-plora) was used to record Raman signals of MB and pNTP molecules on gold film. The laser wavelength, power, exposure time, and collection frequency during the measurement was 638 nm, 20 mW, 1 s, and once, respectively.

3D-FDTD simulation

The electromagnetic (EM) field distribution of Au@CdS NPs on gold substrate was stimulated by three-dimensional finite different time domain (3D-FDTD) on a commercially available Lumerical FDTD Solutions software (version 7.5). A Au@CdS dimer with core size of 55 nm and shell thickness of 5 nm placed on a smooth gold substrate was chosen as the model for the simulations. The thickness of gold substrate was 200 nm, and the region of the refined structure was 1×1×1 nm, respectively. During the simulation, the dimer was illuminated by a linearly polarized plane wave with electric field amplitude of 1 V/m and wavelength of 638 nm.

Additional data and figures

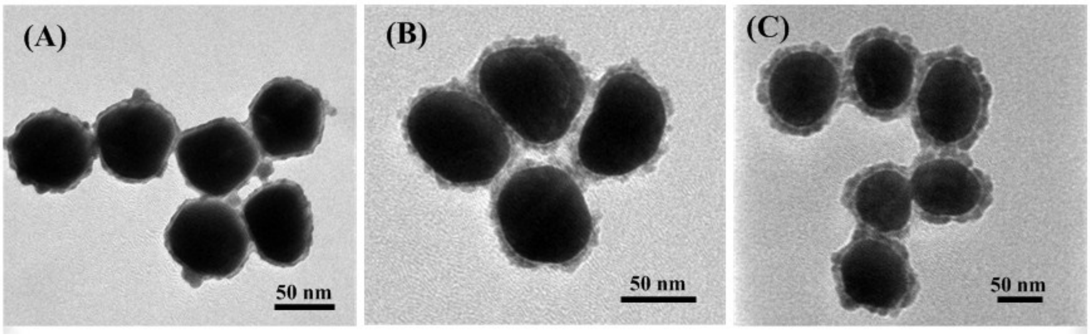

Figure S1. TEM images of Au@CdS with shell thickness of 3 nm (A), 5 nm (B), and 10 nm (C).

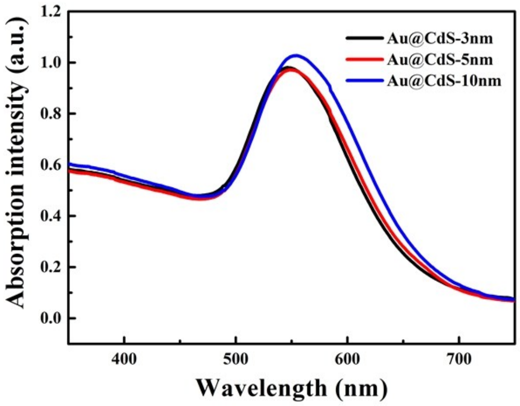

Figure S2. UV-vis absorption spectra of Au@CdS NPs with different CdS shell thickness: 3 nm, 5 nm, and 10 nm.

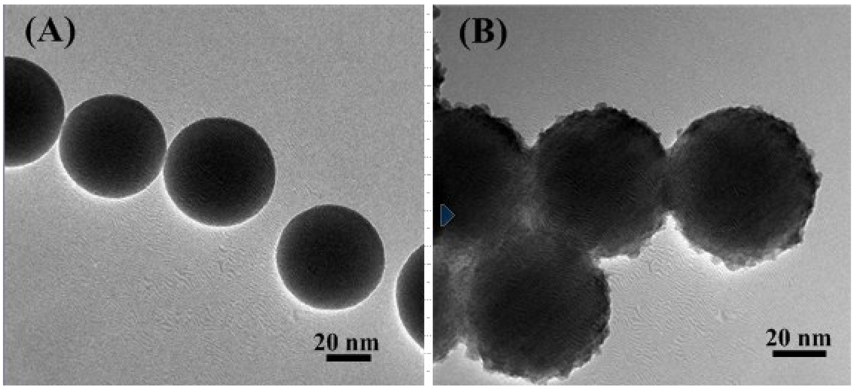

Figure S3. TEM images of SiO_2 NPs and SiO_2@CdS NPs

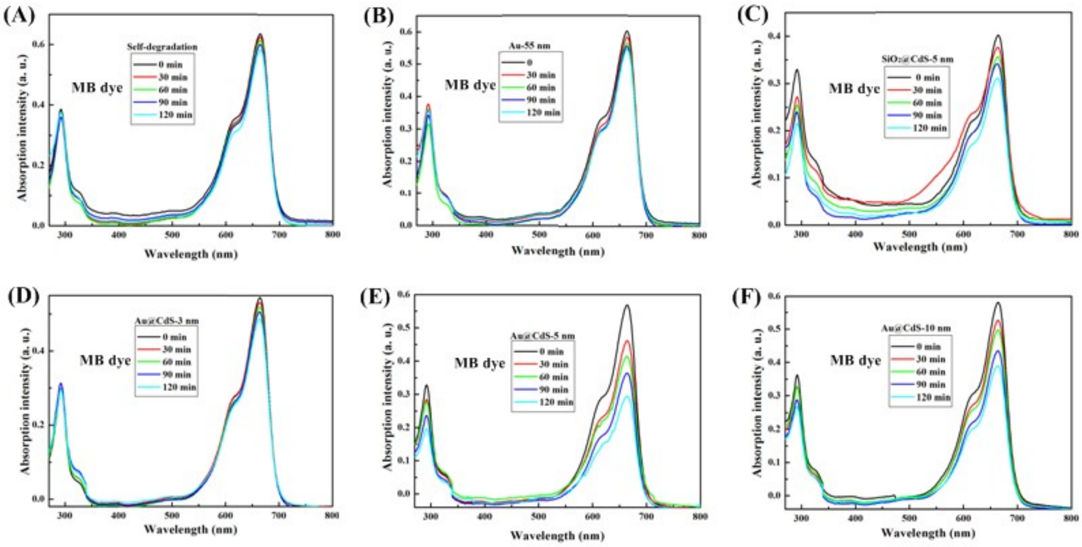

Figure S4. Absorption spectra of MB under different irradiation time using different nanoparticles as catalyst: (A) self-degradation, (B) Au NPs, (C)SiO_2@CdS-5nm (D) Au@CdS-3nm (E) Au@CdS-5nm (F) Au@CdS-10nm.

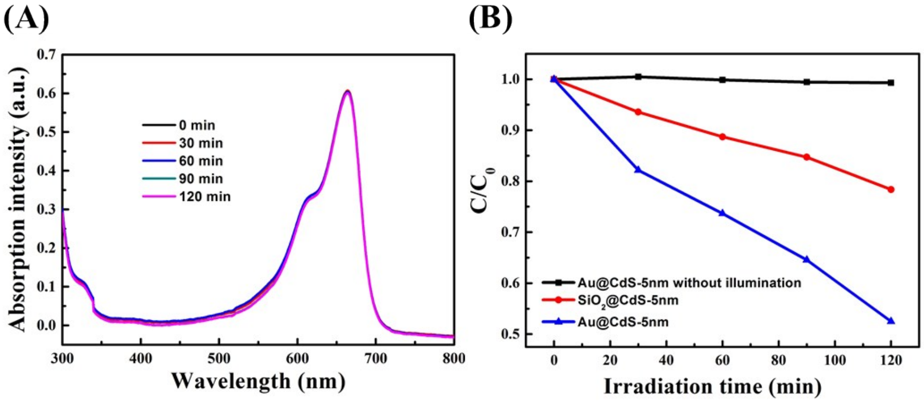

Figure S5. (A) Absorption spectra of MB without light irradiation using Au@CdS-5nm NPs; (B)Time dependent decrease of the MB dye concentration using Au@CdS-5nm NPs with and without 500 nm longpass light illumination, and using SiO_2@CdS-5nm NPs with 500 nm longpass light illumination.

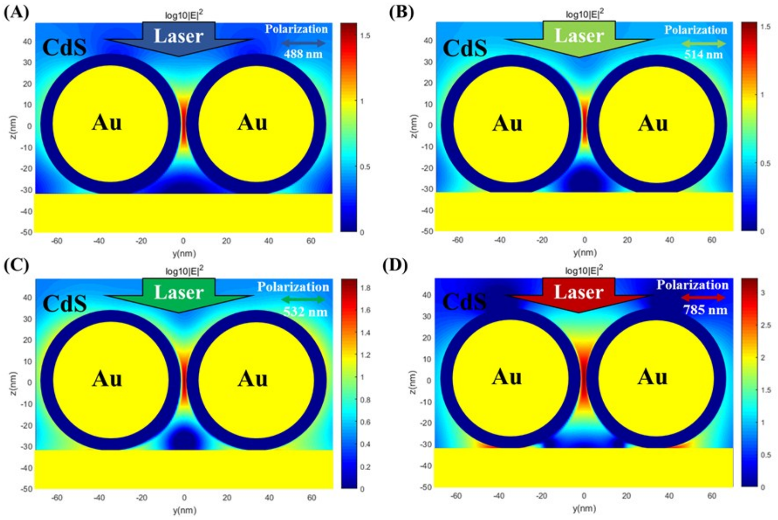

Figure S6. EM field distribution of an Au@CdS dimer on a perfectly smooth Au surface calculated by 3D-FDTD method under the excitation wavelengths of 488 nm (A), 514 nm (B), 532 nm (C), and 785 nm (D).

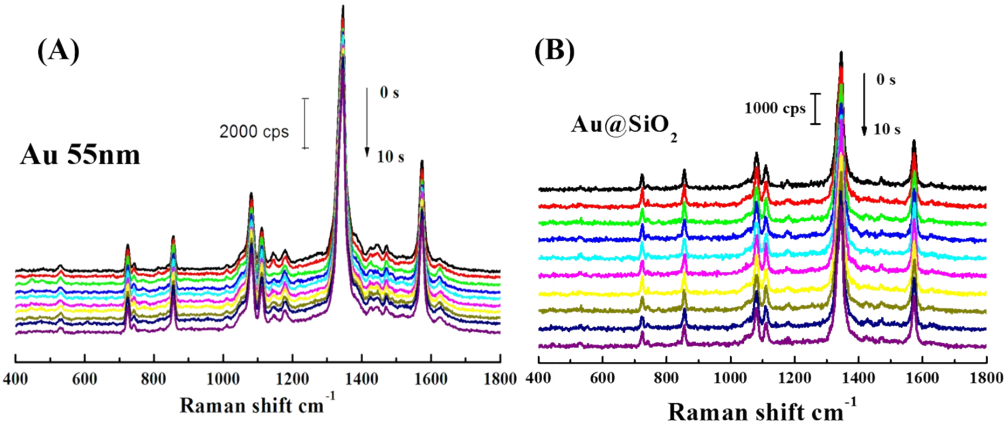

Figure S7. pNTP Raman spectra after different exposures to 638 nm laser irradiation using (A) 55 nm Au NPs and (B) Au@SiO$_2$ NPs with shell thickness of 5nm.