

# Nanogap Enhanced Raman Scattering

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## Abstract

A brief review of Single Molecule SERS area and recent activities of Laboratory for Advanced Molecular Probing (LAMP) of KRICT in this area will be presented.

**Keywords :** SERS(Surface-Enhanced Raman Scattering), Nanogap, Single Molecule Spectroscopy

Since smSERS (single molecule Surface-Enhanced Raman Scattering) was independently reported by S. Nie group and K. Kneipp group in 1997<sup>1,2</sup>, tremendous amount of interest has been shown to this field because Raman spectroscopy can provide molecular fingerprint together with multiplexing capability in bioassay. Regarding to the origin of this smSERS phenomena, so called "SERS hot spot", these two groups argued against each other for several years: Nie group argued sharp edge in nanostructure, such as corners of a silver nanorod or even of a single nanoparticle, can play as a hot spot of smSERS, while Kneipp group argued they could observe smSERS signal only from colloidal aggregation in solution. Later on, Brus group and others showed that SERS hot spots, formed at the junction of two nanoparticles, likely play a major role in smSERS<sup>3,4</sup>. Theoretical calculations also support that SERS electromagnetic enhancement factors (EEM) can approach up to ~10<sup>11</sup> when inter-particle spacing reach down to a few nanometer or less at the junction between nanoparticle pair. However, formation of these smSERS-active nanostructures, mostly dimer or colloidal aggregation of Ag or Au nanoparticles adsorbed with Raman active molecules (e.g., Rhodamine 6G), is a random process driven by salt-induced non-specific aggregation. This fact has been a main hurdle for smSERS toward advanced applications.

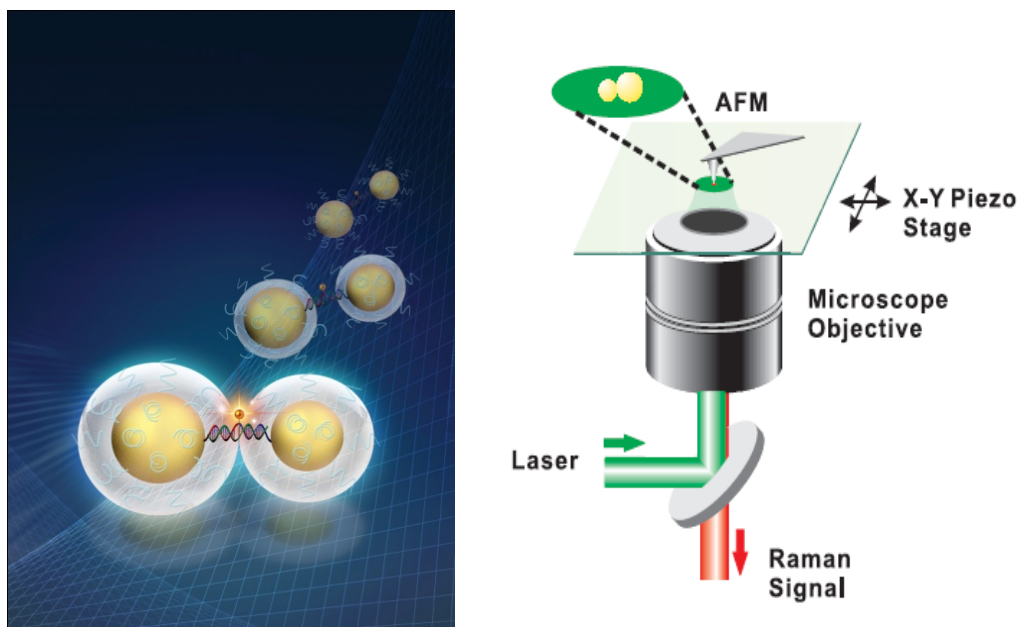


Figure 1: Nanogap-control by single-DNA-tethered heterodimeric Gold-Silver core-shell Nano Dumbbells (GSNDs) (left), and a schematic diagram for AFM-correlated single-particle nano-Raman measurement of the individual GSND particles (right).

Based on the idea that controlling this nano gap between two noble metal nanoparticles is the key to realize reliable smSERS, we have designed a gold-silver nano dumbbell (GSND) and Gold Nanobridged Nanogap Particles (Au-NNP). As for GSND, two gold nano particles with different sizes were linked to each other by double helix DNA (30mer), with a single Raman dye molecule at the center position, to fix the two at a known gap distance (~10 nm). Then we narrowed the gap down to < 1 nm by standard silver staining method to endow the GSND with single molecule sensitivity. We have successfully detected smSERS signals, as well as typical single molecular blinking and polarization behaviors, from each GSNDs by Nano Raman spectroscopy at the single particle level<sup>5</sup>.

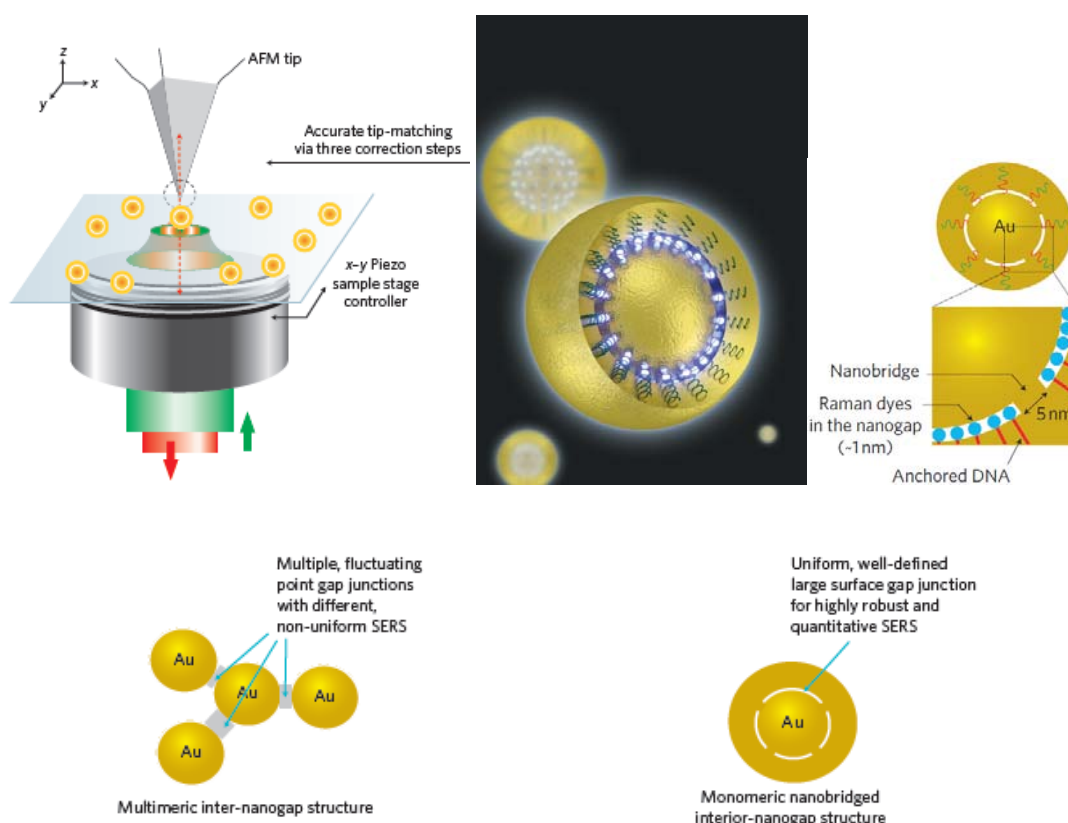


Figure 2: A schematic diagram for AFM-correlated single-particle nano-Raman measurement of the individual Nano-bridged Nanogap Particles (NNPs) (top-left), and Nanogap-control in the NNPs (top-right and bottom).

As for Gold Nanobridged Nanogap Particles (Au-NNP), hollow gap (~1 nm) between the gold core and gold shell can be precisely loaded with quantifiable amounts of Raman dyes labeled on DNA backbone which is anchored at the gold core and then covered by gold shell<sup>6</sup>.

## References

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