博士論文（要約）

Coupled plasmons in nanosphere architecture for surface-enhanced Raman scattering

（金ナノ粒子の配列構造体によるプラズモン結合と表面増強ラマン散乱への応用）

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Miniaturized optical sensors with high sensitivity are beneficial for both human health, and society itself. In particular, surface plasmon resonance (SPR) based detection has been used to develop high sensitivity, fast detection, and high throughput devices that operate with tiny sensing volumes. SPR can be defined as the collective oscillations of free electrons at the boundary between a metal and a dielectric excited by an incident light wave. SPR sustains an evanescent field which rapidly decays with distance from the metal interface, enabling effective surface specific sensing. There are two main types of SPR. One is propagating surface plasmon resonance (PSPR) which can exist at the interface between a thin flat metal film or periodic metallic nanostructures and surrounding dielectric medium, such as gratings, and can be observed by a sharp reflectance or transmittance peak. The other type of SPR is localized surface plasmon resonance (LSPR), which occurs at the surface of metal nanoparticles and results in strong electromagnetic field enhancement. SPR and the aforementioned extensive applications are now positioning themselves as a cutting-edge academic field of research.

LSPR, supported by rapid progress in nano-fabrication technology, and the electromagnetic (EM) field enhancement LSPR provides has enabled novel optical bio-sensing, image processing, and spectroscopy technologies that go beyond the diffraction limit. Recent studies have proven that nanoparticles in close proximity result in coupled plasmons that have strong EM enhancement in the interparticle gaps, called hot spots. Such hot spots can be used in surface-enhanced Raman spectroscopy (SERS) to detect low concentrations of molecules, even single molecules. Gap sizes on the order of several nanometers contribute to large EM enhancements, however the resulting

SERS intensity is found to drastically vary with the size of the small gaps, resulting in lower robustness in terms of reproducibility and quantification.

In this regard, the interaction between a metallic nanoparticle and an underlying film (sphere-film in contact system) is attractive for SERS system for both scientific and engineering reasons. From a scientific point of view, the sphere-film system reveals novel plasmonic phenomena resulting from the interaction of the LSPR resonant nanoparticle and its mirroring charges within the film, which is called plasmonic hybridization. From an engineering point of view, the sphere-film system offers robust geometrical stability providing reproducibility with an easy and low-cost fabrication. Additionally it produces strong enhancement features at sphere-film gap region which is highly attractive in plasmonics and SERS applications.

In this dissertation, we first present how plasmon coupling provides EM enhancement in interparticle gap and sphere-film gap based on fundamental principles. Taking the sphere-film structure as a starting point for its straightforward fabrication technique and well-controlled gaps, we propose a novel nanosphere architecture with aligned gold nanospheres on a metallic thin film for SERS. We show two original nanostructure designs, one being closely spaced gold nanosphere chains (SNC; short nanosphere chain) on Pt mirrors, and the other being gold nanosphere arrays trapped inside inverse pyramidal holes (SIP; spheres in pyramids).

For the SNC arrays, we shows as theoretical study of the plasmonic coupling in the horizontal (interparticle coupling) and vertical (sphere-film coupling) directions. Further we study how SNC arrays achieve effective light concentration by investigating the near-field behavior of the light as the chain length is varied. For the SIP arrays, we exploit a sphere-film contact system in more prominent and direct way. We demonstrate the enhancement of the SIP by focusing on gap plasmons produced by the sphere-film system. We explain the novel plasmonic properties of the SIP arrays found by the mirroring of gap plasmons which has not been reported before. The fabrication techniques used in the making of the SNC and SIP arrays are described in detail, and the SERS results are discussed. For the SIP arrays, we shows quantitative SERS results and compare them to results obtained with the sphere-film structure with ultra-thin spacer (0.6 ~ 0.8 nm) which is theoretically accepted to produce near to maximum of achievable plasmonic enhancement.