

## Supporting Information

# Plasmon-Mediated Nitrobenzene Hydrogenation with Formate as Hydrogen Donor Studied at Single-Particle Level

*Fengxia Tong,<sup>†</sup> Xizhuang Liang,<sup>†</sup> Fahao Ma,<sup>†</sup> Xiaolei Bao,<sup>†</sup> Zeyan Wang,<sup>†</sup>  
Yuanyuan Liu,<sup>†</sup> Peng Wang,<sup>†</sup> Hefeng Cheng,<sup>†</sup> Ying Dai,<sup>‡</sup> Baibiao Huang,<sup>†</sup> and  
Zhaoke Zheng<sup>†\*</sup>*

*<sup>†</sup> State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100,  
China*

*<sup>‡</sup> School of Physics, Shandong University, Jinan 250100, China*

*\*Email: zkzheng@sdu.edu.cn*

## EXPERIMENTAL SECTION

**Materials.** Formic acid (HCOOH, Aladdin, 99%), silver nitrate (AgNO<sub>3</sub>, Sinopharm, 99.8%), sodium tetrachloropalladate (Na<sub>2</sub>PdCl<sub>4</sub>, Aladdin, 99%), tetrachloroauric acid (HAuCl<sub>4</sub>·4H<sub>2</sub>O, Sinopharm, 99%), nitrobenzene (Aladdin, AR, ≥ 99.0%), nitrochlorobenzene (Aladdin, AR, ≥ 99.0%), 5-bromosalicylic acid (BSA, Aladdin, 99%), hexadecyl-trimethyl ammonium bromide (CTAB, Sinopharm, AR, ≥ 99.0%), and ascorbic acid (L-AA, Sinopharm, 99%).

**Preparation of Au NRs (BSA).** The seed-mediated method was used to prepare Au NRs.

*The seed solution:* CTAB (10 mL, 0.1 M), HAuCl<sub>4</sub>·3 H<sub>2</sub>O (250 μL, 0.01 M) and NaBH<sub>4</sub> (0.6 mL, 0.01) were added orderly into 20 ml glass vial under stirring, and aged at room temperature for 30 min.

*The growth solution:* dissolving CTAB (3.6 g) and BSA (0.44 g) in 100 mL of warm water. Then, AgNO<sub>3</sub> (1.92 mL, 0.01M) was added into this solution, and undisturbed for 15 min. Next, adding HAuCl<sub>4</sub>·3H<sub>2</sub>O (100 mL, 1 mM) and gentle mixing of the solution for 15 min. Then, ascorbic acid (L-AA) (510 uL, 0.1 M) was added with vigorously stirring. After the mixture became colorless, 0.32 mL of 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 before used.

**Preparation of Pd-tipped-Au NRs.** Briefly, L-AA (2.25 mL, 0.1 M), Na<sub>2</sub>PdCl<sub>4</sub> (30uL,

0.01 M) and HCl (160  $\mu$ L, 0.1 M) were added into 20 mL of as-made Au-NRs suspension. After gentle mixing of the solution for 2 min, the mixture was left undisturbed for 12 h at 27  $^{\circ}$ C.

**Preparation of Pd-covered-Au NRs.** *Preparation of Au NRs (CTAB):* The method of synthesis of the seed solution is similar to the above.

*The growth solution:* dissolving CTAB (7.288g) in 100 mL of warm water. Then, AgNO<sub>3</sub> (2 mL, 0.01 M) was added into this solution, and undisturbed for 10 min. Next, adding HAuCl<sub>4</sub>·3 H<sub>2</sub>O (100 mL, 0.8 mM) and gentle mixing of the solution for 10 min. L-AA (800  $\mu$ L, 0.1 M) was added with vigorously stirring. After the mixture became colorless, 0.32 mL of seed solution was added to the entire growth solution. The mixture was stirred for 30 s and left undisturbed at 27  $^{\circ}$ C for 12 h before used.

Pd-covered Au NRs were prepared by using the Au NRs (CTAB) as a template.

**FDTD Calculations.** FDTD Solutions (Lumerical Solutions, Inc.) with perfectly matched layers (PML) boundary conditions were used for the finite-difference-time-domain (FDTD) calculations. The tabulated values for bulk gold measured by Johnson and Christy were used as the optical constants of Au. The size of the NRs was determined via TEM maps, and mesh accuracy was set to 0.5 nm.

**Single-Particle PL Measurements by Confocal Microscopy.** Before the single-particle PL measurements, the quartz cover glasses were cleaned by sonication in nitric

acid solution for 40 min, followed by repeated washings with deionized water for 3 times. The as-synthesized Pd-Au NRs suspensions were centrifuged at 12 000 rpm to remove excess surfactant and washed with Milli-Q ultrapure water for 3 times. Finally, the catalysts with a low concentration were spin-coated on the pre-cleaned quartz cover glass. For single-particle PL measurements, a 405-nm continuous wave (CW) laser was used to excite the interband transition of Au NRs.

**Characterization of Materials.** Transmission electron microscopy (TEM), Scanning transmission electron microscopy (STEM) and elemental mapping were performed by JEOL JEM-2100F. The Fourier transform infrared (FTIR) spectra was performed by NICOLET iS10. X-ray photoelectron spectroscopy (XPS) was carried out by X-ray photoelectron spectrometer (ESCALAB 250). Extinction spectra was measured on a UV-vis-NIR spectrophotometer (TU-1810).

**Photocatalytic Reduction of Nitroarenes.** Excess surfactant of Au-Pd NRs aqueous suspensions was removed by centrifugation at 12000 rpm for two times. The catalyst suspensions in H<sub>2</sub>O/2-propanol (9:1) were added into a 20 mL vial contained HCOOH (1 M), HCOONa (1 M) and nitrobenzene (0.05 mmol) and sealed with a rubber septum. For photocatalytic reduction of nitroarenes, the suspensions were irradiated with a 300 W Xenon lamp (Beijing, CEAULIGHT,  $\lambda > 320$  nm). To eliminate temperature interference, the reaction system was connected with a cooling circulating. After 5 h, the resulting mixture was centrifuged at 12000 rpm to remove the insoluble powder.

The conversion and selectivity of the reaction were determined by GC-MS chromatography (GC-MS-QP2010, SH-Rtx-Wax column). Gas chromatography (GC, ShiweipxGC-7806, Shiweipx GC-7920) was used to collect and analyze evolved gas. Total organic carbon concentration (TOC) of before and after nitrobenzene hydrogenation was determined by TOC-V<sub>CPH</sub>. The inductively coupled plasma mass spectrometry (ICP-MS, Optima 2100DV) was used for confirmed the mass of catalysts in the reaction mixture.

The turnover frequency (TOF) value was calculated from the equation as follow:

$$TOF = \frac{n_{nitro}(Conv.)}{n_{Pd} \cdot t}$$

Where  $n_{nitro}$  is the mole amounts of nitrobenzene been converted,

$n_{Pd}$  is the mole amounts of Pd in the catalyst, and  $n_{Pd}$  was confirmed by ICP-MS,  $t$  is the reaction time (h).

The conversion rate and selectivity of the hydrogenation were calculated from the equations as follow:

$$Conv. (\%) = \frac{C_0(nitro) - C_t(nitro)}{C_0(nitro)} \times 100\%$$

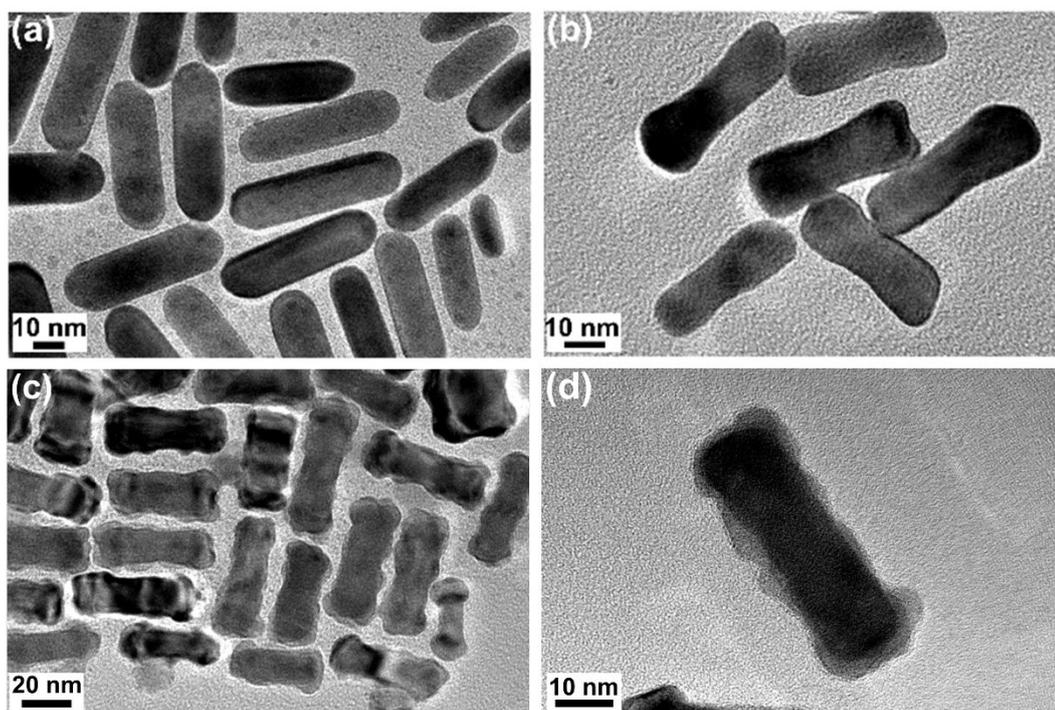
$$Select. (\%) = \frac{C_t(aniline)}{C_0(nitro) - C_t(nitro)} \times 100\%$$

Where  $C_t$  is the concentration of the reactant or product at a certain sampling time, and  $C_0$  is the initial concentration of reactant.

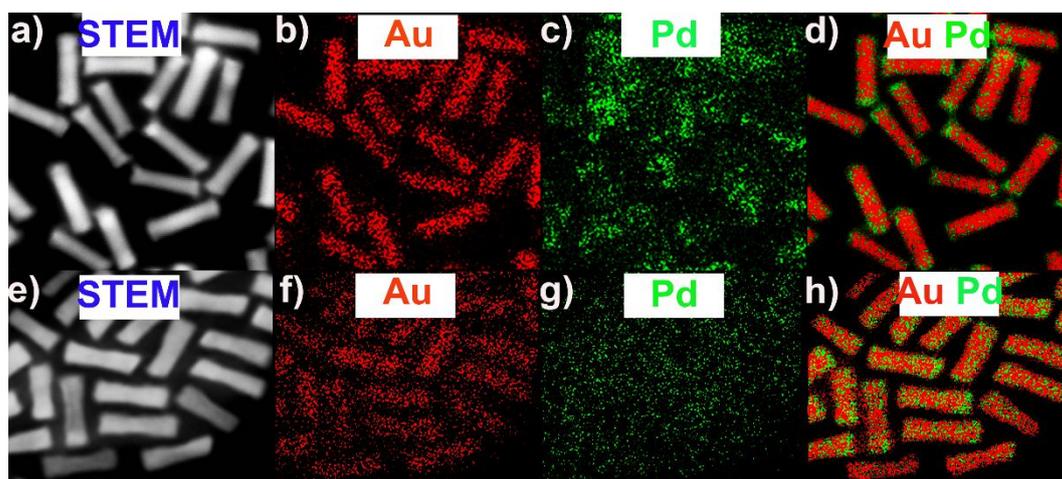
**Catalytic Dehydrogenation of Formic Acid.** The catalyst suspensions and formic acid (4.5mL, 1 M) were placed in a 20 mL glass vials connected with a water bath, and the

glass vials was sealed with a rubber septum. The gas chromatography (GC, ShiweipxGC-7806) was used to collect and analyze evolved gas. For the photo-enhanced formic acid dehydrogenation, a 300 W Xe lamp (Beijing, CEAULIGHT,  $\lambda > 320$  nm) was used to irradiate the suspensions.

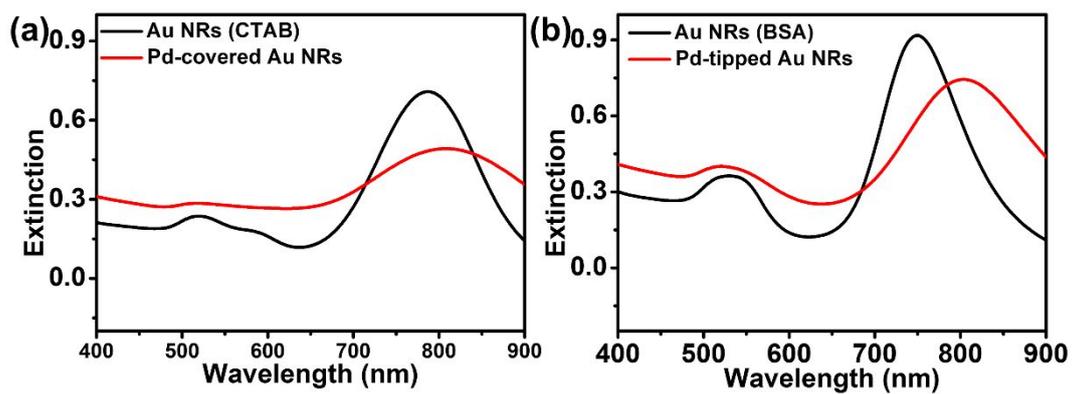
**Photoelectrocatalytic measurements.** The FA oxidation performance of the catalysts was measured on a potentiostat (CHI 660E) at room temperature. A glassy-carbon electrode (GCE) (3 mm in diameter), a saturated calomel electrode (SCE), and a Pt wire were used as the working electrode, reference electrode and counter electrode, respectively. 1 ml Pd-Au NRs were collected by centrifugation and redispersed in 100  $\mu$ L of deionized water. And then 5  $\mu$ L of the catalyst ink was drop-cast onto the GCE and dried naturally, subsequently 5  $\mu$ L of 5 wt % Nafon solution was covered on the surface of the catalyst electrode and allowed to dry again. The linear sweep voltammograms (LSV) curve was measured in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution with 0.5 M FA at a scan rate of 100 mV s<sup>-1</sup>. During photoelectrocatalytic measurements, a xenon lamp (300 W) was used as light source.



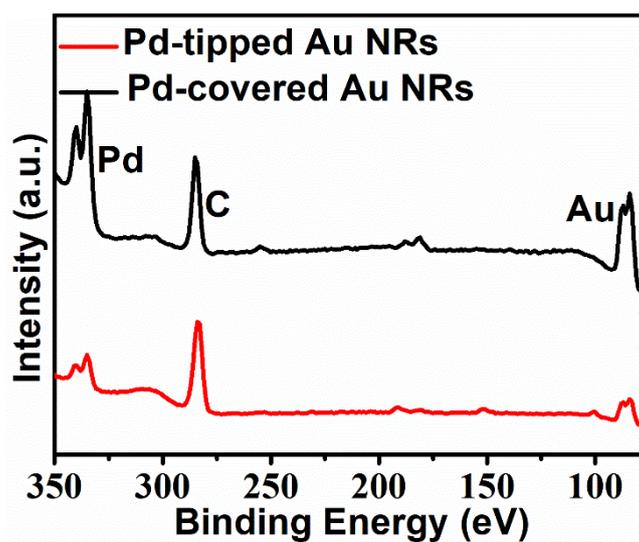
**Figure S1.** (a) TEM image of Au NRs (BSA). (b) TEM image of Au NRs (CTAB). (c-d) TEM images of Pd-covered Au NRs.



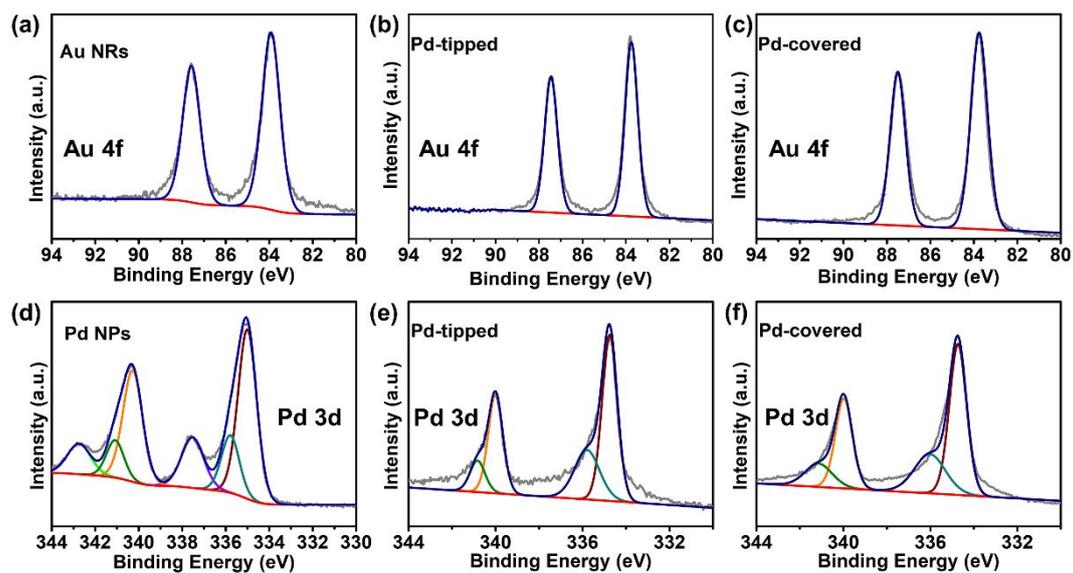
**Figure S2.** STEM images and corresponding STEM-EDS elemental maps of Au, Pd, and Au-Pd: (a-d) Pd-tipped Au NRs; (e-h) Pd-covered Au NRs. The scale bars in all images represent 200 nm.



**Figure S3.** (a, b) UV-vis-NIR extinction spectra of the four samples with the same concentration.



**Figure S4.** XPS spectra of survey scan of Pd-modified Au NRs.



**Figure S5.** The XPS spectra of Au 4f or Pd 3d for Au NRs, Pd NPs and Pd-modified Au NRs.

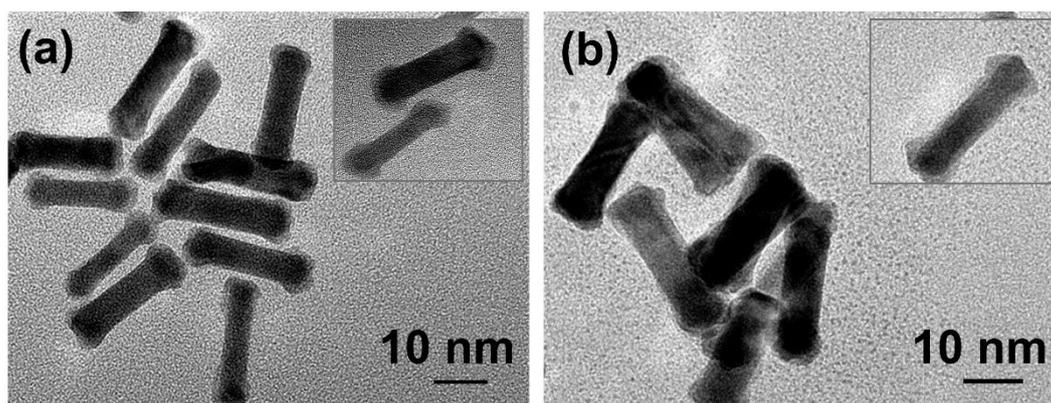
**Table S1.** XPS Data for Pd-modified Au NRs and Pd NPs.

Entry	Catalyst	$3d_{5/2}$	$3d_{3/2}$
1	Pd NPs	335.00	340.20
2	Pd-tipped-Au NRs	334.74	339.99
3	Pd-covered-Au NRs	334.68	339.99

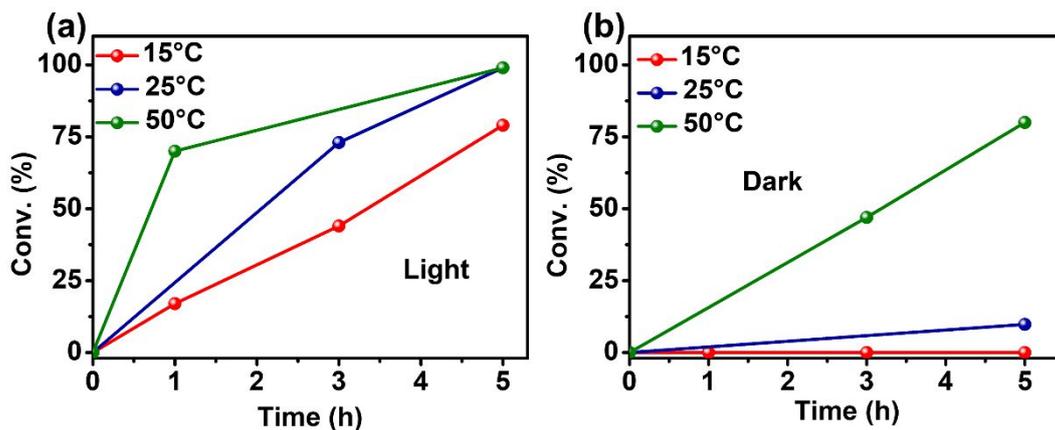
**Table S2. Reduction of Nitrobenzene to Aniline under Light Irradiation**

Entry	Catalyst	Conv. (%)		Select. (%)	
		Dark	Light	Dark	Light
1	Pd covered Au NRs (10%)	36	64	<1	19
2	Pd covered Au NRs (1%)	4	85	5	20
3	Pd tipped Au NRs	9.7	>99	>99	>99
4	Au NRs	<1	32	<1	<1
5	Pd/C	20	20	<1	<1
6	None	0	0	0	0

The catalytic activities of nitrobenzene hydrogenation on Pd-modified Au NRs, Au NRs and commercial Pd/C (5 wt %) at 25 °C. All the reaction time are 5 h and each experiment was performed at least three times.



**Figure S6.** TEM images of Pd-tipped Au NRs (a) before and (b) after nitrobenzene hydrogenation reactions.

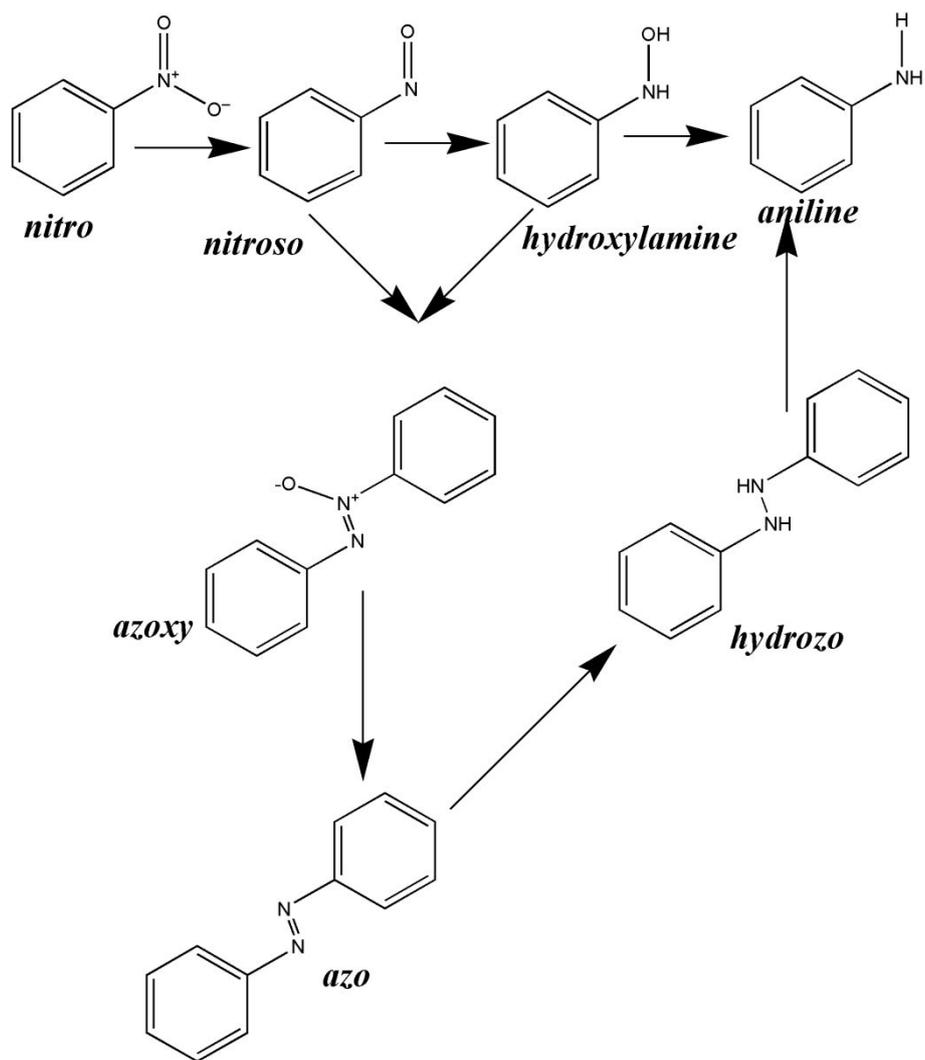


**Figure S7.** The conversion rates of nitrobenzene hydrogenation on Pd-tipped Au NRs at different temperatures under light.

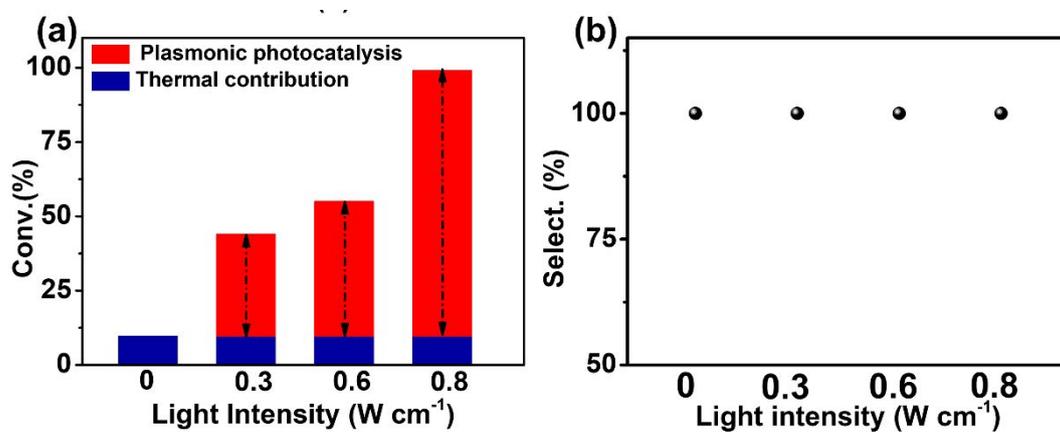
**Table S3. Reduction of Nitrobenzene to Aniline under Light Irradiation at Different Temperature**

Entry	Temperature (°C)	Conv. (%)		Select. (%)	
		Dark	Light	Dark	Light
1	15	<1	79	-	>99
2	25	9.7	>99	>99	>99
3	50	82	>99	64	>99

The catalytic activities of nitrobenzene hydrogenation on Pd-tipped Au NRs at different temperatures. All the reaction time are 5 h and each experiment was performed at least three times.



**Figure S8.** Reaction pathways for the reduction of aromatic nitro compounds to the corresponding anilines.



**Figure S9.** The conversion rates and selectivity of nitrobenzene hydrogenation on Pd-tipped Au NRs at different light intensities at 25 °C.

**Table S4. Redution of Nitrochlorobenzene under Light Irrrdiation**

Entry		Conv. (%)	Select. (%)	TOF (h <sup>-1</sup> )
1	Dark	trace	trace	trace
2	Light	>99	>99	60

The catalytic activities of nitrochlorobenzene hydrogenation on Pd-tipped Au NRs at 25°C.

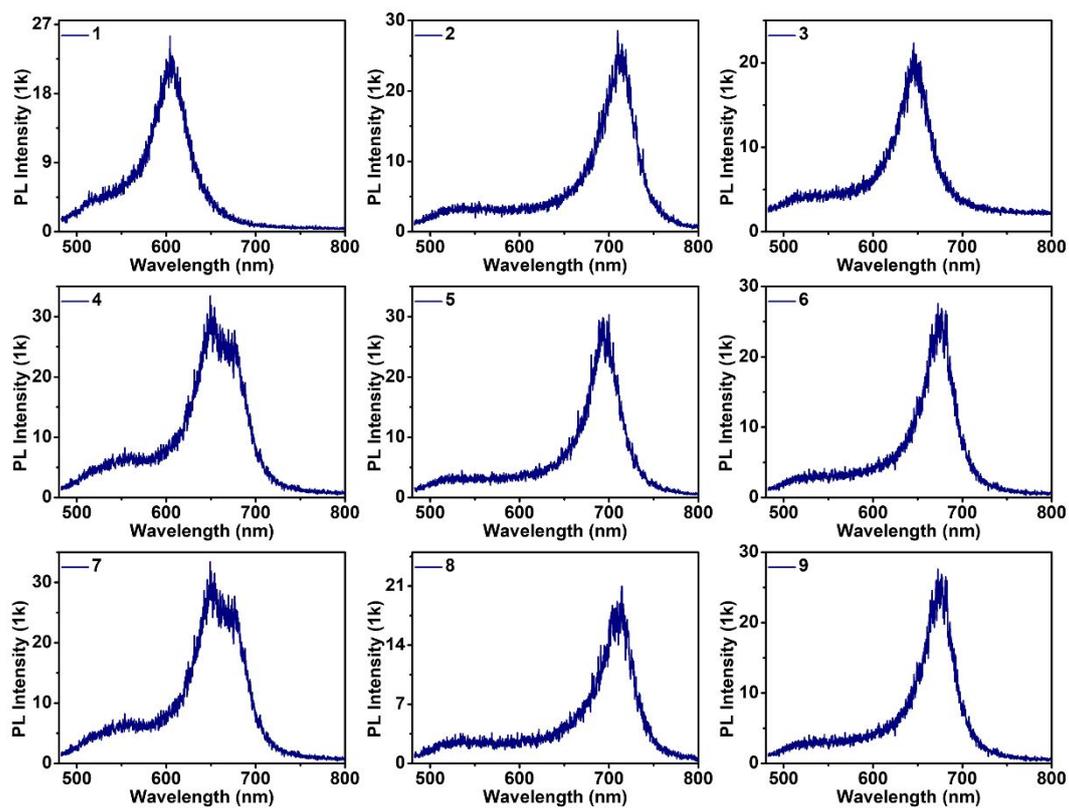
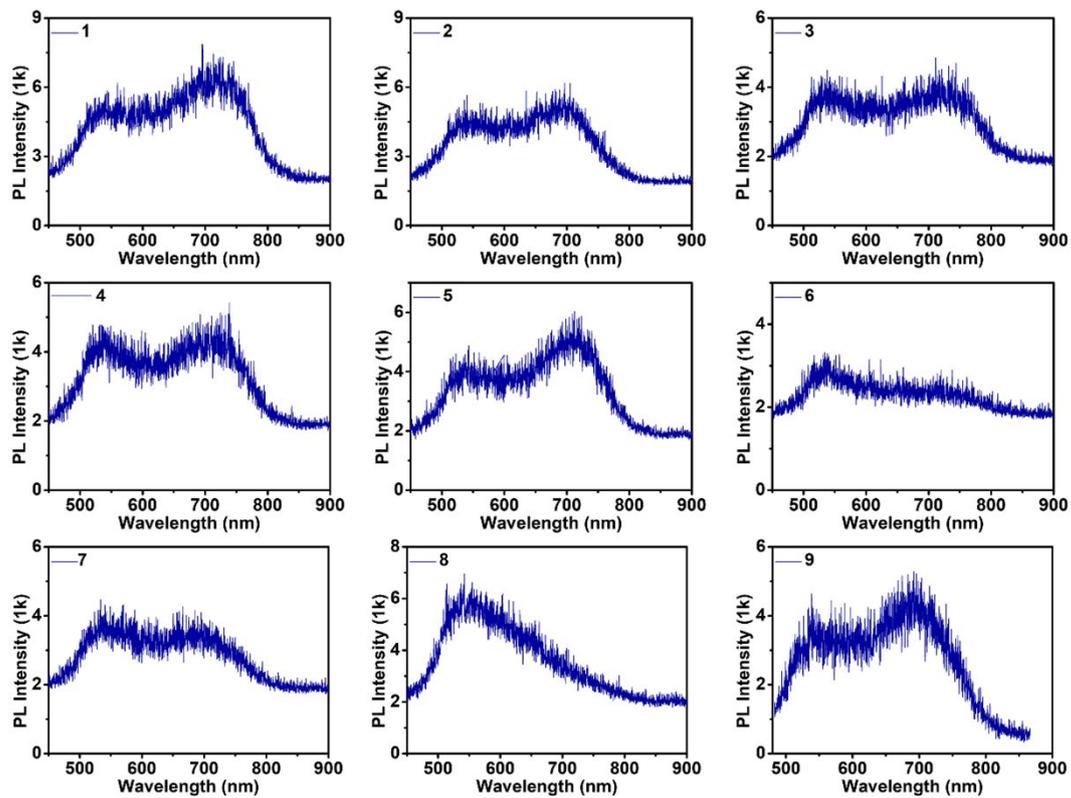
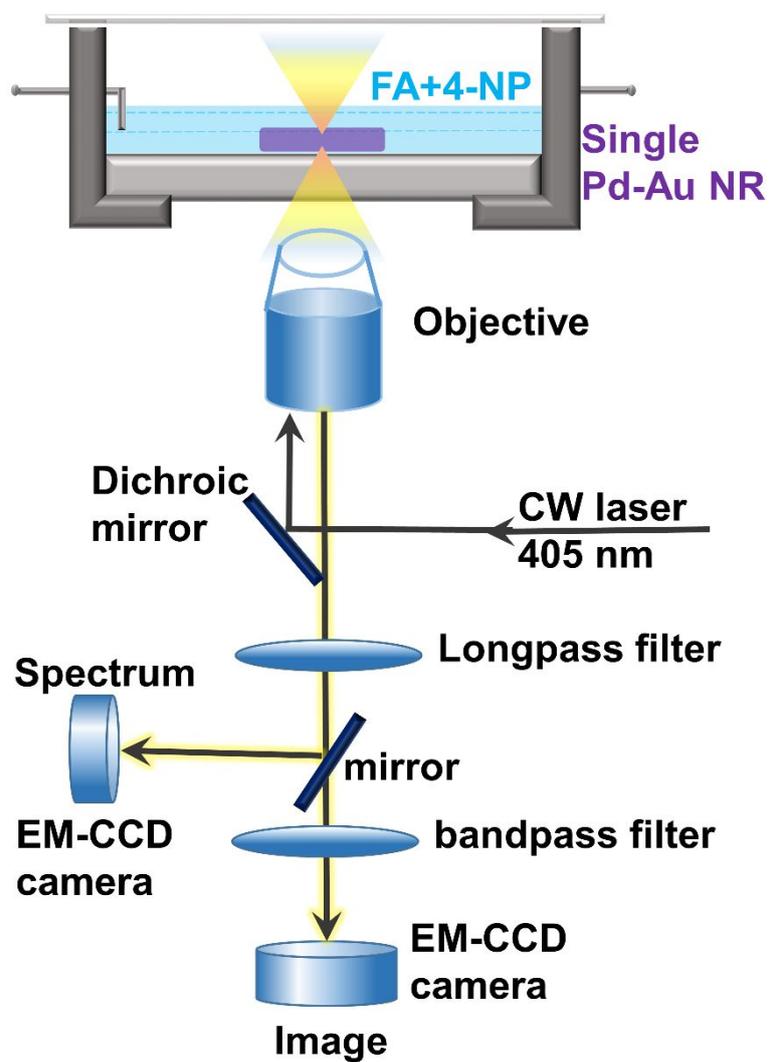


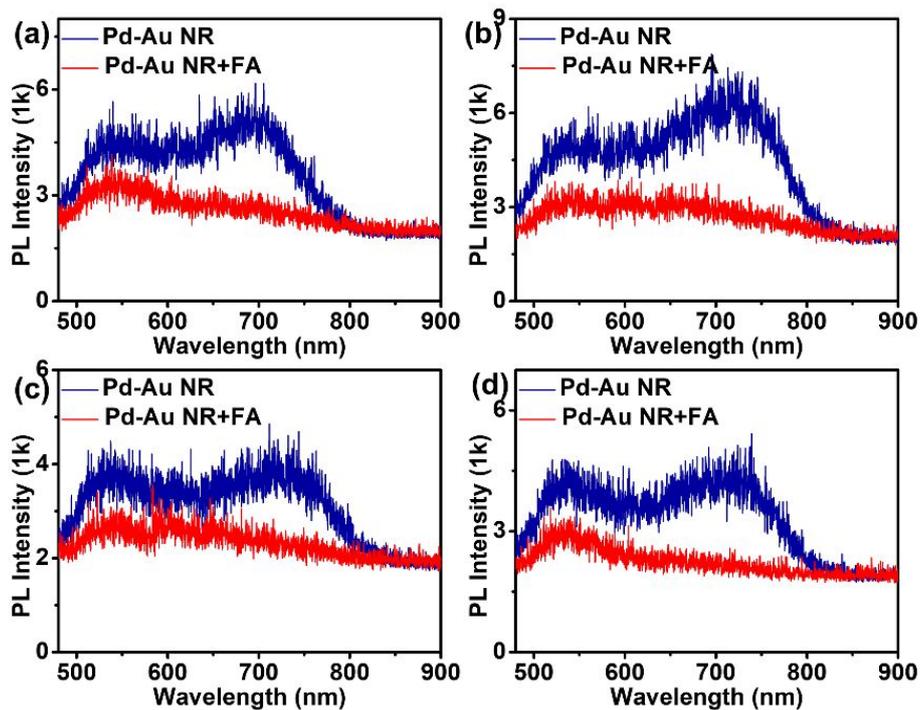
Figure S10. PL spectra of individual Au NRs.



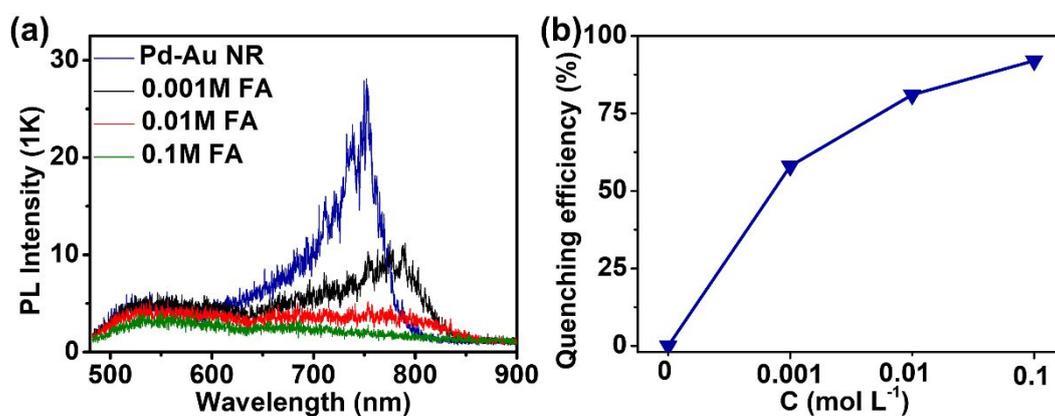
**Figure S11.** PL spectra of single Pd-tipped Au NRs



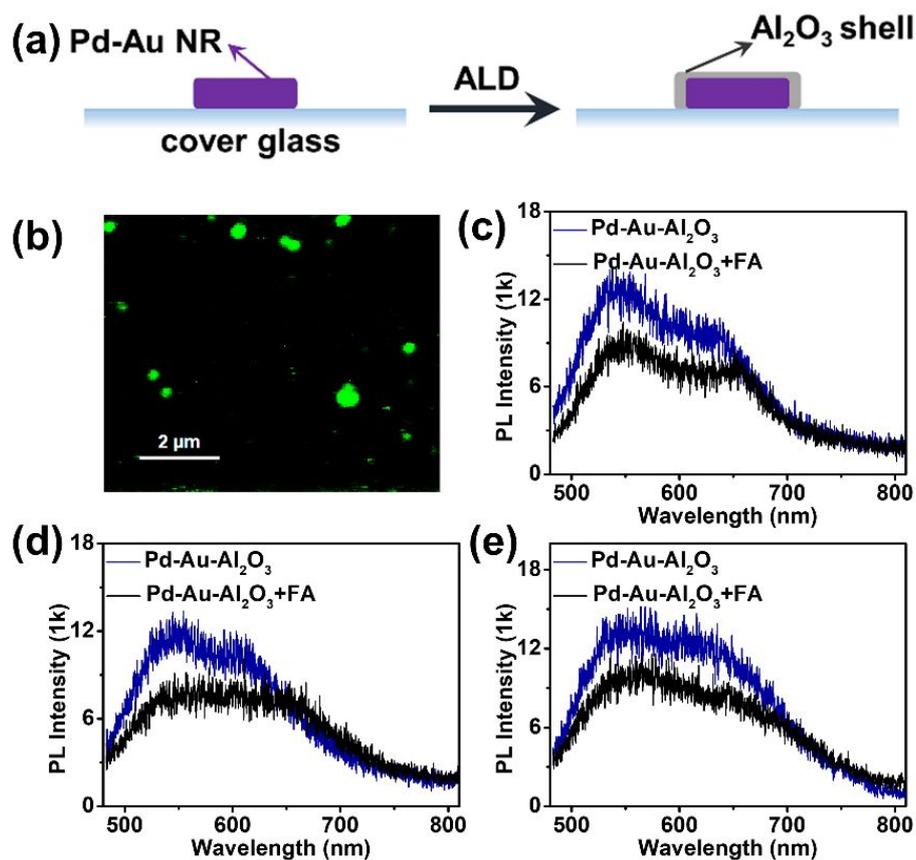
**Figure S12.** Illustration of single-particle PL measurement based on confocal microscope system.



**Figure S13.** PL intensities of single Pd-tipped Au NR immersed in FA (1M).

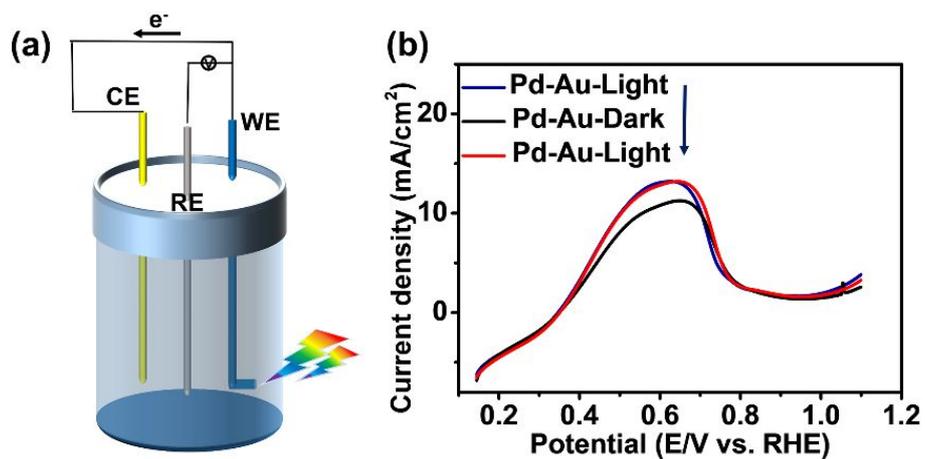


**Figure S14.** (a) PL intensities of single Pd-tipped Au NR immersed in different concentrations of FA solutions. (b) LSPR PL quenching efficiency as a function of the FA solutions concentration.

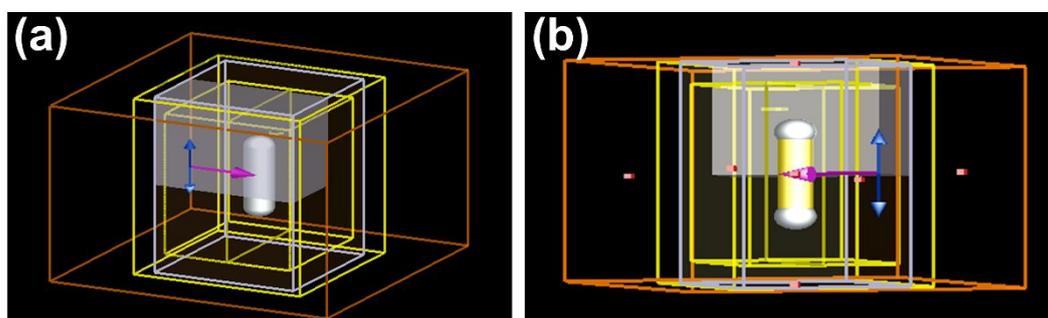


**Figure S15.** (a) Illustration of the experimental setup for the sample preparation. (b) PL images of single Al<sub>2</sub>O<sub>3</sub>-coated Pd- Au NR dispersed on quartz cover glass. (c-e) PL intensities of single Al<sub>2</sub>O<sub>3</sub>-coated Pd- Au NR immersed in FA (1M).

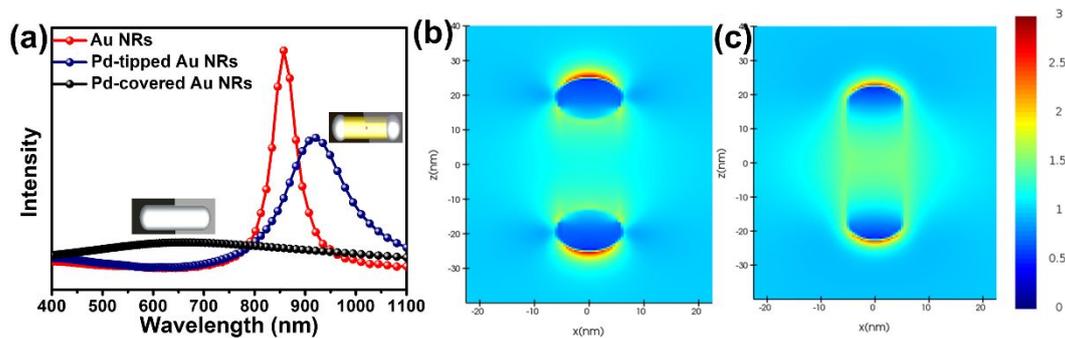
The Al<sub>2</sub>O<sub>3</sub> shell was deposited on the surface of Au-Pd NRs by atomic layer deposition (ALD). Firstly, mono-dispersed Au-Pd NRs with a low concentration were spin-coated on the precleaned quartz cover glass and dried naturally. Then the surface was deposited by a layer of Al<sub>2</sub>O<sub>3</sub> via ALD (100r). For the Au-Pd NRs coated with Al<sub>2</sub>O<sub>3</sub>, there is a change of the TSPR PL peak intensity and a conspicuous red shift of PL peak, confirming the successful coating of Al<sub>2</sub>O<sub>3</sub>.



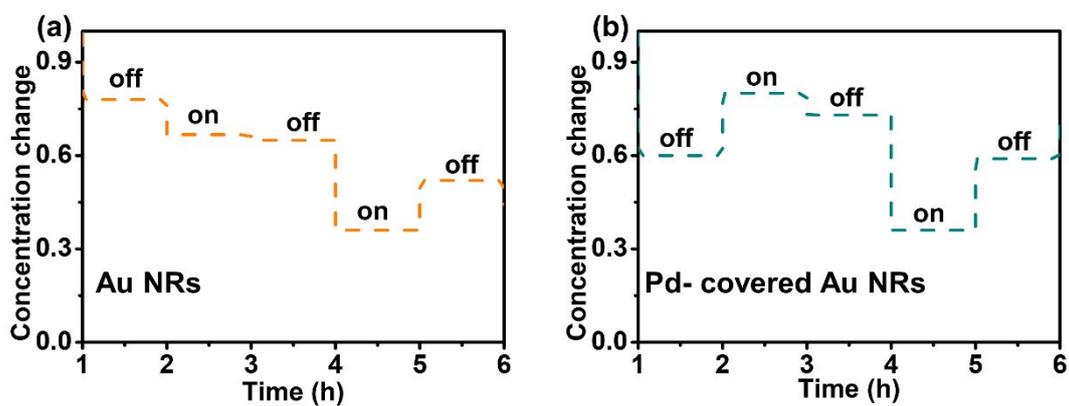
**Figure S16.** (a) Schematic representation of a photoelectrochemical cell with an Pd-Au NRs anode and a Pt cathode. (b) The LSV of Pd-Au NRs in a solution of 0.5 M Formic acid + 0.1 M  $\text{H}_2\text{SO}_4$  with or without light illumination.



**Figure S17.** The FDTD model of (a) Pd-covered Au NRs, (b) Pd-tipped Au NRs.



**Figure S18.** (a) Calculated extinction spectra for Au NRs and Pd–Au NRs using the FDTD method. Spatial distribution of the SPR-induced enhancement of electric field intensity from FDTD simulation calculated at 405nm for Pd-tipped Au NRs (b) and Pd-covered Au NRs (c).



**Figure S19.** Reactant-concentration change on Au NRs and Pd-covered Au NRs in the light-on and light-off cycle process (measured by gas chromatography).

**Table S5. The Concentration of Catalysts**

Entry	Catalyst	$m_{\text{Au}}$ (mg/mL)	$m_{\text{Pd}}$ (mg/mL)
1	Pd-covered Au (10%)	0.08	0.0095
2	Pd-covered Au (1%)	0.1	0.00071
3	Pd-tipped Au	0.055	0.0085

The concentration of catalysts confirmed by inductively coupled plasma mass spectrometry (ICP-MS).