## Supporting information

# Fabrication on AFM Tips for Tip-Enhanced Raman Spectroscopy by Au Nanoparticles Monolayer Film and Electrodeposition

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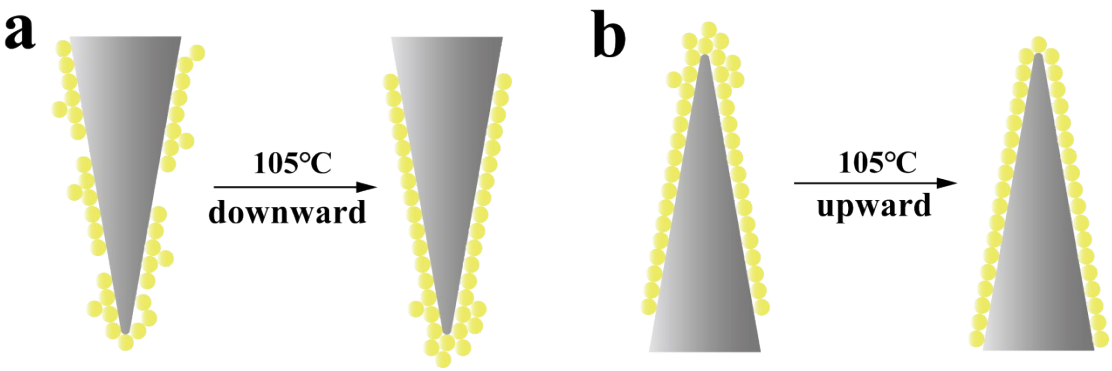


**Fig. S1** Schematic diagram of aggregation of Au nanoparticles in the apex after tip is annealed in a downward direction (a), departure of excess Au nanoparticles from the apex after tip is annealed in a upward direction (b).

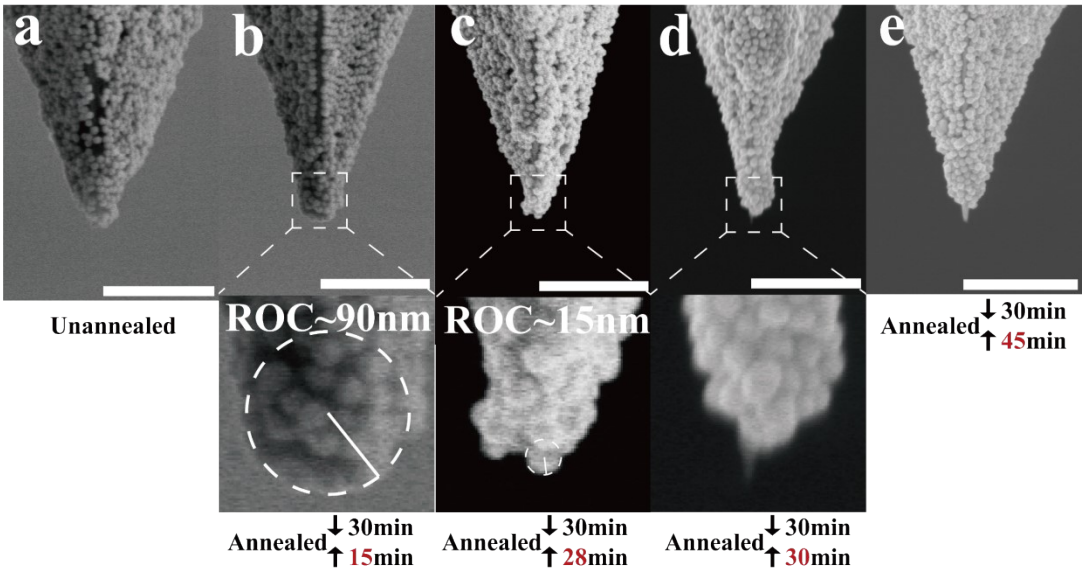


**Fig.S2** SEM images of Au nanoparticles film modified tip without annealling (a), with annealling downward for 30 min and then upward for 15 min (b), 28 min (c), 30 min (d) and 45 min (e). The scale bar is 500 nm.

After annealing downward for 30 min and then upward for 15min, as shown in Fig. S2b, a large number of Au nanoparticles are gathered at the tip apex, leading to an increase in the radius of curvature (ROC) to 90 nm. After annealing downward for 30 min and then upward for 28min, as shown in Fig. S2c, the ROC is decreased to 15 nm. After annealing downward for 30 min and then upward for 30 min and 45 min, as shown in Fig. S2d and Fig. S2e respectively, the tip apex is not occupied by Au nanoparticles, indicating the disappearance of TERS enhancement effect.

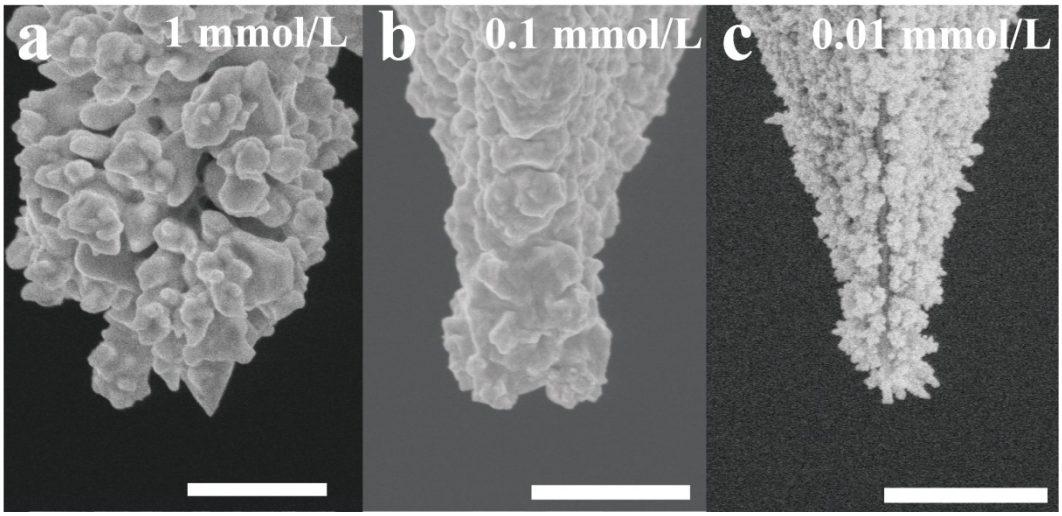


**Fig. S3** SEM images of Au nanoparticles film modified tip with Au outer layer prepared by electrodeposition with different concentration of $HAuCl_4$: 1 mmol/L (a), 0.1 mmol/L (b) and 0.01 mmol/L (c). Potential: 0 to -1.4 V, scan rate：50 mV/s. The scale bar is 500 nm.

To electrochemically deposit an Au outer layer with appropriate thickness on the surface of Au nanoparticles film modified tip, it is necessary to choose a optimal concentration of $HAuCl_4$. Linear voltammetry deposition is conducted on the annealed Au nanoparticles film modified tips in 0.1 mol/L $H_2SO_4$ with different concentrations of $HAuCl_4$. For the $HAuCl_4$ solution of 1 mmol/L, an excessively thick Au layer attaches on the surface of Au nanoparticles film modified tip (Fig. S3a). It indicated that the radius of curvature (ROC) is increased to about 500 nm, resulting in dramatic decrease of spatial resolution. However, the observed micro-structural roughness of the electrodeposited tip surface hinders the efficient laser confinement at the tip apex. It leads to a remarkable degradation in TERS excitation and collection efficiency. Further reducing the concentration of $HAuCl_4$ to 0.1 mmol/L, an excessively thick Au layer is still obtained with the ROC of around 300 nm (Fig. S4b). As the concentration of $HAuCl_4$ is further reduced to 0.01 mmol/L, a relatively suitable Au layer forms on the surface (Fig. S4c). Although the ROC is remarkably decreased to about 100 nm. However, the improvement of the spatial resolution remains significant challenge in such electrodeposition method. Consequently, the deposition parameters is optimized to further control the thickness and morphology of the additional Au outer layer.

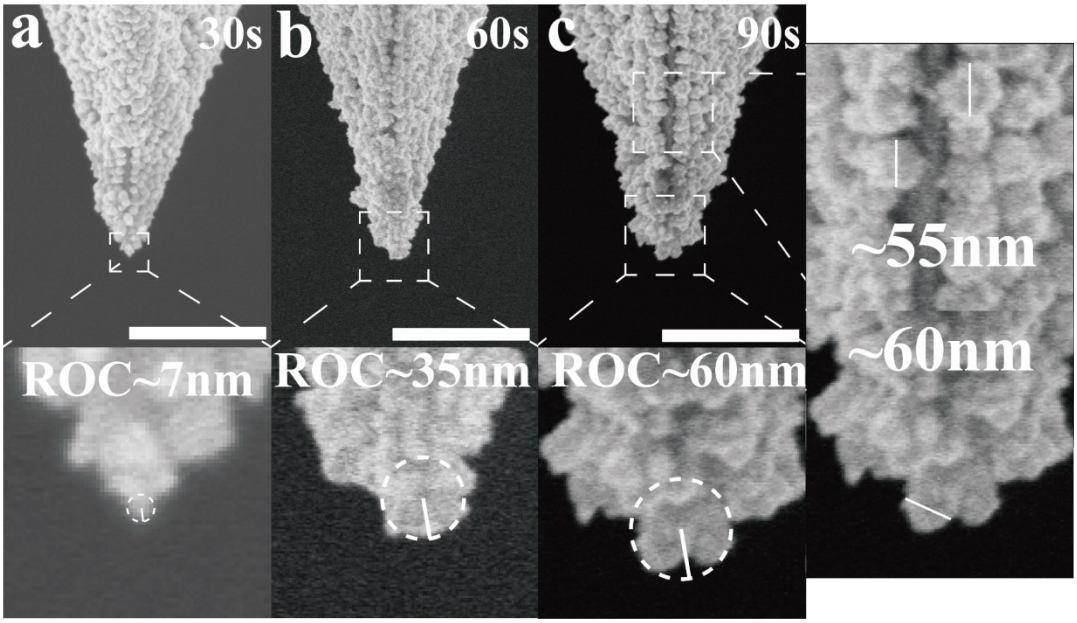


**Fig. S4** SEM images of Au nanoparticles film modified tip with Au outer layer prepared at the initially deposition potential of -1.2 V for 10 s, followed by positive movement of potential to -0.85 V for 30 s (a), 60 s (b) and 90 s (c). The scale bar is 500 nm.

For obtaining appropriate thickness and morphology of the Au outer layer, the potentiostatic deposition is performed. Briefly, a rapid nucleation deposition is carried out at -1.2 V with duration of 10 s, followed by slow growth deposition at -0.85 V for different duration to obtain the desired thickness of Au outer layer. After depositing at -1.2 V for 10 s and then at -0.85 V for 30 s, it can be observed the ROC is significantly decreased to 7 nm (as shown in Fig. S4a). Keeping the initial deposition at -1.2 V for 10 s and increasing the duration at -0.85 V to 60 s and 90 s, the ROC of final modified tip is increased to 35 nm and 60 nm, respectively (as shown in Fig. S4b and 4c).

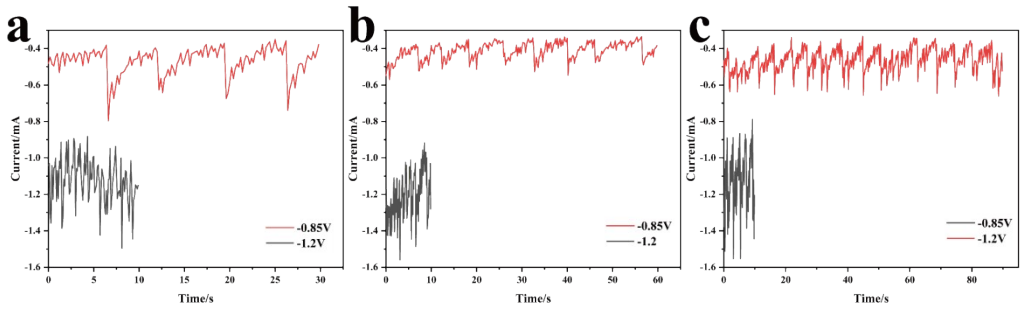


**Fig. S5** Current-time curves of electrodeposition using potentiostatic method on the surface of annealed Au nanoparticles film modified tip. The initial deposition is performed at -1.2 V for 10 s, and followed by deposition at -0.85 V for 30 s (a), 60 s (b) and 90 s (c), respectively.

Actually, it is really difficult to measure the precise thickness of Au outer layer in the present case. Therefore, the thickness of the deposited Au outer layer is estimated by the amount of charge during deposition. The average current is about 1.127 mA ($I1_1$) at -1.2 V, while 0.469 mA ($I2_1$) at -0.85 V (Fig. S5a). For the other experiment with different deposition duration at -0.85 V, the $I1_2$ of -1.21 mA and $I2_2$ of -0.413 mA, and the $I1_3$ of -1.122 mA and $I2_3$ of 0.464 mA are estimated respectively (as shown Fig. S5b and 5c), Thus, the total charge of $Q_{tn}=I1_nt1_n+I2_nt2_n$ during the deposition is about 25.34 mC, 36.88 mC and 53.00 mC corresponding to deposition duration at -0.85 V of 30 s, 60 s and 90 s, respectively. Finally, the relevant thickness of Au outer layer is calculated to about 7 nm, 10 nm and 15 nm, respectively.

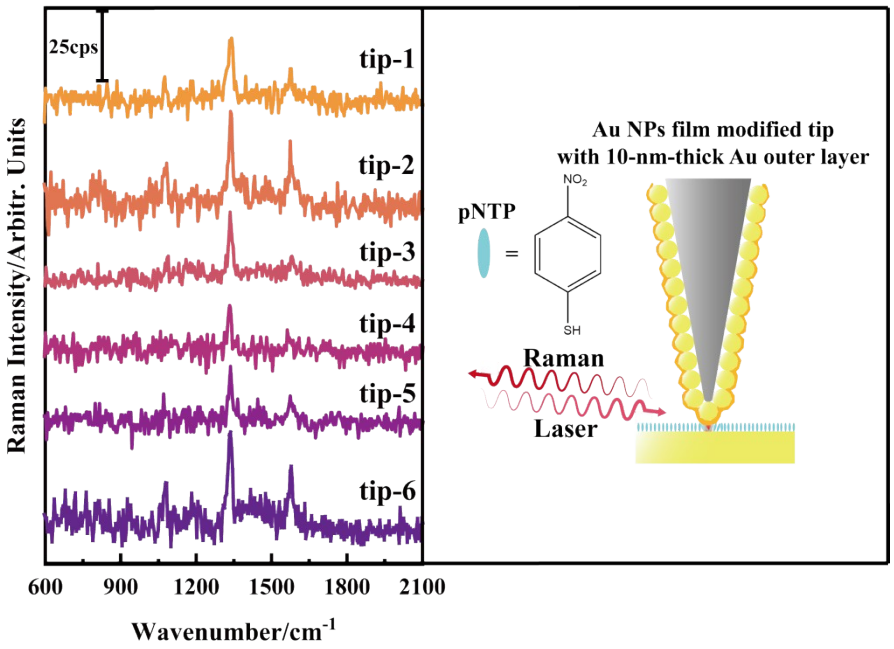


**Fig.S6** TERS spectra of pNTP obtained by different Au nanoparticles film modified tips with 10-nm thick Au outer layer. The spectra are recorded using a 638 nm laser with a power of 0.13 mW and an acquisition time of 1 s.

The Au nanoparticles monolayer film is fabricated by well-defined processing protocol and exhibits the high uniformity in SERS enhancement. It allows to achieve a high success rate for the modification processes. The Fig. S6 presents the TERS spectra of pNTP molecules from 6 different Au nanoparticles film@10 nm Au modified tips. The TERS EF for Au nanoparticles film@10 nm Au modified tips exhibits a range of $1.5\times10^4$ to $3.2\times10^4$. It should be pointed out that the difference in the TERS EF is critically depended on the quality of tips and the properties of substrates (for example the surface structure, coverage etc.) Therefore, the tip fabrication yield is quite high.

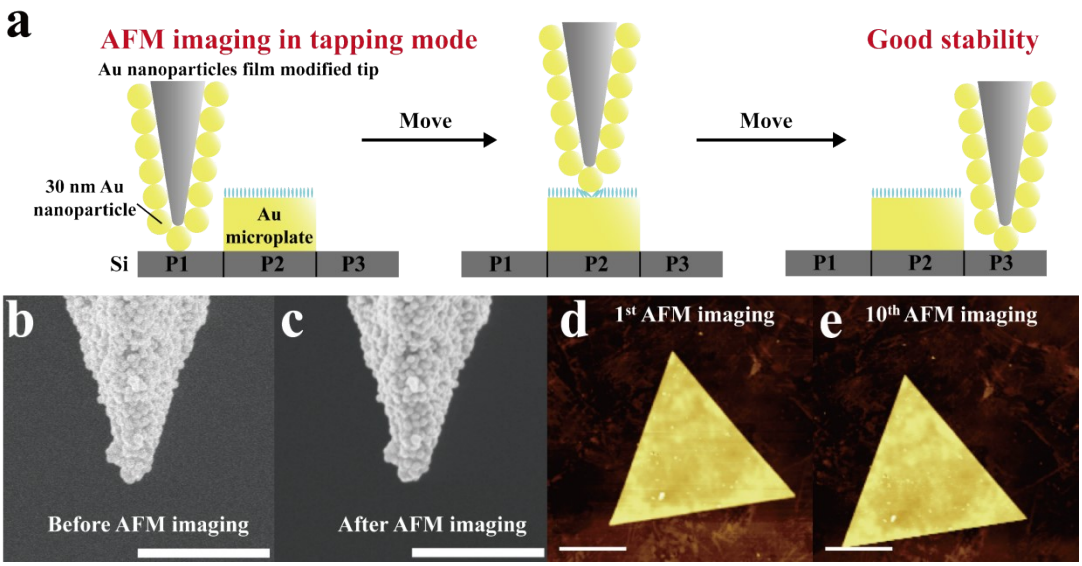


**Fig. S7** Schematic diagram of annealed Au nanoparticles film modified tip for AFM imaging in tapping mode (a). SEM images of annealed Au nanoparticles film modified tip are recorded before (a) and after (b) AFM imaging. The scale bar is 500 nm. AFM images of the Au MP after 1$^{st}$ (c) and 10$^{th}$ (d) scanning by the annealed Au nanoparticles film modified tip. The scale bar is 2 μm.

The stability of annealed Au nanoparticles film modified tips is evaluated during tapping-mode imaging. Firstly, the presence of Au nanoparticles and morphology at the tip apex are observed by SEM (Fig. S7b). Subsequently, the AFM images of Au MP (8 μm × 8 μm) are obtained in tapping mode for ten times by the same tip. The results show that the 10$^{th}$ AFM imaging of Au MP (Fig. S7e) is basically identical to the 1$^{st}$ AFM imaging (Fig. S7d) in terms of details and both maintain a high imaging quality. It indicates the minimal changes in the morphology of the tip apex after multiple AFM imaging measurements. Finally, it is observed that the morphology of the annealed Au nanoparticles film modified tip after AFM imaging remains the initial state. Therefore, the annealed Au nanoparticles film modified tips exhibited optimal AFM imaging stability in tapping mode (Fig. S7a).

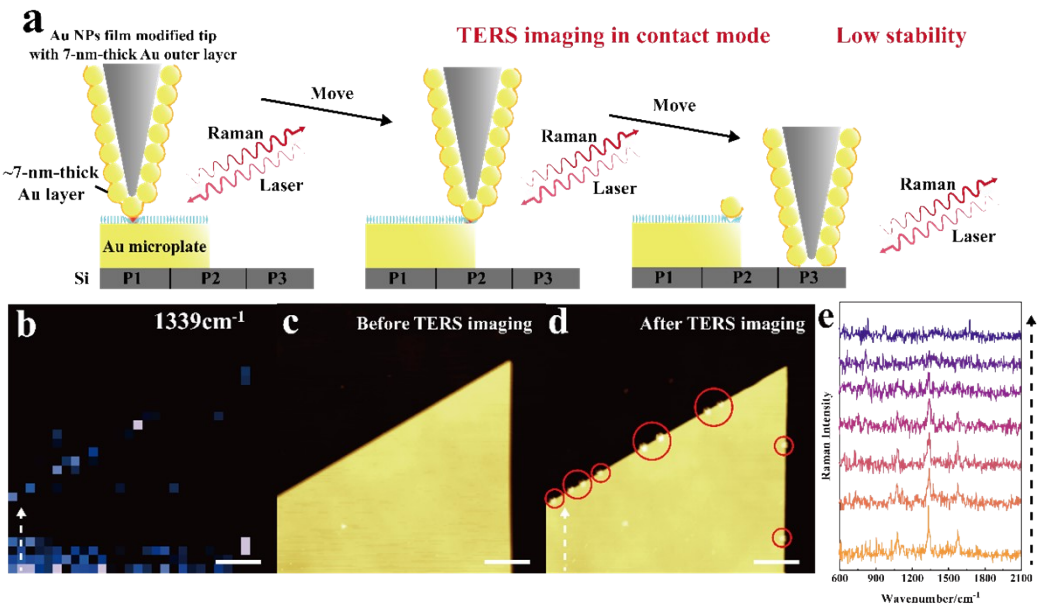


**Fig. S8** Schematic diagram of Au nanoparticles film modified tip with 7-nm thick Au outer layer for TERS imaging in contact mode (a). TERS image of band intensity at 1339 $cm^{-1}$ of pNTP (b). In-situ AFM images of Au MP before (c) and after (d) TERS imaging. The scale bar is 1 μm. TERS spectra are collected at the positions marked by the dotted line in the images. The spectra are recorded using a 638 nm laser with a power of 0.13 mW and an acquisition time of 1 s (e).

The modified tip attached with 7 nm thick Au outer layer exhibited poor stability for the TERS imaging (Fig. S8a). By using Au nanoparticles film modified tip with 7-nm -thick Au outer layer for TERS imaging on pNTP modified Au MP, the spatial distribution of peak intensity at 1339 $cm^{-1}$ of pNTP molecules is presented in Fig. S8b (6 μm × 6 μm, each pixel size is 200 nm × 200 nm). As TERS imaging continues, the TERS signal of pNTP molecules on the surface of Au MP gradually weakens and eventually disappears. It is also confirmed by the signal changes in the TERS spectra (Fig. S8e) from the positions marked by the dotted line in the images. After TERS imaging, it is found that some solid residues appear on the surface of Au MP (Fig. S8d), and the height of these residues is basically consistent with the diameter of Au nanoparticles. Based on the above fact that the TERS signal disappears and residues appear on the surface of Au MP, it reveals that some of the Au nanoparticles on the fabricated tip are detached and deposited on Au MP surface during the TERS imaging. It demonstrates the stability of modified tips with 7 nm thick Au outer layer is too poor to serve as the TERS tips.