Light inhibition of hydrogenation reactions on Au-Pd nanocoronals as plasmonic switcher in catalysis

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Experimental Section

1. Materials: Sodium citrate (98%) was purchased from Macklin. L-ascorbic acid, sodium tetrachloropalladate(II) (Na₂PdCl₄, 98%), tetrachloroauric(III) acid (HAuCl₄) were purchased from Sigma-Aldrich. Phenylacetylene (96%) was purchased from Energy Chemical (Shanghai). Potassium ferricyanide (K₃[Fe(CN)₆], 99%) was purchased from Meryer. Acetonitrile (CH₃CN), cinnamaldehyde (CAL), ethanol and potassium chloride (KCl) were purchased from Aladdin.

2. Preparation of nanoparticles (NPs)

- 2.1. Synthesis of Au NPs (~50nm). Au NPs were synthesized via a seed-mediated method.^[1] Firstly, 0.08516 g sodium citrate (2.2 mM) was added into a 250 mL three-necked flask containing 150 mL H₂O and heated to boiling. Then 850 μ L aqueous solution of HAuCl₄ (1 wt%) was injected under vigorous stirring. Au seeds (~10 nm) were obtained after 10 min. To prepare larger Au NPs, 850 μ L HAuCl₄ aqueous solution (1 wt%) was added when the seed colloid was cooled down to 90°C. After 30 min, another 850 μ L HAuCl₄ aqueous solution (1 wt%) was taken out and the remaining was diluted by adding a mixture of 53 mL H₂O and 2 mL sodium citrate solution (60 mM). This diluted colloid was then used as the seed suspension and Au NPs with a diameter of about 50 nm were obtained after the growth process was repeated for another two times.
- 2.2. Synthesis of Pd NPs (~30nm). 2.24 mL aqueous solution of 10 mM H₂PdCl₄ was added to 30 mL H₂O, then 1 mL sodium citrated aqueous solution (0.112 M) was added under vigorous stirring. After 15 min stirring, 1.2 mL aqueous solution of ascorbic acid (0.56 M) was rapidly injected into the above solution. 30 min later, Pd NPs (~30 nm) were obtained.
- **2.3.** Synthesis of Au-Pd nanocoronals and load on C_3N_4 . 10 mL colloidal Au NPs (~50 nm) were added into an autoclave reactor. 9.5×10^{-3} mmol sodium tetrachloropalladate (Na₂PdCl₄, II) and different amounts of sodium citrate (3.6×10^{-4} , 14.5×10^{-4} , 38.5×10^{-4} and 43.5×10^{-4} M) were added into the colloid under vigorous stirring. After stirring for about 15 min, the reactor was put into an oven set at 100°C for 3 h, and the Au-Pd hybrid NPs were obtained. To ensure the stability of catalysts, Au-Pd nanocoronals were loaded on C_3N_4 via the following steps. 10 mL Au-Pd nanocoronals colloid was washed with water twice and added into a clean glass vial. Then, 50 mg C_3N_4 powder was added into the above vial. The mixture was incubated under ultrasonication for about 0.5 h and a mauve suspension was obtained. Put the product in oven to dry it by evaporation at 60° C for 3 h, after which the dried powders were ground with an agate mortar. Finally, purplish product was obtained, namely, Au-Pd/C₃N₄.
- **3.** Characterization. The SEM image of Au-Pd nanocoronals in Fig. 1b was recorded on a JSM-7900F high-resolution scanning electron microscope. The sample was dispersed in ethanol by ultrasonication and dropped on silicon wafer for measurement. TEM images were obtained by a FEI Talos F200X G2, AEMC high-resolution transmission electron microscope at an accelerating voltage of 200 kV. XPS spectra were recorded on a Thermo escalab 250Xi X-ray photoelectron spectroscope. For *in situ* XPS characterization under light illumination, a xenon

lamp with power density kept at 130.9 mW/cm² was built in to illuminate the sample during the measurements. The binding energy was calibrated by the C 1s peak energy at 284.8 eV. The powder X-ray diffraction (XRD) patterns were obtained by an X-ray diffraction (XRD, Rigaku MiniFlex600) with Cu K α radiation. Extinction spectra were collected on a SPECORD 2010 plus (analytikjena) UV-Vis spectrometer. Raman spectra and SERS were acquired by a Horiba LabRAM HR Evolution confocal Raman microscope with a 633 nm excitation laser.

4. Catalysis

- **4.1.** Thermalcatalytic phenylacetylene hydrogenation. Typically, 3.5 mL acetonitrile (CH₃CN), 0.13 mmol phenylacetylene and 2.5 mg Au-Pd/C₃N₄ were added into a quartz tube. After making catalysts dispersing well in ultrasonication, the tube was put into a bath set at room temperature. H₂ bubbling was used to initiate the reaction at a steady rate of 1 bubble per second. The mixture was tested every 3 min by GC.
- **4.2. Photocatalytic phenylacetylene hydrogenation.** The reaction condition was kept the same as that of the thermalcatalytic phenylacetylene hydrogenation except for light illumination with a 300 W xenon lamp (PLS-SXE300, Beijing Trusttech Co., Ltd.) and the system was also kept at room temperature with a self-built cycle device.
- **4.3. Cinnamaldehyde (CAL) reduction.** 4 mL H₂O, 0.16 mmol CAL and 30 μL colloid of Au-Pd nanocoronals (25 times concentrated from the as prepared colloidal sample) were added into a quartz tube. After making catalysts dispersing well by ultrasonication, the tube was put into a bath at room temperature, under illumination or in dark. H₂ bubbling was used to initiate the reaction at a steady rate of 1 bubble per second. The products were tested by GC.
- 4.4. Potassium ferricyanide reduction. A 0.2 mL aqueous solution of potassium ferricyanide (0.01M) and 0.15 mL Au-Pd nanocoronal colloid were added into a quartz tube containing 3.15 mL H₂O. The next steps were the same as those in 4.1. except for light illumination by a xenon lamp with a >420 nm filter (to circumvent the interference of photosensitivity of potassium ferricyanide itself). The reaction progress was monitored using the UV-Vis spectrometer.
- 5. Electrical measurement. To visualize the reversible electron transfer, open potentials between indium tin oxide (ITO) electrodes modified respectively with Au and Pd NPs were measured before and after light on. Specifically, the Au or Pd NP colloidal suspension was dropped on an ITO glass. After drying, both the ITO glasses were fixed with electrode clamps and then connected respectively to positive and negative electrodes, which were immersed in a 0.5 M aqueous solution of KCl. When the open circuit potential reached a relatively stable value (about 0.377 V), the xenon lamp was switched on. The open circuit potential suddenly and sharply dropped once the light was on, and finally stabilized at about -0.397 V after a slight and tardy growth (shown in Fig. S4). It intuitively visualized and confirmed the phenomenon that the illumination reverses the electron transfer between Au and Pd.
- 6. Theory computations. All the density-functional theory (DFT) computations were performed using the Cambridge Sequential Total Energy Package (CASTEP) based on the pseudopotential plane wave (PPW) method. Electron-ion interactions were described using the ultrasoft (USP) potentials. A plane-wave basis set was employed to expand the wave functions with a cutoff

kinetic energy of 400 eV. For the electron-electron exchange and correlation interactions, the functional parametrized by Perdew-Burke-Ernzerhof (PBE), a form of the general gradient approximation (GGA), was used throughout. During the geometry optimizations, all the atom position were allowed to relax. In this work, the Brillouin-zone integrations were conducted using Monkhorst-Pack (MP) grids of special points with the separation of 0.05 Å⁻¹. The convergence criterion for the electronic self-consistent field (SCF) loop was set to 2×10^{-6} eV/atom. The atomic structures were optimized until the residual forces were below 0.03 eVÅ⁻¹. All adsorptive binding energies (E_{ads}) used in this paper were defined as: $E_{ads}=E_{total}-(E_A+E_B)$, where the E_{total} is the total energy of the frame structure/adsorbate interacting system and E_A and E_B are the energies of the frame structure and the isolated adsorbate, respectively.

а Au NPs (532) b Pd NPs Au-Pd nanocoronals Au-Pd nanocoronals (543) (200) (311) Pd NI (222) (220)(a.u.) Intensity (a.u.) (111) (200) Extinction (220) (311) Au NF Au NPs Au-Pd Pd NPs Pd NPs Au-Pd Au NPs 20 $\begin{array}{ccc} 40 & 50 & 60 \\ 2\theta (degree) \end{array}$ 10 30 70 80 90 100 300 400 500 6<u>0</u>0 7Ó0 Wavelength (nm)

Results and Discussion

Fig. S1. XRD patterns (a) and UV-Vis extinction spectra (b) of Au-Pd nanocoronals, Au NPs, and Pd NPs.



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Fig. S2. TEM images of Au-Pd hybrid NPs, Au-Pd-1 (a), Au-Pd nanocoronals (b), Au-Pd-2 (c), and Au-Pd-3 (d), synthesized by using different amounts of sodium citrate.



Fig. S3. UV-Vis extinction spectra (a) and the corresponding SPR values (b) of the different Au-Pd hybrid NPs shown in Fig. 1h-k.



Fig. S4. (a) The measurement of open circuit potentials between Au and Pd NP-modified ITO electrodes. The dashed purple line notes the time point when light is on. (b) The UV-Vis extinction spectrum of Au NPs (black curve) and the variation values of potential between the two electrodes before and after illumination at different wavelengths (red circles). The line widths of different monochromatic lights are shown at the bottom. The inset shows the electron transfer between Au and Pd under illumination (red arrow) and in dark (navy arrow). (c) The light-intensity dependent open circuit voltage differences.

In order to visualize the plasmon-induced electron transfer between Au and Pd, we measured the open circuit potential (E_{oc}) using two indium-tin-oxide (ITO) glass electrodes coated respectively with Pd (30 nm) and Au NPs (50 nm). The electrons are inclined to transfer from Pd to Au NPs (Fig. S4a, blue curve) with an E_{oc} of ~0.377 V. Interestingly, when the NPs on both sides are illuminated under a xenon lamp (130.9 mW/cm²), the electrons transfer in an opposite direction from Au to Pd NPs (E_{oc} '=-0.397 V).

According to the Schottky effect which describes the effect of the applied field on the work function, the modulus of work function variation (ΔW) can be calculated by equation (1):^[2-4]

$$|\Delta W| = \sqrt{\frac{e^3 |E|}{4\pi\varepsilon_0}} \tag{1}$$

where ε_0 is the vacuum dielectric constant (8.81 × 10⁻¹² F/m); *E* is the applied potential, which approximates the above measured value of E_{oc} . Upon light illumination, ΔW changes from -2.34 × 10⁻⁵ to 2.40 × 10⁻⁵ eV, which means the electron binding capacity of Au and Pd happens reversed, resulting in the opposite electron transfer direction from Au to Pd. The LSPR on Au NPs drives the electron transfer from Au to Pd, which can be confirmed by the monochromatic experiments (Fig. S4b). Under resonant light illumination at 550 nm, the potential change is significantly larger than that at off resonant wavelengths. Additionally, the light-intensity dependent measurements shows a linear relationship (dashed line) between the potential change and intensity (Fig. S4c).^[5, 6]



Fig. S5. DFT calculations of the adsorption configuration and adsorption energy of CAL molecules adsorbed on Au (top row) and Pd (bottom row) through two functional groups, respectively.



Fig. S6. (a) Scheme of atomic force microscopic (AFM) measurement and the table filled with the average adhesion force intensity values between the tips and samples; (b) A typical example of the corresponding force curves. (Here, the tip of AFM made of Pt was coated with 4-MPA by incubating for 24 h.)

AFM is a powerful tool to directly reflect the force intensity between metals and molecules. Here, the adsorption tendency of the alkynyl on different metal surfaces was evaluated by AFM, with the tip modified with 4-mercaptophenylacetylene (4-MPA) to measure the adhesion forces on Au and Pd NPs (as shown in Fig. S6a). It should be noted that before measurements, the tips were washed with ethanol several times to remove the free molecules. In Fig. S6b, the force curves clearly show the different attractions between the tip and samples. And the mean values of dozens of points per sample have been shown in the table. It was found that the Au film presents larger force value (14.33 nN) compared with the Pd film (9.27 nN). The force between the tip and Si wafer (as a blank control) is very weak (0.35 nN), which reflects the reliability of the measurement results. It is reasonable to conclude that compared with Pd, alkynyl tends to adsorb on Au surface.



Fig. S7. DFT calculations of the adsorption configuration and adsorption energy of 4-MPA molecules adsorbed on Pt through two functional groups (a) alkynyl; (b) sulfhydryl, respectively.



Fig. S8. The SERS spectra of PA and 4-MPA on Au and Pt: (a) full spectra; (b) the amplified partial spectra of (a).



Fig. S9. The conversion rates of PA semihydrogenation into styrene on different catalysts including Au-Pd nanocoronals (navy), Pd NPs (orange) and Au NPs (cyan).



Fig. S10. SERS spectra of ferricyanide adsorbed on Au (vermeil) and Au@Pd core-shell NPs (blue).

There are two peaks can be distinguished from the SERS spectra of ferricyanide adsorbed on Au and Au@Pd core-shell NPs. The lower frequency peak is ascribed to the CN E_g vibration, and the higher frequency peak corresponds to the CN A_{1g} vibration.^[7] When potassium ferricyanide adsorbs on the surface of metals, the bonding interaction of the nitrogen via its lone pair to the metal atom results in an increase in the CN force constant, which increases the CN stretching frequency.^[7-9] The stronger the interaction between metals and N, the larger force constant of CN, the greater the blue shift of the two characteristic peaks. The results in Fig. S10 show that the two characteristic peaks measured on Pd are at higher wavenumber than the peaks measured on Au. Therefore, the interaction between CN and Pd is stronger.



Fig. S11. (a) The performance comparison of Fe(III) reduction under different reaction conditions. (b) Schematic illustration of the potassium ferricyanide reduction with (left) and without (right) light illumination. Red arrows note the direction of electron transfer and black arrows indicate the reactants transfer. The columns with different colors show the conversions of the reaction with (red) and without (navy) illumination. (c) The illumination enhancement ratio comparison of the reaction on Au-Pd nanocoronals (navy) and Au@Pd core-shell NPs (red).

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