Supplementary Information

The development of "Fab-Chips" as low-cost, sensitive surface-enhanced Raman spectroscopy (SERS) substrates for analytical applications

Ashley M. Robinson[a], Lili Zhao[a], Marwa Yasmin[a], Paridhi Bhandari[b], Scott G. Harroun[a], Dhananjaya Dendukuri[b], Jonathan Blackburn[c], Christa L. Brosseau[a*]

[a]Department of Chemistry
Saint Mary's University
923 Robie Street
Halifax, N.S
B3H 3C3
Canada

[b]Achira Labs Pvt. Ltd.
57, 1st Main Road
JP Nagar Phase III
Bangalore 560078
India

[c]Institute of Infectious Disease & Molecular Medicine
University of Cape Town
Faculty of Health Sciences
Cape Town, South Africa

*Corresponding Author. Dr. C. L. Brosseau, Saint Mary's University, Halifax, N. S., Canada B3H 3C3. Email: christa.brosseau@smu.ca; Fax: +1 (902) 496-8104; Tel: +1 (902) 496-8175

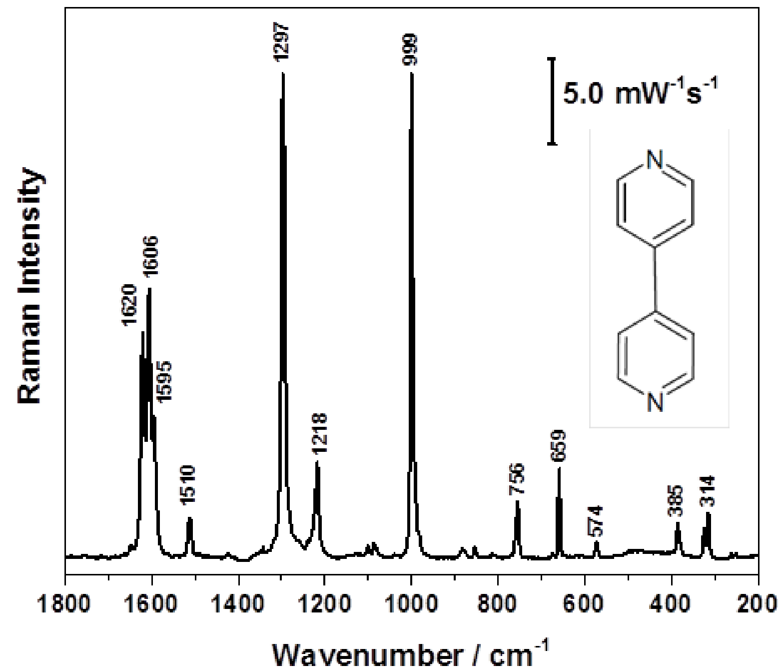

Figure S1. Normal Raman signal of pure 4, 4'-BiPy powder (532 nm, 10 mW, 30 s) and molecular structure of 4, 4'-BiPy.

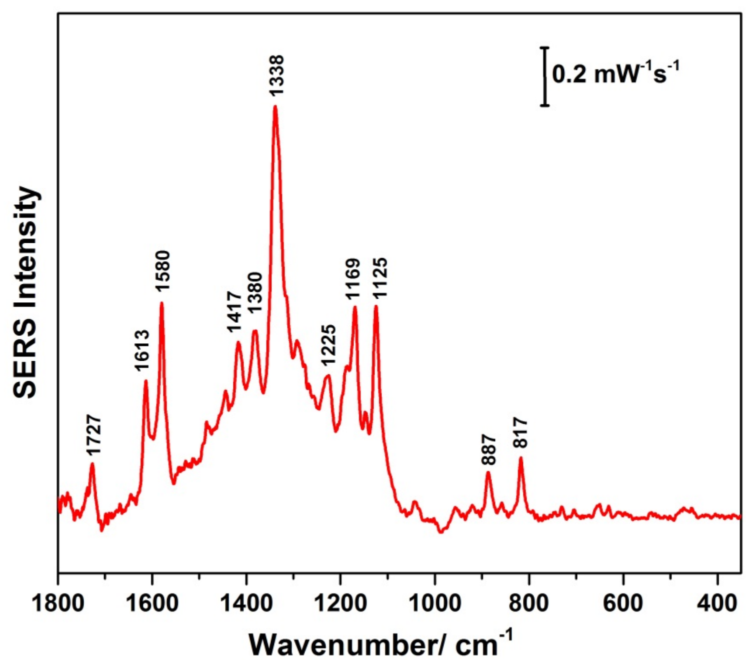

Figure S2. SERS signal of 4, 4'-BiPy on *zari* fabric, collected at 532 nm. No bands for 4, 4'-BiPy can be observed; those from silk dominate the signal.

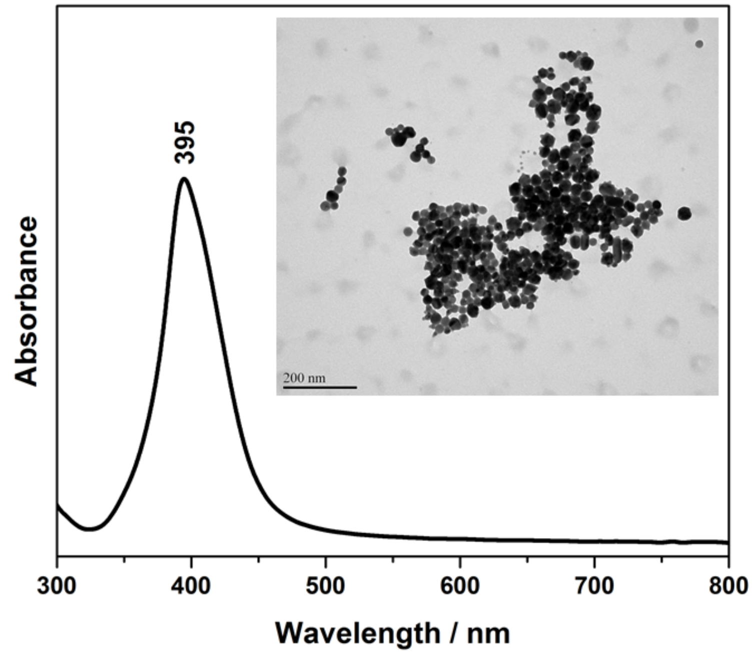

Figure S3. UV-vis spectrum of the modified citrate-reduced AgNPs. Inset: TEM image of the corresponding AgNPs (87,000x).

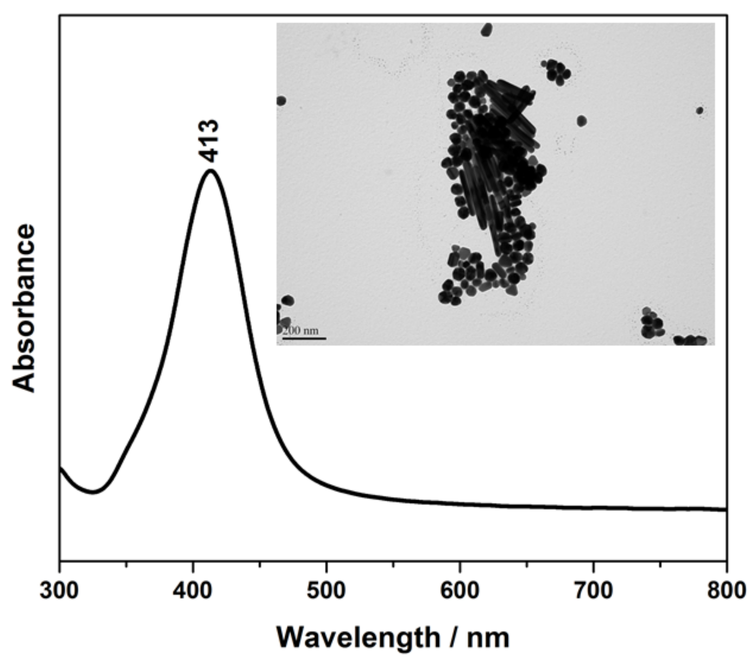

Figure S4. UV-vis spectrum of the silver colloids prepared during the *in situ* modification of the *zari* fabric. Inset: TEM image of the corresponding AgNPs. Many long silver rods can be observed.

Estimation of surface enhancement factor

The enhancement factor can be defined as:

$$EF = (I_{surf} / N_{surf}) / (I_{bulk} / N_{bulk}), \quad (1)$$

where I_{surf} and I_{bulk} denote the integrated intensities of the same band for $BiPy_{ads}$ and $BiPy_{sol}$ respectively, whereas N_{surf} and N_{bulk} represent the number of the corresponding $BiPy_{ads}$ and $BiPy_{sol}$ molecules effectively excited by a laser beam.[1, 2]

The calculation of N_{surf} can be carried out using the following approximation if uniform arrangement of silver nanoparticles and monolayer adsorption is assumed:

$$N_{surf} = ((A/\pi r^2)(2\pi r^2)) / \sigma = 2A / \sigma, \quad (2)$$

Where A is the area of the laser spot and σ is the surface area occupied by an adsorbed BiPy molecule. It has been reported that the cross sectional area is 0.4 nm^2 for BiPy from Corey, Pauling and later improved by Kultun (CPK) molecular model.[3]

Similar to the confocal Raman microscope, the DXR Smart Raman microscope processes a sensitive depth resolution, the term N_{bulk} in Eq. (1) cannot be obtained directly as for a conventional Raman spectroscope. It has to be calculated based on the focal feature of the microscope as reported by Etchegoin and Tian.[1, 2] Figure S3 shows the intensity-distance profile obtained from silicon wafer (solid line). The integrated intensity of the strongest band for Si at 520.2 cm^{-1} was measured as the Si wafer plane was moved front and back.

For the illuminated volume of solution, a plane of solution can be imaginarily considered to move front and back, just like the realistically movable Si wafer. An effective layer (h) is defined, within which, each BiPy molecule yields the same contribution to the Raman signal as those localized in the ideally focused plane. Thus,

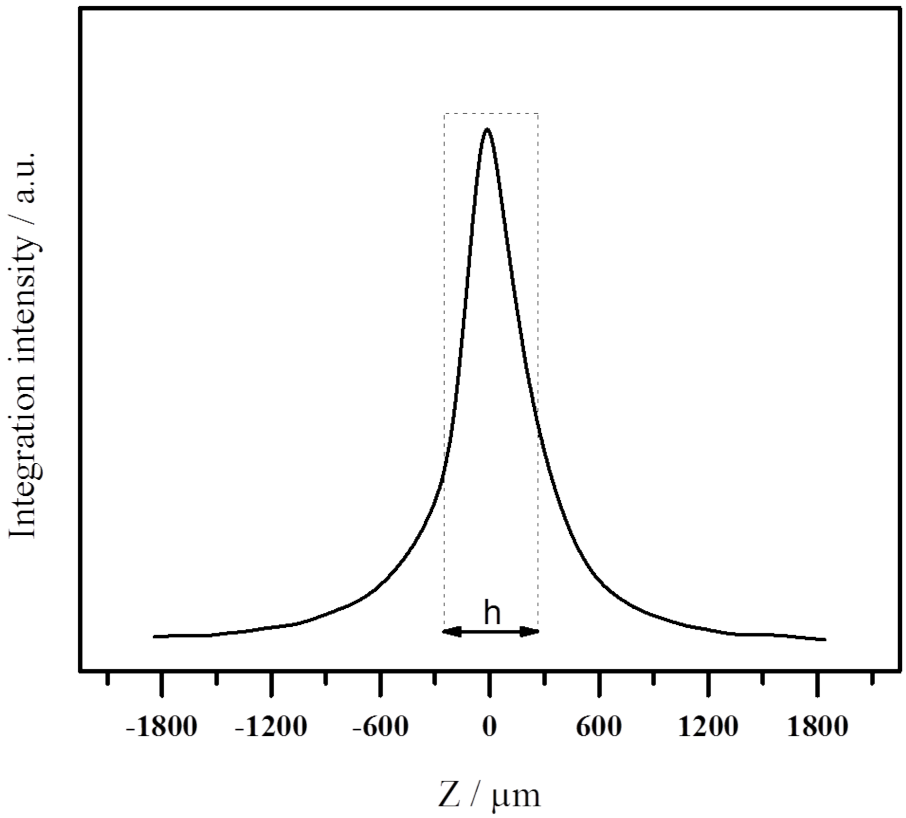

Figure S5. Raman intensity-depth profile of the integrated intensity of 520.2 cm^{-1} band for a Si wafer.

$$h = \left(\int_{-\infty}^{\infty} I(z)dz \right) / I_{max.} \qquad (3)$$

Based on the profile in Figure S3, h can be calculated to be 560 μm. hI_{max} can be presented as a dashed-line rectangle as shown in Figure S5. Therefore, the effectively illuminated number of BiPy molecules in aqueous solution, N_{bulk}, can be written as:

$$N_{bulk} = AhcN_A = 560Ac\, N_A, \quad (4)$$

Where c is the concentration of BiPy solution and N_A is the Avogadro constant. With Eqs. (2) and (4), Eq. (1) can be rearranged as:

$$EF = (560cN_A\sigma I_{surf}) / (2I_{bulk}). \quad (5)$$

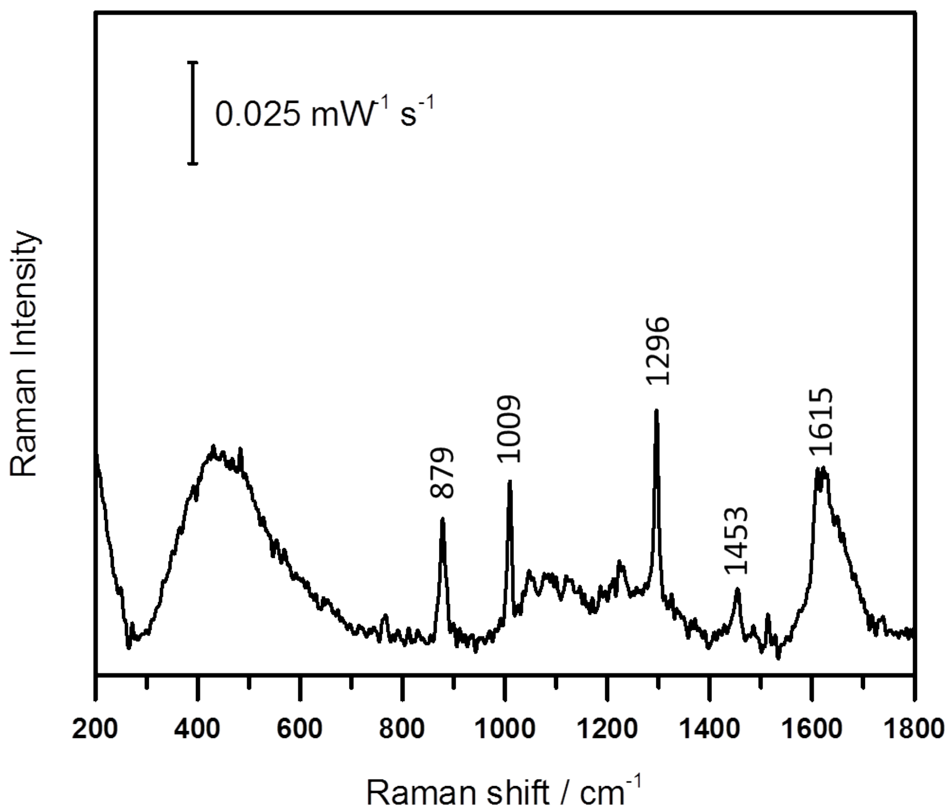

Figure S6. Normal Raman signal of 4, 4'-BiPy solution with concentration of 0.01 M (532 nm, 10 mW, 60 s) .

Thus, the average *EF* value for the fab-chip substrate with deposition of concentrated AgNPs was calculated to be 3.21×10^{8} based on 1009 cm^{-1} band in Figure S6 and 1020 cm^{-1} band shows in Figure 4b in the revised manuscript.

References

1. E. C. Le Ru, E. Blackie, M. Meyer and P. G. Etchegoin, *J. Phys. Chem. C*, 2007, **111**, 13794-13803.
2. W. B. Cai, B. Ren, X. Q. Li, C. X. She, F. M. Liu, X. W. Cai and Z. Q. Tian, *Surf. Sci.*, 1998, **406**, 9-22.
3. M. Suzuki, Y. Niidome and S. Yamada, *Thin Solid Films*, 2006, **496**, 740-747.