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Supporting Information

Creating SERS Hot Spots on Ultralong Single-Crystal β-Ag VO_3 Microribbons

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1. Calculation of SERS Enhancement Factor

The enhancement factor (EF) in SERS is calculated by the following equation:

$$EF = \frac{I_{sample} / (N_{sample} \cdot \rho_{sample})}{I_{ref} / (N_{ref} \cdot \rho_{ref})},$$

where I, N, and ρ represent the measured Raman intensity, the number of molecules probed, and the laser power density (W/m^2) used for Raman excitation, respectively. The "sample" is the 4-ATP molecules on the β-$AgVO_3$ microribbons; the "reference" is the same molecule in solution for which normal (unenhanced) Raman spectrum is obtained.

For the Raman intensities (I_{sample} and I_{ref}), we measured the peak intensities of the 1078 cm^{-1} C−S stretching mode of 4-ATP from the SERS spectrum of the β-$AgVO_3$ microribbons and the normal Raman spectrum of 4-ATP in 0.5 M solution. We obtained $I_{sample} = 852$ and $I_{ref} = 3.6$.

SERS signal arises from the 4-ATP molecules adsorbed on the AgNPs formed on the β-$AgVO_3$ microribbon surfaces. We estimated the number of 4-ATP molecules that contribute to SERS simply by considering the molecules in the laser probe area. For the conservative estimation of the SERS enhancement factor, we assumed that 4-ATP molecules form a monolayer in the probed region with an occupation area of 0.22 nm^2 per molecule.[1] The laser spot in the Raman microscope through a 50× objective was 4.5 μm. Therefore, the number of molecules in the probed area corresponds to 7.2×10^7. Calculation of the number of molecules probed in the solution is a little more complicated. The probe volume for the 0.5 M 4-ATP solution was assumed to be a cylinder. The diameter of the cylinder corresponds to the focal size of laser (785 nm) at the sample through a 10× objective which we used for solution. The length of the cylinder is the confocal parameter. The beam diameter through a 10× objective measured 19 μm. Since the laser beam through an objective still obeys the Gaussian optics, the confocal parameter (b) is calculated by

$$\boldsymbol{b} = \frac{2 \cdot \boldsymbol{\pi} \cdot \boldsymbol{w}_0^{\,2}}{\boldsymbol{\lambda}},$$

where w_0 is the beam waist at the focus (9.5 μm) and λ is the wavelength of light (785 nm).[2] As a result, the calculated cylinder volume was 2.0×10^{-13} m^3. Using the equation above, we obtained the number of molecules probed in 0.5 M solution, 6.2×10^{13}.

The laser power at the sample through 50× and 10× objectives was both 12.0 mW. From these, the enhancement factor is 1.1×10^7.

2. Comparison of the β-$AgVO_3$ Microribbons Treated with 4-ATP and Thiophenol

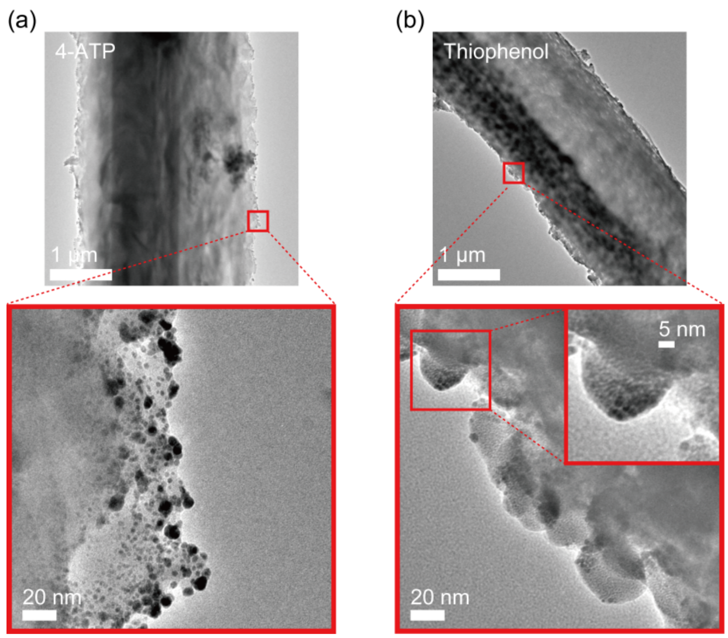

Figure S2. TEM images of β-$AgVO_3$ microribbons treated with (a) 4-ATP and (b) thiophenol.

References

(1) N. Mohri, M. Inoue, Y. Arai and K. Yoshikawa, *Langmuir*, 1995, **11**, 1612-1616.

(2) A. E. Siegman, *Lasers*, University Science Books, Palo Alto, California, U.S.A., 1986.