Supporting Information

Immobilization of Gold Nanorods onto Electrospun Polycaprolactone Fibers via Polyelectrolyte Decoration—A 3D SERS Substrate

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Table of Contents:

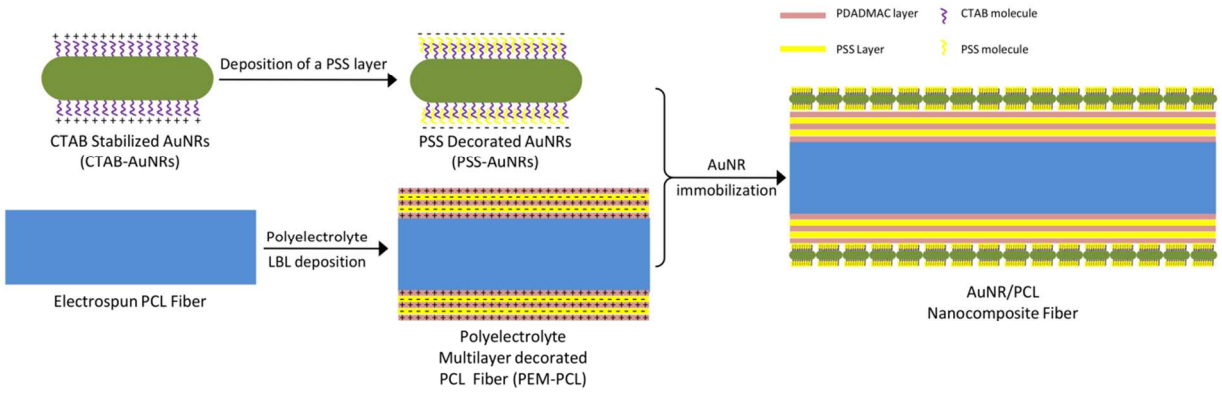

Figure S1. Schematic illustration of the fabrication of AuNR/PCL nanocomposite fibers.

EXPERIMENTAL SECTION

Synthesis of Gold Nanorods. Briefly, hexadecyltrimethylammonium bromide (CTAB, ≥98.0%) stabilized gold nanoparticles were produced by adding 0.6 ml of freshly prepared 0.01M ice-cold sodium borohydride ($NaBH_4$, ≥98.0%) solution to a mixture containing 7.5 ml of 0.1M CTAB and 0.25 ml of 0.01M tetrachloroauric acid ($HAuCl_4$, ≥99.9%). The resulting solution contained the seeds for the growth of AuNRs in the following steps and was stored for over 2 hrs before further use. Subsequently, 0.2 ml of 0.01M $HAuCl_4$, 0.03 ml of 0.01M silver nitrate ($AgNO_3$, ≥99%) and 0.032 ml 0.1M L-ascorbic acid (≥99%) were added to 4.75 ml of 0.1M CTAB solution in the order stated. Finally, 0.01 ml seed solution was added to initiate the growth of AuNRs. A color change of the solution from clear to dark purple occurred during the next ten minutes, suggesting the formation of AuNRs. The AuNR solution was stored overnight to allow for the full growth of the AuNRs.

Fabrication of Electrospun PCL Fibers. Electrospinning was carried out on a conventional setup to fabricate the polycaprolactone (PCL, M_w~65,000 and M_n~42,500) fibrous mesh. Generally, a syringe loaded with the 25% wt/v PCL/chloroform solution was mounted on a syringe pump (NE-300, New Era Pump Systems Inc.) to guarantee a constant flow rate of 0.5

ml/hr. A piece of aluminum foil was placed 25 cm away from the tip of the needle and used to collect the fibers. A Spellman power supply (CZE1000R, SPELLMAN) was employed to apply a potential difference between the needle and the collector (+12kV and -3kV, respectively).

RESULTS AND DISCUSSION

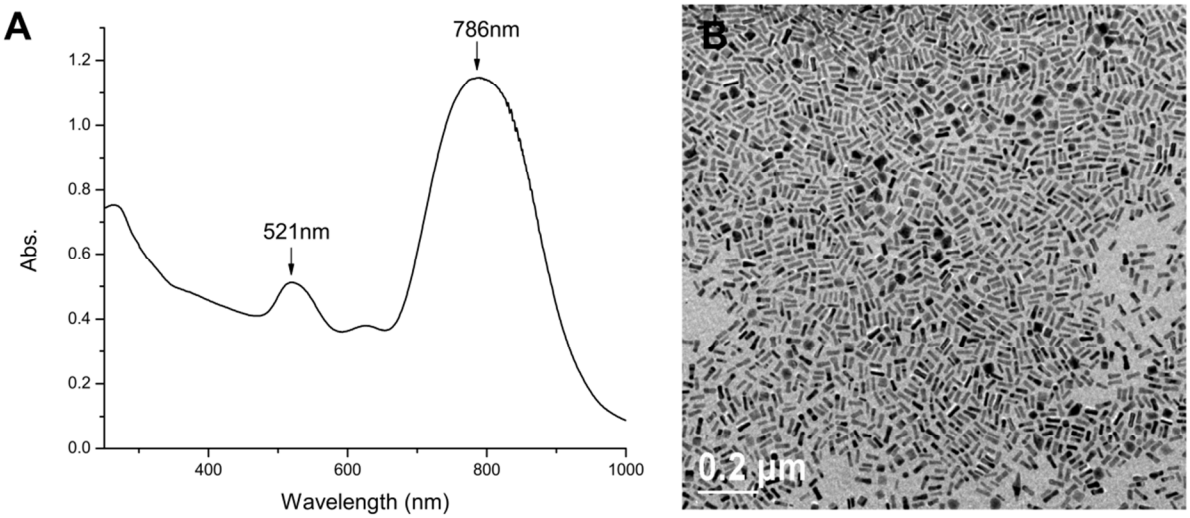

Figure S2. (A) UV-Vis absorption spectrum and (B) TEM image of the as-synthesized AuNRs.

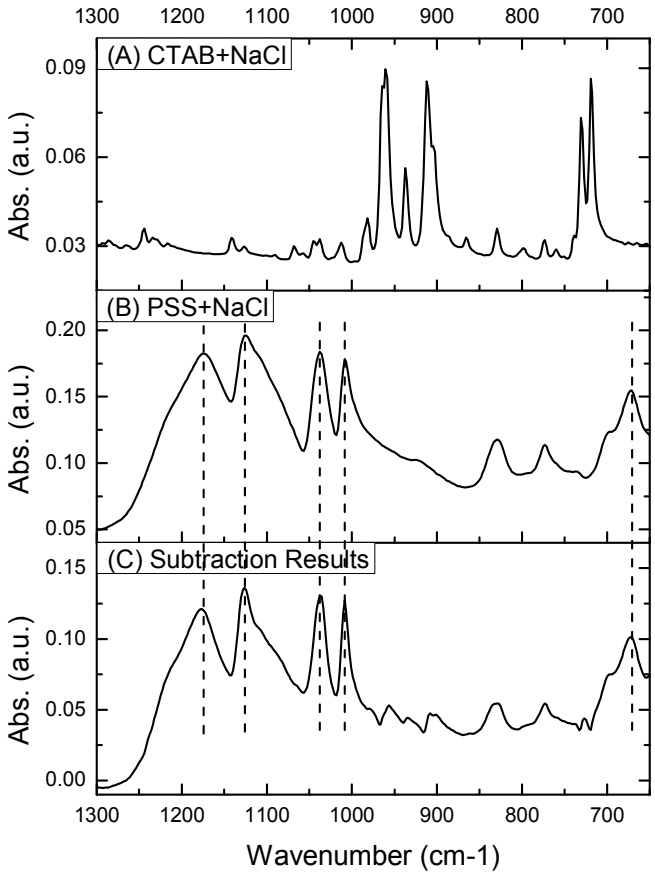

Figure S3. ATR-FTIR spectra of (A) CTAB with the presence of salt (CTAB+NaCl), (B) PSS with the presence of salt (PSS+NaCl) and (C) the spectral subtraction results obtained by subtracting the spectrum of CTAB+NaCl from the spectrum of CTAB+PSS+NaCl.

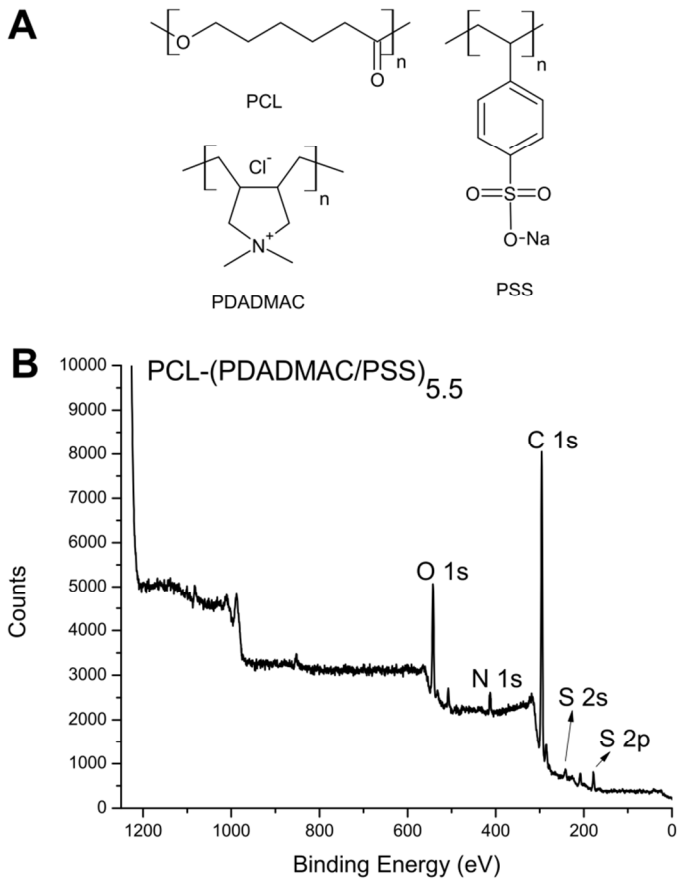

Figure S4. (A) Molecular structures of PCL, PDADMAC and PSS. (B) XPS survey spectrum of PCL-(PDADMAC/PSS)$_{5.5}$.

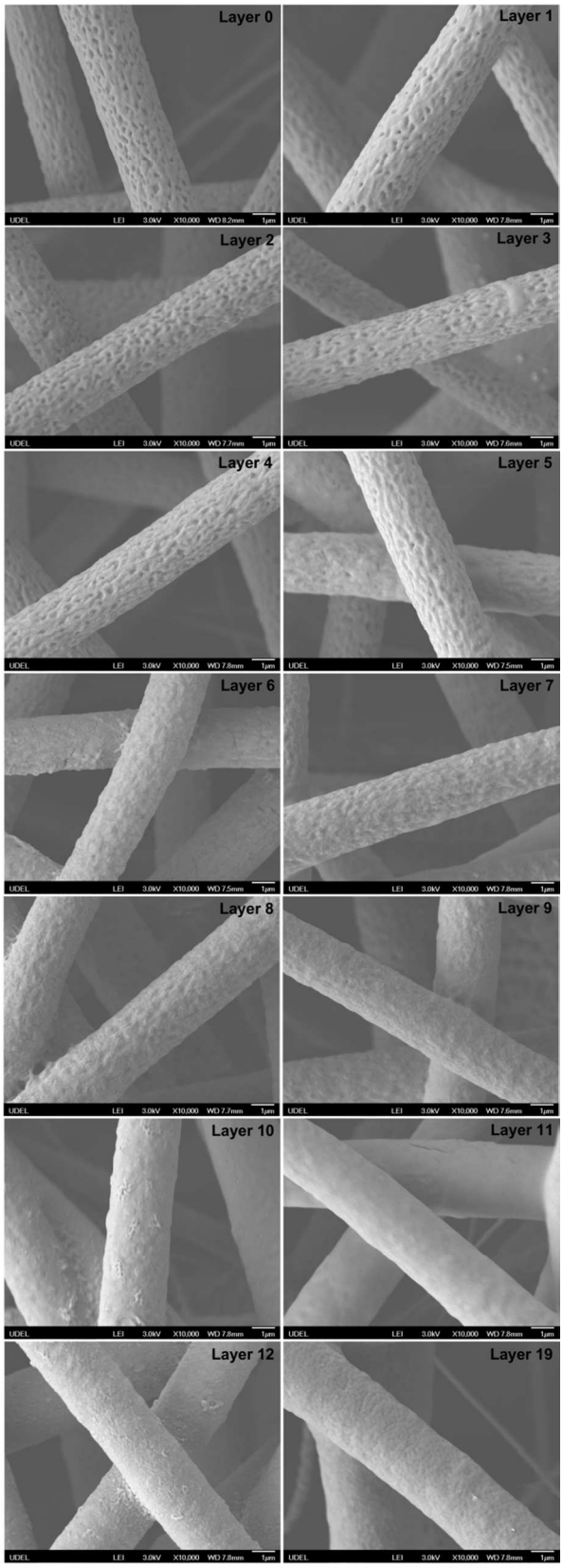

Figure S5. SEM images of PCL fibers coated with various numbers of polyelectrolyte layers.

Theoretical Calculation of Saturation Concentration of 4-MPy

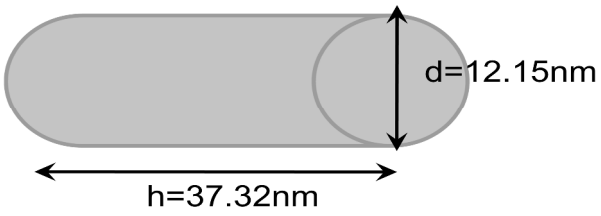

Figure S6. Schematic of a single gold nanorod.

Assumption 1: Gold nanorods take the cylinder shape as shown in Figure S6.

The dimension of AuNR can be estimated from the TEM image shown in Figure S2-B and are determined to be 12.15nm in width (d) and 37.32nm in length (h). The density of gold is 19.3 g/cm^3.

Define: V: Volume of a single AuNR. $V = \frac{1}{4}\pi \times d^2 \times h = 4.325 \times 10^{-18} cm^3$

S: Surface area of a single AuNR. $S = 2 \times (\frac{1}{4}\pi \times d^2) + \pi \times d \times h = 1.655 \times 10^{-11} cm^2$

M: Mass of a single AuNR. $M = V \times \rho = 8.347 \times 10^{-17} g$

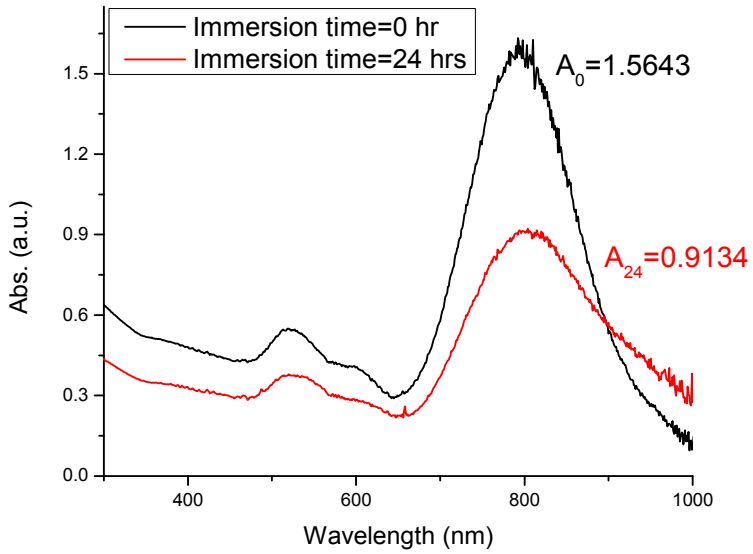

Figure S7. UV-Vis absorption spectra of PSS-AuNR solution before (black curve) and after (red curve) the PEM-PCL mesh had been immersed for 24 hours.

Assumption 2: There is no loss of AuNRs in the centrifugation steps.

The initial concentration of $HAuCl_4$ in the AuNR growth solution $[Au]_{initial}$ can be determined to be 2.655×10^{-4}M from the experimental procedures. The total volume of AuNR solution used for substrate immersion is known to be 9 ml.

Define:

N_0: Number of AuNRs in the initial 9ml AuNR solution.

N_{24}: Number of AuNRs left in the solution after the substrate had been immersed for 24 hours.

N_{ads}: Number of AuNRs being adsorbed onto the PCL substrate and $N_{ads} = N_0 - N_{24}$

A_0: Absorbance of the longitudinal SPR band in the UV-Vis spectrum before substrate immersion and can be read from the UV-Vis spectrum (Black curve in Figure S7).

A_{24}: Absorbance of the longitudinal SPR band in the UV-Vis spectrum after the substrate had been immersed for 24 hrs and can be read from the UV-Vis spectrum (Red curve in Figure S7).

S_{tot}: Total surface area of the AuNRs being adsorbed onto the PCL substrate.

$$N_0 = \frac{Mass\ of\ Au\ in\ solution}{M} = 5.638\times10^{12}$$

According to Beer's law, $A=\varepsilon l c$ where A is the absorbance.

Thus, $\frac{A_0}{A_{24}} = \frac{C_0}{C_{24}} = \frac{N_0}{N_{24}} \Rightarrow N_{24} = 3.292\times10^{12}$

$$N_{ads} = N_0 - N_{24} = 2.346\times10^{12}$$

$S_{tot} = N_{ads} \times S = 38.83cm^2$ Where S is the surface area of a single AuNR.

As has been reported in the literature (Yu, H. Z.; Xia, N.; Liu, A. F. *Anal. Chem*. **1999**, *71*, 1354), when 4-mercaptopyridine (4-MPy) is chemisorbed to the surface of gold with a perpendicular orientation to form a monolayer, the density of 4-MPy is 5×10^{-10} mol/cm^2.

Thus, the saturated amount of 4-MPy that can be adsorbed on the substrate can be determined as:
$38.83cm^2 \times (5\times10^{-10} mol/cm^2) = 1.942\times10^{-8} mol$

The total volume of 4-MPy solution is always kept constant at 7 ml in our SERS experiment, thus the saturation concentration of 4-MPy can be determined as:
$1.942\times10^{-8} mol \div 0.007L = 2.77\times10^{-6} mol/L \approx 3\times10^{-6} M$

Enhancement Factor (EF) Calculation of 4-MPy on AuNR/PCL Nanocomposite Fibers

The enhancement factor can be calculated using the equation as is shown below:

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{NR}/N_{NR}}$$

In this equation, I_{SERS} and I_{NR} are the integrated intensity of a vibrational mode in the SERS spectrum and the intensity of the same vibrational mode in the normal Raman (NR) spectrum, respectively. N_{SERS} and N_{NR} are the number of probe molecules being sampled in the SERS measurements and the normal Raman measurements, respectively. I_{SERS} and I_{NR} can be obtained from the spectra directly while N_{SERS} and N_{NR} need to be calculated.

Calculation of N_{SERS}

In each SERS measurement, a piece of 1 cm^2 (S_{sub}) AuNR/PCL nanocomposite mesh is used as the substrate for 4-MPy adsorption. The laser used in our Raman measurements has a spot size of 10 μm. Therefore, the area illuminated by the laser in the SERS measurements can be calculated as:

$$S_{illum} = \frac{1}{4} \times \pi \times d^2 = 7.85 \times 10^{-11} m^2$$

Assume that the laser penetrates through the thickness of the nanocomposite mesh. As is shown in the calculation of 4-MPy saturation concentration (in the last section), a total of 2.346×10^{12} (N_{ads}) AuNRs have been adsorbed onto the 1 cm^2 PCL mesh which distribute uniformly in the mesh. Therefore, the number of AuNRs illuminated by the laser can be calculated as:

$$N_{illum} = \frac{S_{illum}}{S_{sub}} \times N_{ads} = 1.8416 \times 10^6$$

Also as has been mentioned in the last section, the surface area of each AuNR (S) is 1.655×10^{-11} cm^2 and the immobilized 4-MPy density is 5×10^{-10} mol/cm^2. Therefore, the number of probe molecules being illuminated by the laser can be calculated as:

$$N_{SERS} = N_{illum} \times S \times density \times N_{av} = 9.174 \times 10^9$$

Calculation of N_{NR}

In the normal Raman measurement, the 4-MPy/ethanol solution (0.085 M) is loaded into a NMR tube with an inner tube diameter of 5 mm. Therefore, the illuminated volume (V_{illum}) of the solution can be estimated as a cylinder with a 10 μm diameter and a 5 mm length. Therefore,

$$V_{illum} = \frac{1}{4} \times \pi \times d^2 \times length = 3.925 \times 10^{-13} m^3$$

Since the concentration of the 4-MPy/ethanol solution is known to be 0.085M, then the number of probe molecules being illuminated in the normal Raman measurement can be calculated as:

$$N_{NR} = V_{illum} \times concentration \times N_{av} = 2.008 \times 10^{13}$$

I_{SERS} and I_{NR}

The SERS spectrum and the normal Raman spectrum of 4-MPy are shown in Figure S8. Note that the SERS spectrum is recorded at a different power level than the normal Raman spectrum.

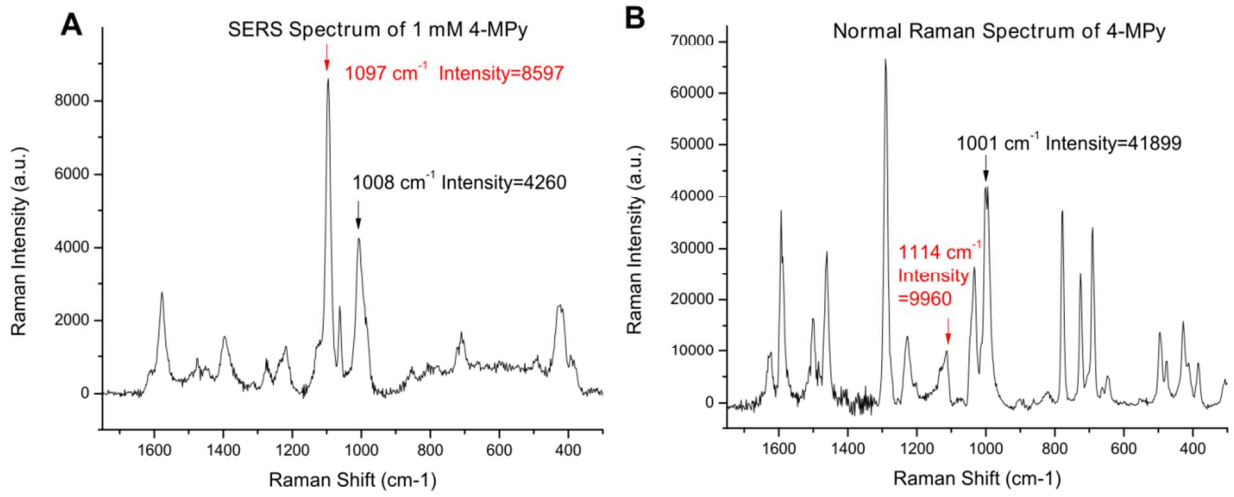

Figure S8. (A) SERS spectrum of 1 mM 4-MPy recorded on the AuNR/PCL nanocomposite fibers at 1.32 mW. (B) Normal Raman spectrum of 4-MPy recorded at 89 mW.

EF calculation using the ring breathing mode

The ring breathing mode of 4-MPy shows up at 1008 cm^{-1} in the SERS spectrum. The corresponding vibrational mode gives rise to a peak at 1001 cm^{-1} in the normal Raman spectrum, as been labeled by the black arrows (Guo H.; Ding L.; Mo Y. *J. Mol. Struct*. **2011**, *991*, 103-107). The intensities of the two peaks can be directly read from the spectra in Figure S8. Therefore,

$$I_{SERS} = 4260 \quad \text{and} \quad I_{NR} = 41899 \times \frac{1.32mW}{89mW} = 621$$

The enhancement factor for the ring breathing mode can be calculated as:

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{NR}/N_{NR}} = 1.5 \times 10^4$$

EF calculation using the ring breathing/CS stretching mode

The ring breathing/CS stretching mode gives rise to a peak at 1097 cm^{-1} in the SERS spectrum and a peak at 1114 cm^{-1} in the normal Raman spectrum, respectively (Guo H.; Ding L.; Mo Y. *J. Mol. Struct*. **2011**, *991*, 103-107). The intensities of those two peaks can be directly read from the spectra shown in Figure S8 (labeled by the red arrows). Therefore,

$$I_{SERS} = 8597 \quad \text{and} \quad I_{NR} = 9960 \times \frac{1.32\ mW}{89\ mW} = 148$$

The enhancement factor for the ring breathing/CS stretching mode can be calculated as:

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{NR}/N_{NR}} = 1.3 \times 10^5$$