Optimizing the SERS Enhancement of a Facile Gold Nanostars Immobilized Paper-Based SERS Substrate

Shuai He[1#], Jefri Chua[1#], Eddie Khay Ming Tan[2], James Chen Yong Kah[1,3]*

[1]Department of Biomedical Engineering, National University of Singapore, Singapore

[2]TechnoSpex Pte. Ltd., Singapore

[3]NUS Graduate School for Integrative Sciences and Engineering, National University of Singapore, Singapore

AUTHOR EMAIL ADDRESS biekahj@nus.edu.sg

Here, we provide an estimate of the number of CV molecules excited for Raman (N_{Raman}) and number of CV molecules excited for SERS with AuNS (N_{SERS}).

Laser spot size

In Raman spectroscopy, the diffraction pattern resulting from the illuminated circular aperture of the laser irradiation has a bright region in the center, known as the Airy disk, as well as a series of concentric bright rings in the surrounding, known as the Airy pattern. Mathematically, the diffraction pattern is characterized by the wavelength of light illuminating the circular aperture, and the aperture's size. The diameter of laser spot can be estimated by the following equation:

$$d \approx \frac{1.22\,\lambda}{\mathrm{n}\sin\theta} = \frac{1.22\,\lambda}{NA}$$

where λ is the laser wavelength and NA is the numerical aperture

In our study, λ = 785 nm, NA = 0.75, so d ≈ 1.3 μm, giving a laser spot size of 1.33 μm^2.

Number of CV molecules excited for Raman (N_{Raman})

After dripping CV on the paper substrate, the observed diameter of CV spot is ≈ 0.8 cm, giving a CV spot size of 0.50 cm^2. For paper substrate without AuNS, initial bulk CV = 10 mM × 5 μL = 5×10^{-8} mole of CV molecules. Assuming homogeneous distribution of CV molecules on paper, The number of bulk CV molecules within laser spot can be calculated from the area ratio of laser spot size (1.33 μm^2) to CV spot size (0.50 cm^2) (i.e. 2.64×10^{-8}) ≈ 1.32×10^{-15} mole of CV molecules. This $N_{Raman} \approx 7.95 \times 10^8$ CV molecules being irradiated by the laser during Raman acquisition on the paper substrate.

Number of AuNS irradiated by laser

Similarly, for paper-SERS substrate, initial AuNS ≈ 100 pM × 100 μL = 10^{-14} mole for single drip and 2 × 10^{-14} mole for double drip. Assuming homogeneous distribution of AuNS immobilized on paper, the number of AuNS particles within laser spot can be calculated from the area ratio of laser spot size (1.33 μm^2) to paper substrate size (0.8 cm × 1.5 cm = 1.2 cm^2 of paper immobilized with AuNS) to be ≈ 66.6 AuNS for single drip and 133.15 AuNS for double drip.

Number of CV molecules excited for SERS with AuNS (N_{SERS})

With AuNS, initial bulk CV dripped on AuNS paper-SERS substrate = 10 μM × 5 μL = 5 × 10^{-11} mole. Assuming uniform adsorption of CV molecules on AuNS surface, the number of adsorbed CV molecules within laser spot can be calculated from the area ratio of laser spot size (1.33 μm^2) to CV spot size (0.50 cm^2) ≈ 1.32 × 10^{-18} mole. Therefore, N_{SERS} ≈ 7.95 × 10^5 molecules of CV being irradiated by the laser under SERS with AuNS.

However, the above is true only if the AuNS on the paper-SERS substrate were not saturated with CV molecules. By modelling AuNS as a sphere with known diameter of ~105 nm and CV size in the literature known to be 120 $Å^2$, the maximum number of CV molecules that could be adsorbed on each AuNS for SERS ≈ 505,109. Since the calculated number of CV molecules per AuNS ≈ 11,938 for single drip and ≈ 5,969 for double drip, which are both below the saturation value.

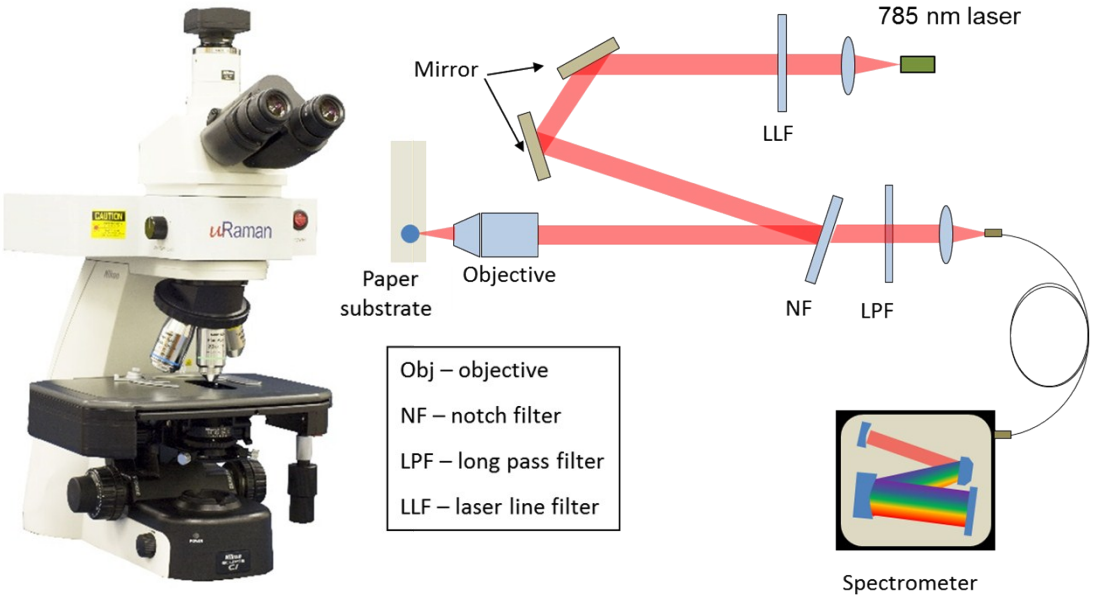

Figure S1. Optical schematic of the uRaman-785-Ci Raman spectroscopy system used for acquiring the Raman spectra of the samples in this study. The system was equipped with a single mode laser operating at 785 nm and with linewidth approximately 100 MHz. The laser optical power at the sample was ~13 mW.

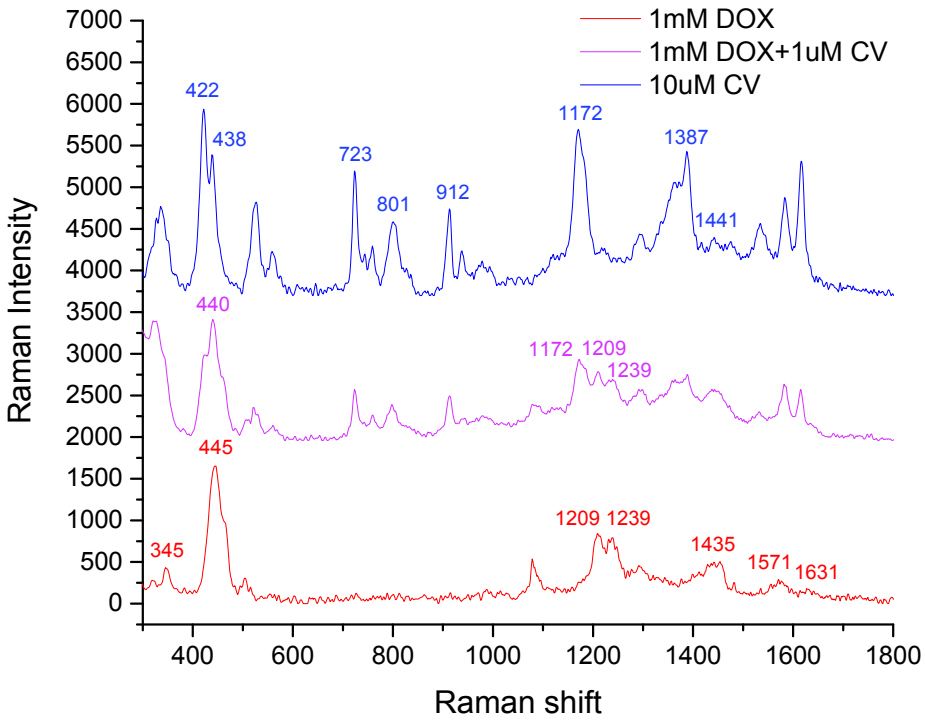

Figure S2. SERS spectrum of 1 mM Doxorubicin, 1 mM Doxorubicin mixed with 1 μM CV and 10 μM CV on AuNS-filter paper substrate acquired under the optimal condition of dry substrate-wet analyte configuration, double dripping strategy and sodium citrate treatment. A relatively high concentration of Doxorubicin (1 mM) was used mainly because the excitation wavelength of Doxorubicin is 480 nm, which is far from the laser wavelength of 785 nm. As a result, the SERS enhancement was not optimized in this setup. The SERS spectrum of Doxorubicin mixed with CV presents characteristic Raman peaks of both Doxorubicin and CV, demonstrating the potential for multiplexing detection.

Table S1. Peak assignment for the SERS spectrum of Doxorubicin

SERS Peak (cm^{-1})	Band Assignment
345	Ring deformation, C-O-H wagging, C-H_2 wagging
445	Ring deformation, C-H wagging, C=O deformation
1200-1300	C-O in-plane bending
1435	Skeletal ring, C-O-H, C-H bending
1571	Skeletal ring
1631	Ring stretching, C-O-H deformation, C=O stretching