

Large Area Metal Nanowire Arrays with Tunable Sub-20 nm Nanogaps

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Supporting Information

Figure S1 shows high-resolution scanning electron microscopy (SEM) images that are representative of Ag-NW arrays fabricated with the technology reported in this article. The SEM images clearly demonstrate the effectiveness of this fabrication technology for manufacturing high quality uniform functional metal NW arrays with well-controlled sub-20 nm separation nanogaps.

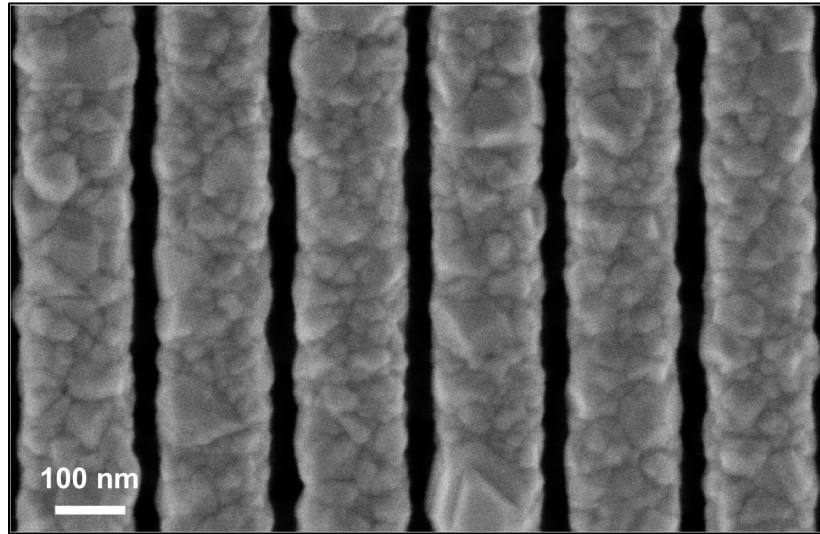


Figure S1. High-resolution SEM image of fabricated Ag-NW array with pitch $\lambda_g=200$ nm and $g=20$ nm nanogap spacing.

Figure S2 shows the curve fitting results from measured nanogap widths g that were realized with different combinations of template dimensions, λ_g and w , and nominal metal thickness t_z , the nanogap

can be estimated with an empirical relationship $g \approx we^{-\alpha t_z}$, where α , the nanogap reduction parameter, has been estimated for the different dimensions and metal deposition conditions.

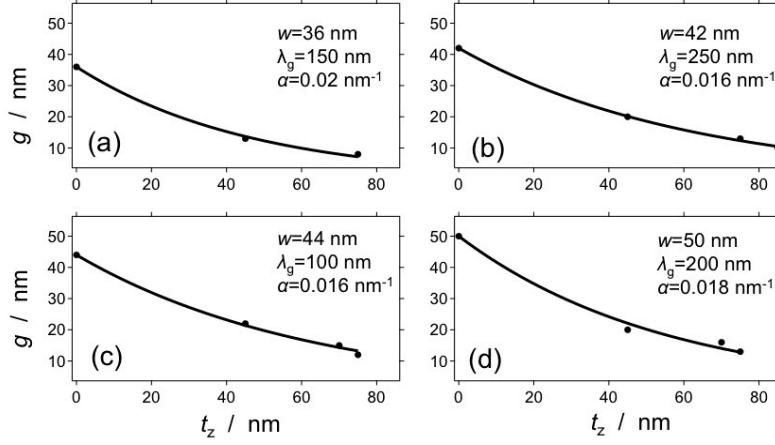


Figure S2. Exponential model fitting of lateral Au deposition rate that forms the nanogap region of the Au-NW array.

Figures S3 and S4 show example cross-section, prepared with focused ion-beam milling, SEM images of Au-NW array with $\lambda_g=100$ nm, $w=50$ nm, $t_z=70$ nm, and $g=10$ nm.

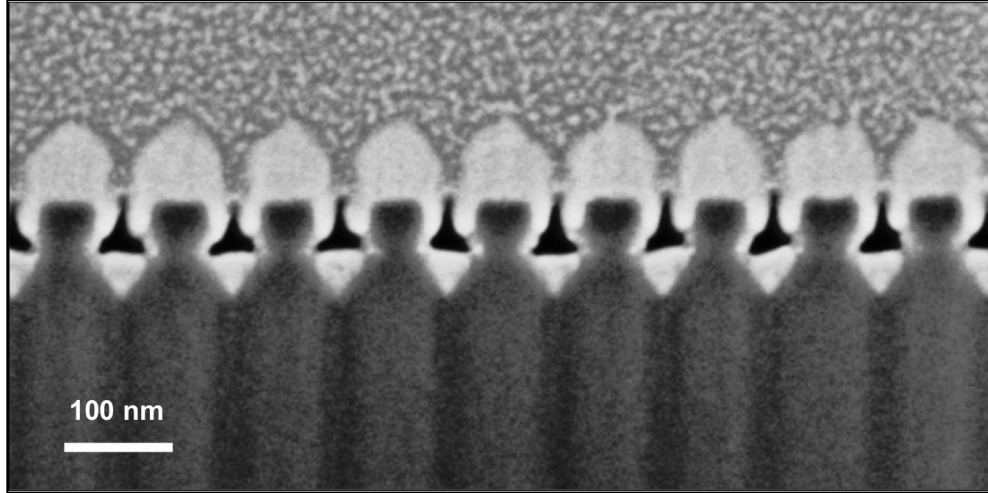


Figure S3. High-resolution SEM images of a fabricated Au-NW array cross-section with sub-wavelength pitch $\lambda_g=100$ nm surfaces with $g=10$ nm nanogap spacing. The cross-section was prepared with focused ion-beam milling.

Figure S4 shows that the major axis e_x of the Au-NW cross-section elliptical shape can be reduced to a circular shape, i.e. $e_x \approx e_z$, as the array pitch λ_g is reduced.

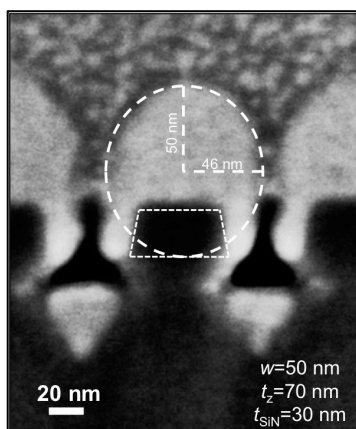


Figure S4. High-resolution SEM image of Au NW array cross-section prepared with focused ion-beam milling with $\lambda_g=100$ nm and $g\approx 10$ nm. Short white dashed lines indicate SiN template layer profile. Long white dashed lines indicate the near circular surface profile.

Figure S5 shows the molecular details of the benzenethiol molecule. Figure S5b shows that the UV-VIS absorption spectrum is well into the UV portion of the spectrum and far away from commonly used laser excitation sources used for surface enhanced Raman spectroscopy (SERS), which are in the visible portion of the spectrum, e.g. 532 nm, 632.8 nm and 785 nm. Figure S5c shows the dominant Raman vibration modes of BT.

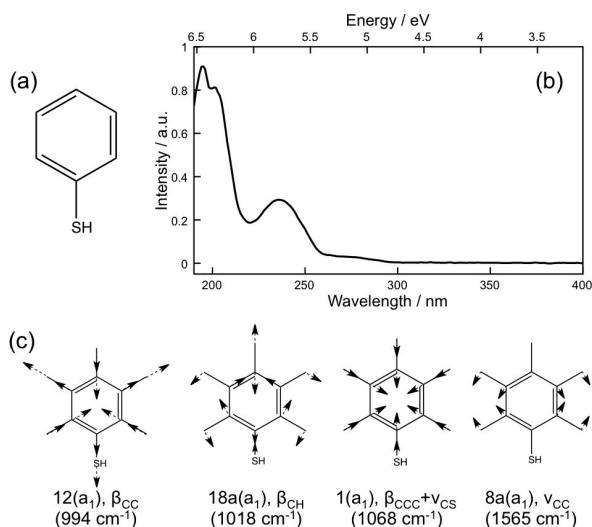


Figure S5. Benzenethiol molecular details. (a) schematic diagram of molecular structure; (b) UV-VIS absorption spectrum; (c) dominant Raman vibration modes.

Figure S6 shows conventional Raman measurements of neat BT in solution sealed in a glass vial. The number of molecules was estimated from the confocal volume of the Raman microscope with the 100 \times /0.9 NA microscope objective. The 917 cm^{-1} band represents the S-H bond vibration in free solution, which is missing from the chemisorbed BT SERS measurements.

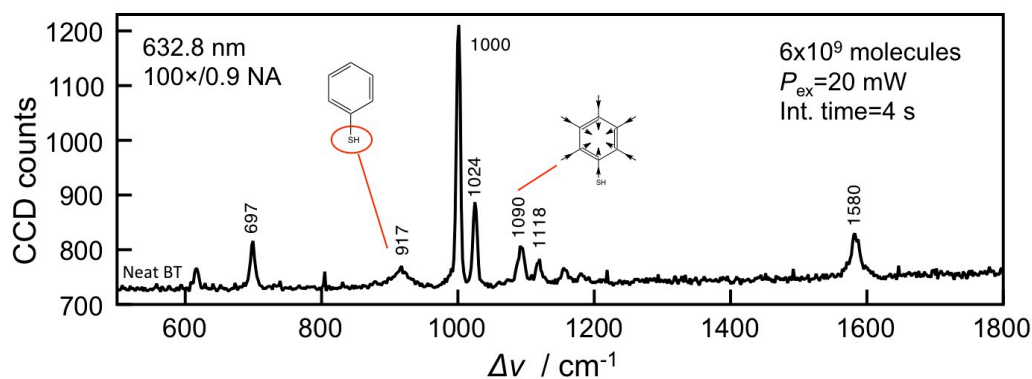


Figure S6. Conventional Raman measurements of neat BT sealed in a glass vial. The number of molecules was estimated from confocal volume of the measurement system. The 917 cm^{-1} band represents the S-H bond vibration.

Figure S7 shows a representative surface enhanced Raman spectrum of BT chemisorbed on a Ag-NW array surfaces is shown with the different Raman active vibrational modes of the BT monolayer 416 cm^{-1} , 691 cm^{-1} , 994 cm^{-1} , 1018 cm^{-1} , 1068 cm^{-1} and 1565 cm^{-1} , which have been previously reported.

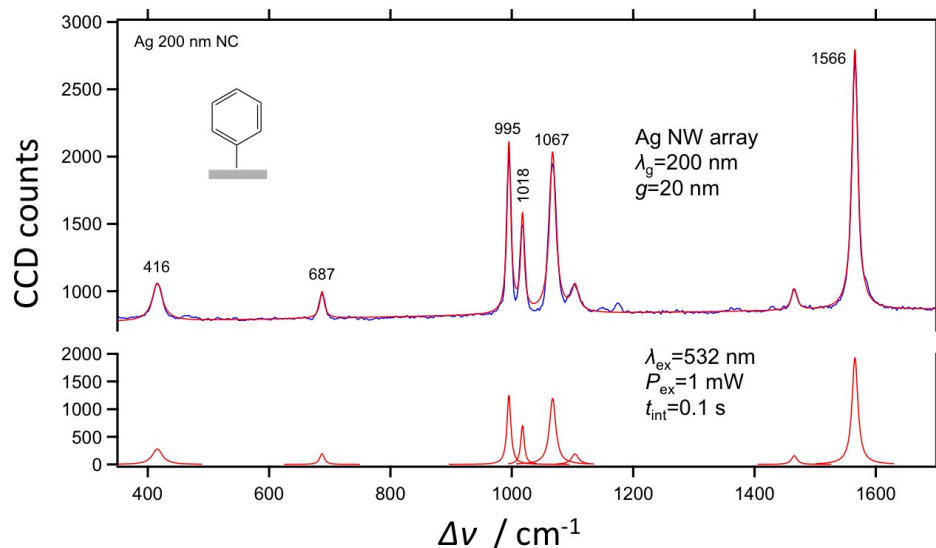


Figure S7. Measured Raman spectra of BT chemisorbed on Ag-NW array surfaces. Top: Measured (blue) spectra from surface with pitch $\lambda_g=200\text{ nm}$ and measured $g=20\text{ nm}$, and modeled Lorentzian bandshapes (red); Bottom: Modeled Lorentzian bandshapes (red) without the background.

REFERENCES

1. M. Jin, H. van Wolferen, H. Wormeester, A. van den Berg, and E.T. Carlen, *Nanoscale*, 4, 4712, 2012.