Electromagnetic Field Enhancement in the Multilayer of Metallic Nanomesh Films: Synthesis and Application as Surface-Enhanced Raman Scattering Substrates

Ho Young Jang,† Seong Kyu Kim,‡ and Sungho Park§,*

†Department of Energy Science and ‡Department of Chemistry, Sungkyunkwan University, Suwon 440-746, South Korea

ABSTRACT: We have fabricated uniform, large-area, and two-dimensional arrays of gold (and silver) nanomesh structures via metal sputtering on an anodic aluminum oxide substrate. We studied the localized surface plasmon resonance originating from the edges of nanopores in the nanomesh structure. The resulting metal nanomeshes exhibited strong surface-enhanced Raman scattering (SERS) signals, and the measured SERS response was highly uniform throughout the whole surface area. The localized surface plasmon enhancement at the edge of the nanopores in the metal nanomesh structures is believed to be responsible for the strong SERS response. Also, we fabricated Au/Ag multilayer nanomesh structures with different stacking orders to further enhance the SERS response by utilizing the junctions between Ag and Au nanomesh films. The irradiated light can effectively penetrate deep into the multilayer metal nanomesh films through the nanopores. The SERS enhancement is maximized when the nanomesh structures are stacked alternately with Au and Ag nanomeshes as compared to homogeneous Au/Au or Ag/Ag stacked nanomesh films.

INTRODUCTION

Surface-enhanced Raman scattering (SERS) is a useful analytical technique to acquire vibrational information about organic and inorganic materials at surfaces due to their corresponding unique fingerprint spectral profiles. It is a phenomenon resulting from the significantly increased electromagnetic field where molecules are in close proximity to nanometer-sized metallic structures.1,2 Therefore, SERS has often been utilized to characterize molecules that are present as a monolayer (or even a single molecule) and has variable applications in chemical and biological sensors.3−5 It is generally understood that the SERS on properly roughened coinage metals (Cu, Ag, and Au) originates from two major contributions. One is the local electromagnetic field enhancement induced by metal nanostructures, and the other is a charge-transfer resonance between the metal surface and an absorbed molecule.6 The first case is often referred to as the “electromagnetic mechanism” (EM) and the second case is the “chemical mechanism” (CM). CM enhancement is induced by electronic resonance charge transfer between the adsorbate and the metal surface. In contrast to CM enhancement, EM enhancement is induced by local EM field enhancement at either the surfaces of particles or the gaps of the nanostructures. Recently, researchers proved both theoretically and experimentally that EM fields are greatly enhanced at the gaps or junctions in nanostructures, which are called “hot spots.”7−9 When the gap distance between two particles decreases, their EM field at the junctions is greatly enhanced. Therefore, several methods for the fabrication of nanostructures to enhance EM fields have been developed such as nanoparticle arrays,10−12 lithographically patterned nanostructures,13−15 and electrochemically deposited junctions.16−18 Among these nanostructures, metal nanoparticles have been intensively investigated in order to fabricate highly sensitive SERS substrates. Ag or Au nanoparticles show a high SERS enhancement of (on the order of 106) when the particles are arrayed in close proximity with each other.2,19 There are various fabrication methods for SERS substrates using nanoparticles such as self-assembly10 or water/hexane interface-utilized array methods.11 However, the nanoparticle-arrayed films usually form small areas of hot spots; the uneven distribution of hot spots within the films often leads to random EM field enhancement.7 In order to solve these limitations, electron-beam and focused-ion-beam lithography have been used to create uniform patterns on the nanometer scale. However, these methods have several drawbacks such as high cost, complex fabrication steps, and long fabrication time. Alternative methods to avoid these problems, including phase-shift lithography,20 nanosphere lithography,21 and nanoporous templates, have been used. Among these methods for the fabrication of SERS substrates,
the utilization of nanoporous templates of anodized aluminum oxide (AAO) has attracted enormous interest due to this material’s long-range ordering and facile controllability of a variety of pore sizes. Furthermore, AAO templates are self-stable, rigid, and well-defined. The nanopores can be tuned by changing the anodization voltage, which can lead to a suitable nanotemplate for plasmonic nanostructures. A few groups have fabricated nanomesh structures and investigated their application as SERS substrates. Polymer beads and e-beam lithography are commonly adopted to synthesize nanomeshes. In a previous report, we investigated metal nanomesh structures using AAO membranes as stretchable electrodes. Herein, we report how one can fabricate three-dimensional stacked nanomesh structures and the application of these materials as SERS substrates, mainly utilizing the high EM enhancement from the edge of nanopores and the junctions along the vertical directions with three-dimensional stacking. The resulting three-dimensional nanomesh films showed strong, reusable SERS signals over large areas; these
signals mainly originate from uniformly generated hot spots on the edges and at junctions.

**EXPERIMENTAL SECTION**

**Fabrication of Au and Ag Nanomesh Films.** An AAO template was prepared according to a method published in the literature. The pore sizes of the AAO templates were controlled by the anodizing voltage. AAO templates show pore diameters of 79, 60, and 48 ± 1 nm (Figure S1, Supporting Information). The metal layer (Au and Ag) was deposited using an Ar plasma sputter-coater (Cressington 108 auto) with a current level of 20 mA for 60 s onto the prepared AAO templates. The pore sizes were 69, 50, and 41 nm, with corresponding standard deviations of 2, 2, and 1 nm, respectively (Figure 2). Then, a polymer coating layer was formed using a PMMA solution dissolved in dichlorobenzene (MICRO CHEM 950 PMMA C 4) and deposited with a spin-coater (3000 rpm for 1 min). The AAO template under the Au-sputtered layer was dissolved using a 3 M NaOH solution and washed repeatedly with DI water. It was then transferred onto a clean substrate (either a SiO2 wafer or glass substrate) and dried in an oven at 80 °C. To obtain the pure Au and Ag nanomeshes on the substrates, the PMMA layer was dissolved by immersion in acetone for 30 min.

**SERS Measurements.** A confocal Raman spectrometer was used to record the SERS. A He–Ne laser (632.8 nm) and a Nd:YAG laser (532 nm) were used for excitation. All of the samples were dipped into 0.1 M mercaptobenzene in an ethanol solution for 3 h for the SERS measurement.

**Characterizations.** Field-emission scanning electron microscopy (FESEM; JEOL 7600F) was used to observe the surface and structural properties of the Au nanomesh structures. The extinction spectra of the Au nanomeshes were obtained by a UV–visible (UV–vis) spectrometer (Scinco S-3100). A confocal Raman spectrometer (WiTec alpha 300R) was used to record the SERS spectra. The extinction was given by a He–Ne laser at 632.8 nm and a Nd:YAG laser at 532 nm. For the finite difference time domain (FDTD) calculations, a MEEP program, developed by Johnson, was used.

**RESULTS AND DISCUSSION**

The synthetic routes of the stacked metallic nanomesh films are illustrated in Figure 1. By employing AAO templates and metal sputtering methods, a thin Au or Ag layer with a controlled thickness could be deposited onto the AAO templates. Then, a PMMA adlayer was formed on top of the metal via spin-coating. After dissolving the bottom AAO template, the film was transferred to the surface of water and relocated to a silicon substrate. The PMMA layer is critical for floating the film on the water surface and maintaining the nanomesh architecture without causing any structural collapse. The PMMA layer could be easily removed by acetone. In order to construct multilayer metal nanomesh films, the same procedure was repeated until the desired number of layers and compositions was obtained.

Typically, the morphology of Au nanomeshes is investigated by FESEM, as shown in Figure 2. The resulting metal nanomeshes exhibited large, ordered, and tunable two-dimensional arrays, with a controlled pore diameter ranging from ~41 to 69 nm. The Au nanomeshes are a replica of the AAO, and their pore size and periodicity can be readily tailored by controlling the morphology of the AAO templates. When we sputtered Au for 60 s at 20 mA using the AAO templates with 79 nm pores, the Au nanomesh showed a rim thickness of 19 ± 2 nm (Figure 2A). This width increased up to 33 ± 3 nm when the pore size of the AAO templates was changed to 48 ± 1 nm (Figure 2C). Regardless of the pore size, each sample could be multistacked without structural collapse due to the strong van der Waals interactions among the Au nanomeshes. It is noteworthy that the Au nanomeshes adhered to the silicon substrate strongly enough to survive the transfer processes of subsequent nanomesh layers. As clearly represented in Figure 2G–I, the fourth Au nanomesh showed a similar top morphology to the monolayers corresponding to Figure 2A–C.

As expected, the nanomeshes with larger holes exhibited a higher transmittance in the UV–vis spectrum, as shown in Figure 3A. All of the investigated multilayer nanomesh films showed high transparency (over 80%) within the spectral window ranging from 600 to 1000 nm. Each spectrum containing the Au nanomesh layer also exhibited a distinct shoulder feature at 518 nm, which typically represents the surface plasmon resonance of Au on the nanometer scale. The
multilayer of the Au/Ag nanomesh films will be explained later. Since the Au nanomesh films exhibit characteristic surface plasmon resonance features when their size is on the nanometer scale, we tested their SERS as a function of pore size. For this experiment, we adopted benzenethiol as a testing molecule (Figure 3B). The assignment of peaks in the SERS spectra has been previously reported and will not be mentioned here because the purpose of this report is to compare the relative SERS enhancement of different pore sizes in nanomesh films. As represented in Figure 3B, all of the investigated nanomeshes showed strong enhancement. The nanomesh with a pore size of \( \sim 50 \) nm showed the strongest SERS response among those tested. The estimated enhancement factor (EF) was \( 3.5 \times 10^6 \), and the detection limit was about \( 10^{-6} \) M (Figure S4, Supporting Information). To better understand the details of the interactions between the light and nanomeshes with a given pore size, we employed a computational method: the FDTD calculation (Figure 3C). In this simulation, the pore sizes are set to be 70, 50, and 40 nm. This simulation area was 180 nm \( \times \) 180 nm for all samples. The electromagnetic field distribution of the Au nanomesh films was calculated at an incident light wavelength of 633 nm. The electromagnetic waves were directed along the z axis. In Figure 3C, their corresponding electric-field enhancement (\( E^2/E_0^2 \)) is displayed with color contrast, representing the strongest enhancement in nanomeshes with 50 nm pores, which is in a good agreement with experimental SERS measurements.

Of central interest here is the comparison of observed SERS in nanomeshes with multilayers. Different magnitudes of SERS peaks were observed for nanomeshes with different numbers of monolayers (ML) and pore sizes, as represented in Figure 4A–C. In general, the SERS increases as the number of layers increases, regardless of the pore size. Similarly to the monolayer films, the nanomesh with \( \sim 50 \) nm pores showed the strongest SERS response. By comparing the band intensity centered at 1580 cm\(^{-1}\), the SERS enhancement for the different nanomeshes is compared (Figure 4D). The SERS intensity linearly increased as the number of layers increased up to four. The thickness of this nanomesh is \( \sim 29 \) nm, and the light penetration depth of light toward bulk Au is typically 15 nm. The linear increase in the SERS intensity is mainly due to the successful light penetration, through nanopores, reaching the bottom layer. The light can be absorbed by each nanomesh layer and consequently induces localized surface plasmon resonance within each layer. Figure S4A (Supporting Information) shows the variation in SERS intensity from the 50 nm pore sized Au nanomesh when the number of layers was changed from 1 to 10. The SERS intensity of the Au nanomesh increased with the number of layers up to 8 ML before saturation. The surface plasmon coupling between nanomesh layers are effectively operative, leading to the generation of large area hot spots at the junctions. One of the interesting observations from the FDTD field distribution is that most of the electric field is concentrated on the edges of the rims. This
is consistent with the well-known lightening rod effect that occurs in elongated nanostructures, where a large field is more concentrated on the highly curved tips than on flat surfaces. The edges of the nanomeshes are highly curved domains and are analogous to the tips of elongated nanostructures. The electric-field enhancement between the first and second layers (from the bottom) is as strong as the enhancement in the interlayer between the second and third layers. The strongest field enhancement was obtained between the third and fourth layers because the light is irradiated from the top direction. This is the case because light can successfully penetrate deep into the bottom nanomesh through the nanopores (Figure 4E). The resulting multistacked nanomesh films also showed very stable morphology under a harsh chemical environment. The adsorbed organic molecules can be eliminated by exposure to O$_2$ plasma. Therefore, because there is no structural collapse in the nanomesh films, the SERS substrate can be reused repeatedly (Figure S2, Supporting Information). As a control experiment, we fabricated multistacked spherical Au nanoparticle films and tested their reusability by applying the same O$_2$ plasma treatment. There was a significant morphology change caused by severe, irreversible aggregation, and the SERS enhancement was substantially dampened (Figure S3A, Supporting Information). In contrast, the Au nanomesh films retained their SERS enhancement after several O$_2$ plasma treatments, mainly due to the fact that there was little change in their morphology (Figure S3C, Supporting Information). In line with this observation, the confocal Raman mapping (where the homogeneity of an electromagnetic field can be estimated over a large area) exhibited very even Raman signal intensities over the investigated areas (40 μm × 40 μm) of nanomesh films (Figure S3B, D, Supporting Information). Usually, nanoparticle films show uneven SERS intensity distributions due to the inhomogeneous morphology that is commonly observed in nanoparticle films, originating from the uneven distribution of an electric field. Our metal nanomesh films showed good reusability and homogeneous field distributions, both of which are suitable for universal SERS substrates.

An interesting phenomenon was found in the behavior of the alternately stacked (Au and Ag) nanomeshes as compared to homogeneous Au/Au or Ag/Ag films. Our multilayer nanomesh films could be compositionally tailored by adopting different metal nanomeshes. The strong SERS signals were usually observed when adsorbrates are on substrates on a nanometer scale, typically consisting of coinage metals, Cu, Ag, and Au. Ag nanomeshes can be synthesized via the same procedure that is utilized to construct Au nanomeshes by replacing the sputtering source with Ag (although the surface is rougher for Ag nanomeshes compared to Au nanomeshes) (Figures S5 and S6, Supporting Information). Typically, a Ag nanomesh showed a rim thickness of 39 ± 3 nm when we sputtered Ag for 60 s at 20 mA. By varying the transferring order, we could tune the composition of the metal nanomesh films. We fabricated three-layer nanomesh films consisting of pure and mixed multilayers of Ag and Au nanomeshes. Their corresponding UV–vis spectra (i.e., multilayer Au/Au/Au, Au/Ag/Au, and Ag/Au/Ag nanomeshes) are shown in Figure 3A. A single layer of Ag nanomesh exhibited broad absorbance over the investigated spectral window (purple trace). Mutilayer nanomeshes showed a characteristic band at 518 nm and around 400 nm originating from Au and Ag, respectively. In order to test the versatility toward different excitation wavelengths, two excitations (532 and 633 nm) were adopted. The corresponding SERS spectra are plotted in panels A and B, respectively, in Figure 5 and Figure S7 (Supporting Information). For systematic comparison, Figure 5C shows the variation in the SERS intensity of the band at 1580 cm$^{-1}$ (C–C stretching mode of benzenethiol) as a function of the nanomesh compositions for the three-layer films. As shown in Figure 5C, regardless of the excitation wavelength, the general intensity trends as a function of composition are very similar. When the films are heterogeneously composed with mixed layers of Ag and Au nanomeshes (i.e., Au/Ag/Au or Ag/Au/Ag), the strongest SERS intensity was observed. Although the difference in intensities is not significant, stronger SERS was observed when the heterojunctions between Ag and Au are located close to the incident light as opposed to when the heterojunctions are closer to the bottom. The observed SERS intensity is directly related to the different magnitudes of the electric-field enhancement at the junctions, indicating that the maximum field enhancement occurs at the junctions between Ag and Au layers. It is noteworthy that surface plasmon coupling in nanoparticles is most effective when the coupling direction is in the same plane as the electric field of the incident light. In the stacked multilayer nanomeshes represented here, it is expected that the direct radiation-induced coupling will be weak along the z axis. However, electron-induced coupling between two layers should occur when electron oscillation in one nanomesh can induce oscillation of the image charge in the next nanomesh. Therefore, a z-axis-polarized oscillating dipole is produced at the junctions. When the junction is heterogeneous, we propose that the different degree of electronegativity of the two metals attribute to inducing more readily the image charges to each other when compared to the...
homogeneous (Ag/Ag or Au/Au) nanomesh films. In order to investigate the experimental observations more thoroughly, we carried out FDTD calculations for representative three-layer nanomeshes by varying the stacking order using a 633 nm wavelength laser, as shown in Figure 6. For all of the investigated orderings, the heterojunctions between Ag and Au nanomeshes generated strong electric-field enhancement. When the Ag nanomesh is located on top of the Au nanomeshes, as shown in Figure 6A, the strongest field occurred at the junction between the first Ag and second Au nanomeshes, while the junction from the bottom Au nanomesh exhibited a slight electric-field enhancement. In contrast, when the Ag nanomesh is sandwiched between two Au nanomeshes, both the top and bottom junctions showed strong electric-field enhancement, as shown in Figure 6B. When the Ag nanomesh is on the bottom, the strongest electric field was generated at the bottom heterojunction. The sum of the electric fields at the two junctions directly correlates with the observed experimental SERS intensities, representing a good agreement between our experimental and theoretical results.

**CONCLUSION**

In conclusion, we found a simple synthetic approach to fabricate highly ordered multilayers of metal nanomeshes by using AAO templates, water-floating the nanomeshes, and then, subsequently transferring the nanomeshes to a silicon plate to create reusable SERS substrates with strong enhancement. The resulting multilayers of metal nanomeshes retained their structural morphology under harsh chemical environments (i.e., O₂ plasma cleaning conditions), which is unique for nanomeshes with continuous morphologies. However, it is noteworthy that the noncontinuous Au nanoparticle films showed severe aggregation under the same experimental conditions, leading to significant dampening in SERS. We found the optimized SERS enhancement conditions as a function of pore and rim sizes. Among Au nanomeshes with various pore sizes, Au nanomeshes with 50 nm pores and a rim thickness of 25 ± 2 nm exhibited the strongest SERS response. The calculated electric-field simulation with FDTD supported the experimental observations. The multilayered metal nanomeshes showed a linear increase in SERS enhancement as the number of layers increased. The observed linear increase is attributed to the presence of nanopores, through which light can penetrate and reach the bottom layer of the nanomeshes to enhance the electric field. Interestingly, the heterojunctions formed with multilayers of Ag and Au nanomeshes exhibited stronger SERS enhancement than the analogous homojunctions with pure Ag or Au nanomeshes. The experimental results correlate well with the theoretical calculations of FDTD. The induced dipole along the z axis between the Ag and Au nanomeshes can be readily generated due to the difference in the electronegativities of the two metals, which more readily induces the image charge in the neighboring nanomeshes.

**ASSOCIATED CONTENT**

3 Supporting Information

SEM images of AAO, Au nanomeshes before and after O₂ plasma treatments, and Ag nanomesh; SERS images of Au nanomeshes and Au nanoparticle films; graphs for SERS intensities versus the number of Au nanomesh layers; SERS spectra of multilayers of Au and Ag nanomeshes; and EDS spectra of Au and Ag nanomeshes. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b01926.

**AUTHOR INFORMATION**

Corresponding Author
* E-mail: spark72@skku.edu.

Notes
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the National Research Foundation of Korea (National Leading Research Lab: 2011-0027911). S.P. thanks the Human Resources Development program (no. 20124010203270) of the Korea Institute of Energy Technology Evaluation and Planning(KETEP) grant funded by the Korea government Ministry of Trade, Industry and Energy.

**REFERENCES**


(16) Li, X. D.; Li, M. C.; Cui, P.; Zhao, X.; Gu, T. S.; Yu, H.; Jiang, Y. J.; Song, D. D. Electrodeposition of Ag Nanosheet-Assembled Microsphere@Ag Dendrite Core–Shell Hierarchical Architectures and Their Application in SERS. CrystEngComm 2014, 16, 3834–3838.


