

Plasmon-Induced Hot Electron Transfer in Au-ZnO Heterogeneous Nanorods for Enhanced SERS

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Supporting Information

Synthesis of Au-ZnO NRs

Typically, 0.05 mmol of gold(III) chloride hydrate (20 mg), 4 ml of benzyl alcohol, 2 ml of 1-octadecene, 3 mL of oleylamine, and 0.5 mmol of zinc acetate dehydrate (109mg, pre-annealed at 110 °C for 10 min) were added into a three-neck flask and heated to 120 °C. The reaction contents were kept at 120 °C for 20 min. During this procedure, the color of solution change from yellow to colorless first, then to brown which means the formation of 10 nm Au nanoparticles. The solution was further heated to 180 °C, kept at this temperature for 30 min with magnetic stirring and cooled slowly to room temperature. The Au-ZnO NRs were washed with ethanol to remove oleylamine surfactants and collected by centrifugation (6000 rpm, 10 min, RT). The precipitate was dissolved and stored in hexane at room temperature.

The Au seeds were obtained by directly extracting a small amount of reaction solution at 120°C following a washing with ethanol and re-dispersing with hexane. ZnO nanorods were prepared by removing Au seeds from Au-ZnO NRs by a two-phase etching treatment. KI (800mg) and iodine (200mg) were mixed in deionized water (10 ml) was added to a vial containing Au-ZnO NRs (ca.30 mg) in a hexane

dispersion. The mixture was shaken for two hours, and the colourless hexane phase was collected in a centrifuge tube. Etched ZnO nanorods were separated by adding ethanol and centrifugation.

Au seeds, ZnO nanorods, and Au-ZnO nanostructures were deposited on the SiO₂/Si substrates for SERS measurements, respectively. A total of 100 μ L of hexane dispersion of the hydrophobic nanoparticles was dropped onto the 1×1 cm² SiO₂/Si wafer with a 300 nm SiO₂ top layer and dried under ambient conditions. Then, this Si wafer was put into a 5 mL beaker containing 1 mL of 1×10^{-5} M Dopamine solution. After 12 hours, Si wafers covered the different samples were washed three times with ethanol and dried in air.

Characterizations of the crystalline structures of Au-ZnO NRs

Powder X-ray diffraction (XRD) data were collected on a D2 PHASER X-ray diffractometer (Cu K α radiation, $\lambda = 0.154$ nm). Fig. S1 shows that the XRD pattern of the Au-ZnO NRs.

Raman spectra of dopamine solid powders

We measured the Raman spectrum of dopamine solution with a high concentration of 2M by a Via-Reflex spectrometer with 532 nm radiation from a solid-state laser. The predominant bands in the spectrum of dopamine solid powders (Fig. S2) are located at 1602, 1356, 1294, 792, and 753 cm⁻¹.

FDTD simulation of Au-ZnO heterogeneous nanorods

The finite-difference time-domain (FDTD) simulation method was used to elucidate the electric field distribution of Au-ZnO hybrid nanostructures with a commercial software package provided by Lumerical. Fig.S3 shows the details of simulation. we used the finite-difference time-domain (FDTD) simulation method to elucidate the features connecting geometrical and electronic structures for Au-ZnO nanorods.

Degradation of 4-CP with different nanoparticles

Fig.S4 shows the degradation of 4-CP under visible-light irradiation ($\lambda > 420$ nm) over different nanoparticles: Au seeds, ZnO nanorods, and Au-ZnO heterogeneous nanorods.

Femtosecond Mid-IR Absorption Spectroscopy.

The laser source of the homemade femtosecond mid-IR spectroscopy system is a commercial Ti: sapphire laser (Spitfire Ace, Spectra Physics) centered at 800 nm with a pulse duration of 35 fs working at a repetition rate of 1 kHz. At first, the 800 nm pulse was split into two beams. One beam is used pump an optical parametric amplifier (TOPAS prime, Spectra Physics) to generate the 360 and 520 nm excitation pulse. The other beam is used to generate a broadband mid-IR source as the mid-IR probe via four-wave mixing (FWM) through filamentation in air. During the FWM process, the second harmonic generation (SHG) of the fundamental 800 nm pulse was generated through a BBO crystal and then both the SHG and the fundamental pulses were focused simultaneously and collinearly by an aluminum concave mirror into the air. The collimated the mid-IR light after a concave mirror

was then focused onto the sample by a parabolic mirror. After sample, the transmitted mid-IR light was collected and sent into a spectrometer (iHR 320, HORIBA Jobin Yvon) and acquired by a 64-channel MCT array detector (FPAS-0144, Infrared Systems Development).

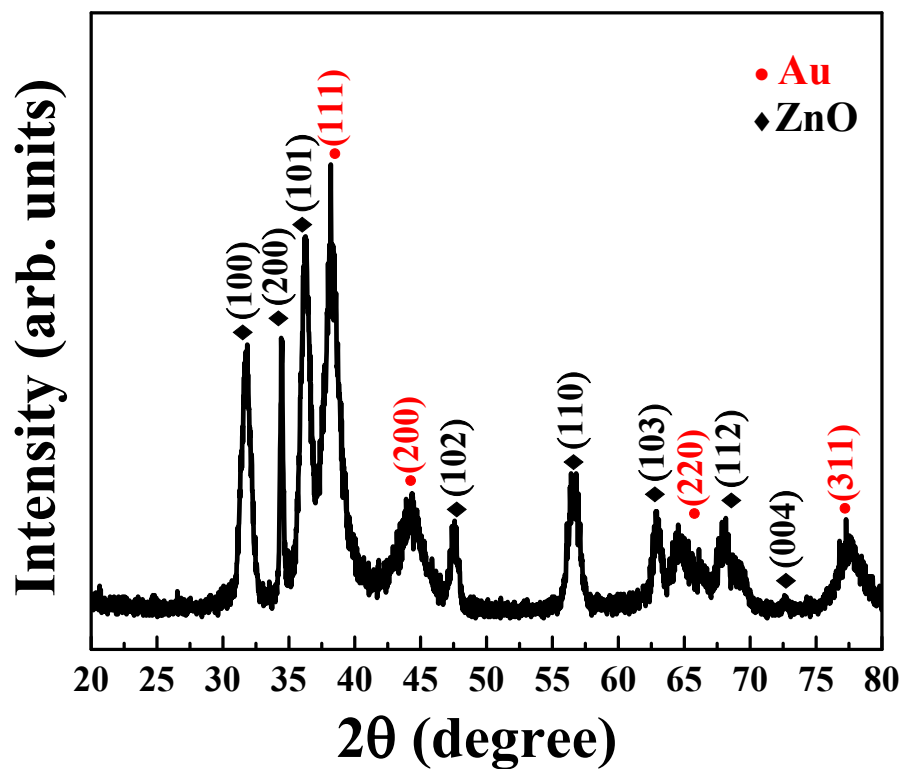


Fig. S1 XRD patterns of the Au-ZnO nanorods

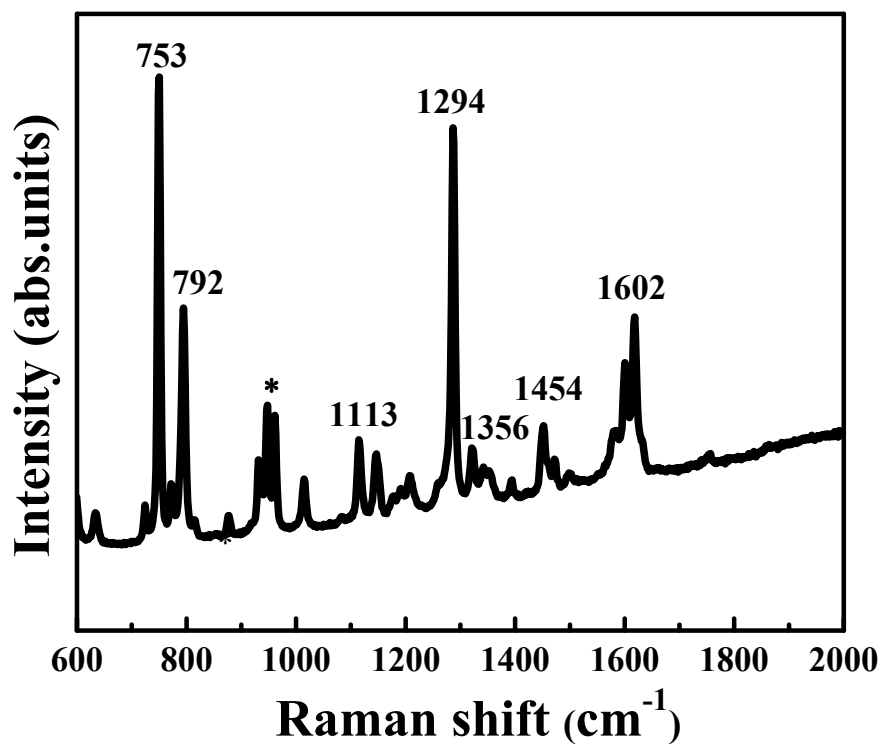


Fig. S2 Raman spectra of dopamine solution with a high concentration of 2M with 532 nm laser excitation.

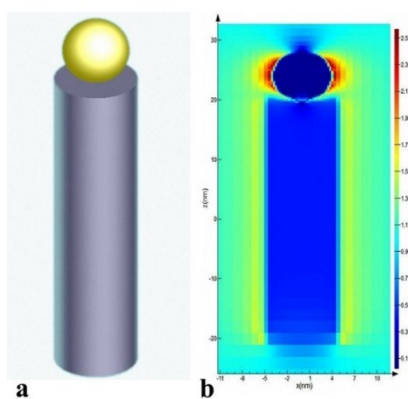
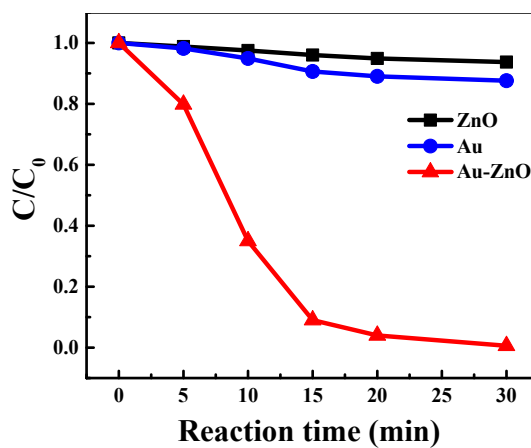


Fig. S3 (a) Model of the Au-ZnO nanorods used in FDTD simulation (b) Two-dimensional electric field distribution of Au-ZnO nanorods along x-z plane. No obvious hot-spots appear.



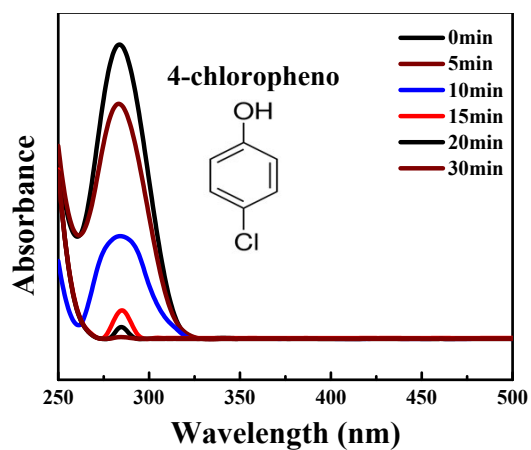


Fig. S4 Photocatalytic performance of 4-CP under visible-light irradiation with different nanostructures

Table S1 Fitting parameters for plasmon-induced charge separation and recombination in 360 and 520 nm excited nanostructures. The time scale is ps if no special note is in the table.

Excitation	Sample	Rising time	Decay time			
			τ_1	τ_2	τ_3	τ_4
360 nm	Au	---				
	ZnO NRS	0.059 ± 0.004	3.5 ± 0.4	16.0 ± 1.0	110.0 ± 12.0	~ 3.0 ns
	Mixed	0.064 ± 0.003	3.8 ± 0.3	18.0 ± 1.0	111.0 ± 13.0	~ 3.0 ns
	Au-ZnO NRs	0.083 ± 0.010	2.4 ± 1.3	25.0 ± 5.0	280.0 ± 140.0	> 3.0 ns
520 nm	Au-ZnO NRs	0.720 ± 0.120	3.6 ± 0.7	86.0 ± 25.0	~ 2.5 ns	

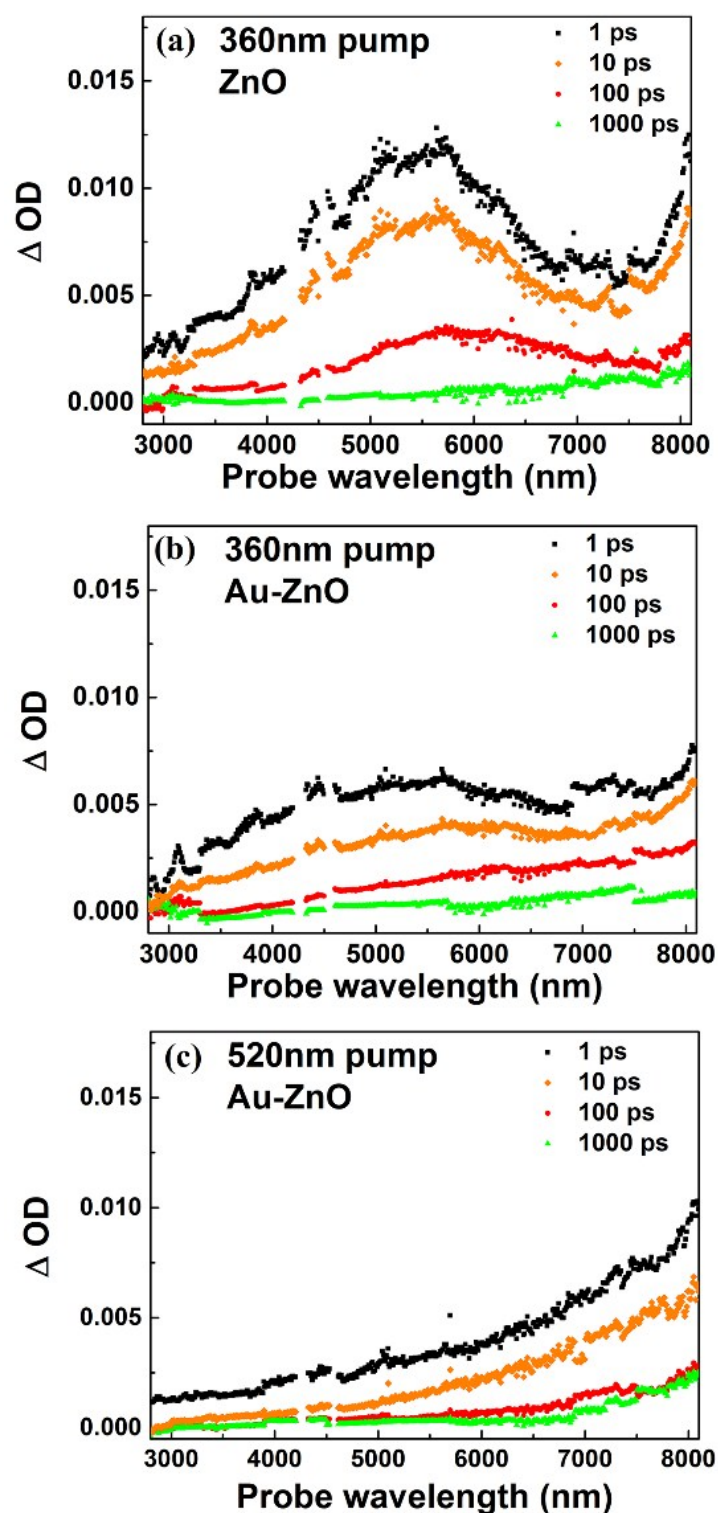


Fig. S5 The time-resolved transient spectra of ZnO nanorods and Au-ZnO hybrid nanorods at different excitation wavelength.

The transient mid-IR absorption spectra have been measured at four delay times. The 360 nm laser pulse pump-probe experiment was conducted for both ZnO and Au-ZnO nanorods which gave an excitonic state excitation. It is found that the transient

spectra dominated by a feature of distinct absorption peak around 5500 nm and it is assigned to the exciton intraband absorption. In the case of Au-ZnO pumped by 520 nm laser pulse, the transient spectra only show a monotonic increasing tendency towards to the longer wavelength which follows the derude formula very well giving the free electron intraband absorption in ZnO band. This is the evident of hot electron transfer from Au tip to the conduction band of ZnO.

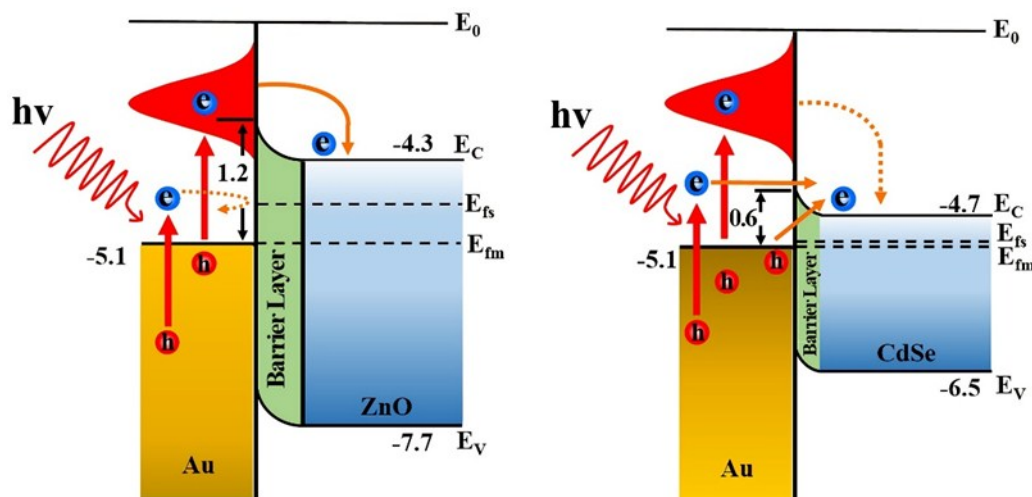


Fig. S6 Band diagram schematic of a Au–ZnO and Au–CdSe Schottky device. Au with a workfunction of about 5.1 eV is liable to form Schottky barrier with ZnO and CdSe of n-type semiconductor. The Schottky barrier prevents the carriers with low energy to cross over and barrier layer with a very low electron density has a low conductivity. The plasmon excitation decays to hot electrons and holes due to Landau damping, in which a plasmon quantum is transferred into an intraband excitation within the conduction band of the metal and an interband excitation between occupied bands (usually d bands) and the conduction band when the plasmonic nanostructures are usually smaller than 20 nm. Since the Schottky barrier of Au–CdSe NRs is only 0.6 eV and the Femi level of Au is very close to the valence band of CdSe, the decay of Au plasmons could directly excite an electron in the conduction band of CdSe and a hole in the Au due to the strong coupling and mixing between Au and CdSe energy levels and a narrow barrier layer. The hot electrons with a low energy can also tunnel into the conduction band of the CdSe through narrow barrier layer. However, the Schottky barrier of Au–ZnO is as high as 1.2 eV and the difference between the valence band of ZnO and the Femi level of Au is 0.8 eV, which results in a wide barrier layer and poor mixing between Au and CdSe energy levels. Only hot electrons with high energy can transfer to the conduction band of ZnO and the direct tunneling of plasmon-induced hot-electrons from the Au to ZnO even with a fine interface between them become very difficult.

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