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Tailoring Optical Properties of a Large-Area Plasmonic Gold Nanoring Array Pattern

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Abstract

A new fabrication route, which combines nanosphere lithography with silicon-based clean-room microfabrication processes, has been developed to produce large-area long-range ordered gold nanoring array patterns in a controllable fashion. Both the experimentation and the finite-difference time-domain (FDTD) simulation show that the surface plasmon resonance peak (SPR) of the nanoring array pattern can be tuned systematically in a large spectral range by varying the geometry parameters such as the ring thickness, the ring height, the ring outer diameter, and the gap between neighboring rings. For the Au nanoring arrays with a large gap in the absence of plasmon coupling between neighboring rings, the local electromagnetic (EM) field enhancement occurs at both the outer and inner surfaces of individual nanorings; and the periodicity of Au nanoring array has no any effect on the plasmonic properties. For the Au nanoring arrays with a small gap, plasmon coupling takes place between neighboring rings. As a result, the characteristic plasmonic band is split into two new peaks corresponding to a bonding SPR mode and an antibonding SPR mode. The local EM field enhancement becomes stronger with a decrease in the gap between neighboring rings, but the SPR peaks shift away. Therefore, to maximize the surface-enhanced Raman scattering signal, the geometry parameters of the Au nanoring array need to be tuned to balance the contributions from the resonance excitation (spectral overlap) and the local EM field enhancement.

Graphical abstract

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Supporting Information

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The electromagnetic (EM) field distribution of a pair of Au nanorings with gaps of 2 nm (a), 4 nm (b), 6 nm (c), 8 nm (d), 10 nm (e), 20 nm (f), 50 nm (g), and 100 nm (h) (PDF)

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Notes

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INTRODUCTION

Surface-enhanced Raman scattering (SERS) and surface plasmon-coupled emission (SPCE) spectroscopy are finding increasing applications in biosensing and bioimaging.^{1–5} In SERS and SPCE, plasmonic nanostructures are employed as substrates to amplify the SERS or SPCE signals. Plasmonic metal nanoparticles have been used extensively in SERS and SPCE. Free-standing bare metal nanoparticles tend to aggregate in a solution with high ionic strength. Hence, the surface modification of metal nanoparticles is often performed to preserve the stability of colloidal nanoparticles.⁶ Besides freestanding nanoparticles, two-dimensional (2D) metal nanoarray patterns have received increasing attention.^{7–10} The optical properties of 2D nanoarray patterns can be tuned systematically and predicted theoretically using numeric methods such as the finite-difference time-domain (FDTD) and finite element analysis (FEA), which in return helps guide the design of 2D nanoarrays.^{11,12} Long-range ordered 2D nanoarray patterns not only show good reproducibility but also extend the dynamic detection range of sensors due to the extension of the enhanced electromagnetic (EM) field in space. It still remains a challenge in massive production of large-area long-range ordered metal nanoarray patterns at low cost.

Among the panoply of 2D metallic nanoarrays, Au nanoring arrays display meritorious features.^{13–19} First, Au nanoring array patterns have a wide spectral range of tunable plasmons, which have advantages over Au nanohole and nanoparticle arrays whose optical property tuning is severely limited by the extent of size-dependent plasmon shift. Second, the EM field can be concentrated at both the inner and outer surfaces of the ring, considerably extending the spatial distribution of “hot spots” for surface-enhanced spectroscopies. Third, the overall size of Au nanoring arrays can remain largely unchanged during optical tuning by simply changing the shell thickness of rings. In contrast, tailoring the optical properties of the Au nanohole and nanoparticle arrays is always at the expense of significantly varying the size or periodicity, which compromises the overall performance. In addition, Au nanoring arrays have been theoretically predicted to have a high orientation-independent plasmon resonant absorption in the visible to near-infrared spectral range, which has implications in plasmon-enhanced photothermal heating.²⁰ Thanks to these advantageous properties, colloidal Au nanorings have been chemically synthesized using sacrificial Co nanoparticles for SERS applications.^{21,22} These colloidal Au nanorings obtained have an outer diameter from 25 to 40 nm with a shell thickness of 5 nm, which

allows the LSPR to be tuned from 651 to 760 nm. Moreover, Au nanoring array patterns have been fabricated by nanosphere lithography (NSL), electron-beam and focused-ion beam lithography, and etc.^{13,14,17–19} Electron-beam and focused-ion beam lithography can create ultrasmall features in an accurate and controllable fashion, but it is expensive and impossible to produce the large-area nanoarray patterns massively. For example, Au nanoring arrays, fabricated by e-beam lithography, only had an area of $60 \times 60 \mu\text{m}$.²³ In contrast, NSL is a powerful, versatile, and cost-effective fabrication method for fabrication of large-area periodic nanoarray patterns. NSL uses polystyrene (PS) beads as the template, and these can be easily tailored by simply changing the PS bead size, the etching time, and the metal deposition thickness. The reliability of NSL has been manifested in the development of Au nanohole arrays and Au nanotriangle arrays for SERS and SPCE applications.^{7,24,25} Among those Au nanoring array patterns reported previously, the plasmonic bands of most of them are located in the mid-infrared and near-infrared range (typically $>900 \text{ nm}$). This does not meet the requirement for SERS sensing, because most of current SERS sensing signals are excited by the 785, 633, and 532 nm lasers. Although NSL has been demonstrated to fabricate the Au nanoring arrays in combination with electrochemical deposition, the nanoring structure obtained is irregular and disordered, making it difficult to achieve the optimal performance.²⁶ Also, the gap of nanorings is generally too large to have plasmonic coupling between neighboring rings, leading to no “hot spots” between neighboring rings. In addition, so far few studies have been performed to systematically investigate the EM enhancement distribution and the optical properties of nanoring array patterns.

In the present work, NSL is combined with the silicon-based clean-room fabrication processes to fabricate the large-area long-range ordered Au nanoarray patterns at low cost. FDTD simulation is employed to predict the optical properties and the EM field distribution in the Au nanoarray patterns with systematical variation of the geometry parameters such as the periodicity, the ring thickness, height, and the overall size of the rings. The systematic FDTD studies on the optical properties will provide guidelines for designing the optimum plasmonic Au nanoring array pattern for SERS sensing. The Au nanoring array patterns investigated in this work show two unique features for SERS. First, the wide tunable spectral range of plasmon across the visible-light and near-infrared light regions enables the plasmon band to match the typical spectral wavelength of excitation laser sources. Second, the local EM field enhancement at the gap of neighboring rings provides a strong near-field.

EXPERIMENTAL METHODS

Chemicals and Reagents

Silicon wafers were purchased from University Wafers Inc. (Boston, MA). Polystyrene microspheres with diameters of 500, 600, and 1000 nm were purchased from Thermo Scientific (Waltham, MA). Deionized (D.I.) water was produced by the Milli-Q Integral 3/5/10/15 system (18.2 M Ω cm, Millipore Corp., U.S.A.).

Instrumentation

An Oxygen Plasma Asher (March PX-250 Plasma Asher) was used to etch the PS beads. Inductively Coupled Plasma (ICP Trion Technology Minilock III RIE) was used to etch silicon. An E-beam Evaporator (Kurt J. Lesker) was used for metal deposition. A scanning electron microscope (JEOL-JSM-7600F) was used to characterize the Au nanoring array patterns. Reflection spectra of Au nanoring array patterns were acquired using an Ocean Optics USB 4000 spectrometer and DT-MINI-2-GS.

Fabrication of Au Nanoring Array Patterns

The Au nanoring array patterns were fabricated based on the modified NSL method,⁸ as shown in Figure 1. Initially, the silicon substrate was cleaned in acetone, methanol, and DI water for 5 min, respectively. It was further made hydrophilic by immersion into piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 3:1$) at 90°C for 2 h. *Caution: Piranha solution is very dangerous; caution must be taken!* Subsequently, a monolayer of PS beads was hexagonally patterned on the silicon substrate. After natural drying, the monolayer was treated under oxygen plasma to reduce the PS sphere size. Inductively coupled plasma and reactive-ion etching (ICP-RIE) with Cl_2 gas was then used to etch the silicon substrate with the PS beads as a mask. The PS beads were etched again using oxygen plasma to further reduce the size. After that, a layer of 12 nm thick Ni was deposited on the substrate. After removal of the PS beads by sonication in methanol, ICP-RIE with CF_4 gas was used to etch silicon with the Ni layer as the mask. Hence, a hexagonally patterned silicon nanoring array pattern was obtained after removal of the Ni layer using nitric acid. Finally, the Au nanoring array pattern was obtained after a successive deposition of a 5 nm thick Ti film and a 20 nm thick Au layer, where Ti acted as an adhesion layer, connecting the Si substrate with the Au layer. Given that the 5 nm Ti adhesion layer is completely masked by a layer of Au film, it would only minimally affect, if any, the surface plasmons generated at the interface between the air and the Au nanoring pattern. In addition, no gold is deposited on the undesired place if there is no any defect in the PS template. Even though Au is deposited on the undesired place on the Si substrate due to the existence of some defects in the PS template, its contribution to the plasmonic features to the reflectance spectra can be negligible. The reason is that SPPs cannot be excited due to the momentum mismatch between the incident light and the surface plasmon polariton (SPPs) on a planar gold film.

Finite-Difference Time-Domain (FDTD) Simulation

Optical properties of Au nanoring arrays were studied using FDTD simulations. The software Optiwave FDTD is commercially available from Optiwave Inc. A grid size of 1 nm was used to construct the simulation cells. A continuous plane wave from 400 to 1200 nm was used as the input light source. The refractive index was taken from the data of Palik.²⁷ Periodic boundary conditions were imposed for all simulations to replicate periodic Au nanoring array patterns.

RESULTS AND DISCUSSION

Morphology of Au Nanoring Array Patterns

Figure 2a shows that the fabricated Au nanoring array pattern had a typical physical size comparable with that of a coin. Figure 2b–f shows the SEM images of the Au nanoring array patterns fabricated using the PS spheres with different sizes. In Figure 2b, the overall ring size (i.e., the outer ring radius) was 920 nm, the ring thickness was 75 nm, the ring height was 120 nm, and the periodicity (center-to-center distance) was 1000 nm. The periodicity of the Au nanoring arrays is determined by the size of the unetched PS beads used. The overall ring size and the gap size, which is the closest distance between two neighboring rings, can be varied by changing the duration of sphere etching (Figure 1c); and the ring height is dependent on the Si etching. The ring thickness, which is defined as the difference between outer and inner ring radius, can be tuned by controlling the oxygen plasma etching duration in Figure 1e, while the hexagonally patterned monolayer of PS beads renders a long-range order of Au nanoring array pattern as shown in Figure 2e,f. The parameters such as the size of PS beads and the etching duration allow a high degree of tunability of the optical properties.

Optical Properties of Au Nanoring Array Patterns

The optical properties of Au nanoring arrays can be described by the plasmon hybridization model.^{28–30} An Au nanoring array is considered to be created by an Au nanodisk array perforated with an Au nanohole array; hence, its optical properties include the contributions from both the elements. The elementary nanodisk and nanohole plasmons contribute to the oscillating charges at both the outer and inner surface of the ring. Because of a finite ring thickness, these oscillating charges interact with each other and produce two new plasmon resonances corresponding to a bonding mode at a longer wavelength and an antibonding mode at a shorter wavelength. The bonding localized surface plasmon resonance (LSPR) mode of an Au nanoring array is identified as the reflection dip at a spectral wavelength of 750 nm for the Au nanoring array with a periodicity of 500 nm (Figure 3a); the dip red-shifted to a spectral wavelength of 880 nm when the Au ring periodicity increased to 600 nm. Due to the cancellation of opposite charges at the outer and inner surfaces of the ring for the antibonding mode, the corresponding reflection dip has a much lower intensity and is thus of less significance.

The plasmon hybridization description of the Au nanoring arrays with periodicities of 500 and 600 nm predicted by FDTD simulation was consistent with the experimental data of reflection spectra (Figure 3a). The intense bonding LSPR mode was further confirmed by the dipolar behavior observed in the simulated local EM field distribution extracted at the LSPR wavelength, as shown in Figure 3b. The Au nanoring array acts as a plasmonic lens. It concentrates the EM radiation at both the outer and inner surfaces of the ring, considerably extending the spatial distribution of “hot spots” for surface-enhanced spectroscopies. In comparison, “hot spots” are limited to the outer surface of circular nanodisks.

Optimization of Au Nanoring Array Patterns

To achieve an optimal performance in surface-enhanced spectroscopies, the plasmonic band of the nanostructure needs to be overlapped with the spectral wavelength of the excitation laser source, and the local EM field enhancement needs to be maximized. The spectral overlap between the excitation light source and the SPR band ensures a resonance excitation; and the local EM field enhancement helps modulate various near-field optical processes.^{29–31} As identified above, the manifold parameters such as the ring thickness, height, and overall ring size are found to affect the optical properties of the Au nanoring array patterns. Therefore, they all need to be studied and optimized.

In case of the Au nanoring arrays with a large gap where plasmonic coupling among neighboring rings can be ignored, the behavior of individual nanorings just needs to be considered, and the periodicity of nanoring had no effect, as shown in Figure 4(a,c,e). For any individual nanoring, among the parameters of the ring thickness, height, and overall ring size, each parameter was varied with all the other parameters fixed to study the plasmonic properties using FDTD simulation. For example, Figure 4a shows the effect of the ring thickness on the spectral wavelength (position) of the plasmon peak, while the ring height, the overall ring size, and the periodicity are kept constant. A decrease in the ring thickness was found to red-shift the plasmon peak because of an increasingly stronger plasmonic coupling between charges at the outer and inner surfaces of the ring. A similar red-shift behavior of the plasmon peak was found for an increase in the ring height and the overall ring size, which was characteristic of the dipolar plasmon resonance of nanoparticles. By taking an advantage of the nanosphere lithography-based technique, all three parameters can be manipulated in a controllable manner so that the plasmon resonance can be tuned to the visible wavelength range. It was found that the plasmon peak can be tuned 100–200 nm by merely varying one of the three tuning parameters above. The wide spectral tunability of Au nanoring arrays allows the resonance excitation of SPR by overlapping the SPR band with the wavelength of the excitation laser source.

Dependence of the plasmon peak sensitivity on the tuning parameters was also studied to reveal the parameter regions where the optical properties are most sensitively affected. The plasmon peak sensitivity is defined as the plasmon peak shift for every 1 nm change of each tuning parameter. The plasmon peak was found to be more sensitive at a smaller ring thickness, as shown in Figure 4b. The plasmonic coupling between charges at the outer and inner surfaces of the ring became weaker as the ring thickness increased. At a large ring thickness, there was almost no plasmonic coupling between charges at the outer and inner surfaces of the ring, which explained why varying the ring thickness barely shifted the plasmon at larger ring thicknesses. The plasmon peak was found to be largely equally sensitive to the ring height and overall ring size in a wide parameter region, since the spectral dependence of the plasmon peak on both tuning parameters scale linearly, as shown in Figure 4d,f.

For the Au nanoring arrays where plasmonic coupling among neighboring rings is strong, the plasmonic properties were studied in a pair of rings by varying the gap, as shown in Figure 5. The plasmonic coupling between two approaching rings was found to become increasingly intensified, as manifested by the split of the plasmon peak into two new peaks

corresponding to a bonding SPR mode and an antibonding SPR mode as shown in Figure 5a, which was also experimentally observed in Figure 5b. When the gap of the Au nanoring array with a period of 500 nm changed from 100 to 2 nm, the plasmon peak at 750 nm was split to two peaks (i.e., the antibonding SPR peak at 700 nm and the bonding SPR peak at 920 nm), as shown in Figure 5a. For the Au nanoring array with a periodicity of 600 nm, reducing the gap from 90 to 12 nm made the 850 nm peak split to the antibonding SPR peak at 790 nm and the bonding SPR peak at 900 nm (Figure 5b).

In case of the Au nanoring arrays with a large gap where plasmonic coupling among neighboring rings can be ignored, the local EM field enhancement $(E/E_0)^2$ for an individual nanoring was only $\sim 5.0 \times 10^2$, as shown in Figure 3b. In case of the Au nanoring arrays with a small gap where plasmonic coupling among neighboring rings occurred, the simulated local EM field enhancement $(E/E_0)^2$ increased significantly with a decrease in the gap, reaching 4.3×10^4 at a gap of 2 nm as shown in Figure 5c. The corresponding local EM field distribution transitioned from being localized at the outer surface of the ring to being increasingly delocalized at the gap between neighboring rings, as shown in Figures 5d and S1. The local EM field enhancement can significantly mediate the performance of Au nanoring arrays in surface-enhanced spectroscopies through near-field interaction. However, maximizing the local EM field enhancement by coupling neighboring rings shifts the plasmon peak and thus could result in the breakdown of the resonance excitation. Practically, the minimum gap that can be spatially resolved by SEM is 8 nm. Hence, we only presented the experimental data on the Au nanoring pattern with the gap 8 nm.

Guideline for Fabrication of Optimized Au Nanoring Array Patterns

The analysis above reveals two approaches to optimize Au nanoring arrays for surface-enhanced spectroscopy. First, the wide spectral tuning range allows the resonant excitation of SPR by overlapping the excitation wavelength with that of the SPR band. This is made possible by varying either the ring thickness, height, or the overall ring size. The three tuning curves obtained (represented as yellow dashed arrows in Figure 4) provide a general guideline in choosing the optimal parameters for Au nanoring array fabrication. Second, the strong local EM field enhancement can be achieved on the closely packed Au nanoring arrays due to plasmonic coupling. It is noted that maximizing local EM field enhancement could break down the resonance excitation, since the plasmonic coupling could shift the plasmon resonance peak, resulting in no spectral overlap. Therefore, to achieve an overall optimized performance, a compromise could be made to balance the resonance excitation and the local EM field enhancement, depending on the weight of each contribution to surface-enhanced spectroscopy.

CONCLUSIONS

In summary, the large-area long-range ordered Au nanoring array patterns were fabricated using the modified NSL technique. The plasmon resonance peak position can be tuned in a large spectral range by manifold parameters such as the ring thickness, the ring height, and the overall ring size. For example, the plasmon resonance peak position can be controlled to be spectrally overlapped with the wavelength (785 nm) of the excitation laser, which is

widely used in SERS sensors. The local EM field enhancement can be achieved nearby the outer and inner surface of individual nanorings; and the local EM field became stronger with a decrease in the gap between neighboring nanorings by forming the “hot spots”. For maximizing the enhancement effect in SERS or SPCE, the contributions from the resonance excitation (spectral overlap) and the local EM field enhancement need to be balanced. The knowledge obtained can guide the design of optical and optoelectronic devices in surface-enhanced spectroscopy.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Fabrication protocol for Au nanoring array pattern.

Figure 2.

(a) Optical image of a large-area Au nanoring array chip compared to a coin; (b) SEM image of the Au nanoring pattern (periodicity: 1000 nm, outer radius: 920 nm, thickness: 75 nm, and height: 120 nm); (c) pattern (periodicity: 600 nm, outer radius: 500 nm, thickness: 50 nm, and height: 120 nm); (d) pattern (periodicity: 500 nm, outer radius: 440 nm, thickness: 30 nm, and height: 120 nm); (e,f) the Au nanoring array patterns with large-scale area.

Figure 3.

(a) Experimental (P500-exp) and FDTD-simulated (P500-fdtd) reflection spectra of Au nanoring arrays with periodicities of 500 and 600 nm, respectively; (b) EM field distribution with a local EM field enhancement $(E/E_0)^2$ of $\sim 5.0 \times 10^2$ at the plasmon peak wavelength for an Au nanoring with an outer radius of 200 nm, a ring thickness of 40 nm, a height of 100 nm, and a periodicity of 500 nm. The white arrow indicates the polarization direction of the incident light.

Figure 4.

Optimization of optical properties of Au nanoring arrays. Dependence of the plasmon resonance peak on (a) the ring thickness, (c) the height, and (e) the overall thickness. The yellow dashed arrow shows the trend of the plasmon peak position evolution. Plot of the plasmon peak sensitivity with respect to each tuning parameter extracted from Figure 4a–c. The plasmon peak sensitivity is defined as the plasmon peak wavelength change for every 1 nm variation of each tuning parameter. The refractive index used for the Si substrate in FDTD simulations is 3.42. The spectral range below 500 nm is avoided, because the interband transitions of gold occur at around 475 nm, which damps the plasmon.

Figure 5.

Plasmonic coupling between a pair of rings. (a) Simulated reflection spectra for the Au nanoring array with a periodicity of 500 nm; (b) experimental reflection spectra for the Au nanoring array with a periodicity of 600 nm. The olive dashed arrow shows the splitting of the plasmon peak into a bonding resonance mode (longer wavelength) and an antibonding resonance mode (shorter wavelength); (c) gap-dependent EM field enhancement of a pair of Au rings; (d) the EM field distribution of a pair of rings with a gap of 2 nm. The magnitude of the EM field enhancement in (d) is presented as $\log_{10}(E/E_0)^2$.