Supporting Information

Ultrasensitive vapor detection with SERS-active gold nanoparticle immobilized flow-through multi-hole capillaries

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1. Normal Raman spectra of pyridine and 4-nitrophenol

As a control experiment, normal Raman spectra of pyridine and 4-nitrophenol were investigated, as shown in Figure S1a, and b, respectively. The Raman measurements were done at 785 nm, 12 mW laser power, and acquisition time of 2 seconds.

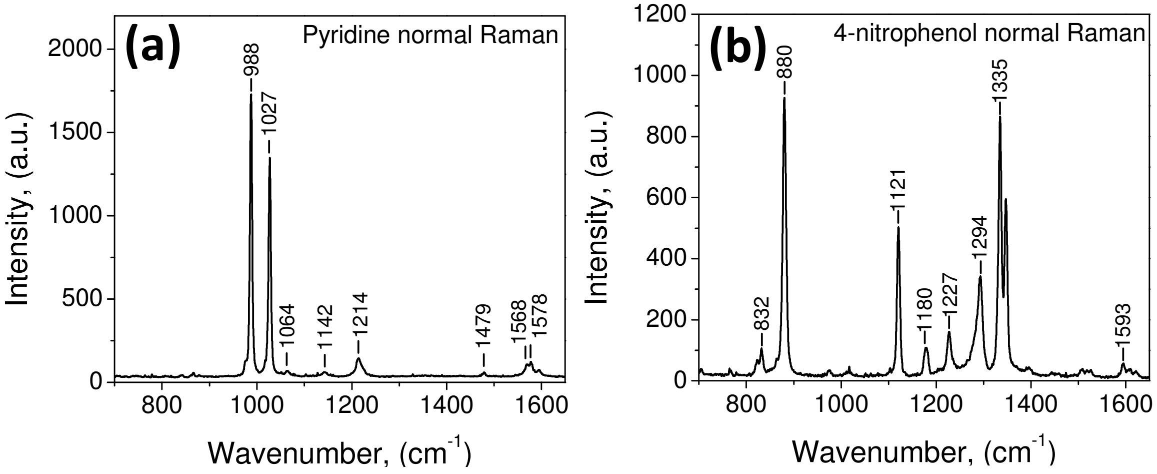

Figure S1. Normal Raman spectra of (a) pyridine and (b) 4-nitrophenol

Pyridine and 4-nitrophenol normal Raman frequency and mode assignments, as well as their corresponding SERS peaks (obtained from our experimental results), are tabulated in Table S1, and S2, respectively.

Table S1. Assignment of pyridine normal Raman and SERS peaks

Mode assignment[1]	**Normal Raman of pyridine Frequency, (cm^{-1})**	**SERS of pyridine Frequency, (cm^{-1})**
Symmetric Ring breathing	988	1021
Asymmetric Ring breathing	1027	1045
In-plane CH bending	1064	
In-plane CH bending	1142	
In-plane CH bending	1214	
Ring stretching	1479	
Ring stretching	1568	
Ring stretching	1578	

Table S2. Assignment of 4-nitrophenol normal Raman and SERS peaks

Mode assignment[2]	**Normal Raman of 4-nitrophenol** **Frequency, (cm^{-1})**	**SERS of 4-nitrophenol** **Frequency, (cm^{-1})**
C-H out of plane bending	832	
C-H out of plane bending	880	869
C-H in plane bending/ NO_2 asymmetric stretching	1121	1120
C-H in plane bending/ NO_2 symmetric stretching	1180	
C-H in plane bending/ NO_2 asymmetric stretching	1227	
C-H in plane bending	1294	
C-H in plane bending	1335	1341
Ring deformation	1593	

2. Determination of laser excitation volume

As shown in Figure S2a, a focal image was taken at ZX plane using a CMOS camera (DCC1545M, Thorlabs). Notations of a three dimensional Cartesian coordinate system is shown in the lower left corner of Figure S2a. A 785 nm laser was excited into a gold colloidal medium (contrast agent) to generate strong scatter light around a focal point. The camera attached with 2× tube lens was focused at the focal point of 785 nm excitation. Then focal point image was taken and analyzed using OriginPro 8 software (see Figure S2b). The image resolution of 2.5 μm/pixel was achieved. It was observed that a mode filed diameter (MFD) of 70 μ m (Figure S2c), and a penetration depth of 1082 μm at the focal point (Figure S2d). The mode field diameter and the penetration depth are considered the region where the laser intensity is larger than $1/e^2$ of the maximum intensity.

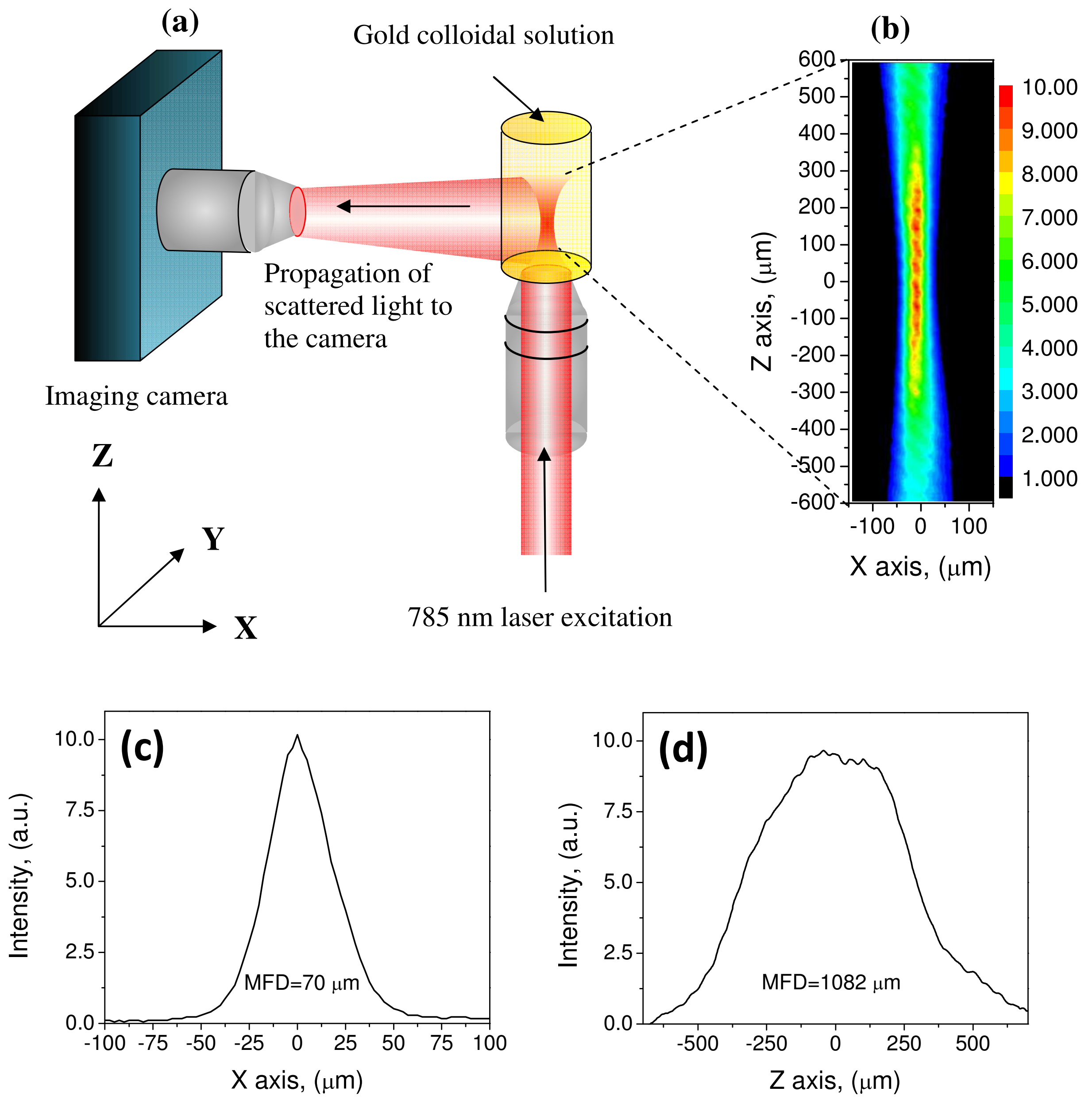

Figure S2. (a) Schematic of imaging system (b) focal point image taken at Z X plane (c) mode field profile at the focal point in X axis, and (d) penetration depth at the focal point along the Z axis. (Z=light propagation direction, and X or Y = perpendicular to the excitation light)

3. Flow rates of multi-hole capillaries

The flow of each capillary was measured using solid state flow meter (Restek 6000), and the flow rates were calculated using Hagen–Poiseuille equation (Eq. 1). The data are shown in Figure S3.

$$\Delta P = \frac{128 \eta L Q}{\pi d^4} \qquad (1)$$

where:

ΔP = pressure drop

η = coefficient of viscosity

L = length

Q = volumetric flow rate

d = diameter of capillary

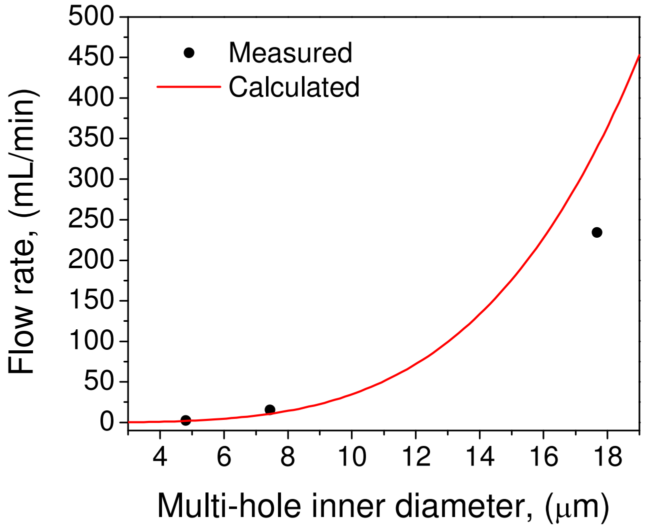

Figure S3. Calculated (red curve) and measured (black dot) flow rate of different inner diameter of multi-hole (2700 holes) capillaries

References

1. Bilmes, S. A. *Chem. Phys. Lett.* **1990,** 171, 141-146.
2. Perry, D. A.; Son, H. J.; Cordova, J. S.; Smith, L. G.; Biris, A. S. *J. Colloid Interface Sci.* **2010,** 342, 311-319.