

Nanogap-Enhanced Raman Spectroscopy (NERS) controlled by DNA

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Since smSERS (single molecule Surface-Enhanced Raman Scattering) was independently reported by S. Nie group and K. Kneipp group in 1997 [1][2], 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”, Nie group argued sharp edges 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 [3][4]. Theoretical calculations also support that SERS electromagnetic enhancement factors can approach up to $\sim 10^{11}$ when inter-particle spacing reaches down to a few nanometer or less at the junction between two nanoparticle pair. However, formation of these smSERS-active nanostructures with a nano-gap at the SERS hot-spot junction, 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.

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) to exhibit Nanogap-Enhanced Raman Scattering (NERS) controlled by DNA. 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 [5]. As for Au-NNP, hollow spherical 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 [6].

1. S. Nie and S.R. Emory, *Science* **275**, 1102 (1997).
2. K. Kneipp, Y. Wang, H. Kneipp, L.T. Perelman, I. Itzkan, R.R. Dasari, and M.S. Feld, *Phys. Rev. Lett.* **78**, 1667 (1997).
3. A.M. Michaels, M. Nirmal, and L.E. Brus, *J. Am. Chem. Soc.* **121**, 9932 (1999).
4. Y.D. Suh, G.K. Schenter, L. Zhu, and H.P. Lu, *Ultramicroscopy* **97**, 89 (2003).
5. D. Lim, K.-S. Jeon, H.M. Kim, J.-M. Nam, and Y.D. Suh, *Nature Materials* **9**, 60 (2010)
6. D. Lim, K.-S. Jeon, J.H. Hwang, H.Y. Kim, S.H. Kwon, Y.D. Suh, and J.-M. Nam, *Nature Nanotechnology* **6**, 452 (2011).