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Coupled plasmons of nanoparticles for single molecule spectroscopy and nanoscopy

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ABSTRACT

Noble metal (Ag or Au) nanoparticles and nanostructures exhibit useful optical responses such as field enhancement and resonance shifts. Such properties can be utilized for ultra-sensitive spectroscopy of small organic molecules and optical imaging with sub-diffraction limit spatial resolution. Here, I will introduce what is currently possible with such optical properties for single-molecule vibrational spectroscopy and nano-scale optical imaging.

1. INTRODUCTION

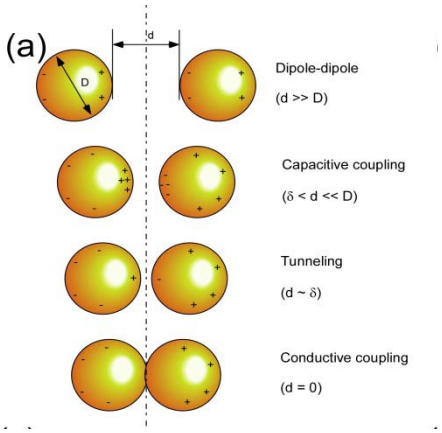

Fig. 1. Schematic illustration of plasmonic coupling of nanoparticles

Optical excitation of silver or gold nanostructures leads to coupled oscillation of conduction electrons of metals (e^-) and the electromagnetic field nearby (E_{loc}). Such coupled oscillation is called the localized surface plasmon (LSP). Such LSP of nanostructures leads to drastic enhancement of electric field around the structure, which is called the local field enhancement. In addition, the LSP oscillation has, as in

mechanical oscillator, characteristic resonance frequencies, which sensitively changes with the dielectric functions of surrounding environment. When two or more nanoparticles are brought close together, the characteristics of respective LSPs change, resulting in coupled plasmon modes. In particular, when the separation between the two nanoparticles are much smaller than the sizes of the nanoparticles, positive charges of one nanoparticle and the negative charges of the other particle strongly attract each other, resulting in extremely strong local field at the inter-particle gap, and also the plasmons of the dimeric structures are completely changed. The intensities of strongly localized field at the gap can be 10,000 times stronger than that of excitation light, and as such the gap-plasmons can be used to amplify weak spectroscopic signals from the molecules positioned at the gap. Such coupling not only allows one to observe faint spectroscopic signals of molecule, but it also allows one to develop a microscopy technique that beats optical diffraction limit of light microscopy. Below, we outline the technique that can directly visualize the localized surface plasmons of nanoparticles, and gap-plasmon enhanced Raman spectroscopy of individual molecules.

2. DIRECT VISUALIZATION OF LOCALIZED PLASMON MODES

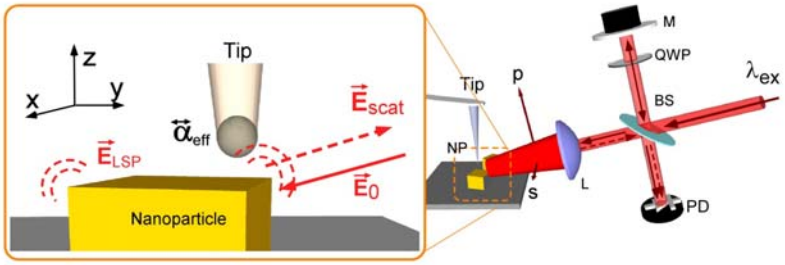

Fig. 2. The operation principle of the sSNOM (left) and the detailed detection schemes (right). E_{scat}= scattered field, E_0 = incident field, and E_{LSP}= localized plasmonic field, α_{eff} = effective polarizability of the tip, M = mirror, QWP= quarter-wave plate, BS = 50/50 beam splitter, NP = nanoparticle, and PD = photodiode.

To visualize the LSP modes of nanoparticle directly, we employ the scattering-type scanning nearfield microscopy [1] (sSNOM, Figure 2). The setup is a combination of a laser, a tapping mode atomic force microscope (AFM), a Michelson interferometer and a photo-diode. Linearly polarized light from a laser is focused onto the tip-sample junction via an objective lens. Back-scattered light from the tip-sample junction is collected by the same lens and interferometrically detected. The tip-end serves as a dipole-polarizable nanosphere that samples the intensity and phase of the plasmonically enhanced local field just above the nanostructure.

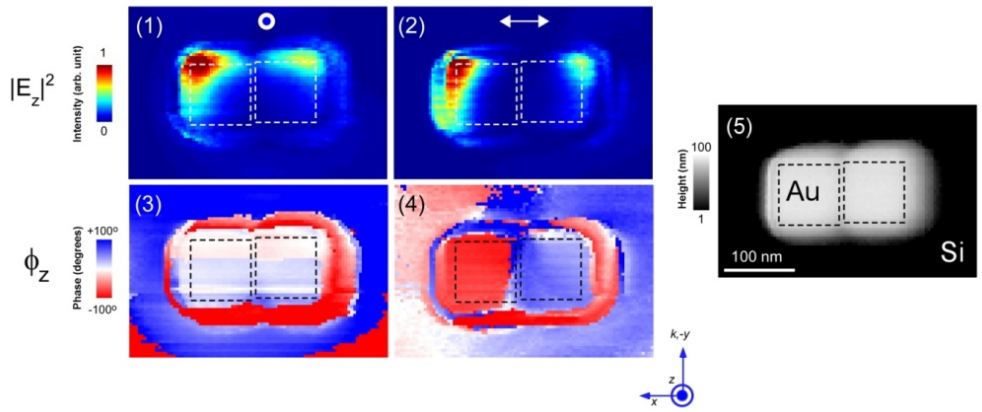

Fig. 2. Coupled LSPs of nanocube dimer obtained with Si-tip. 1&2, sSNOM intensity, 3&4 phase, and 5, topography images of a nanocube dimer obtained with p- (1 and 3) and s- polarized (2 and 4) λ_{ex} = 633 nm light. White arrows represent the excitation polarization directions, dotted squares represent the expected positions and sizes of nanocubes, and scale bar represent 100 nm.

Figure 2 shows an example of the coupled LSP mode of a dimeric Au nanocube imaged by sSNOM technique, in which we can clearly observe a characteristic capacitively-coupled dimeric plasmons. The near-field images of self-assembled nanocube dimers (interparticle distance/particle size ~ 0.04) reveal anti-symmetric field distributions that are qualitatively different from those of the monomers and, which is are fully reproduced by the electrodynamic simulation. The results definitely confirm that, for the closely-spaced dimers, the Coulombic attraction between the charges at the inter-particle gap dominates over the intra-particle charge oscillations, resulting in a hybridized dimer plasmon mode that is qualitatively different from a the simple superposition of the two dipolar plasmons.

3. DETECTION OF A SINGLE-MOLECULE USING A GAP-PLASMON

We have measured the surface-enhanced Raman scattering (SERS) of individual gold nanoparticle –molecule – gold film junctions to investigate the SERS spectra of individual organic molecules. The characteristic spectral shift of Raman peaks and the temporal on / off blinking allows us to unambiguously prove that overall (chemical and and electromagnetic) enhancement of ~10^7 is sufficient to observe the single-molecule SERS of an electronically off-resonant molecule [2].

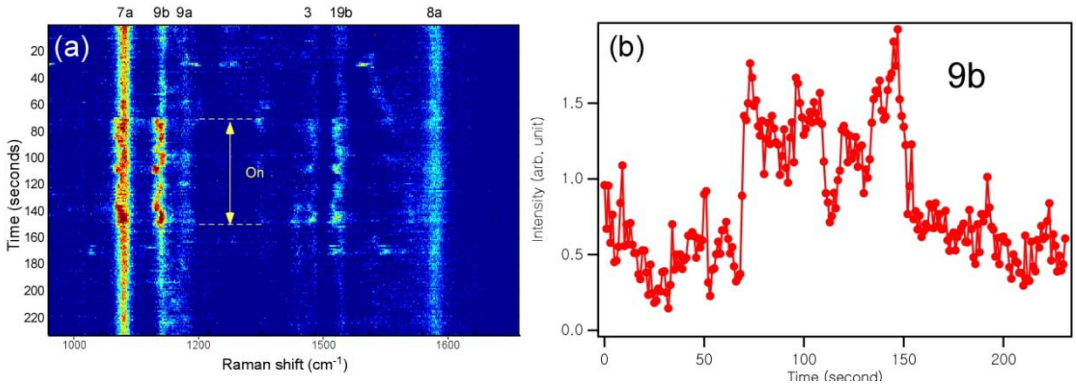

Fig. 3. Examples of single-molecule SERS trajectories that show mode-specific on / off blinking. (a) The SERS trajectory that shows off / on events. Sampling time is 1 second. (b) Intensity trajectory of 9b-band sampled from (a).

3. CONCLUSIONS

To conclude, one can make, measure, and model the plasmonic nanostructures and associated plasmon modes with modern near-field microscopy and spectroscopic techniques. Such well-defined plasmons can be used to detect the vibrational spectra of individual molecules, which reveals 1 nm scale heterogeneity of metal-molecule interfaces, and quite possibly the chemical reaction at metallic surfaces.

4. REFERENCES

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