

Supporting Information

Hybrid Plasmonic Nanoprobe Using Polyvinylpyrrolidone-Capped Bimetallic Silver-Gold Nanostars for Highly Sensitive and Reproducible Solution-based SERS Sensing

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Calculation for determination of the concentration of GNS-PVP, BGNS-Ag-PVP-1, BGNS-Ag-PVP-2, and BGNS-Ag-PVP-3.

We first calculated the concentration of GNS-PVP according to the equation (1)-

$$C = \frac{M \text{ (number of moles of Au)}}{N \times 0.05(L)} \quad (1)$$

Where C is the concentration of the GNS-PVP (mol/L), M is the number of moles of gold present in GNS-PVP solution, and N is the number of gold atoms present in one nanostar. The GNS-PVP volume was 50 mL. The gold concentration was determined from ICP-MS measurement. The gold concentration was 200.6 µg/L for GNS-PVP. The number of gold atoms in a gold nanostar is determined from the nanostar volume and gold density. The volume was calculated according to the reported equation (2).¹

$$V = \frac{4}{3}\pi a^3 + \sum_{t=1}^n \left\{ \frac{h_i}{3}\pi(R_i^2 + R_i^2 r_i + r_i^2) + \frac{2}{3}\pi r_i^3 - \frac{\pi}{6}(a - \sqrt{a^2 - R_i^2})[3R_i^2 + (a - \sqrt{a^2 - R_i^2})^2] \right\}$$

(2)

Where a is the radius of the spherical core of the GNS (25 nm), R_i is the base radius near the core of a spike (10nm), r_i is the radius of the hemispherical tip of a spike (2 nm), and h is the spike length measured from the base to tip of the spike (90 nm). The atomic density is 59 atoms per nm^3 .¹ The volume of the GNS-PVP was calculated to be 289580.416 nm^3 . The concentration of the GNS-PVP was calculated to be 3.5 pmol/L. For our SERS study, GNS-PVP was concentrated 2.5 times, and the final concentration of GNS-PVP was 8.75 pmol/L. The concentration of BGNS-Ag-PVP-1, BGNS-Ag-PVP-2, and BGNS-Ag-PVP-3 was calculated by following the previous calculation method. The gold concentration was 202.8, 205.4, and 200.5 $\mu\text{g/L}$ for BGNS-Ag-PVP-1, BGNS-Ag-PVP-2, and BGNS-Ag-PVP-3, respectively. The concentration of the BGNS-Ag-PVP-1, BGNS-Ag-PVP-2, and BGNS-Ag-PVP-3 was calculated to be 3.53, 3.58, and 3.49 pmol/L, respectively. The final concentration of the BGNS-Ag-PVP-1, BGNS-Ag-PVP-2, and BGNS-Ag-PVP-3 was concentrated and adjusted to 8.75 pmol/L.

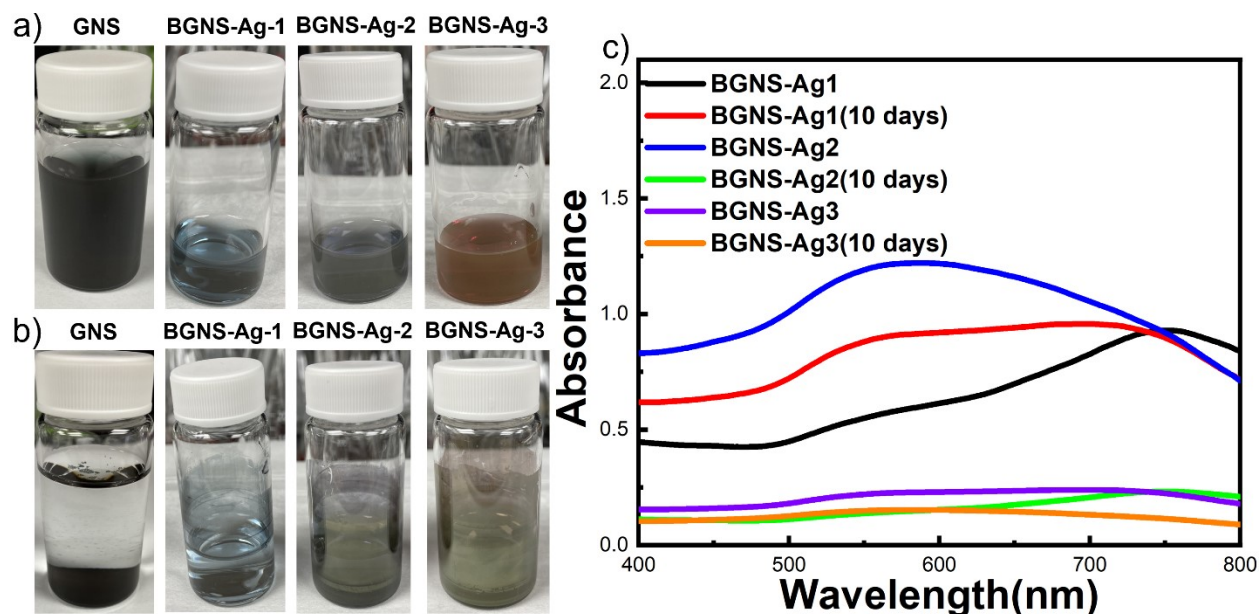


Figure S1. Images of GNS, BGNS-Ag-1, BGNS-Ag-2, and BGNS-Ag-3 after 0 days of synthesis (a), and after 10 days of synthesis (b) indicating aggregation of nanoparticles. UV-vis absorbance spectra of GNS, BGNS-Ag-1, BGNS-Ag-2, and BGNS-Ag-3 after 0 days of synthesis, and after 10 days of synthesis (c).

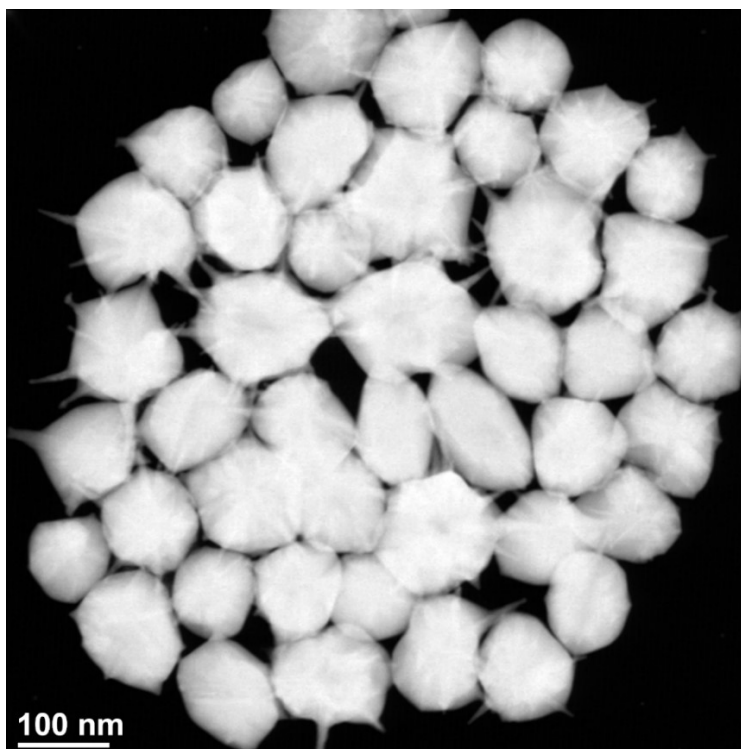


Figure S2. STEM image of BGNS-Ag-PVP-3 after 90 days of synthesis.

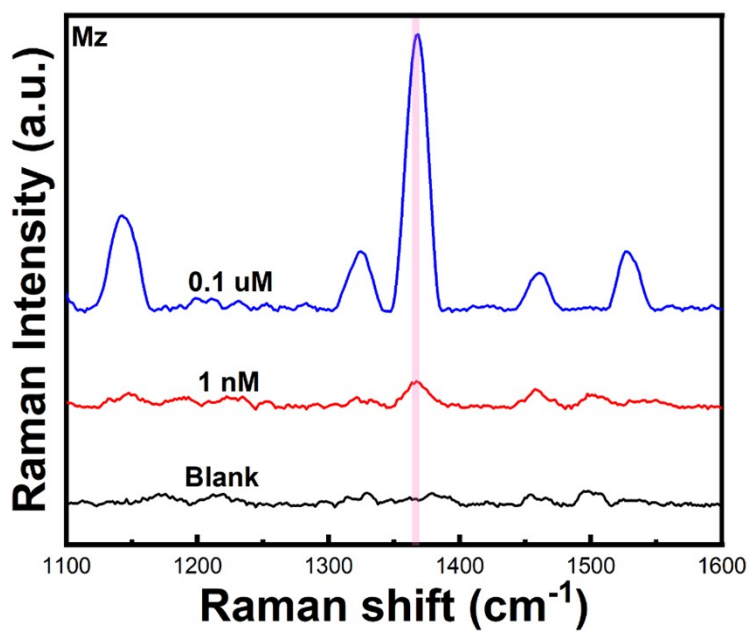


Figure S3. The SERS spectra of Mz at 0.1 uM and 1 nM concentration.

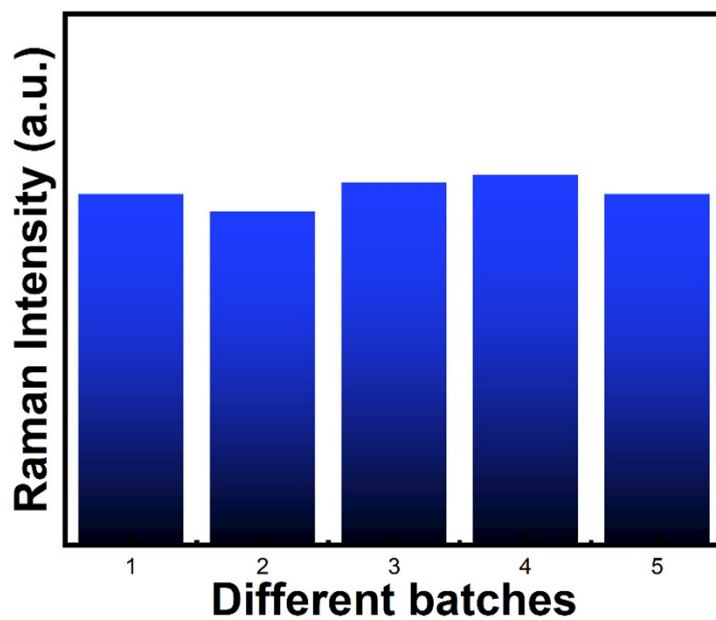


Figure S4. The Raman band intensity of Mz is at 1365 cm^{-1} of five different batches of BGNS-Ag-PVP-3.

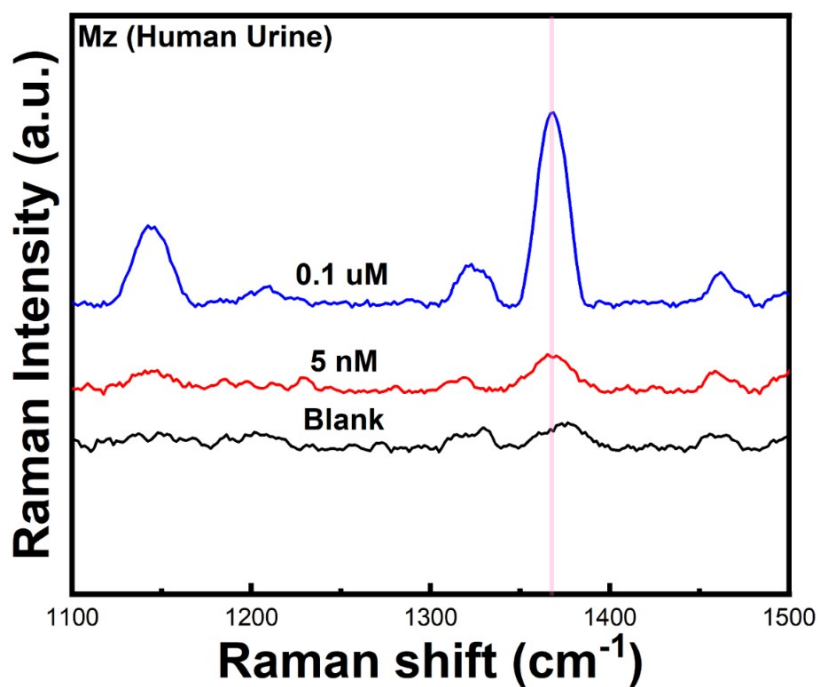


Figure S5. The SERS spectra of Mz at 0.1 uM and 5 nM concentration where Mz is spiked with human urine.

Reference-

1. Tsoulos, T. V.; Han, L.; Weir, J.; Xin, H. L.; Fabris, L., A closer look at the physical and optical properties of gold nanostars: an experimental and computational study. *Nanoscale* **2017**, *9* (11), 3766-3773.