Surface Enhanced Infrared Absorption of Self-Aligned Nanogap Structures

Yajing Li[1], Mathieu L. Simeral[1], Douglas Natelson[1,2,3,]*

[1]Department of Physics and Astronomy, MS 61, Rice University, 6100 Main St., Houston, Texas 77005 USA

[2]Department of Electrical and Computer Engineering, MS 366, Rice University, Houston, TX 77005 USA

[3]Department of Materials Science and Nanoengineering, MS 325, Rice University, Houston, TX 77005 USA

Corresponding Author:

*To whom correspondence should be addressed. Emails: natelson@rice.edu

Baseline subtraction methods

Here we compare different approaches to approximating the smooth plasmonic extinction background, so that the underlying SEIRA lineshape from the SiO_2 may be extracted. Figure S1 (a) shows the baseline shape including the Si-O stretch peak fitted using Asymmetric least square method. Gaussian fit gives a less distorted baseline shape since it excludes the contribution from the fano peak of Si-O stretch.

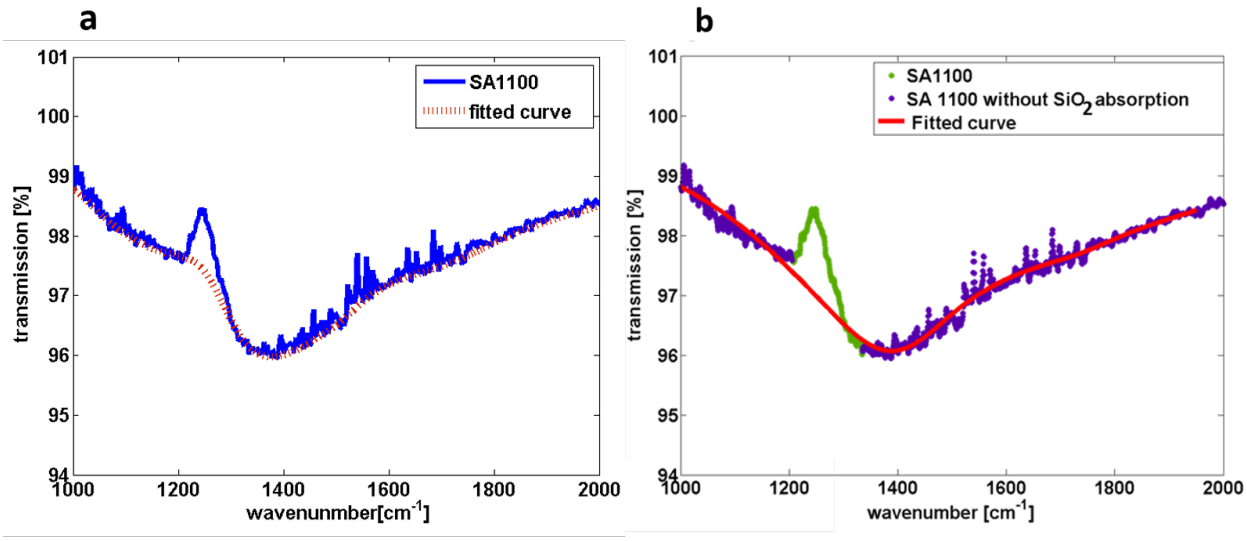

Figure S1 Comparison of baseline in data set shown in Figure 3 fitted using (a)AsLS[1] and (b) Gaussian.

Baseline subtraction result in different Si-O features in transmission spectra due to different baseline shape resolved from AsLs and Gaussian fitting methods. The corresponding spectra are presented in Figure S2 and S3. The baseline corrected transmission spectras generated from both methods show the same trend: the nanogap dimers exhibit stronger signal of the Si-O stretch than the nanorods; the longitudinal coupled dimers provide a better enhancement than the vertically coupled dimers.

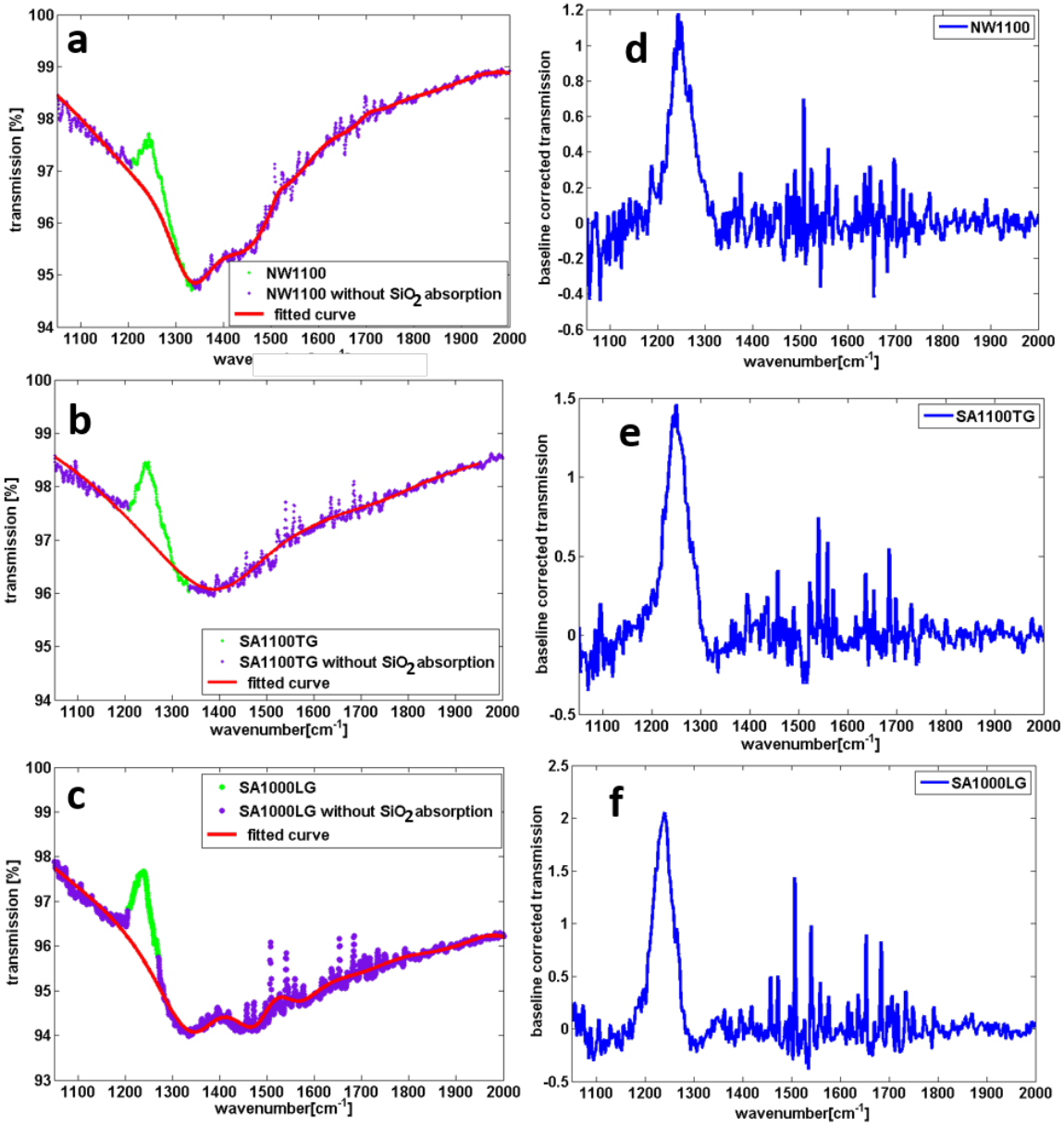

Figure S2 (a)-(c) Transmission with baseline fitted to Gaussian function subtracted from the experimental curve of nanorod, vertical aligned nanogap dimers and longitudinal aligned nanogap dimers. Green curve is data points of the Si-O phonon mode in transmission mode, purple curve is the remaining part of the data points and the red curve is a curve fit. (d)-(e) Transmission with baseline subtracted from the experimental curve in (a)-(c).

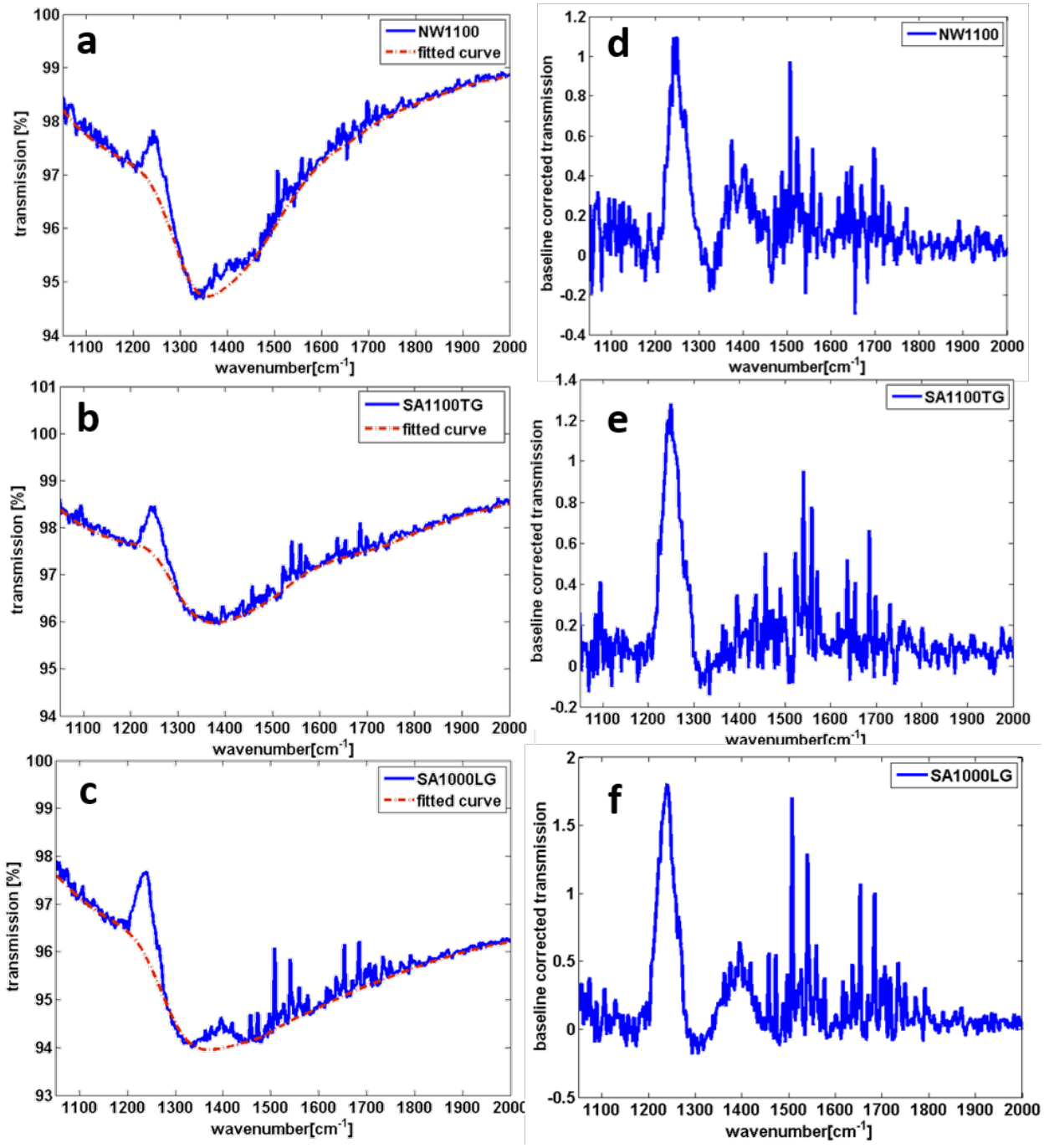

Figure S3 (a)-(c) Transmission with baseline fitted based on AsLS method and subtracted from the experimental curve of nanorod, vertical aligned nanogap dimers and longitudinal aligned

nanogap dimers. Blue curve is experimental data points. Red curve is the fitted curve. (d)-(e) Transmission with baseline subtracted from the experimental curve in (a)-(c).

FDTD simulations

In FDTD simulations performed in this work, the Si and SiO_2 dielectric constants are adapted from data published in ref[2]. The thickness of the SiO_2 is chosen to be 2nm to match the minimum mesh size in the FDTD simulation. All three sets of calculations were done with the same incident intensity. The incoming electromagnetic field is polarized in the *x* direction

To evaluate the effect of the broken symmetry on plasmonic field enhancement of the vertical nanogap structures, electric field enhancement was calculated from FDTD simulations and compared on vertical dimers consisting two identical rods in Figure S4 (b) and (d) and dimer with a notch at the end of the bottom component shown in Figure 4S (a) and (c). The presence of the gap in the simulations reduces the narrowest gap to 2nm between two vertical components. The induced broken symmetry increases the electric field intensity inside of the closest gap as well as in the SiO_2 dielectric layer. The electric field enhancement in x-z plane was also calculated and compared between the longitudinally coupled and vertically coupled dimers. The field enhancement is stronger at the gap between the two rods in the horizontal direction, which suggest the coupling between the two rods is stronger in the longitudinal direction.

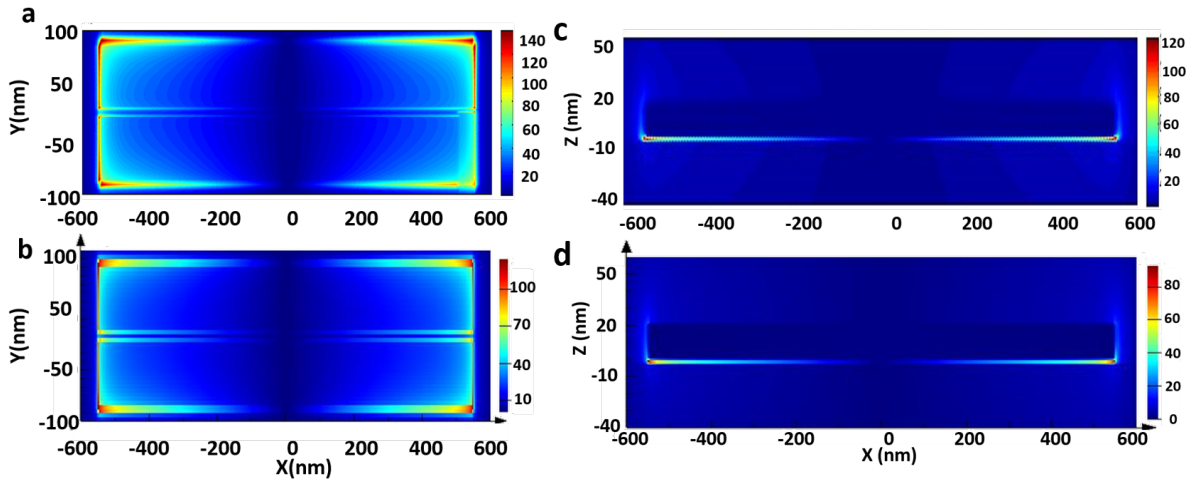

Figure S4. Spatial plots of electric field enhancement from FDTD simulation on vertical coupled dimers with one notch at the +x end of the bottom rod in (a) x-y plane and (c) x-z plane. (b) and (d) are corresponding plots of the vertical dimers consisting two identical rods. All data was calculated at 1387 cm^{-1} for nanogap structures with component length of 1100 nm.

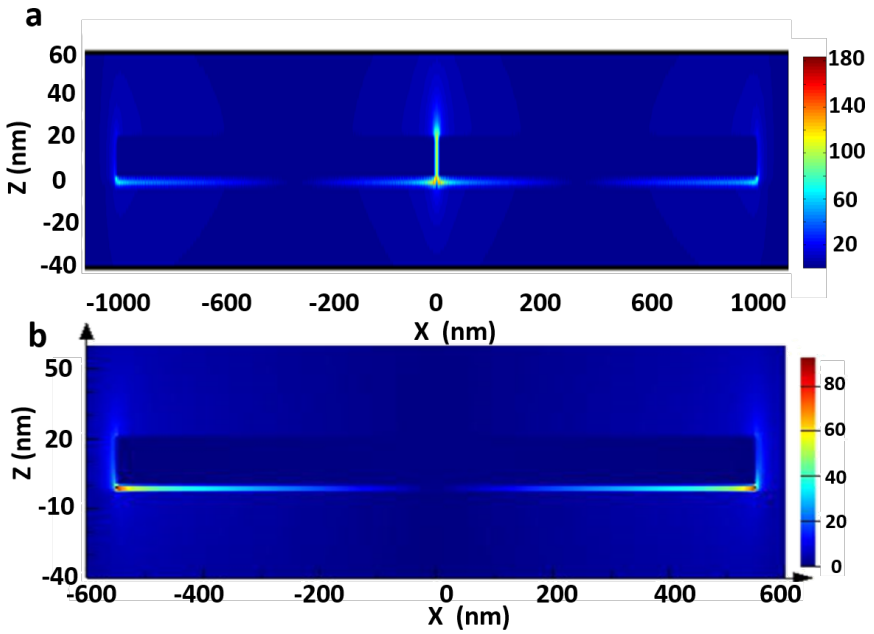

Figure S5. Spatial plots of electric field enhancement in *x-z* plane from FDTD simulation on (a)longitudinally coupled dimers and (b) the vertical coupled dimers All data was calculated at the incident light with wavenumber of 1387 cm^{-1}

Reference

(S1) Peng, J.; Peng, S.; Jiang, A.; Wei, J.; Li, C.; Tan, J. Asymmetric Least Squares for Multiple Spectra Baseline Correction. *Anal. Chim. Acta* **2010**, *683*, 63–68.

(S2) Philipp, H. R. Silicon Dioxide (SiO_2) (Glass) Palik, Edward D. In *Handbook of Optical Constants of Solids*; Academic Press: Boston, 1985; pp 749–763.