

**Supporting Information for:**

**An Array of Optical Antennas on a Fiber Facet for *In Situ* Surface Enhanced Raman Scattering Detection**

Elizabeth J. Smythe<sup>1</sup>, Michael D. Dickey<sup>2</sup>, Jiming Bao<sup>1</sup>, George M. Whitesides<sup>2</sup>, and Federico Capasso<sup>1\*</sup>

1. School of Engineering and Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, Massachusetts 02138

2. Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138

**Surface Plasmon Resonance Spectra of Nanorod Arrays**

The SPR resonances measured from the array of nanorods transferred to the facet of a fiber are shown in Figure S1. When the incident light was polarized along the length of the nanorods, a strong resonance centered around  $\lambda \approx 650$  nm was generated (red curve). With the polarization perpendicular to the length of the nanorods, the resonance of the nanorods at  $\lambda \approx 650$  nm was no longer measurable (blue curve).

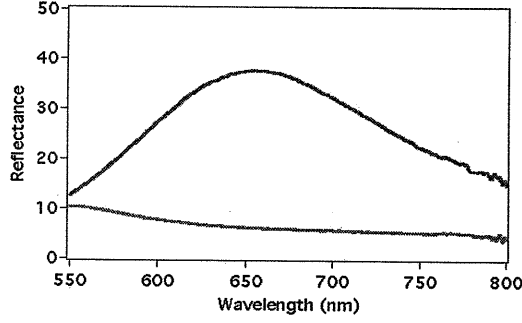


FIG S1: Surface Plasmon Resonance (SPR) measured from arrays of nanorods transferred to the facet of an optical fiber. The red curve shows the resonance measured with incident light polarization parallel to the length of the nanorods. The blue curve shows the spectra measured with the incident light polarization perpendicular to the length of the nanorods.

#### External Illumination: Calculation of External EF

The average SERS EF of the transferred nanorod array undergoing ‘external’ illumination is given by

$$EF = \left( \frac{I_{sers}}{N_{sers}} \right) \left( \frac{N_{neat}}{I_{neat}} \right) \quad (S1)$$

where  $I_{sers}$  is the height of a SERS peak measured when the objective lens focused light directly on the nanorod array (coated with benzenethiol),  $I_{neat}$  the height of the same Raman peak measured when a sample of liquid neat benzenethiol replaced the nanorod array,  $N_{sers}$  the number of benzenethiol molecules contributing to the SERS signal of the array, and  $N_{neat}$  the number of molecules contributing to the neat benzenethiol signal.<sup>1</sup>

$I_{sers}$  and  $I_{neat}$  are the heights of Raman bands of benzenethiol determined from spectra taken over a 10 second integration while 0.46 mW of power focused onto the sample. We

measured the height of the Raman peaks from the nonzero baseline of the collected spectra, and examined four different Raman-active vibrational modes: the measured peak heights are shown in Table 1.

To calculate  $N_{sers}$  and  $N_{neat}$  we followed the methodology outlined by Le Ru et al.<sup>1</sup>, in which  $N_{sers}$  is defined as

$$N_{sers} = A_{illum} F_{sers} \mu_{sers}$$

where  $A_{illum}$  is the illuminated area of the array,  $F_{sers}$  is the fraction of illuminated surface area containing benzenethiol molecules contributing to the Raman signal, and  $\mu_{sers}$  is the packing density of adsorbed benzenethiol molecules.

We used a value of  $6.8 \times 10^{14}$  molecules/cm<sup>2</sup> for  $\mu_{sers}$ . This is the largest reported packing density of benzenethiol<sup>2</sup>: use of a lower packing density would increase the calculated EF. To determine  $A_{illum}$  we determined the area of the array illuminated in the focus of the objective lens. The lens focused to a spot  $\sim 10 \mu\text{m}$  in diameter, giving  $A_{illum} = \pi (5000)^2 \text{ nm}^2$ .  $F_{sers}$  is the ratio of exposed nanorod surface area  $SA_{rod}$  to the nanorod 'unit cell'  $A_{UC}$ :

$$F_{sers} = \frac{SA_{rod}}{A_{UC}}$$

We transferred nanorods 65 nm long, 40 nm thick, and 50 nm wide, giving  $SA_{rod} = 12450 \text{ nm}^2$ . Gaps of 25 nm separated the nanorods along their long axis and 100 nm along their short axis, making  $A_{UC} = 13500 \text{ nm}^2$ . The fractional surface area is  $F_{sers} = 0.922$ ; this can be used to determine  $N_{sers} = 4.9 \times 10^8$ .

$N_{neat}$  is given by

$$N_{neat} = A_{obj} H_{obj} \rho_{neat}$$

where  $A_{obj}$  is the area of the spot size of the objective lens ( $A_{obj} = \pi(5000)^2 \text{ nm}^2$ ),  $H_{obj}$  is the height of the volume of neat benzenethiol contributing to the Raman signal, and  $\rho_{neat}$  is the density of the neat benzenethiol ( $5.9 \times 10^{21}$  molecules/cm<sup>3</sup>; Sigma Aldrich). The product  $A_{obj} H_{obj}$  is the volume of neat benzenethiol contributing to the measured Raman signal.

We determined  $H_{obj}$  for the measurement configuration by moving a silicon <100> wafer in 1  $\mu\text{m}$  increments through the focal plane of the 20x objective lens, and (at each point) recording the strength of the Raman signal of the silicon at 520.6  $\text{cm}^{-1}$ . We calculated  $H_{obj} = 62.6 \mu\text{m}$  by integrating the strength of the Raman signal over distance and dividing the result by the largest measured signal. The resulting value, 62.6  $\mu\text{m}$ , represented the height of a cylindrical volume (with radius = 5000 nm) in which the signal generated by each molecule of neat benzenethiol can be considered equal to the signal of a molecule found in the focal plane of the objective lens.<sup>3</sup> We determined  $N_{neat} = 2.9 \times 10^{13}$ .

Table 1: Measured values of Raman scattering from a vial of neat benzenethiol, SERS signals measured from the externally illuminated array of nanorods, and the calculated external EF factors

Wavenumber	Neat Benzenethiol	SERS Signals from Array	External EF
995 $\text{cm}^{-1}$	122	558	$2.7 \times 10^5$
1020 $\text{cm}^{-1}$	131	566	$2.6 \times 10^5$
1075 $\text{cm}^{-1}$	116	1012	$5.1 \times 10^5$
1583 $\text{cm}^{-1}$	173	928	$3.2 \times 10^5$

Measurements taken over a 10 second integration period: the objective lens focused 0.46 mW of power on the samples.

### Internal Illumination: Calculation of 'Effective' Internal EF

We could not use equation S1 to calculate the EF of the internally illuminated nanorods

because the reference measurement needed to obtain  $I_{neat}$  values proved too weak to detect. Instead, we determined an ‘effective’ internal EF value for the nanorods,  $EF_{eff}$ :

$$EF_{eff} = \beta \left( \frac{I_{sers}}{N_{sers}} \right) \left( \frac{N_{neat}}{I_{neat}} \right) \quad (S2)$$

where  $I_{sers}$  equaled the height of the Raman peak in the SERS spectrum measured from the internally illuminated array and  $I_{neat}$  the height of the same Raman peak when the objective lens focused light into a vial of neat benzenethiol: these heights were determined from the nonzero baselines of the spectra. We set  $N_{sers}$  and  $N_{neat}$  equal to the number of molecules contributing to  $I_{sers}$  and  $I_{neat}$ , respectively, and included a scaling factor  $\beta$  to compensate for differences between the internal SERS measurements and the reference measurements of the neat benzenethiol.

We used the SERS spectra measured from the internally illuminated array of nanorods to determine  $I_{sers}$  values.  $N_{sers}$  equaled the number benzenethiol molecules contributing to this SERS signal, and we determined the value of  $N_{sers}$  with the same formula used to determine the  $N_{sers}$  of the external EF calculation ( $N_{sers} = A_{illum} F_{sers} \mu_{sers}$ ): the two calculations differed only in the illuminated area ( $A_{illum}$ ) of nanorods. Nanorods across the entire core of the fiber underwent internal illumination, making the internal  $A_{illum} = \pi(31250)^2 nm^2$  and  $N_{sers} = 1.9 \times 10^{10}$ . We measured the internal illumination over a 40 second integration while coupling 5.4 mW of power into the fiber.

We determined values of  $I_{neat}$  from the Raman spectrum acquired from a vial of neat benzenethiol placed directly in the focus of the objective lens, and let  $N_{neat}$  equal the number of neat benzenethiol molecules contributing to this signal. The value of  $N_{neat}$  for this internal EF calculation remained unchanged from the  $N_{neat}$  value used in the external EF calculation, since

the two references shared the same measurement configuration:  $N_{neat} = 2.9 \times 10^{13}$ . We used a 40 second integration to acquire this reference spectrum, but focused only 0.46 mW of power into the neat benzenethiol.

The scaling factor,  $\beta$ , accounted for fundamental differences between the internal illumination measurement and the reference measurement. We defined

$$\beta = \eta_{ins} \eta_{coll}$$

and considered differences in the intensity of illumination ( $\eta_{ins}$ ) and the collection efficiency ( $\eta_{coll}$ ) of the two measurement configurations.

Different intensities of light illuminated benzenethiol molecules in the two measurements. The objective lens illuminating the neat benzenethiol focused 0.46 mW of power ( $P_{neat}$ ) in a beam with a spot size of diameter  $\sim 10 \mu\text{m}$  (area of  $A_{obj} = \pi (5000)^2 \text{nm}^2$ ). We assumed that in internal illumination the 5.4 mW of light coupled into the fiber ( $P_{sers}$ ) spread evenly across the core (62.5  $\mu\text{m}$  in diameter, core area of  $A_{core} = \pi (31250)^2 \text{nm}^2$ ). Consequently, light with lower intensity illuminated the benzenethiol molecules absorbed on the gold nanorods than irradiated the neat benzenethiol molecules. We accounted for this difference in the intensity of illumination because the intensity of Raman scattering from a molecule is linearly proportional to the intensity of light illuminating the molecule. We defined  $\eta_{ins}$  to normalize the  $I_{sers}$  and  $I_{neat}$  values in Equation S2 to the intensity of the light illuminating the benzenethiol absorbed on the gold nanorods and the neat benzenethiol, respectively.

$$\eta_{ins} = \left( \frac{A_{core}}{P_{sers}} \right) \left( \frac{P_{neat}}{A_{obj}} \right)$$

The ability of the two setups to collect Raman signals also differed: we used  $\eta_{ins}$  to account

for this discrepancy. The percentage of total SERS signals generated by the array that were collected during internal illumination differed from the percentage of total Raman signals collected from the neat benzenethiol because (i) the numerical apertures (NA) of the objective lens and the fiber differed and (ii) the spectrometer detected only a portion of the SERS signals coupled into the fiber during internal illumination.

The NA values of the objective lens and the fiber limited the total Raman scattering collected by each component. The illuminated neat benzenethiol molecules produced Raman scattering that radiated in all directions, but the spectrometer measured only light collected by the objective lens: the numerical aperture ( $NA = 0.42$ ) of the objective lens determined the amount of collected light. Assuming the neat benzenethiol emitted Raman signals in all directions, the percentage of total scattered light collected by the objective lens is

$K^{obj} = \frac{1}{2} [1 - \cos(\arcsin(NA))] = 4.6\%$ . The NA of the fiber ( $NA = 0.275$ ) indicates that a smaller percentage ( $K^{fib} = 1.9\%$ ) of light scattered in all directions couples into the fiber.

The NA of the fiber also dictates the range of angles assumed by light exiting the fiber. The lower NA of the fiber (compared to the NA of the objective lens) indicates that the range of angles spanned by light exiting the fiber core is smaller than the range of incident light angles accepted by the objective lens: this implies that light exiting the fiber (that falls within the focal spot of the objective lens) is collected by the lens and directed to the spectrometer.

We compensated for the different NA values of the objective lens and the fiber by adding a scaling factor to enable comparison of the ‘total’ Raman scattering generated in each measurement, rather than comparing the Raman scattering collected in each measurement. To make this adjustment in Equation S2 we scaled  $I_{sers}$  by  $K_{fib}^{-1}$  and  $I_{neat}$  by  $K_{obj}^{-1}$ .

We assumed equal Raman enhancement from all the internally illuminated nanorods,

resulting in a uniform distribution of collected SERS signals across the core of the fiber (62.5  $\mu\text{m}$  in diameter). The smaller spot size of the objective lens ( $\sim 10 \mu\text{m}$  in diameter) allowed only a portion of the signals distributed across the core ( $\sim 2.5\%$ ) to be detected by the spectrometer. To enable to the comparison of ‘total’ generated Raman scattering in Equation S2, we scaled the value of  $I_{\text{SERS}}$  by  $\frac{A_{\text{core}}}{A_{\text{obj}}}$ . Accounting for differences in collection efficiency between the two measurement setups gave

$$\eta_{\text{coll}} = \frac{K_{\text{obj}}}{K_{\text{fib}}} \frac{A_{\text{core}}}{A_{\text{obj}}}$$

Thus  $\beta = \left( \frac{A_{\text{core}}}{P_{\text{SERS}}} \frac{P_{\text{neat}}}{A_{\text{obj}}} \right) \left( \frac{K_{\text{obj}}}{K_{\text{fib}}} \frac{A_{\text{core}}}{A_{\text{obj}}} \right) = 314.7$ . We used this scaling factor  $\beta$  in Equation S2 to

obtain the effective internal EF values shown in Table 2.

Table 2: Values of Raman scattering measured from an illuminated vial of neat benzenethiol, SERS signals measured from an internally illuminated array of nanorods, and the resulting effective internal EF.

Wavenumber	Neat Benzenethiol	SERS Through Probe	‘Effective’ Internal EF
995 $\text{cm}^{-1}$	899	776	$4.2 \times 10^5$
1020 $\text{cm}^{-1}$	764	813	$5.1 \times 10^5$
1075 $\text{cm}^{-1}$	931	1238	$6.4 \times 10^5$
1583 $\text{cm}^{-1}$	944	1277	$6.5 \times 10^5$

Measurements taken over a 40 second integration period: the objective lens focused 0.46 mW of power in the neat benzenethiol, while 5.4 mW of power illuminated the array of nanorods.

We used two different Raman spectra to obtain values of  $I_{\text{neat}}$  in Table 1 and Table 2. Both spectra were acquired by focusing 0.46 mW of power into a vial of neat benzenethiol, and were taken over 10 second (Table 1) and 40 second (Table 2) integrations. The measured values of  $I_{\text{neat}}$ , however, do not simply scale by a factor of 4. The two reference spectra were both acquired immediately after measurement of the corresponding SERS spectrum from the array of



nanorods. The alignment of the optical components guiding the light from the samples into the spectrometer changed slightly between the measurements of these two sets of data, resulting in different coupling of the neat benzenethiol signals into the spectrometer.

## References

1. Ru, E. C. L.; Blackie, E.; Meyer, M.; Etchegoin, P. G., Surface enhanced Raman scattering enhancement factors: a comprehensive study. *Journal of Physical Chemistry C* **2007**, 111, (37), 13794-13803.
2. Wan, L. J.; Terashima, M.; Noda, H.; Osawa, M., Molecular orientation and ordered structure of benzenethiol adsorbed on gold(111). *Journal of Physical Chemistry B* **2000**, 104, (15), 3563-3569.
3. Cai, W. B.; Ren, B.; Li, X. Q.; She, C. X.; Liu, F. M.; Cai, X. W.; Tian, Z. Q., Investigation of surface-enhanced Raman scattering from platinum electrodes using a confocal Raman microscope: dependence of surface roughening pretreatment. *Surface Science* **1998**, 406, (1-3), 9-22.