Supporting Information for:

Surprisingly Long-Range Surface Enhanced Raman Scattering (SERS) on Multisegmented Nanowires

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Theoretical Calculations

The local electric field SERS enhancement factors $(|E|^2)$ of the cylindrical multisegmented nanowires (Figure S4) were calculated in vacuum using the discrete dipole approximation (DDA) method.¹⁻³ The structure used in the calculations consists of two Au nanodisks, each 120 nm in thickness and 360 nm in diameter, that are separated by a gap of 28 nm, plus a 600 nm Ni nanowire with 360 nm diameter that is separated from the nearest Au nanodisk by 120 nm (other nanowire lengths were considered, and these led to similar results). The grid size used was 4 nm. The quantity plotted in Figure S4 is $|E|^2$ with the initial polarization vector taken to be along the axis of the segments and initial wavevector pointing down (Other polarization directions produce smaller enhancements). The planes used for the SERS enhancement estimates were taken to be 4 nm away from Ni nanowire surface that is closest to the Au nanodisk pair. The electromagnetic enhancement was calculated by averaging $|E|^2$ over this surface. Enhancements were also calculated for the other possible particle surfaces, but the only one which shows significant enhancement with

the Ni nanowire/Au nanodisk pair structure compared to the Ni nanowire alone is the plane on the Ni nanowire that is nearest the Au nanodisk pair.

The SiO2 film is not included in these calculations, so a small blue shift in plasmon resonance wavelengths is expected from the model compared to the experiments, but otherwise the model structures are chosen to be realistic. The working wavelength used in calculating the enhanced local electric fields between the Au nanodisk pair is chosen to be the excitation wavelength of 632.8 nm in what we present. We also have examined results at 669 nm (the mean of the incident and Stokes-shifted wavelengths) and the results are similar.

(1) Qin, L.; Zou, S.; Xue, C.; Atkinson, A.; Schatz, G. C.; Mirkin, C. A. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 13300-13303.

(2) Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C. J. Phys. Chem. B 2003, 107, 668-677.

(3) Draine, B. T.; Flatau, P. J. "User guide to the Discrete Dipole Approximation Code DDSCAT 6.1" **2004**, <u>http://arxiv.org/abs/astro-ph/0409262v2</u>.



Figure S1. SERS spectrum of phthalic acid (benzene-1,2-dicarboxylic acid) on Au-Ni multisegmented nanowires. The intense $v_s(COO^-)$ mode of the carboxylic group at 1346 cm⁻¹ was used to generate all Raman images.



Figure S2. (a) Scanning electron microscopy and (b) optical microscopy images of three individual Au nanodisk pairs that are similar to the Au nanodisk pair in Figure 1a. (c) 2D-confocal Raman microscopy images of above Au nanodisk pairs created by integrating the intensity of the Raman spectra at 0 cm⁻¹ (reflection light), which indicates the position of the nanostructures during the Raman scanning. (d) 2D-confocal Raman microscopy images of above Au nanodisk pairs at 1346 cm⁻¹. No SERS of phthalic acid is observed for all three Au nanodisk pairs. (e) Top: Raman scattering of phthalic acid in solid; bottom: average of SERS of phthalic acid taken from the three Au nanodisk pairs.



Figure S3. (a) Scanning electron microscopy image of Au-Ni multisegmented nanowires: a 1.5 μ m Au nanowire (360 nm diameter) separated by 78 ± 8 nm from a 2.0 μ m Ni nanowire. (b) The corresponding confocal Raman microscopy images for nanowires in "(a)" functionalized with phthalic acid. (c) From top to bottom: Raman scattering of solid phthalic acid; SERS of phthalic acid taken from the Ni segment 78 nm from the Au nanowire (point B in (b)); SERS of phthalic acid taken from the other end of the Au nanowire that is not adjacent to the Ni nanowire (point A in (b)) and Ni segment end not associated with Au nanowire (point C in (b)). (d) Dark field extinction spectra of an individual Au nanowire (black) and a Ni nanowire (red). The red dotted line indicates the wavelength of the laser (632.8 nm) used in the Raman spectrum measurement.



Figure S4. Image shows the electric field enhancement factor $(|E|^2)$ of a nanodisk pair (dark blue rectangles, left) and a longer nanowire-like portion (dark blue large rectangle, right). The field enhancement is modeled at 632.8 nm radiation for a multisegmented nanowire that contains two 120 nm long Au nanodisks separated by a 28 nm gap and a Ni segment that is 120 nm from the Au nanodisk pair. The calculation was performed in vacuum using the discrete dipole approximation (DDA) method.