MONOTONIC TUNING OF PLASMON RESONANCE USING DEFORMABLE NANOPLASMONIC MEMBRANE FOR SURFACE-ENHANCED RAMAN SCATTERING

M. Kang, J. -J. Kim, Y. -J. Oh and K.-H. Jeong*
* Korea Advanced Institute of Science and Technology (KAIST), Korea
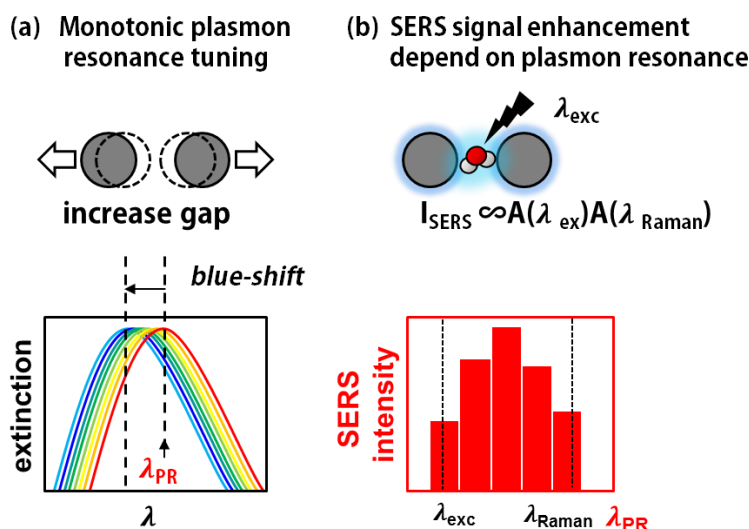
ABSTRACT

Localized surface plasmon resonance (LSPR) is strongly associated with inelastic scattering of biochemical molecules near metal nanostructures, i.e., surface enhanced Raman scattering (SERS). Systematically exploration of the relationship between surface-enhanced Raman spectroscopy (SERS) and the plasmon resonance wavelength has been an experimental limitation due to the lack of reliable and tunable techniques for controlling the LSPR wavelength. In this work, plasmon resonance was actively tuned by mechanical stretching with 1nm resolution for direct investigating of the relationship between the plasmon resonance and SERS. The functional substrates feature nanoplasmonic metal nanostructures on a stretchable elastomer. The elastomeric membrane is uniformly deformed in all directions, resulting in precise change of inter-particle distance. The inter-particle distance gives dynamic tuning of plasmon resonance. The SERS signal enhancement is directly observed by changing the plasmon resonance. This work enables as a guideline for how to select plasmon resonance of substrates to achieve extreme sensitivity of SERS for targeted molecule.

KEYWORDS Plasmonics, SERS, Localized surface plasmon resonance

INTRODUCTION

Plasmonics has become a promising technology that aims to exploit the unique optical properties of metallic nanoparticles. The signature optical property of theses metallic nanoparticles is the localized surface plasmon resonance (LSPR) that is charge density oscillations confined to metallic nanoparticles. The wavelength corresponding to the extinction maximum, λ_{PR}, of the LSPR is highly dependent on the size, shape, and dielectric properties of the metal nanostructures. Whereas theoretical and experimental studies of the role of these properties provided a fundamental understanding of how plasmons are influenced by local structure and environment, the LSPR as a sensing modality for detecting molecules of both biological and chemical interest led to the field of surface-enhanced Raman scattering (SERS). The highly sensitivity of SERS is achieved through the strong coupling between the LSPR of substrates, excitation laser and vibrational mode of a molecule. Therefore, the tunability of plasmon resonance holds great promise for high sensitive SERS and it is desirable to design the SERS substrate that it's the LSPR wavelength suitable for excitation laser and targeted molecules. However, the relationship between plasmon resonance and SERS enhancement was not clearly revealed due to the lack of reliable and tunable techniques. Alternative approach utilizing optical, electronic[1,2], ferroelectric[3], or thermal[4] methods has been reported as a part of active plasmonics. However, those previous works for tuning of the LSPR wavelengths by changing dielectric properties have remaining problem for practical SERS application including small range of tuning, limitation of the number of data point, slow speed, and high cost fabrication.

Here, we report a monotonic tuning of plasmon resonance using mechanical stretching. An elastomeric membrane with silver nanoislands on an elastomeric chamber is continuously deformed into a concave shape by applying negative pressure drop. The plasmon resonance of metal nanoislands is monotonically blue-shifted due to the increase of the nanogap spacing between those neighboring nanoislands. Uniform and stable stretching of the elastomeric membrane allows large, and continuous adjustment in the plasmon resonance. This device can be utilized for investigating the selection rules for determining the plasmon resonance to induce highly intense surface enhanced Raman scattering. (Figure1)

(a) Monotonic plasmon resonance tuning

increase gap

blue-shift

extinction

λ_{PR}

λ

(b) SERS signal enhancement depend on plasmon resonance

λ_{exc}

$I_{SERS} \propto A(\lambda_{ex})A(\lambda_{Raman})$

SERS intensity

λ_{exc} λ_{Raman} λ_{PR}

Figure1. Monotonic tuning of plasmon resonance by mechanical stretching and SERS signal enhancement depend on plasmon resonance. (a) The plasmon resonance of metal nanoislands on an elastomeric membrane is monotonically blue-shifted due to the increase of the spacing between those neighboring nanoislands. Uniform and stable stretching of the PDMS membrane allows large and continuous adjustment in the plasmon resonance (λ_{PR}). (b) Maximum SERS enhancements are obtained when the plasmon resonance wavelengths match with the center wavelength of excitation and Raman shifted wavelength.

EXPERIMENT AND RESULT

Micro-nanofabrication procedures for deformable nanoplasmonic membrane are shown in Figure2. The device was fabricated by transferring silver nanoislands onto a thin elastomeric membrane of polydimethylesiloxane (PDMS). The uniform formation of silver nanoislands was done by solid immersion metal dewetting (SIMD). First, fluorocarbon thin film as an anti-adhesion layer is deposited on a borofloat wafer by using plasma enhanced chemical vapor deposition. Thin silver film is thermally evaporated on the thin fluorocarbon film, followed by spin-coating of uncured PDMS. After curing the PDMS, silver nanoislands were formed and simultaneously transferred on to the PDMS by thermal annealing. An elastomeric membrane with silver nanoislands is deformed into a concave shape by applying negative pressure drop. The relationship between the thin circular membrane center deflection and the applied uniform pressure can be approximated by by solving differential equations for bending of a uniformly loaded distensible circular plate.
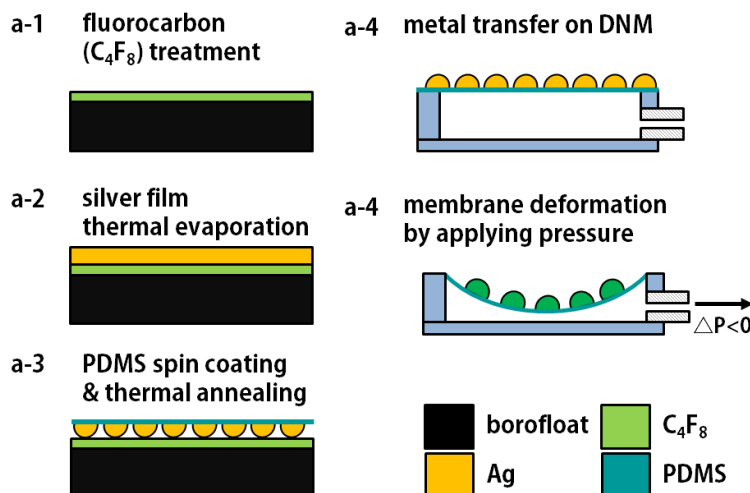
Figure2. Micro- and nanofabrication of deformable nanoplasmonic membrane. Large area deformable nanoplasmonic membrane with uniform silver nanoislands were fabricated by using solid immersion metal dewetting (SIMD) and metal transfer to PDMS. Thin silver film was thermally evaporated on the thin fluorocarbon film. 100 µm thick PDMS monomer was spin-coated on the silver film and cured at room temperature. The thin silver film between fluorocarbon and PDMS was annealed on a hot plate at $120\,℃$ for 180 minutes and transformed into silver nanoislands. Finally, the thin PDMS membrane with silver nanoislands was permanently bonded to a thick PDMS slab with a hole and microfluidic channel by using an oxygen plasma treatment. The nanoplasmonic membrane was deformed into a concave shape by applying negative air pressure drop through the channel.

Several silver nanoisland arrays with different size and inter-particle spacing were fabricated by varying initial thickness of silver film. The plasmon resonance wavelength has been characterized by using deformable nanoplasmonic membrane. The plasmon resonance of silver nanoislands is monotonically blue-shifted due to the increase of the nano gap spacing. Normalized extinction spectra of an initial film thickness 9nm and 12nm are presented in Figure3(a-top). The plasmon resonance wavelength tuning is plotted as a function of strain and initial film thickness in Figure3(a-bottom). The results obviously show that nanoplasmonic membrane's color is blue-shifted as strain and initial film thickness increased.

The enhancement of SERS signals were experimentally demonstrated by using deformable nanoplasmonic membrane with initial film thickness 9nm by controlling the plasmon resonance wavelengths. The plasmon resonance wavelength was continuously tuned by using deformable nanoplasmonic membrane with the tuning range by 40 nm, i.e., from 524 nm to 484 nm. SERS signal was obtained using Crystal violet 100µM with 488nm excitation. The five peaks of Crystal Violet, in descending cm^{-1} shift order, correspond to the following molecular vibrational modes: in-plane C-C, stretching vibration of N-phenyl ring, C-H in-plane bending, and C-H out-of plane bending. They are located at approximately 1625, 1400, 1187, 931 and 838cm^{-1}. With the 488nm laser-excitation, these peaks are located, on the wavelength scale, at approximately 530, 524, 518, 511, and 508nm respectively. Figure 3(b-top) shows that SERS signal of crystal violet 100µM (vertically offset for clarity) when the plasmon resonance of deformable nanoplasmonic membrane were λ_{PR}=524nm, 504nm, and 488nm, respectively. SERS signal intensities at one of the major Raman-shifted wavelength (1400cm^{-1} or 524nm with the 488nm laser-excitation) are plotted as a function of the plasmon resonance (λ_{PR}) in Figure3(b-bottom). SERS signals demonstrate maximum enhancement at plasmon resonance λ_{PR}=504nm, which is the center wavelength of excitation and Raman shifted wavelength. It clearly shows that the maximum of the SERS effect to depend on both excitation and Raman scattering wavelength. This dependence is in good agreement with the surface induced Raman intensity in the case of island film. The product of optical extinction signals at both Raman wavelength and excitation wavelength becomes maximize when the plasmon resonance wavelength is equal to $(\lambda_{ex}+ \lambda_{RS})/2$.
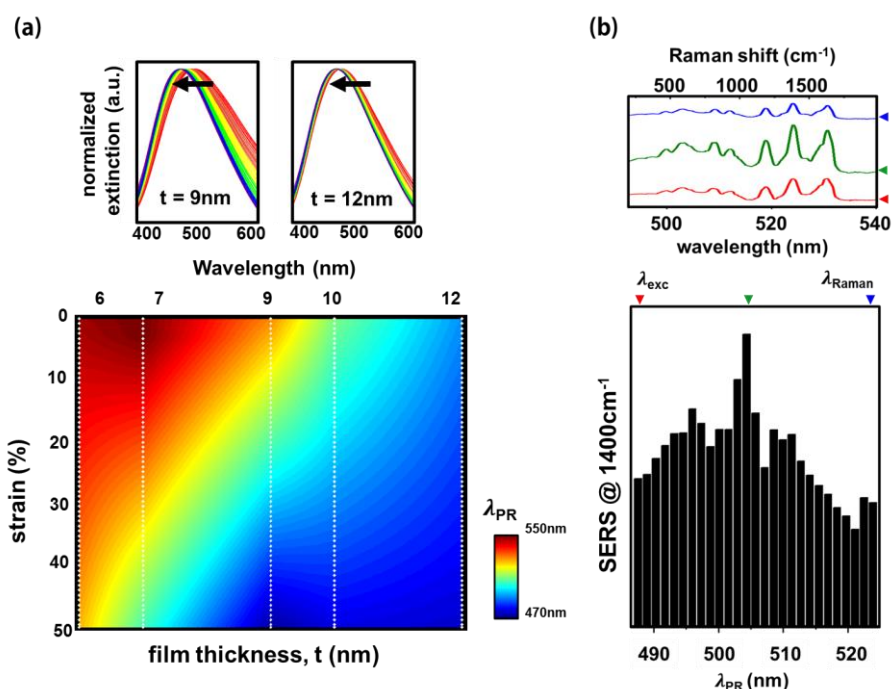
Figure3. (a) The plasmon resonance has been characterized by using deformable nanoplasmonic membrane of silver nanoislands. The plasmon resonance is blue-shifted as the mechanical strain (top). The plasmon resonance tuning is plotted as a function of strain and initial film thickness. The plasmon resonance is blue-shifted as strain and initial film thickness increased (bottom). (b) Enhancement of SERS peaks depending on the plasmon resonance. The plasmon resonance wavelength is continuously changed by using the deformable nanoplasmonic membrane. SERS signal of crystal violet 100μM (vertically offset for clarity) when the plasmon resonance of deformable nanoplasmonic membrane were λ_{PR}=524nm, 504nm, and 488nm respectively. SERS signals at major Raman scattering wavelength (1400cm^{-1}) vary with the plasmon resonance changes. (SERS intensities are divided by the scattering intensity) SERS signals demonstrate maximum enhancement with plasmon resonance λ_{PR}=504nm, which is the center wavelength of excitation and Raman shifted wavelength.

To conclude, this work directly shows systematic investigation of the relationship between the plasmon resonance and SERS by using active plasmonics. Until now the study of the correlation between the plasmon resonance and SERS was indirectly carried out on ensembles of discrete nanostructures fabricated by electron beam lithography or nanosphere lithography. However, the matching condition between the incident wavelength, Raman shifted wavelength, and the plasmon resonance wavelength is difficult to guarantee without precise control over the plasmon resonance control in the order of 1nm or less. The precise control of the plasmon resonance wavelengths in the order of 1nm by employing active plasmonics enables to understanding these relationship with SERS. In this work, plasmon resonance was actively tuned by mechanical stretching with 1nm resolution for direct investigating of the relationship between the plasmon resonance and SERS. The functional substrates feature nanoplasmonic metal nanostructures on a stretchable elastomer. The circular elastomeric membrane is uniformly deformed in all directions, resulting in precise change of inter-particle distance. The inter-particle distance gives dynamic tuning of plasmon resonance. The SERS signal enhancement is directly observed by changing the plasmon resonance. This research enables as a guideline for how to select plasmon resonance of substrates to achieve extreme sensitivity of SERS for targeted molecule. Selection rule and active platform will allow the Raman detection of low concentration level molecules. In particular, active platform can also be integrated with diverse techniques of nanofluidic manipulation for advanced high-throughput small molecular bioassays.

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CONTACT
Ki-Hun Jeong +82-42-350-4323 or kjeong@kaist.ac.kr