Supporting Information

Ultrasensitive Optofluidic Surface-Enhanced Raman Scattering Detection With Flow-Through Multi-Hole Capillaries

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1. Determination of laser illumination and Raman collection depth, and effective surface area in the transverse detection

The laser detection volume is determined by both the excitation laser and Raman signal collection optics. In our Raman measurements, a 785 nm excitation laser was used, and was focused onto a spot of approximately 3 μm in diameter.

In order to determine the effective laser illumination and Raman collection depth, we performed a control experiment using a 180-μm-thick glass slide as a reference sample. The glass slide was put perpendicularly to the light propagation direction, and its normal Raman spectrum was measured and shown in Fig. S1(a), which had a characteristic Raman shift at 1380 cm^{-1}. To test the response of the Raman system to the 180-μm thick glass slide, we adjusted the relative distance between the laser focal point and the glass slide, and measured the change of the Raman intensity of glass at 1380 cm^{-1}, shown in Fig. S1(b). Using the convolution theory, we estimated the effective light illumination and Raman collection depth was about 120 μm.

The normal Raman or SERS signal, P, can be expressed as follows:

$$P \propto \sigma IN \qquad (1)$$

where σ is the normal Raman or SERS cross section, $I = P_0 / S$ is the excitation intensity determined by the input laser power P_0 and the illuminated cross-sectional area S, and $N = nSd$ is the total number of molecules within the laser detection volume determined by the molecule volume density n, the illuminated surface area S, and the illumination/collection depth d. Thus, Eq. (1) can be rewritten as:

$$P \propto \sigma(\frac{P_0}{S})(nSd) \propto n\sigma P_0 d \qquad (2)$$

The above equation shows that the Raman or SERS signal P is independent of the illuminated cross-sectional area S. In our experiment, although the laser beam size along the propagation direction varies with the distance from the focal point, the Raman or SERS signal per unit depth remains unchanged. For simplicity, we assume that the illuminated cross-sectional area remains the same as the focal spot (*i.e.*, 3 μm in diameter) along a depth of 120 μm. Therefore, the total effective detection volume was approximately 850 μm^3 (*i.e.*, 0.85 pL) for the multi-hole capillary used in our SERS experiments. Since the multi-hole capillary has a surface to volume ratio of 0.87 μm^{-1}, the total effective illuminated surface area is estimated to be 740 μm^2.

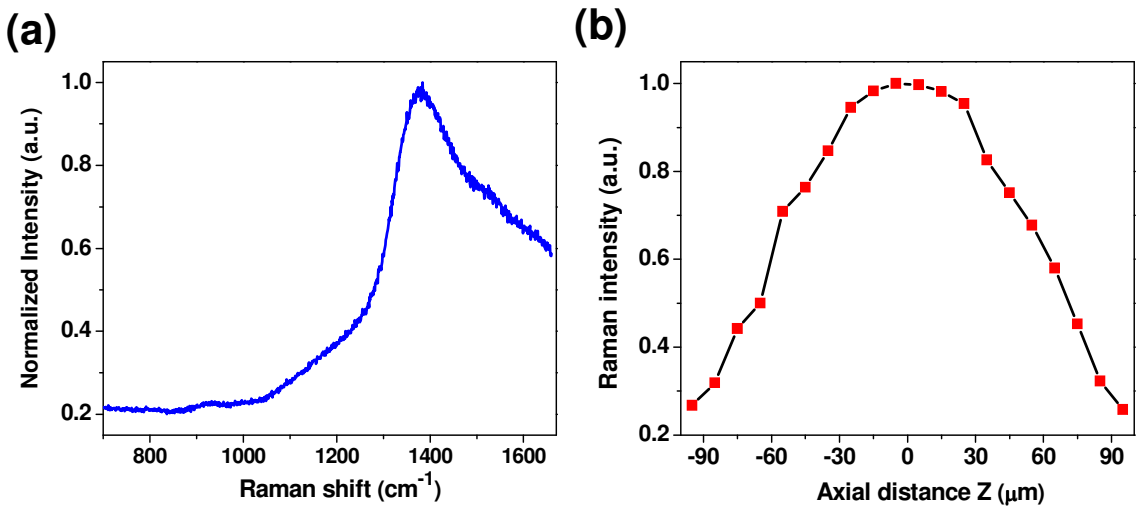

Figure S1 (a) The typical normal Raman spectrum of a glass slide. (b) The Raman intensity at 1380 cm^{-1} of the glass slide varies with the relative distance between the laser focal point and the glass slide.

2. Extinction spectrum of gold nanoparticles

Fig. S2 shows the extinction spectrum of the gold nanoparticles in solution that we used in the experiments. The gold nanoparticles have the maximal extinction at 570 nm, twice as high as at 785 nm (our excitation laser wavelength used in the experiments).

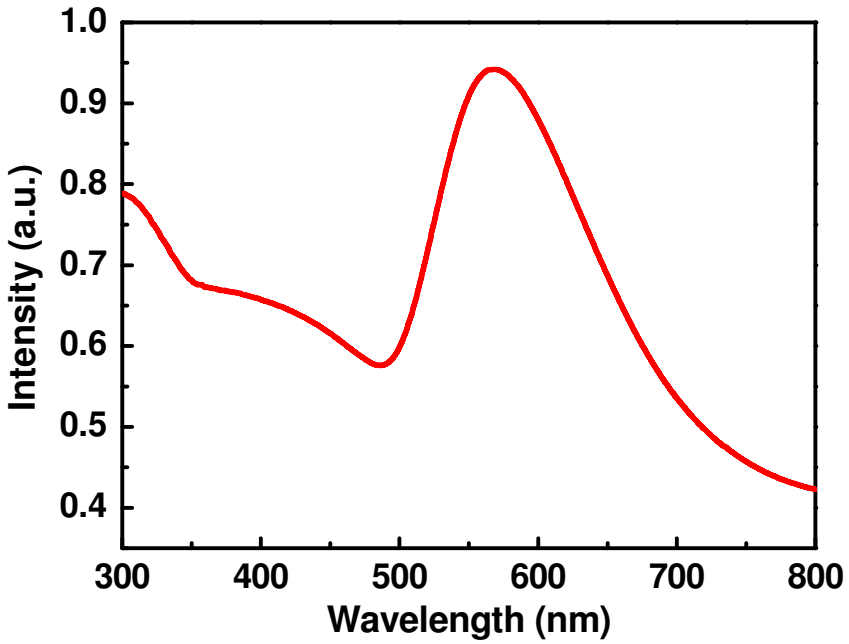

Figure S2. The extinction spectrum of gold nanoparticles measured in solution.

3. Enhancement of the multi-hole capillary

To investigate the enhancement contribution from the multi-hole capillary, we performed a control experiment, where the normal Raman spectra of 1×10^{-2} M R6G loaded in a 1-mL glass cuvette and in the multi-hole capillary (without gold nanoparticle immobilization) were measured, respectively. The results in Fig. S3 show that over 20 fold enhancement was achieved using the multi-hole capillary by comparing the Raman intensity of characteristic R6G band at 1369 cm^{-1}.

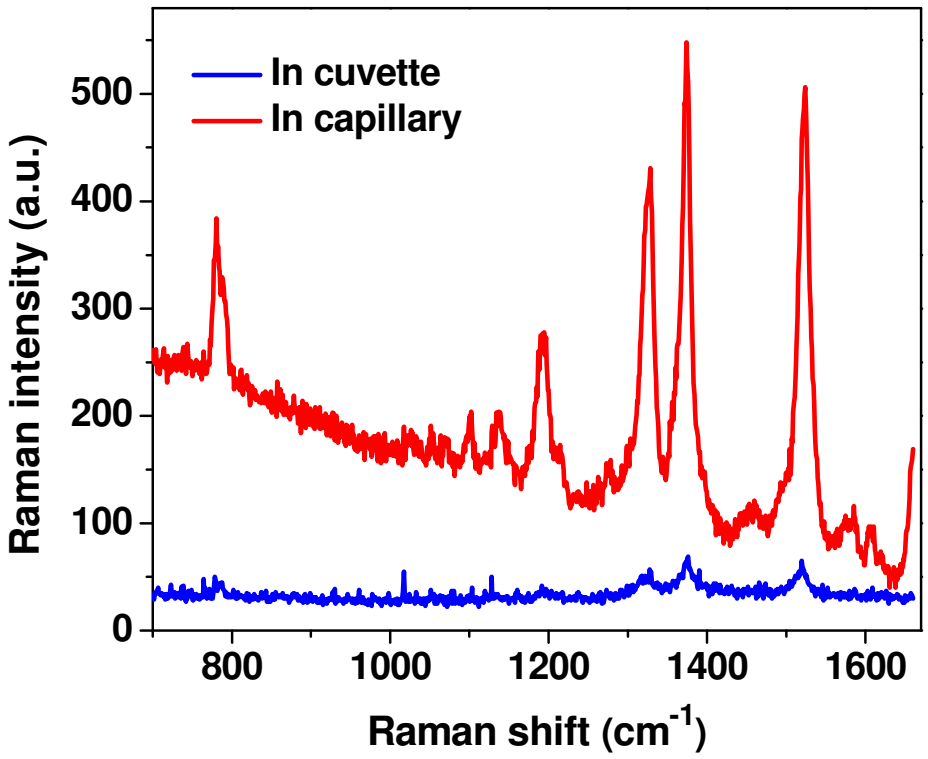

Figure S3. The normal Raman spectra of 1×10^{-2} M R6G in a 1-mL glass cuvette and in the multi-hole capillary, respectively.

4. Images of the light from the endface of a multi-hole capillary

We took the images of the light from the endface of a bare multi-hole capillary (without gold nanoparticles) in the following two scenarios, when the laser light of 785 nm was launched in the longitudinal direction.

(1) The launched laser was tightly focused (*i.e.*, the beam spot size was 3 μm). In this scenario, the light illuminated the central region with a mode field diameter of 30 μm (considering the region where the laser intensity is larger than $1/e^2$ of the maximum intensity), as shown in the following Fig. S4(a). This shows that light can be guided in the high-index walls (*e.g.*, silica) and quasi-guided by the low-index holes (*e.g.*, water).

(2) The launched laser was loosely focused, the light illuminated a much larger region with a mode field diameter of 100 μm, as shown in Fig. S4(b). This shows that the input light was able to be coupled into many walls and holes simultaneously.

As explained in Section 1 of Supporting Information, the total Raman or SERS signal is independent of illuminated cross-sectional area (for a given excitation power). However, the signal collection efficiency highly depends on the optical arrangement, absorption and scattering losses introduced by the nanoparticles within the illuminated volume. Therefore, there is a trade-off among the illuminated volume and the signal collection efficiency. In our experiments, we tuned the launched laser spot size to maximize the detected SERS intensity.

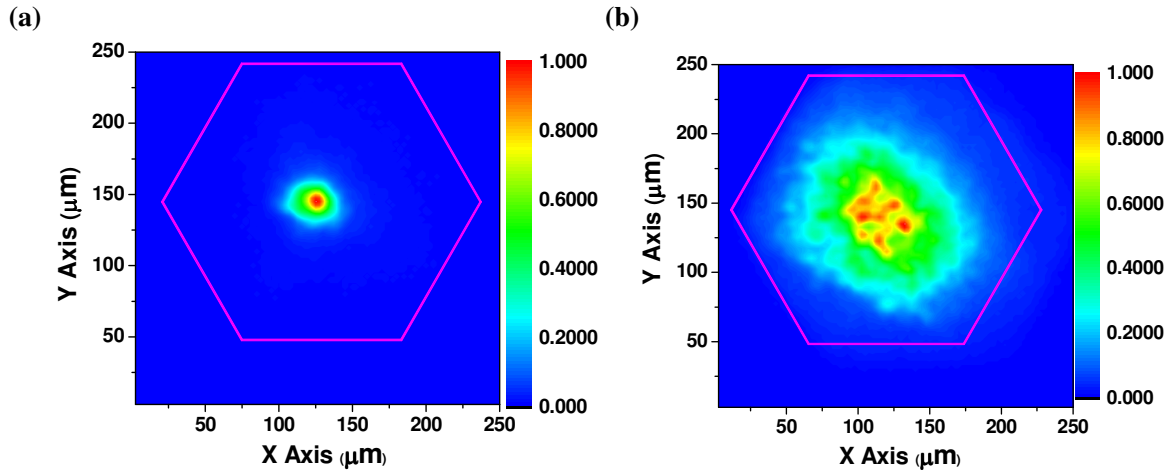

Figure S4. The images of the light from the endface of a multi-hole capillary when the launched laser beam is (a) tightly focused, (b) loosely focused. The hexagon shows the outline of the capillary.

5. Measurement of transmission loss

In order to determine the transmission loss of a short-length capillary (~ 3 mm) immobilized with gold nanoparticles, we adopted the experimental configuration as shown in Fig. S5. The laser light from the excitation source (785 nm diode laser) was transmitted via a multi-mode fiber with a core diameter of 50 μm (AFS50/125Y, Thorlabs, Inc.) into the multi-hole capillary in the longitudinal direction, and it was absorbed and scattered by the gold nanoparticles immobilized in the capillary. The scattered light at a certain position was collected using an objective lens into a spectrometer. By comparing the intensity of the scattered light at a series of positions along the light propagation direction, we were able to calculate the transmission loss within the multi-hole capillary, as shown in Fig. 5(b).

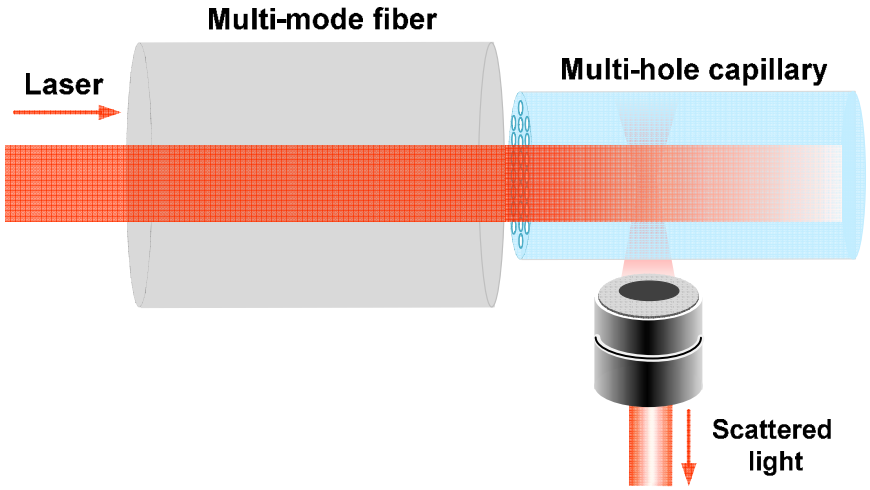

Figure S5. Schematic of experimental setup measuring the transmission loss of a multi-hole capillary immobilized with gold nanoparticles.