審査の結果の要旨

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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）

PhD thesis defended by Yaerim LEE

Plasmonic nanostructures have been used in a wide range of applications covering bio-sensing and light energy conversion. Plasmonic resonances confine light on nanostructures and therefore enhance light-matter interaction, enabling superior energy conversion and sensing performance. The plasmonic nanostructures consist of metal nanoparticles, which can be assembled from colloidal solutions. The particles dispersed in colloids are available in a wide range of sizes, shapes and materials, so that colloids are widely used in the fabrication of plasmonic structures. Colloids have been used to obtain randomly dispersed particles on substrates. However, a control of the particle spatial arrangement at the nanometer level is predicted to result in enhanced properties. Particularly the formation of nanogaps between nanoparticles is being extensively investigated. To achieve such high enhancements, further investigations into particle configurations and their respective fabrication techniques are required. LEE proposes two types of particle configurations, namely, aligned spheres on a mirror and trapped spheres in inverse pyramids.

The manuscript consists of five chapters.

Chapter One introduces surface plasmons and their ability to produce very large electric field on metal nanostructure surfaces. The enhancement of the electric field arising from surface plasmons is first quantitatively described in the case of a single metal nanosphere. Then, the case of the nanosphere dimer is considered to introduce plasmons coupling and define gap plasmons. The geometry of the sphere on film systems is then introduced and the plasmons coupling for the sphere-film geometry explained. Advantages of the sphere-film geometry in forming small and reproducible gaps near the sphere-film contact point and the large enhancement of the electric field in these gaps are emphasized. The potential of fabricating nanostructures sustaining robust and high electric field enhancement for sensing purposes based on the sphere-film geometry is mentioned. The basic principles of surface enhanced Raman spectroscopy are delineated.

Chapter Two described the performance of the sphere-film structure in terms of electric field enhancement and observed SERS spectra. This chapter introduces the calculation done on the sphere-film geometry and reports the dependence of the enhancement on the incidence angle of light. This will be used in Chapter five to understand the property of the sphere in pyramid. Also, the experimental technique is first described, and explanations are given about the normalization of the SERS signal, cleaning of the colloids and the use of a spacer of a known thickness between the sphere and the film as a reference for SERS signal comparison purposes.

In Chapter Three, aligned spheres standing on a film and separated by a gap is investigated to understand how light can be concentrated in the gaps between the spheres standing on a mirror. Plasmons coupling is found to control the light “focusing” behavior of the aligned sphere configuration. To control the gap distance between the spheres, LEE develops a fabrication technique resorting on a resist pattern that controls the gap and can be removed. Although the technique is successful in forming 10-nm gap, it involves a sequence of complicated steps not amenable to production. Due to the effective light concentration of the structure, the aligned sphere structure demonstrates strong surface enhanced Raman scattering.

In Chapter Four, gold nanospheres trapped in inverse gold pyramids is proposed as a plasmonic nanostructure and applied to surface enhanced Raman spectroscopy. The nanostructure achieves high electric field enhancement as evidenced by its sensitivity toward a monolayer of benzenethiol molecules adsorbed on the nanostructure. By trapping single colloid nanoparticles in inverse nanopyramids, LEE obtains a complex structure with well-defined nanogaps that cannot be fabricated by a top-down technique because the gap dimensions are in the range of a few nanometers, which is beyond the resolution limit of electron-beam lithography, and the gaps have three dimensional shapes. The sphere in the pyramid structure concentrates light in the structure due to a quadrupolar-like charge distribution on the nanosphere and strongly amplify the Raman signal of the target molecules giving a finger print signature of the molecules even at very low concentration. LEE investigates theoretically the three-dimensional nanostructure consisting of an array of single nanosphere trapped in inverse pyramid. The region near the contact points between the sphere and the inverse pyramid surface exhibits very high electric field enhancement due to hybridization of the gap mode plasmon and film plasmon. The sphere-in-pyramid configuration enables charge to accumulate in the vicinity of the contact points and therefore achieves high electric field enhancements. The accumulation of charges for the sphere-in-pyramid resonance contrasts with the charge transfer for the conventional sphere-on-film resonance, for which the charges flow through the contact points and hamper electric field enhancement. The charge distribution of the sphere in sphere-in-pyramid structure appears in the form of a quadrupole-like distribution. The performance of the field enhancement for the sphere-in-pyramid structure is given in terms of the percentage of the maximum enhancement of the electric field obtained for a nanogap (0.7 nm) separating a sphere from a film. It is noted that this structure has not been applied in sensing because the field is enhanced in the nanogap or spacer which is made before exposure to target molecules. The proposed structure achieves 55% of the maximum electric field enhancement obtained with the 0.7 nm nanogap.

The conclusions of the manuscript are given in Chapter Five.

In summary, LEE thesis introduces an original nanostructure consisting of spheres trapped in inverse pyramids (sphere-in-pyramid structure) for use in sensing and offers new physics with the explanation of the origin of the high charge concentration developed in the sphere-in-pyramid structure. Also, LEE demonstrates state-of-the-art nanofabrication for the proposed sphere-in-pyramid structure and reports an improved sensitivity toward adsorbed molecules using surface enhanced Raman detection.

LEE has published ten journal papers, among which three were as a first author (ACS Photonics, Appl. Phys. Lett., Sens. Actuators B) and five were as a second author.

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