Supporting Information

Enhanced Raman Scattering from Nanoparticle-Decorated Nanocone Substrates: a Practical Approach to Harness In-Plane Excitations

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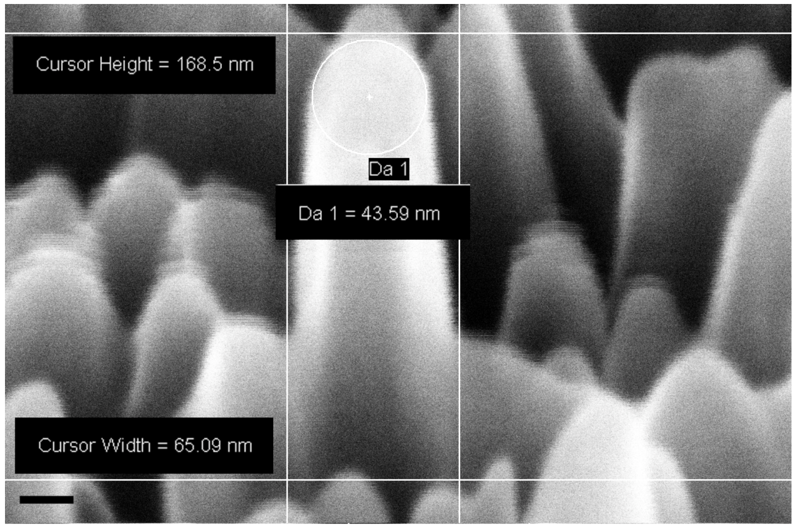
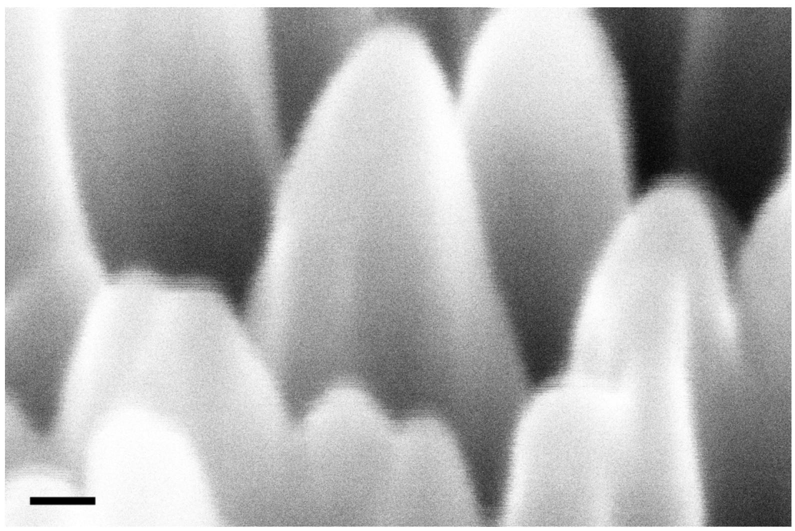
Characterization of the morphology of the nanocones

We used a PointProbe Plus Force Modulation tip (Nanosensors Inc, Neuchatel, Switzerland) to obtain the AFM measurements shown in Figure 3 in the manuscript. The AFM tip has a guaranteed radius of curvature less than 10 nm. In Figure S1, we show SEM images of representative SiGe nanocones tilted at 36 degrees. Figure S1a displays a nanocone with a peak curvature of ~ 22 nm (diameter ~ 44 nm) and a height of ~ 103 nm, both of which are sufficiently larger than the curvature of the AFM tip. Figure S1b shows nanocones of similar dimensions. Please note that all the numerical values of the heights displayed in the SEM images as well as given in the texts are tilt-angle-compensated.

In Figure S2, we show two section analyses of the AFM scan. The dimensions of the nanocone peak curvature, base diameter and height are listed in Table S1. Further analysis revealed that nanocones typically have heights ranging from 80 to 130 nm, and base widths ranging from 60 to 100 nm (base radius 30 - 50 nm). The dimensions are consistent with the SEM analysis. Thus, we expect the artifacts in the AFM scan (*i.e.* dilation effect from the AMF tip) to be negligible.

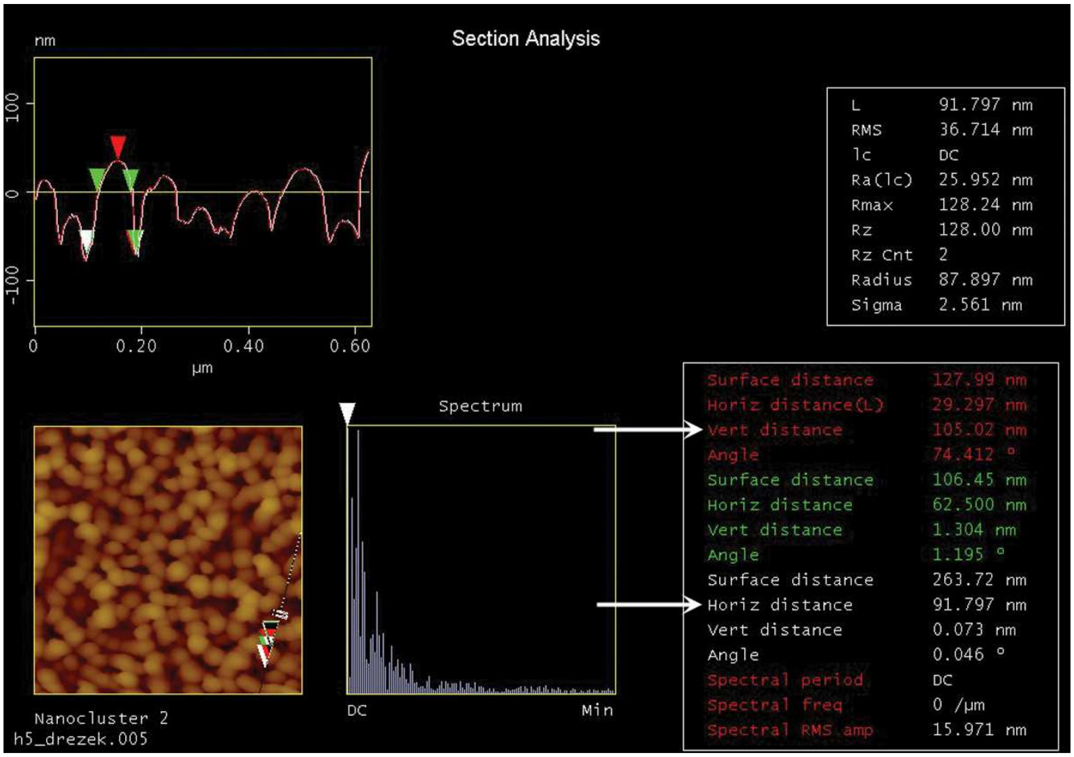


(a)

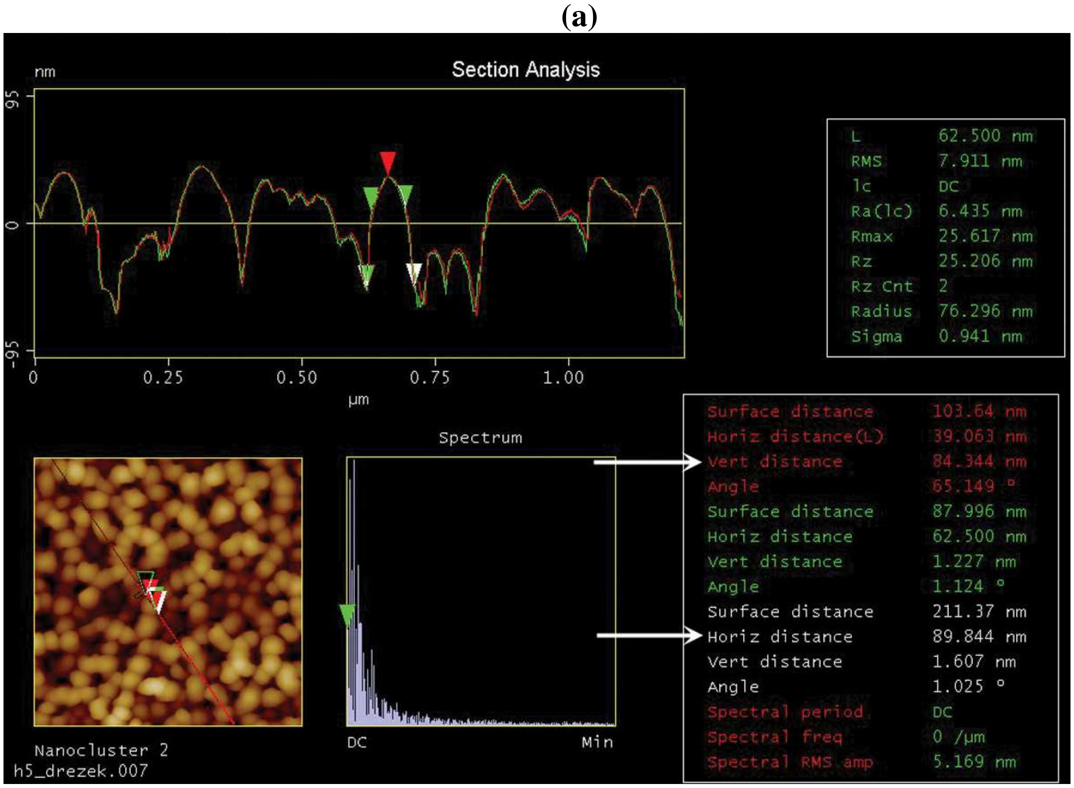


(b)

Figure S1. SEM images of SiGe nanocones tilted at 36 degrees, (a) a nanocone with its dimensions labeled, (b) nanocones of similar dimensions. Scale bar is 20 nm. The height given in (a) is tilt-angle-compensated.



(a)



(b)

Figure S2. AFM cross-section analysis of two nanocones: dimensions shown are base diameter (in red), peak radius (in green), and height (in white).

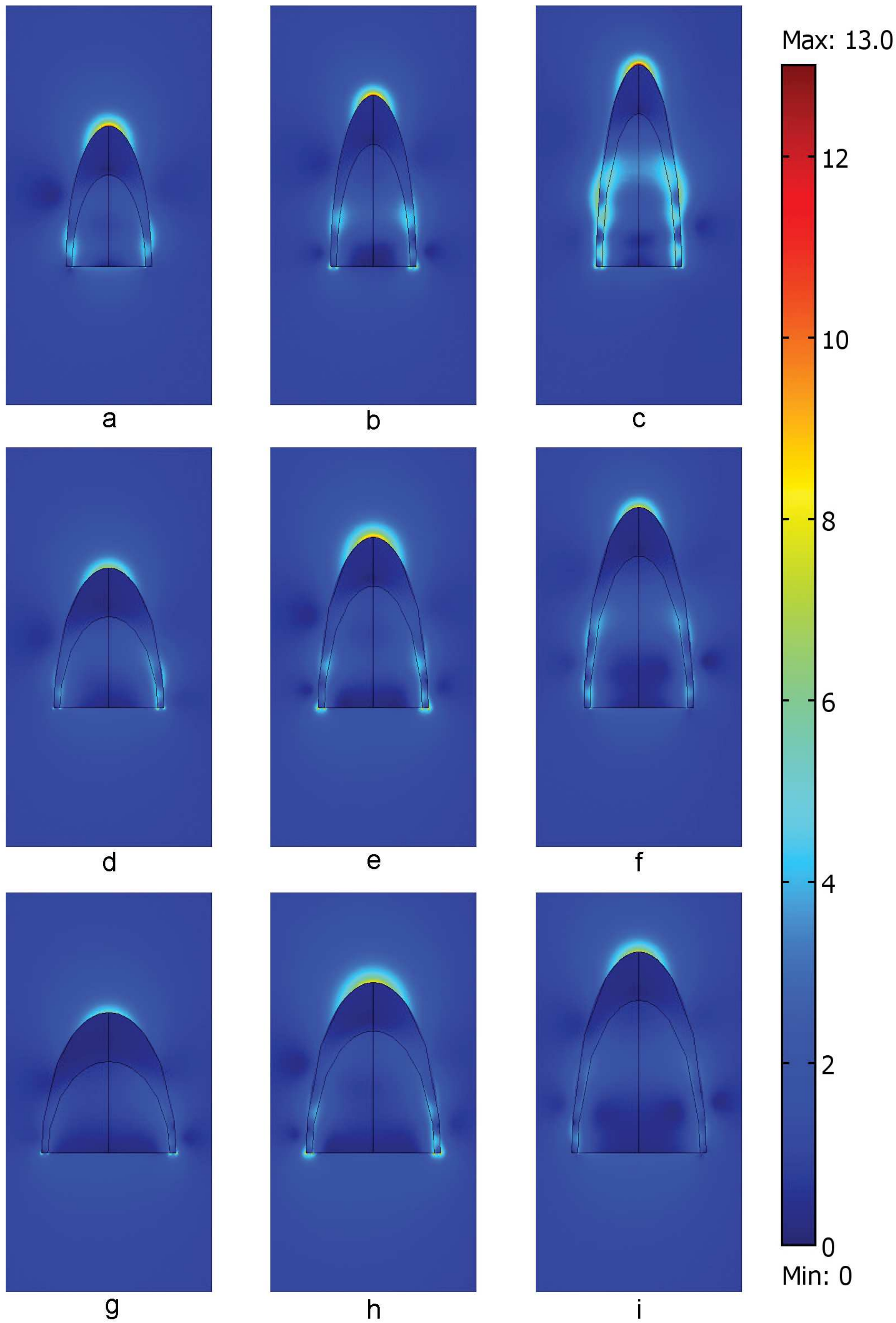
Table S1. Dimensions of the nanocones from section analysis in Figure S2.

	Peak curvature [nm]	Base diameter [nm]	Height [nm]
Nanocone 1 (Figure S2a)	63	92	105
Nanocone 2 (Figure S2b)	63	90	84

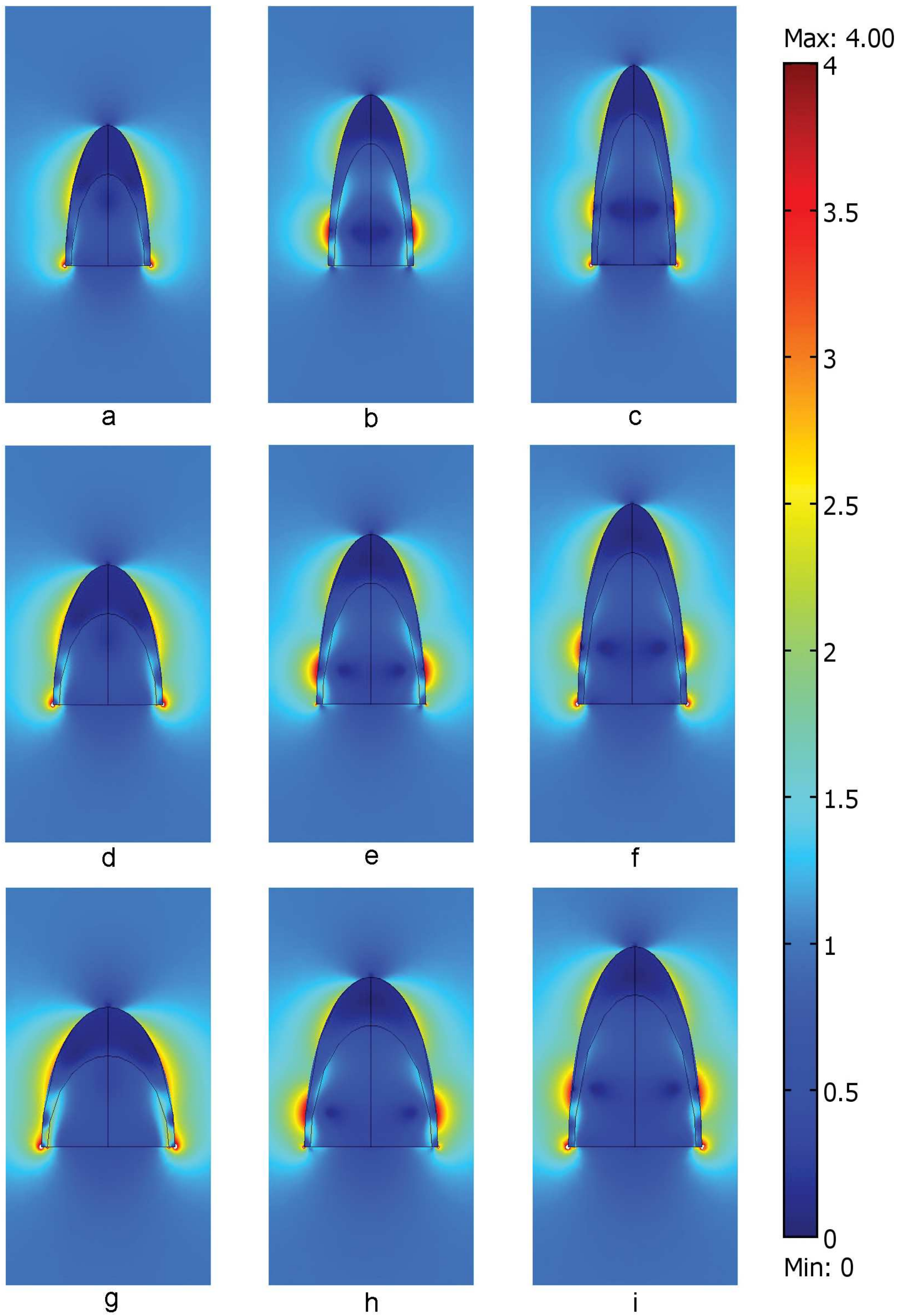
Geometry effect on the electric-field distribution on the nanocones

We provided in the manuscript the electric-field distribution on a nanocone with the specific dimensions (80 nm base and 100 nm height) at four different wavelengths and two excitation polarizations. AFM and SEM images, however, revealed a range of dimensions for the nanocones. Here we simulate SiGe nanocones with ±25% variations in base diameter and height from the aforementioned geometry while assuming the same thickness for the gold coating. The electric-field distributions at 785-nm excitation are plotted in Figure S3a for axial polarization and in Figure S3b for transverse polarization. The dimensions of the SiGe are listed in Table S2.

It can be observed that axial polarization still generates larger field enhancement than transverse polarization, as indicated by the color scale. For axial polarization, a sharper peak (*i.e.* resulted from a larger aspect ratio between the height and the base diameter) results in larger field enhancement (*i.e.* from left to right in each row). A more elongated nanocone also supports more modes along the sidewall. For transverse polarization, the peak curvature does not affect the field distribution due to left-right symmetry. A more elongated nanocone does not generate stronger field enhancement. Dipole resonances can be observed on the sidewall of the nanocone where the gold layer is thinner. Moreover, the strength of the field enhancement appears to be more sensitive to the height of the nanocone than to its base diameter. Overall, the behavior of the nanocone is similar among all geometries presented in Figure S3 and we expect the effect of variation in dimensions to be small on the enhancement characteristics of the nanocone substrate.



(a)



(b)

Figure S3. Normalized electric field distribution of the gold-coated SiGe nanocones with dimensions shown in Table 2, a) axial polarization, b) transverse polarization. For all geometries, the gold thickness is 40 nm on the peak and tapers down to 5 nm at the base. Excitation wavelength is 785 nm.

Table S2. Dimensions of the SiGe nanocones simulated in Figure S3. Base diameters in rows and heights in columns.

Base dia./Height [nm]	75	100	125
60	a	b	c
80	d	e	f
100	g	h	i

Incubation time *vs.* SERS intensities

To estimate an optimal incubation time in conjunction with the concentration of BPE solution, we incubated seven nanocone substrates in 5-ml solutions of 50-μM BPE solutions for 1, 6, 12, 18, 24, 48, and 72 hours, followed immediately afterward by SERS measurements. As shown in Figure S4, the intensity of the 1200 cm^{-1} mode increases approximately linearly from 1 to 24 hours, and gradually levels off around 48 hours. This observation led to the choice of the 24-hr incubation time, which is likely to produce a sub-monolayer surface coverage.

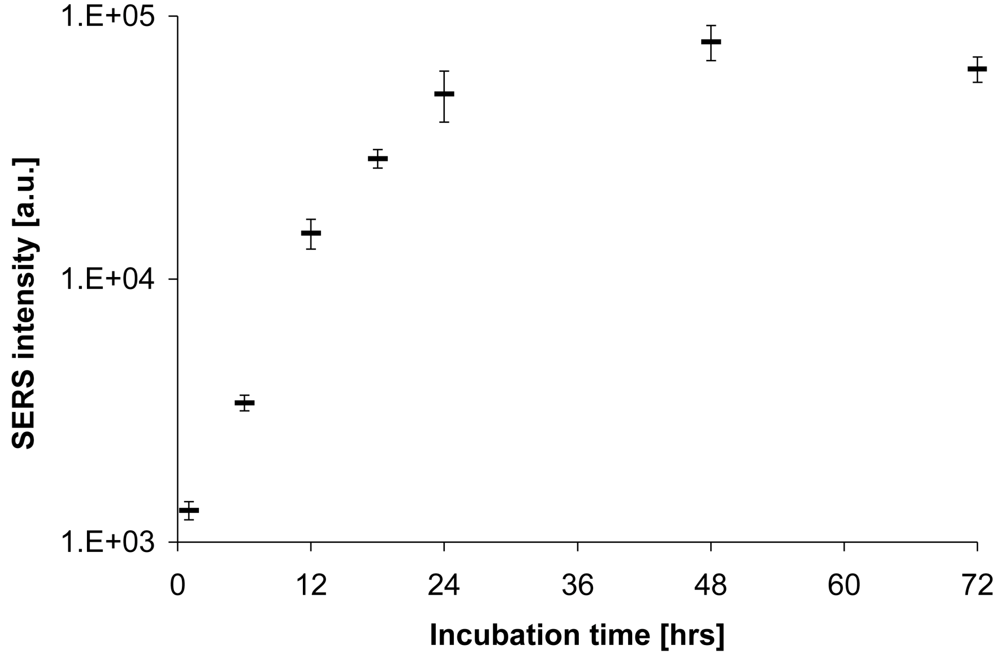


Figure S4. SERS intensity of the 1200 cm^{-1} mode from the substrate, which was incubated for different time periods.