Electronic Supplementary Information (ESI)

# Dispersive Pd island-deposited gold nanorods for *in situ* SERS monitoring of catalytic reactions

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## ■ Experimental Section

### Materials Synthesis.

**Chemicals**: Gold(III) chloride trihydrate ($HAuCl_4$), CV (Crystal Violet), Hydrochloric acid (HCl), palladium chloride ($PdCl_2$, 99%), and 4-nitrothiophenol (4-NTP) were purchased from Sinopharm group chemical reagent Co. Ltd. Hexadecyltrimethylammonium bromide (CTAB) and sodium borohydride ($NaBH_4$) were obtained from Sigma-Aldrich, 5-iodosalicylic acid (5-ISA), L-ascorbic acid (AA) and silver nitrate ($AgNO_3$) were obtained from Aladdin. Potassium iodide (KI) was purchased from Alfa Aesar. Milli-Q water was obtained from Milli-Q Advantage water purification System. All materials were directly used without any further purification.

**Synthesis of AuNRs**. An improved seed growth procedure was used to obtain gold nanorods (AuNRs). Briefly, 10 mL of 0.2 M CTAB solution was first mixed with 105 μL of 1 wt% $HAuCl_4$. Then, 0.6 mL of ice-cold 0.01 M $NaBH_4$ was added to the mixed solution with vigorous stirring for 2 min. The solution changed from dark-yellow to brown and was maintained for 1 h at room temperature before use. The 1 mL seed solution was diluted to 5 mL with 0.1 M CTAB, shaken well and placed for 30 min.

Next, the growth solution was prepared by mixing aqueous solution of CTAB (0.1 M, 70 mL), $AgNO_3$ (0.01 M, 0.7 mL), $HAuCl_4$ (1 wt%,1.44 mL) and $HNO_3$ (1 M, 1.4 mL). A freshly prepared aqueous ascorbic acid (AA) solution (0.05 M, 0.91 mL) was then added. Finally, 0.45 mL pre-diluted seed solution was added with stirring for 5 min. The liquid mixture was carried out in a water bath at 28-32 °C for at least 12 h.

**Surface Modification of the Au Nanorods by CTAB/5-ISA.** 10 mL as-synthesized Au NRs solution was first centrifuged at 6000 rpm for 10 min and subsequently redispersed in 10 mL of aqueous CTAB/5-ISA solution (0.1 M CTAB and 0.02 M 5-ISA). Then, the solution was centrifuged again at 5500 rpm and redispersed in 10 mL of deionized water. The nanoparticle aqueous dispersions were used for the synthesis of AuNRs@Pd islands.

**Synthesis of the AuNR@Pd materials.** The Pd precursor ($H_2PdCl_4$) was prepared by dispersing 88.7 mg of $PdCl_2$ powder into 100 mL of 0.1 M HCl solution at 60 °C. After that, 568 µL AA (0.1 M), 990 µL as-prepared $H_2PdCl_4$ (1 mM), 80 µL 0.01 M HCl were added to the CTAB/ISA AuNRs solution. The synthesis process was carried out by shaking the solution gently and keeping it at room temperature for 20 h. The synthesized AuNR@Pd islands were rinsed using deionized water and were centrifuged at 6000 rpm for 10 min. while the AuNR@Pd Shell was synthesized directly from AuNR without surface modification.

**UV-vis measurement**

1 mL of 0.1 M fresh $NaBH_4$ was added into 2 mL 4-NTP ($10^{-4}$ M) solution, and then added 500 µL water-dispersed AuNRs@Pd. The catalytic 4-NTP reduction process was recorded *in situ* at the range of 250-500 nm by UV-visible absorption spectrophotometer (UV-2550, Shimadzu, Japan).

**SERS measurement**

1 mL nanoparticles were mixed with 0.5 mL of $10^{-5}$ M 4-NTP solution and incubated at room temperature for 12 h, and then the 4-NTP-functionalized nanoparticles were washed with Milli-Q water twice and concentrated to 100 µL. the solution was dropped on a silicon wafer and dried by air to measure. Then 10 µL of $10^{-3}$ M $NaBH_4$ aqueous solution was dropped on the silicon wafer. In order to avoid liquid evaporation, an ultra-thin quartz slide was placed on the sample. Raman spectra (LabRAM HR800, Horiba Jobin Yvon, France) were collected *in situ* at different reaction time using a 633 nm laser with a 50x objective lens. The acquisition time of each spectrum was 10 s.

**Calculation of catalytic rate constant K ($min^{-1}$)**

The catalytic rate constant can be obtained from the pseudo first order kinetic equation, as shown in Formula 1.

$$\ln (C_t/C_0) = -K_{app}t \qquad \text{(Formula 1)}$$

The relationship between the absorbance value and the concentration of the light-absorbing substance conforms to Lambert-Beer 's law:

$$A= Kbc \qquad \text{(Formula 2)}$$

$C_t$ and $C_0$ are the concentrations (mol/L) of 4-NTP at time t and 0, respectively. A is absorbance. K is the molar absorption coefficient. The absorbance value is proportional to the concentration of the light-absorbing substance, so ln ($C_t/C_0$) is directly proportional to ln ($A_t/A_0$). The corresponding reaction rate constants are calculated.

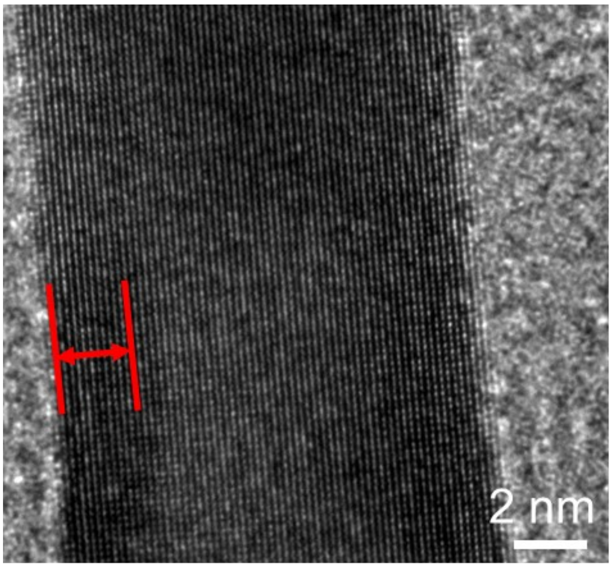

Fig. S1 HRTEM of AuNR@Pd Shell

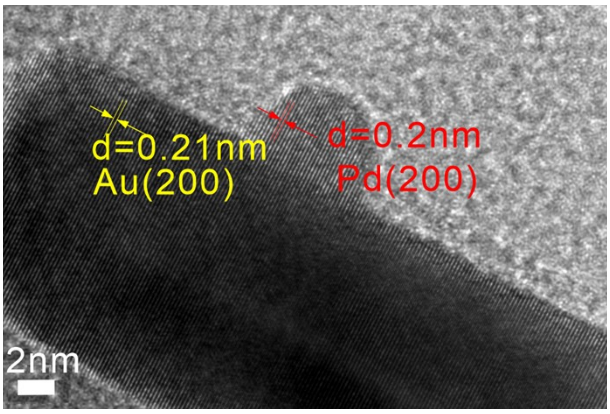

Fig. S2 HRTEM of AuNR@Pd islands

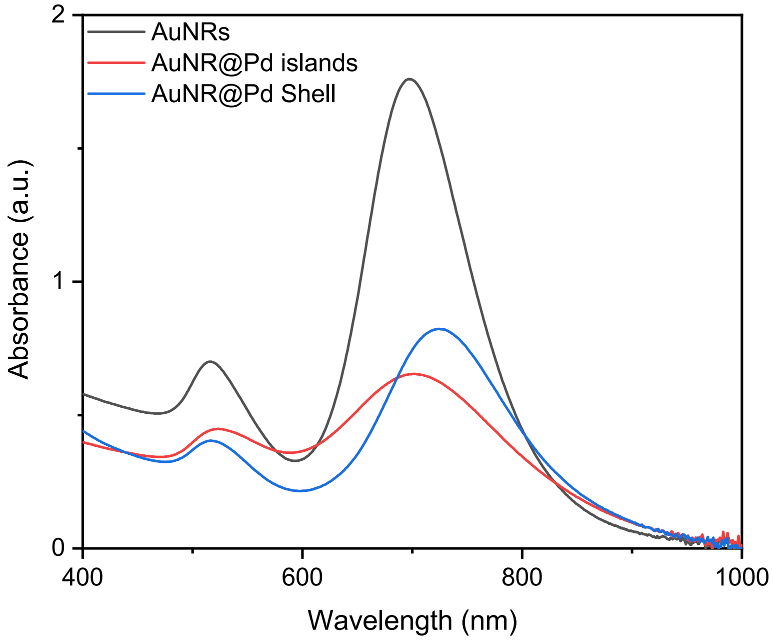

Fig. S3 UV-vis spectra of AuNRs、AuNR@Pd islands and AuNR@Pd Shell

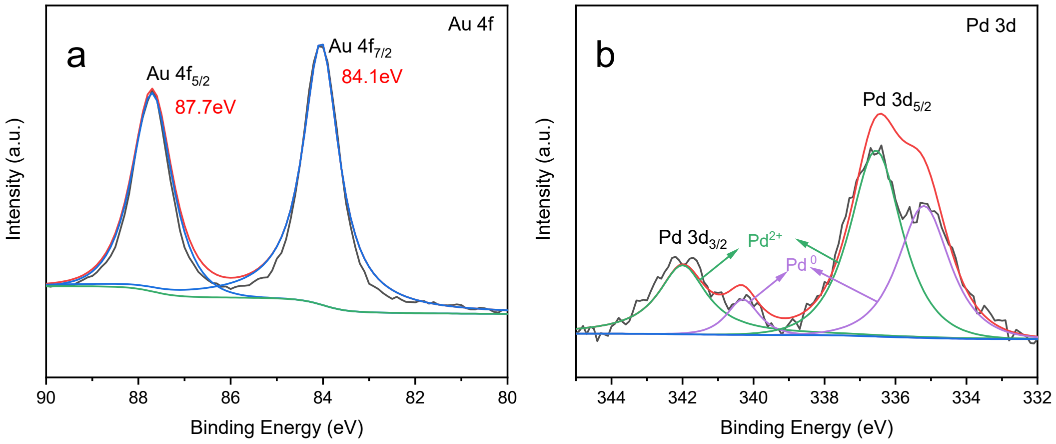

Fig. S4 XPS spectra of AuNR@Pd Shell: (a) Au 4f, (b)Pd 3d

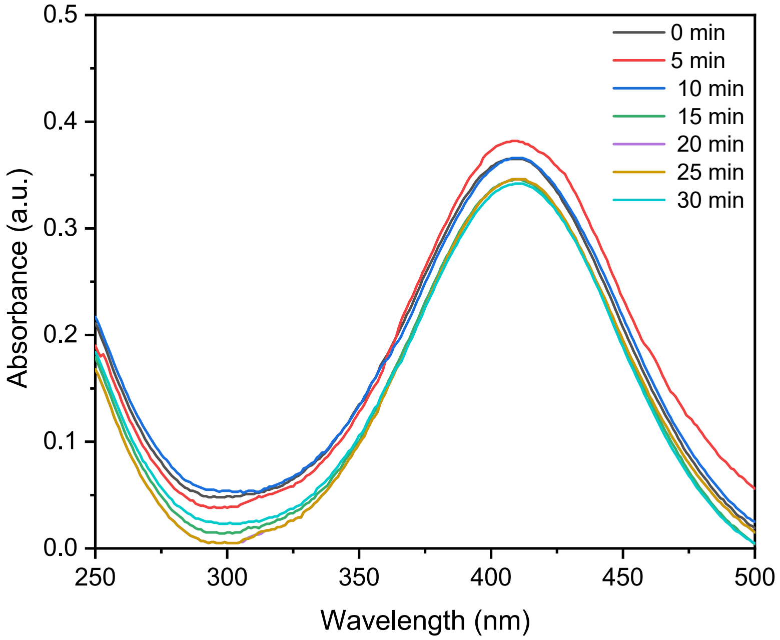

Fig. S5 UV-vis absorption spectra of 4-NTP after adding $NaBH_4$

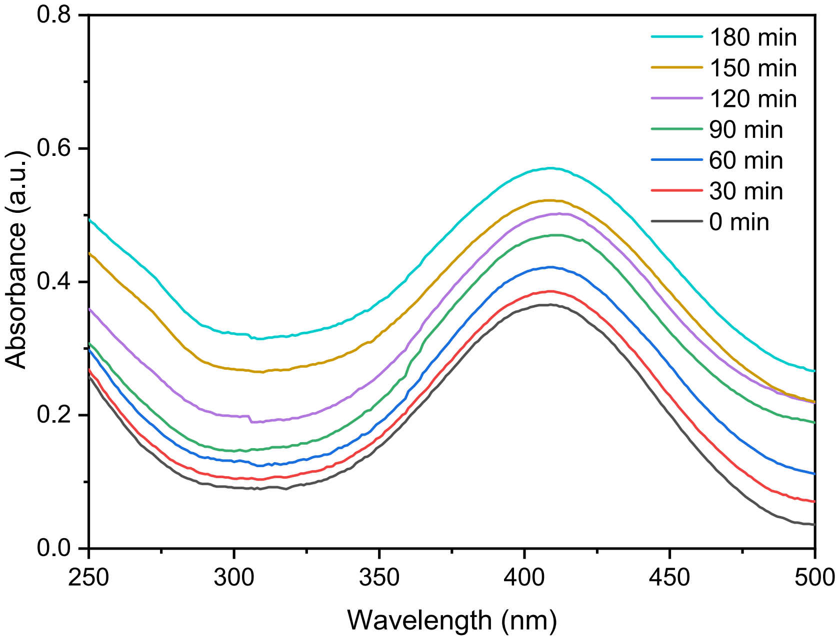

Fig. S6 UV-vis absorption spectra of catalytic reduction of 4-NTP with AuNRs

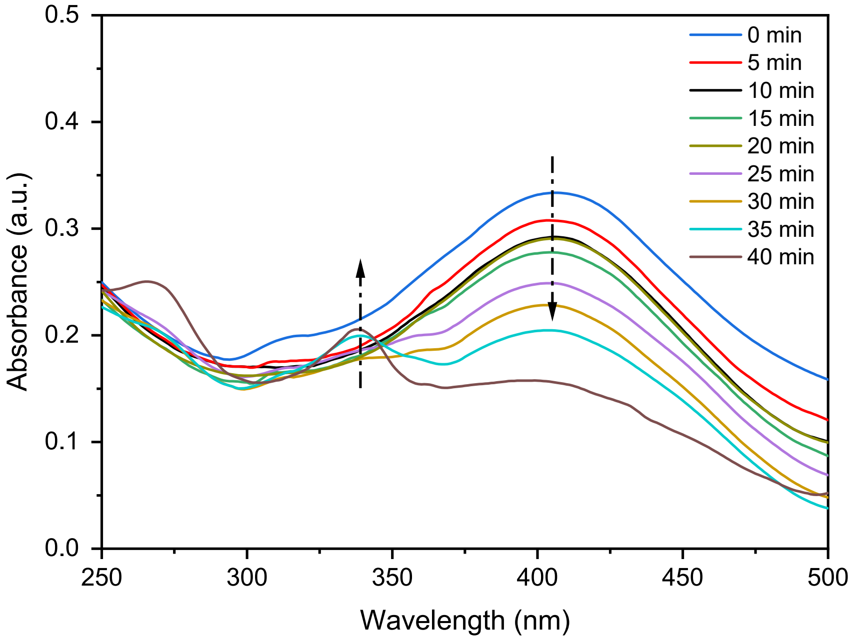

Fig. S7 UV-vis absorption spectra of catalytic reduction of 4-NTP with AuNR@Pd Shell

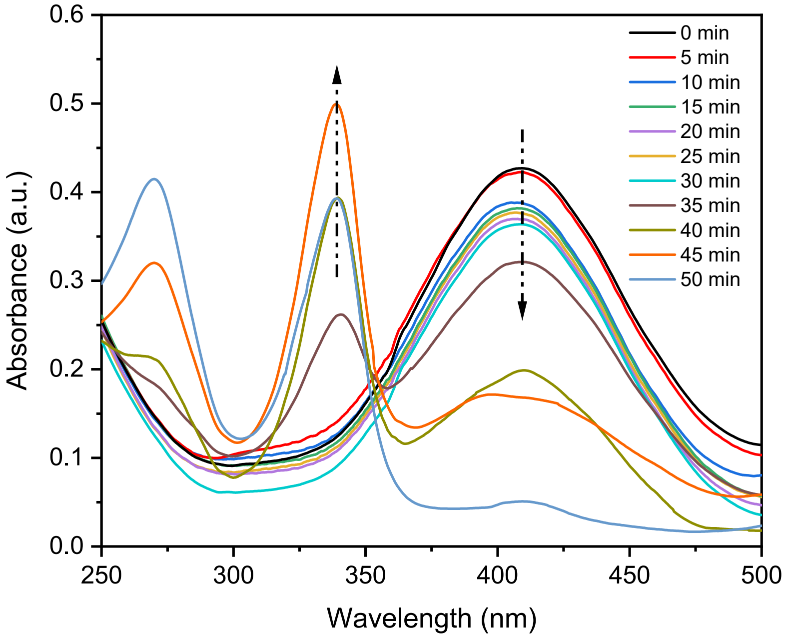

Fig. S8 UV-vis absorption spectra of 4-NTP reduction catalyzed by AuNR@Pd islands1/2

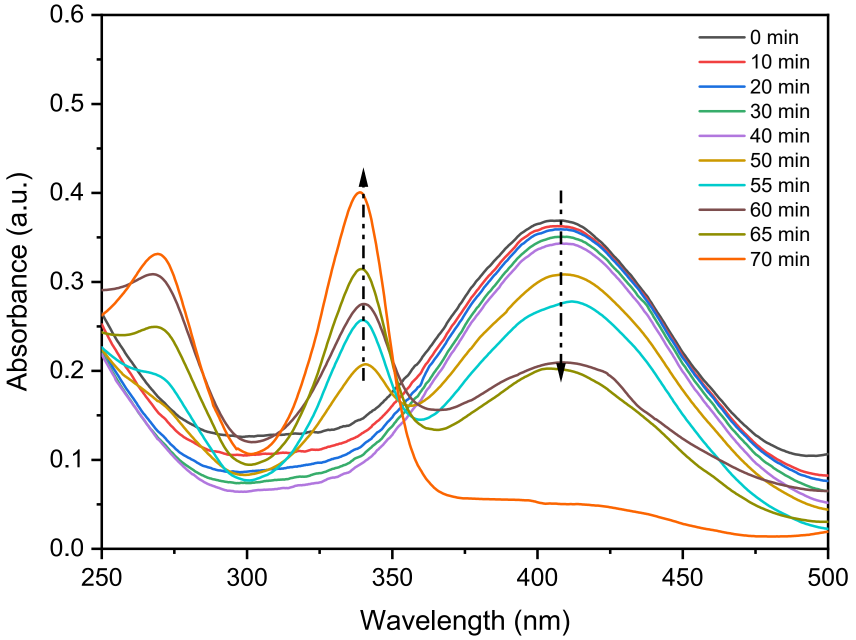

Fig. S9 UV-vis absorption spectra of 4-NTP reduction catalyzed by AuNR@Pd islands1/4

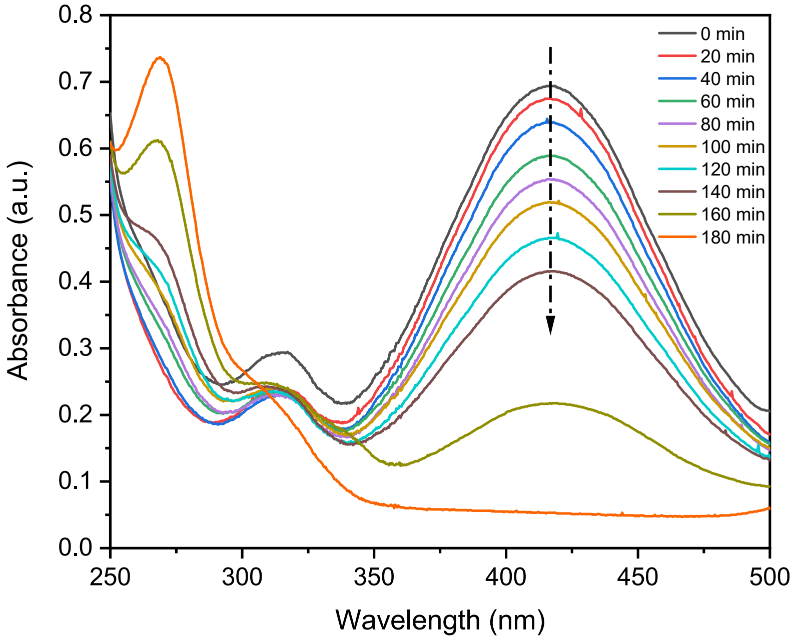

Fig. S10 UV-vis absorption spectra of 4-NTP reduction catalyzed by AuNR@Pd islands1/8

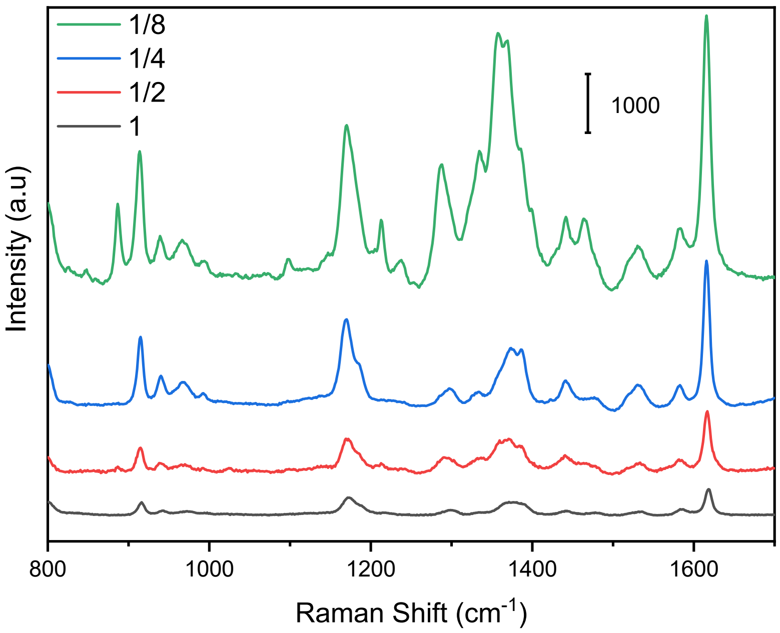

Fig. S11 SERS spectra of CV acquired from different AuNR@Pd islands

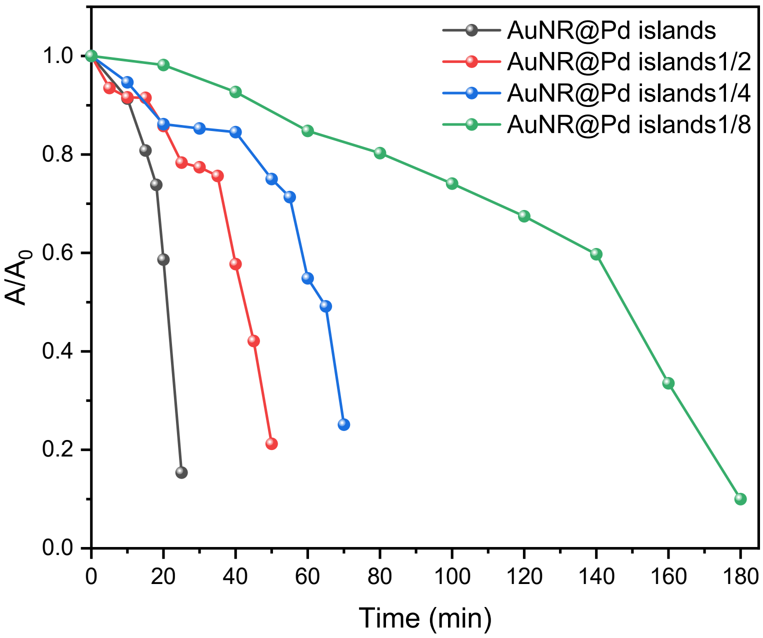

Fig. S12 Absorption at 400 nm as a function of reaction time in the presence of different AuNR@Pd islands

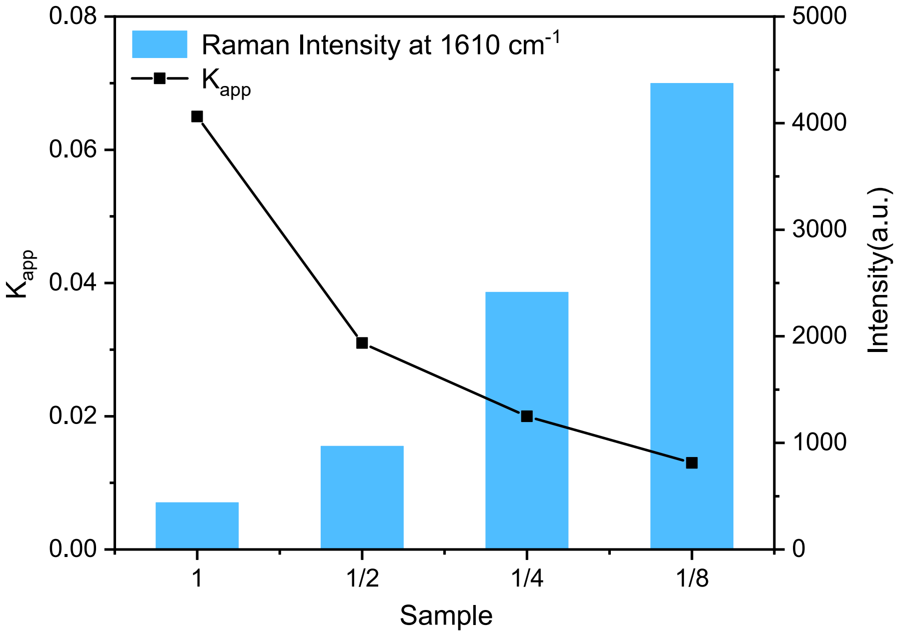

Fig.S13 Diagram of reaction kinetic constant ($K_{app}$) and SERS intensity of CV at 1610 cm$^{-1}$ of different AuNR@Pd islands

Table S1. Synthesis of AuNR@Pd islands with different Pd amounts

| Sample | Volume of 0.1 M AA | Volume of 1 mM $H_2PdCl_4$ | Volume of 0.01 M HCl |
|---|---|---|---|
| AuNR@Pd islands | 568 μL | 990 μL | 80 μL |
| AuNR@Pd islands1/2 | 284 μL | 495 μL | 40 μL |
| AuNR@Pd islands1/4 | 142 μL | 248 μL | 20 μL |
| AuNR@Pd islands1/8 | 71 μL | 124 μL | 10 μL |

Table S2. The K(min$^{-1}$) of four types of AuNR@Pd islands with different Pd content

| Sample | $K_{app}$ (min$^{-1}$) |
|---|---|
| AuNR@Pd islands | 0.065 |
| AuNR@Pd islands1/2 | 0.031 |
| AuNR@Pd islands1/4 | 0.020 |
| AuNR@Pd islands1/8 | 0.013 |

Table S3. The SERS shifts and assignments of 4-NTP and 4-ATP

| | Raman shifts ($cm^{-1}$) | Assignment |
|---|---|---|
| 4-NTP | 1108 | O-N-O stretching |
| 4-NTP | 1326 | O-N-O stretching |
| 4-NTP | 1569 | phenyl-ring mode |
| 4-ATP | 1078 | C-S stretching |
| 4-ATP | 1173 | C-H in plane bending |
| 4-ATP | 1590 | phenyl-ring mode |