

Supporting Information

Rapid Separation and On-Line Detection by Coupling High Performance Liquid Chromatography with Surface- Enhanced Raman Spectroscopy

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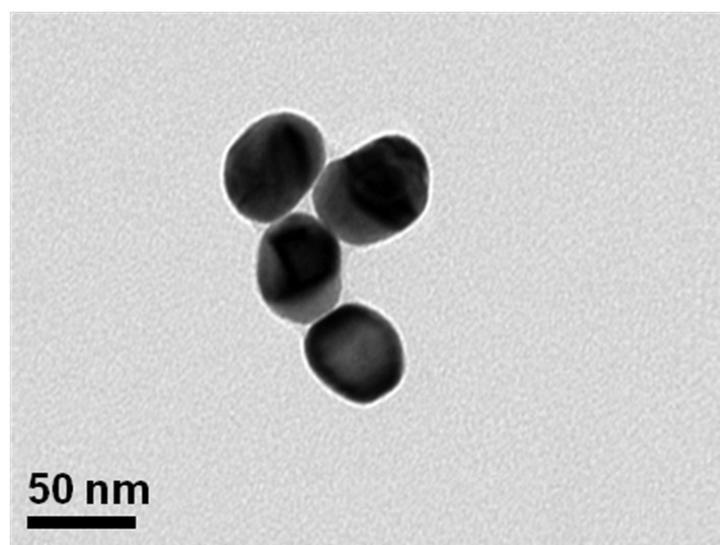


Figure S1. TEM image of the as-prepared Au nanoparticles with a diameter of 55 nm.

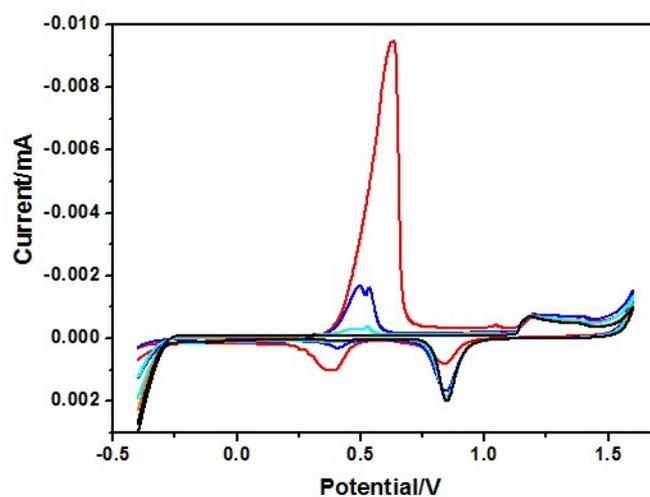


Figure S2. Cyclic voltammetry of Au@Ag nanoparticles with Au pinholes on a glassy carbon (GC) electrode in $0.5 \text{ mol}\cdot\text{L}^{-1}$ of H_2SO_4 aqueous solution. Totally 5 circles with a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$. Scan range: -0.4 V to 1.6 V .

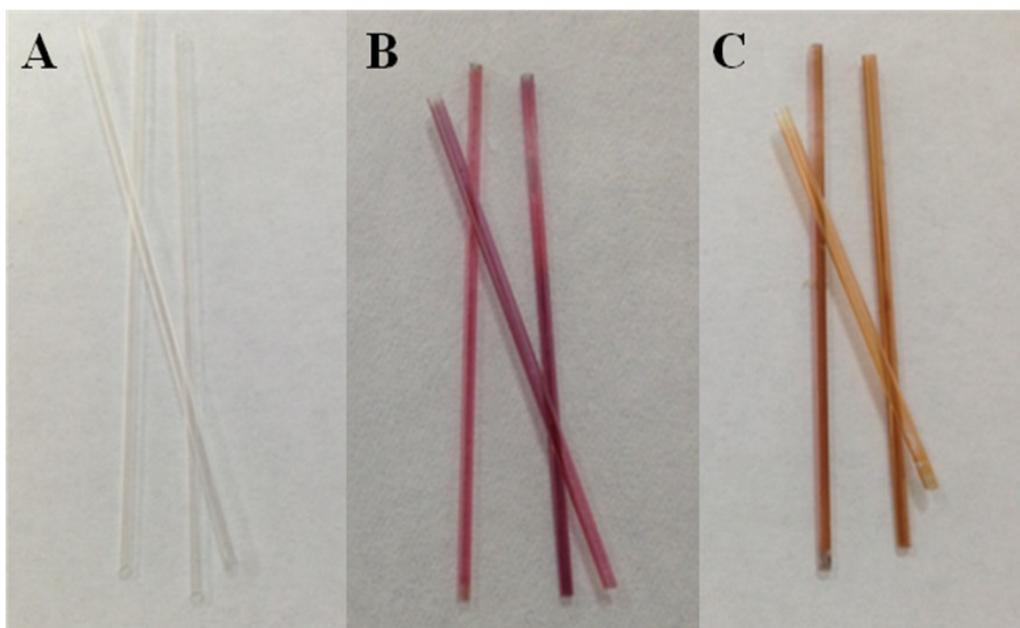


Figure S3. Photographs of bare capillary (A), Au nanoparticles-modified capillary (NPMC) (B) and Au@Ag NPMC (C).

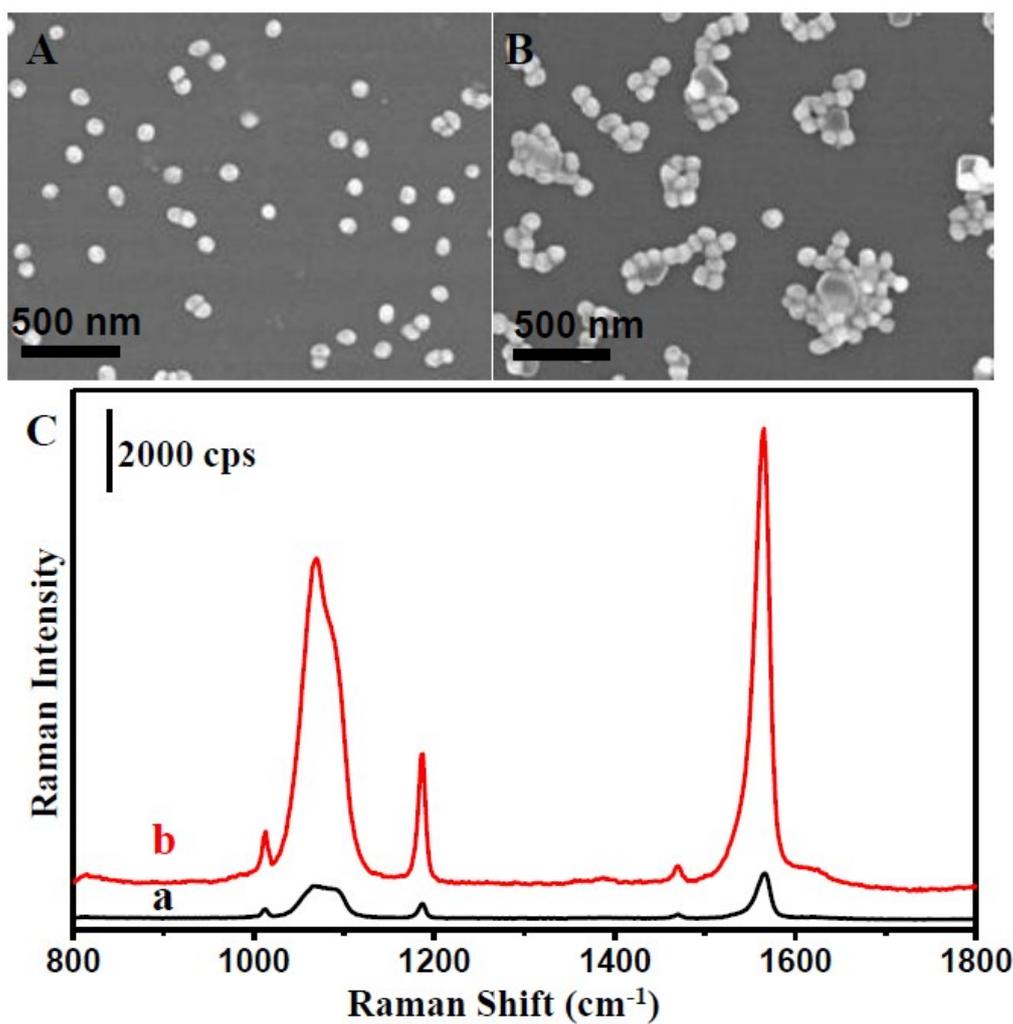


Figure S4. (A, B) SEM images of Au@Ag NPMC before (A) and after (B) treatment with 0.1 mol·L⁻¹ KCl aqueous solution. (C) SERS spectra of 10⁻⁵ mol·L⁻¹ 1,4-benzenedithiol taken by Au@Ag NPMC without any pretreatment (a) and with treatment by 0.1 mol·L⁻¹ KCl aqueous solution (b).

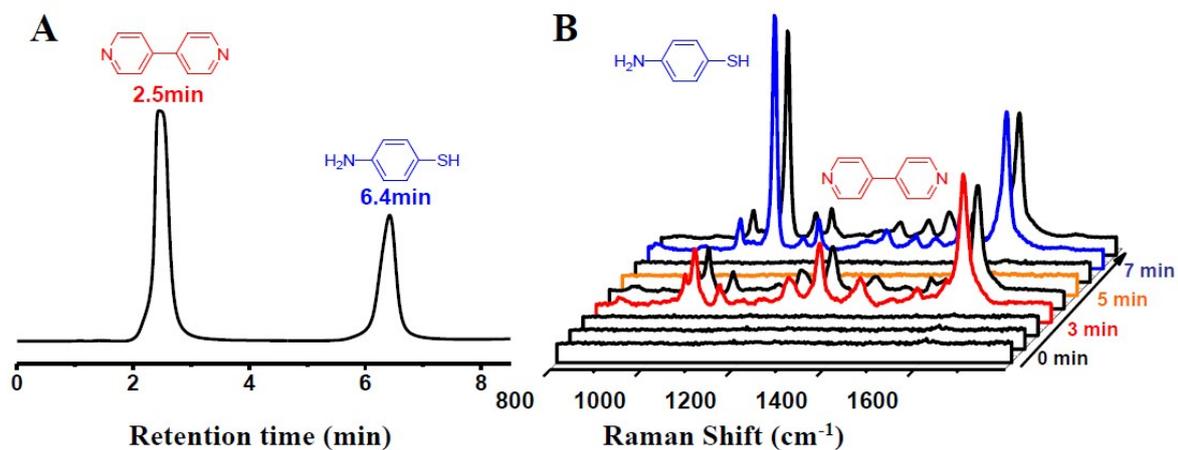


Figure S5. Chromatogram (A) and time-dependent SERS spectra (B) of the mixture containing 4,4-bipyridine and 4-aminothiophenol. Note that the interval time between each line in SERS spectra is one minute.

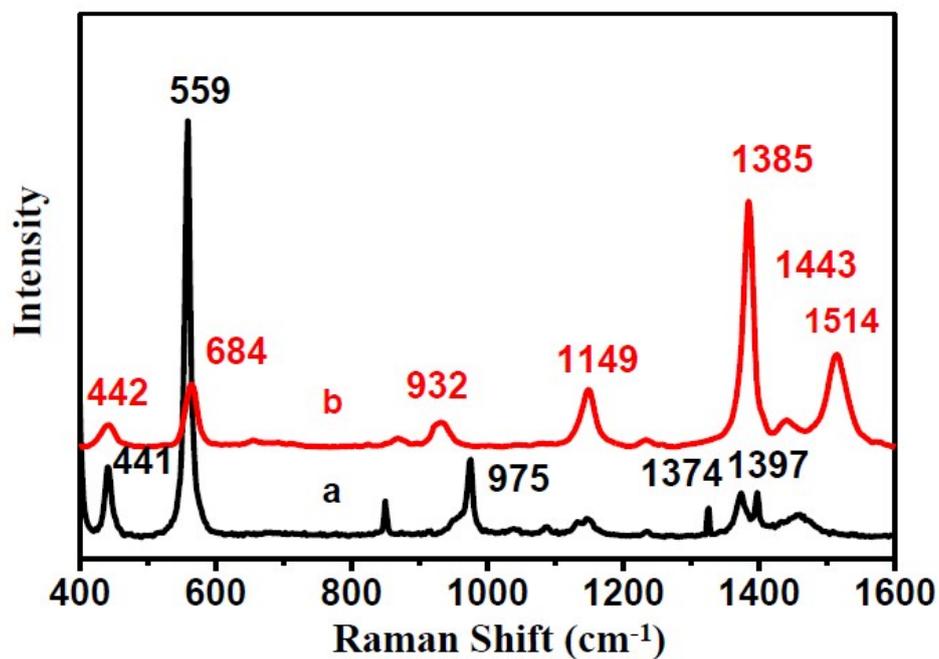


Figure S6. Normal Raman (a) and SERS spectra (b) of thiram molecules. Compared to the normal Raman signals, the SERS signals have much stronger intensity. The characteristic peak of thiram molecules at 684 cm⁻¹ ($\nu(\text{S-S})$), 1149 cm⁻¹ ($\rho(\text{CH}_3)$; $\nu(\text{C-N})$), 1385 cm⁻¹ ($\rho(\text{CH}_3)$) and 1514 cm⁻¹ ($\nu(\text{C-N})$) could be clearly observed.

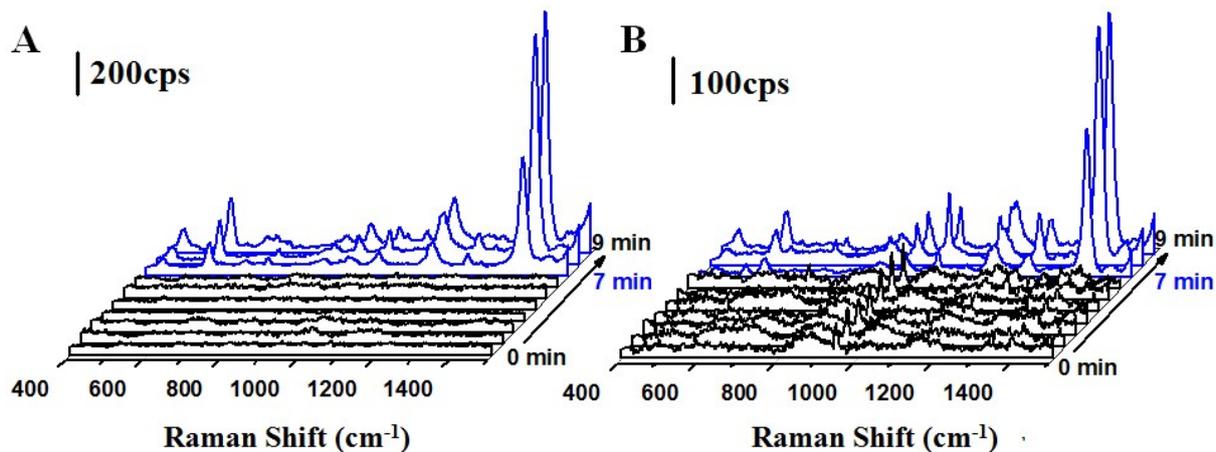


Figure S7. Time-dependent SERS spectra of the effluent liquids of $10^{-4} \text{ mol}\cdot\text{L}^{-1}$ (A) and $10^{-5} \text{ mol}\cdot\text{L}^{-1}$ (B) thiram through HPLC. The interval time between each line in SERS spectra is one minute.

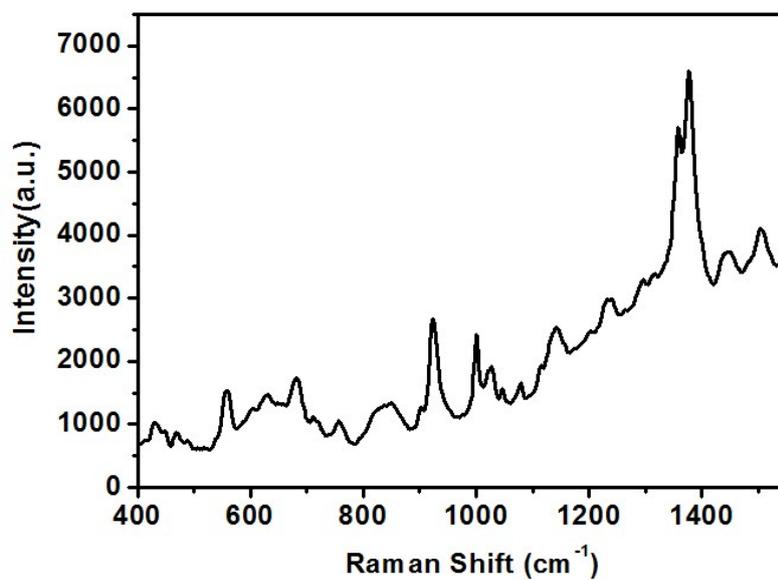


Figure S8. SERS spectrum of the extracted orange solution taken by Au@Ag NPMC.