Electronic Supplementary Material (ESI) for Analyst

The Chemical Origin Of Enhanced Signals From Tip-Enhanced Raman Detection Of Functionalized Nanoparticles.

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Figure S1: (A) TERS map with simultaneously obtained topographic features and Raman characteristics from 50 nm biotinylated-GNP probe adsorbed onto a streptavidin surface. Scan size: 2x2 μm, step-size 55nm. Color represents the Raman intensity of a streptavidin marker band (816cm^{-1}). (B) Plot of the representative TERS spectra extracted from 5 pixels along the line y= 0.19 μm circled in (A). (1) x=1.81 μm, (2) x=1.75 μm, (3) x=1.69 μm, (4) x=1.64 μm, (5) x=1.58 μm.

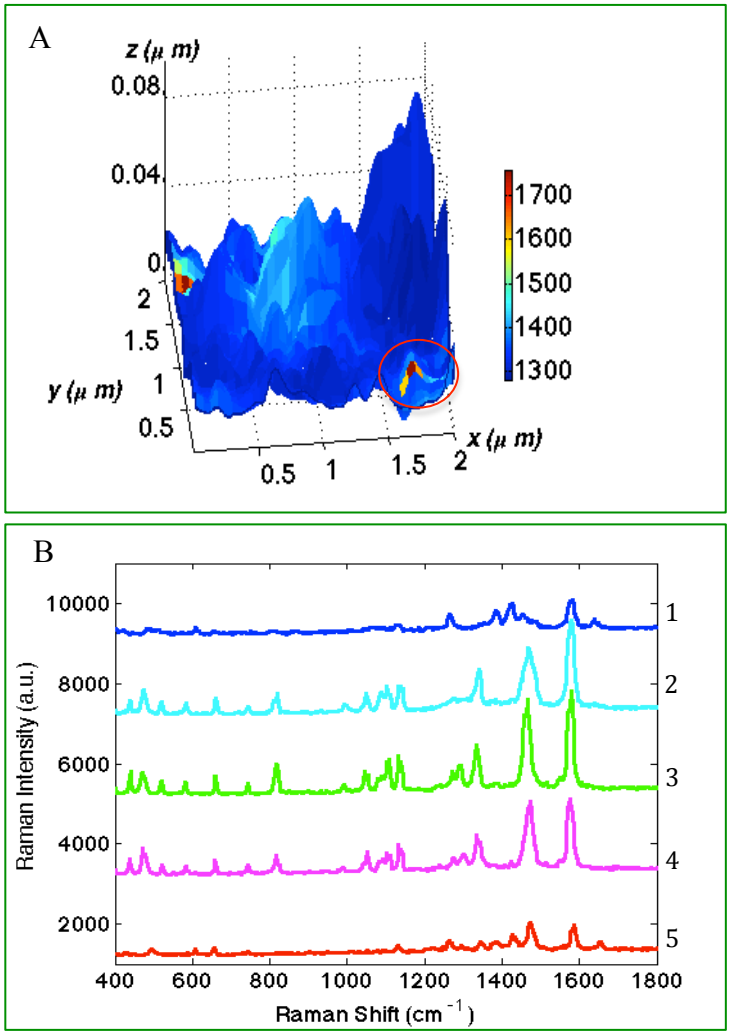
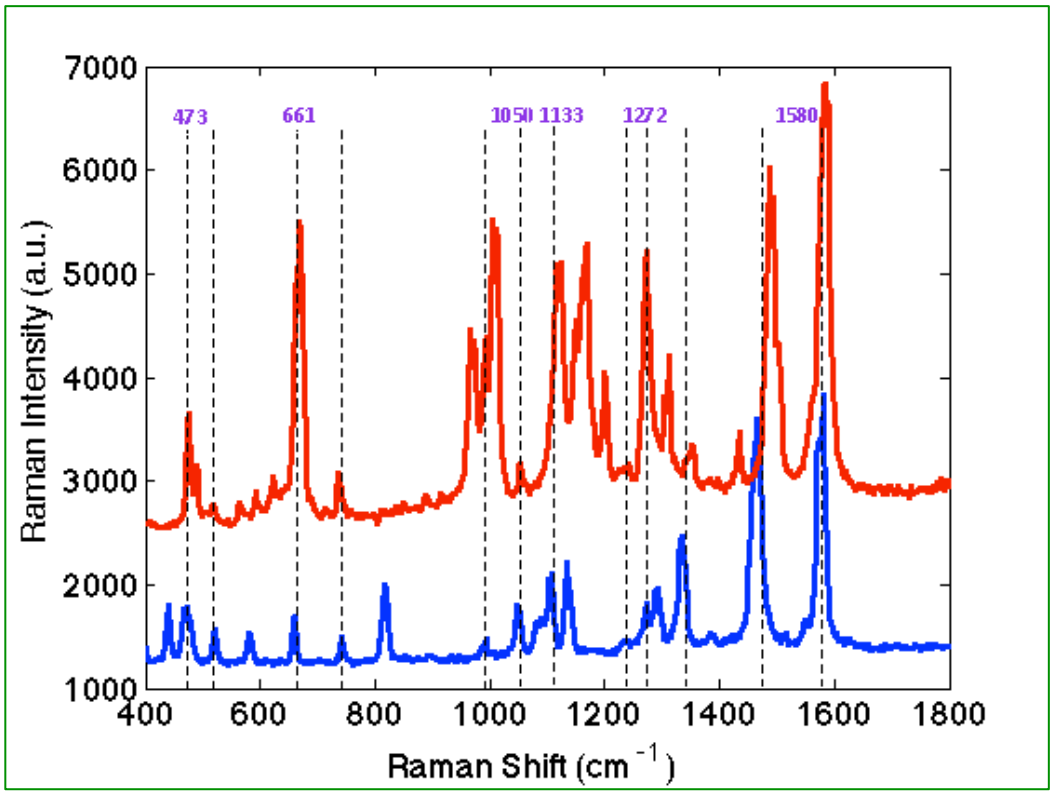


Figure S2: A comparison of TERS spectra from single biotinylated-GNP probes of different sizes bound to streptavidin derivatized slides: 80 nm biotinylated-GNP (red), 50 nm biotinylated-GNP (blue).



Peaks observed in both spectra include 473, 661, 742, 993, 1050, 1133, 1272, 1580 cm^{-1}, as shown in Table 1, attributable to Phe, ν-C-S, Trp(W18), Biotin/Phe, Biotin, Trp(W13), Biotin/AmideIII, ν-C-N respectively. These bands indicate the presence of biotin and various amino acid residues in streptavidin. Intensities of these bands vary depending on the size of the nanoparticle. Stronger signals were observed with the 80 nm biotinylated-GNP probe than the 50 nm, indicative of either a stronger electric field or a greater amount of analytes residing in the sampled volume by a larger plasmonic nanoparticle probe.