Electronic Supplementary Information (ESI)

Experimental Section:

Materials and Reagents. Chloroauric acid tetrahydrate ($HAuCl_4.4H_2O$), hydroxylamine hydrochloride ($NH_2OH.HCl$), trisodium citrate, sulfuric acid (H_2SO_4, 95–98%), hydrogen peroxide (H_2O_2, 30%), and ethanol were analytical reagents and purchased from Sinopharm Chemical Reagent Co., Ltd. Polyvinylpyrrolidone (PVP) was obtained from Acros organics. Si(111) wafer was used as the substrate for trapping Au nanoparticles monolayer film. All aqueous solutions were prepared with Milli-Q water (resistivity≥18.2 MΩ·cm).

Apparatus. The scanning electron microscope (SEM) images were recorded using a Hitachi S-4700 with an accelerating voltage of 15 KV and transmission electron microscope (TEM) images were recorded using a TECNAI F30 with an accelerating voltage of 200 KV. SERS measurements were carried out on an XploRA PLUS confocal micro-Raman system from HORIBA, the width of the silt and the pinhole were 300 μm and 100 μm, respectively. All the measurements were performed by using the excitation wavelength of 639 nm with a power of about 20 mW on the substrates. All SERS spectra were acquired for at least 3 times. Raman signals were collected by a 50× long-working-length objective (≈8 mm) which was based on an Olympus BX41 system.

Preparation of Au nanoparticles seed. Au nanoparticles seed with the mean diameter of 15 nm were prepared by the classic Frens' approach[1]. Briefly, 100 ml of aqueous solution of $HAuCl_4$ (100 $\mu g \cdot mL^{-1}$) was added to a round-bottomed flask (250 ml) and heated to boiling with vigorous stirring. Then 2 ml of trisodium citrate (10 $mg \cdot mL^{-1}$) was quickly injected into the solution. The color of the solution changed from light yellow to pink within 3 min. The mixed solution was kept boiling for another 15 min and then cooled to room temperature.

Preparation of 35 nm Au nanoparticles. Au nanoparticles with the average diameter of 35 nm were prepared by the way of epitaxial growth using 15 nm Au nanoparticles as the seeds[2]. Typically, 25 ml of as-prepared 15 nm Au nanoparticles seed was added to a round-bottomed flask (100 ml), accompanied by the addition of 1 ml of trisodium citrate

(10 mg·mL^{-1}), 1 ml of Polyvinylpyrrolidone (PVP, Mw=10000) (10 mg·mL^{-1}) and 20 ml of $NH_2OH·HCl$ (25 mmol·L^{-1}). Subsequently, 20 ml of aqueous solution of $HAuCl_4$ (1 mg·mL^{-1}) was added into the solution dropwisely under stirring. The device was kept stirring for another 1 h after the addition was complete. The color of the solution changed from pink to wine red, indicating the growth of seeds, which could also be clearly observed from the corresponding UV-vis spectra.

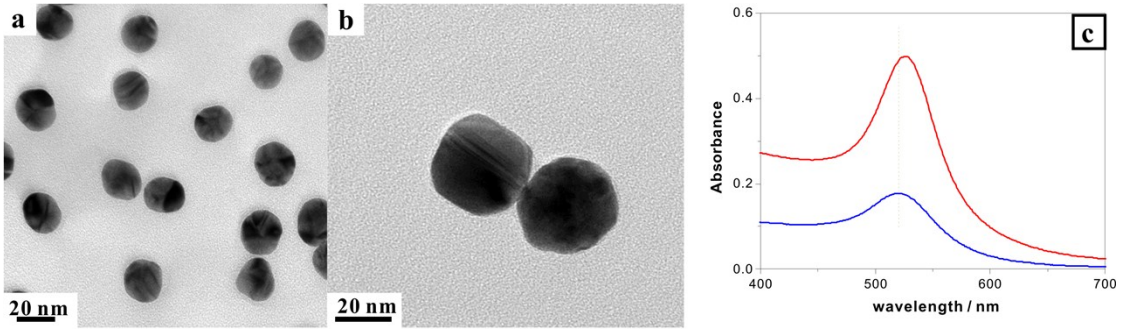

Fig. S1 TEM images of the as-prepared Au nanoparticles with the mean diameter of (a) 15 nm and (b) 30 nm. (c) the corresponding UV-vis spectra of the as-prepared Au nanoparticles.

Preparation of Au nanoparticles monolayer film. Au nanoparticles monolayer film was obtained at the air-water interface. Briefly, 3 ml of the as-prepared 35 nm Au nanoparticles sol was added to a home-made evaporation device into a vacuum drying oven for 16 h at 40 ℃ for the formation of a bright and compact monolayer film of Au nanoparticles. Then the film was transferred to a substrate for characterization.

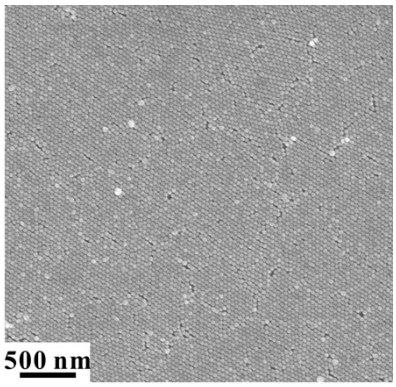

Fig. S2 SEM image of Au nanoparticles monolayer film

The SERS uniformity characterization of the Au nanoparticles monolayer film.

It was characterized with the probe of TP.

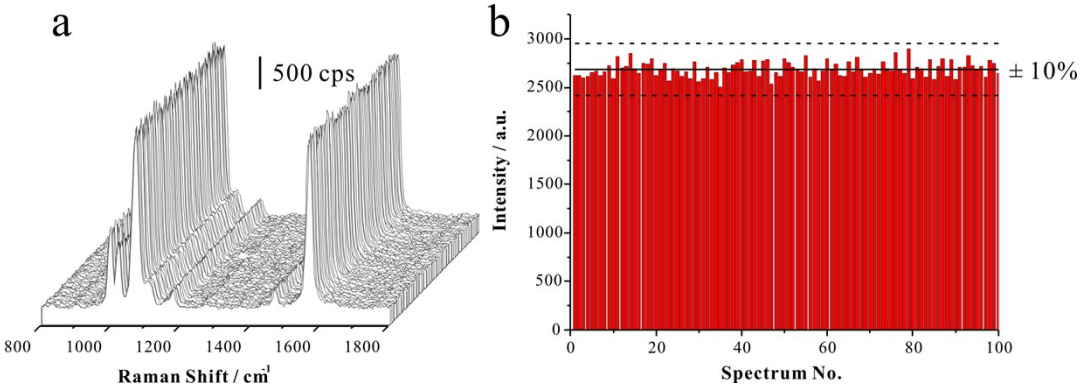

Fig. S3. SERS spectra of TP from 100 randomly selected spots on the Au nanoparticles film (a). The corresponding SERS intensities of TP at 1072 cm^{-1} (b). The average SERS intensity (solid line) was estimated to be about 2700 cps with the relative standard deviation smaller than 10%.

The SPR-driven catalytic reaction uniformity characterization of the Au nanoparticles monolayer film.

It was characterized with the probe of PATP.

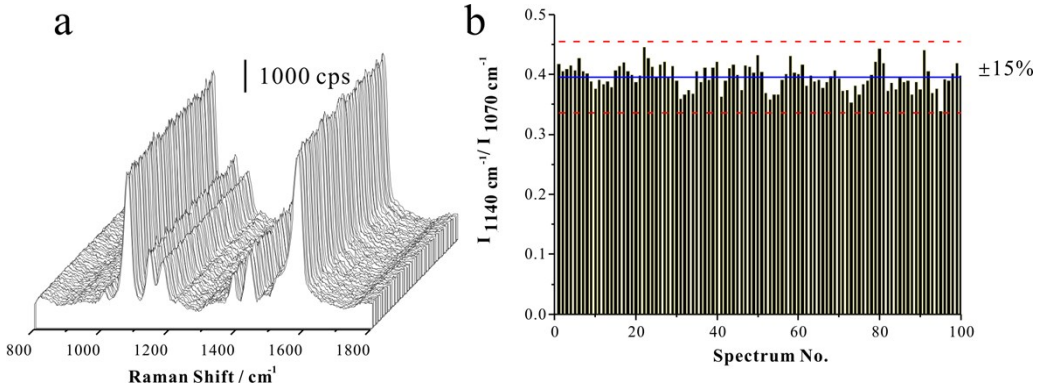

Fig. S4 SERS spectra of PATP from 100 randomly selected spots on the Au nanoparticles film (a). The corresponding SPR catalytic efficiency (blue line) was estimated to be about 0.4 with the relative standard deviation smaller than 15% (b).

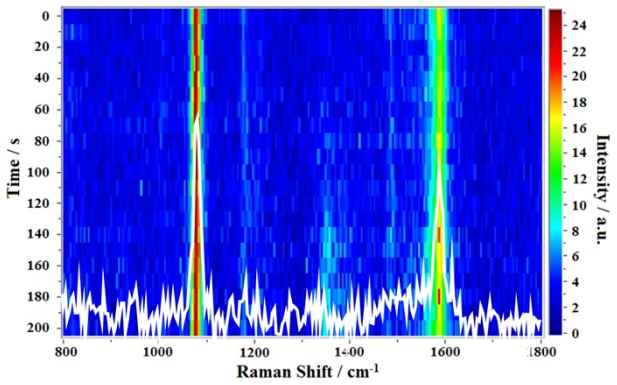

Fig. S5 Time-dependent SERS mapping image of PATP absorbed on Au MLF under dry state.

Theoretical calculation. A commercial finite-element method simulation software (COMSOL Multiphysics) was applied to modeling the Au nanoparticles monolayer film. A heptamer was used to model the Au nanoparticles film and the silicon substrate was assumed to be semi-infinite. A spherical domain was created around the heptamer and perfectly matched layers (PMLs) were employed to simulate an open boundary. The average diameters of Au nanoparticle were 35 nm, which were based on the SEM images of the Au nanoparticles film. And the distance between the Au nanoparticles and the silicon substrate was 2 nm. In order to simulate the distribution of the average SERS EF in the wavelength range from 400 nm to 1000 nm during the evaporation process, the gap between the adjacent Au nanoparticles was decreased from 20 nm to 1 nm. The permittivity values of Au nanoparticle were taken from Johnson and Christy[3], while the refractive index of the silicon substrate was taken from Ref. 3[4]. The medium over the substrate was set to be air, with a refractive index of n = 1, or water, with a refractive index of n = 1.33.

References

1. G. Frens, *Nature, Phys. Sci.*, 1973, **241**, 20-22.
2. Q. H. Guo, M. M. Xu, Y. X. Yuan, R. A. Gu and J. L. Yao, *Langmuir*, 2016, **32**, 4530-4537.

3. P. B. Johnson and R. W. Christy, *Phys. Rev. B*, 1972, **6**, 4370-4379.
4. E. D. Palik, in *Handbook of Optical Constants of Solids*, Academic Press, Burlington, 1997, pp. 187-227.