

Tuning plasmonic interaction between gold nanorings and a gold film for surface enhanced Raman scattering

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We investigate the plasmonic properties of gold nanorings in close proximity to a gold film. The rings have been fabricated using nanosphere lithography and are optimized to boost their near-infrared surface enhanced Raman scattering (SERS) effects. A SERS enhancement factor as large as 1.4×10^7 has been achieved by tuning the separation between the gold nanorings and the gold film. In addition, we have numerically and experimentally demonstrated an enhanced tunability of the plasmon resonance wavelength and a narrowing of the plasmon linewidth for increasing ring-film interaction. © 2010 American Institute of Physics. [doi:10.1063/1.3504187]

Strongly enhanced Raman scattering of adsorbates occurs on the surfaces of metallic nanostructures that exhibit local plasmon resonances and consequently an enhanced local electromagnetic (EM) field at the wavelength of the stimulating laser beam. In addition, the chemical interaction between adsorbed molecules and the metallic nanostructures may provide an additional enhancement based on the charge transfer between the metal and the molecules. These two mechanisms give rise to the well-known surface enhanced Raman scattering (SERS) spectroscopy, which even has single molecule resolution.¹ Although early experiments generally were performed in the visible frequency range, there is increasing interest in SERS-based sensing or imaging in the near-infrared (NIR) optical ranges of 650–900 and 1000–1350 nm, because they are the most appropriate wavelength ranges for SERS experiments in the bovine plasma environment and *in vivo* detection.²

Gold (Au) nanorings have been proposed and demonstrated for NIR SERS application^{3,4} because they have highly tunable optical properties in the NIR region.^{4–6} E-beam lithography has been extensively applied to fabricate the nanorings but is limited by a low throughput and high cost.^{7–9} As an alternative, one turns to look for some simple, productive, and cheap methods to prepare the nanorings such as nanosphere lithography.^{4,5,10} In addition, depositing metallic nanostructures in a close proximity to a metal film has been proved to be an effective way to tune the plasmon resonance and to enhance the local electric field.^{11–13} For example, Lévêque and Martin have reported on that the plasmon resonance wavelength can be modified over 600–900 nm by changing the spacer thickness between Au nanosquares and a Au film.¹² Crozier *et al.*¹³ also found that the strong coupling between the localized and propagating surface plasmons in a structure of a Au nanodisk array near a Au film could enhance the electric near-field largely. In this letter, we use the nanosphere lithography method to fabricate Au nanorings near a Au film on a substrate for the NIR SERS application. By controlling the plasmonic interaction between the Au nanorings and a Au film with different thicknesses of the

SiO₂ spacer, the NIR SERS enhancement factor (EF) can reach values as large as 1.4×10^7 , an improvement with a factor of 50 times compared to the Au nanorings. We have also numerically and experimentally demonstrated an enhanced tunability of the plasmon resonance position and a narrowing of the plasmon linewidth in the composite structures.

Figure 1(a) and 1(b) show the schematic illustration of Au nanorings on a Au film with a SiO₂ spacer (Au nanorings–SiO₂–Au film) and Au nanorings, respectively. The Au nanorings–SiO₂–Au film structure was fabricated by performing nanosphere lithography onto a Au film with a SiO₂ layer on the top. First, a quartz substrate was covered by sputter deposition with a 50 nm thick Au film and a SiO₂ layer with a variable thickness. Then 100 nm sized polystyrene (PS) sulfate latex particles were deposited on the functionalized SiO₂ surface by the electrostatic self-assembly, followed by sputtering a 30 nm thick Au layer on the top.¹⁰ Next, a Xe ion milling process was performed on the Au film. Finally, an oxygen plasma treatment was used to remove the remains of the PS particles. Figure 1(c) displays that the nanorings (around 130 nm in diameter) are distributed randomly with a constant density onto the SiO₂ surface and are isolated with an interparticle spacing of around

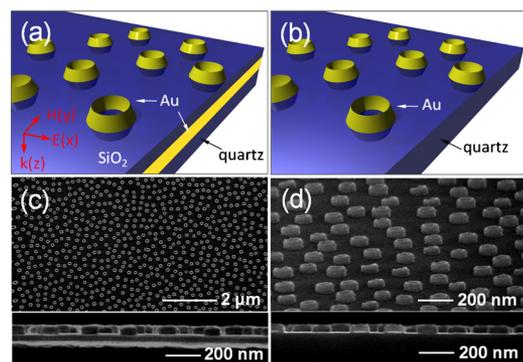


FIG. 1. (Color online) Schematic illustrations of (a) Au nanorings–SiO₂–Au film and (b) Au nanorings on quartz and their corresponding electron micrographs in (c) and (d), respectively. Bottom parts in (c) and (d) panels are the cross-section images.

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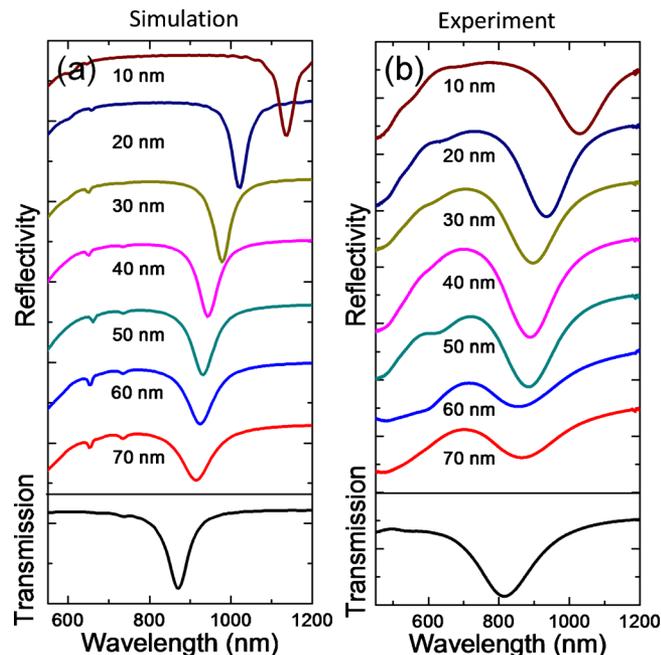


FIG. 2. (Color online) (a) Simulated and (b) experimental reflection spectra of Au nanorings-SiO₂-Au film with different thicknesses of the SiO₂ layer (top) and transmission spectra of Au nanorings (bottom).

200 nm. The maximum area of a single continuous nanoring domain can reach a few square centimeters after optimization. Furthermore, a cross-section electron micrograph [bottom part in Fig. 1(c)] shows the smooth and flat Au and SiO₂ film under the nanorings and all free standing Au nanorings possess sharp edges and opened surface morphology, which is favorable for SERS. For a comparison, nominally identical Au nanorings were fabricated directly onto the quartz substrate without a Au film and a SiO₂ film underneath [Fig. 1(d)].

To investigate the optical properties of the Au nanorings-SiO₂-Au film structure, simulated and experimental reflection spectra are analyzed in Fig. 2. Numerical simulations were performed by employing a finite difference time domain method.¹⁴⁻¹⁶ The structure was excited by normally incident light with its polarization along the *x*-direction [Fig. 1(a)]. The empirical dielectric functions of Au and SiO₂ have been described in our previous work.¹⁶ For the sake of simplicity, we assumed periodic boundaries although the structures are randomly distributed in our samples. We have observed some periodicity induced effects, which we will discuss later, but in general there is good agreement with the experimental results. Experimental spectra were measured by a Bruker spectrometer (Vertex 80 V) with a Hyperion 2000 microscope.

Figure 2(a) (top) presents the simulated reflection spectra of the Au nanorings-SiO₂-Au film structures with different thicknesses of the SiO₂ spacer. We can observe a strong reflectance dip in the NIR range for all structures, which is attributed to the coupling and the plasmon hybridization between the localized surface plasmon (LSP) of nanorings and the delocalized surface plasmon (DSP) of the Au film. With the decrease in the SiO₂ spacer thickness from 70 to 10 nm, the dip shifts to longer wavelengths and becomes narrower.¹⁷ The transmission spectrum of Au nanorings onto the quartz substrate is shown in Fig. 2(a) (bottom)

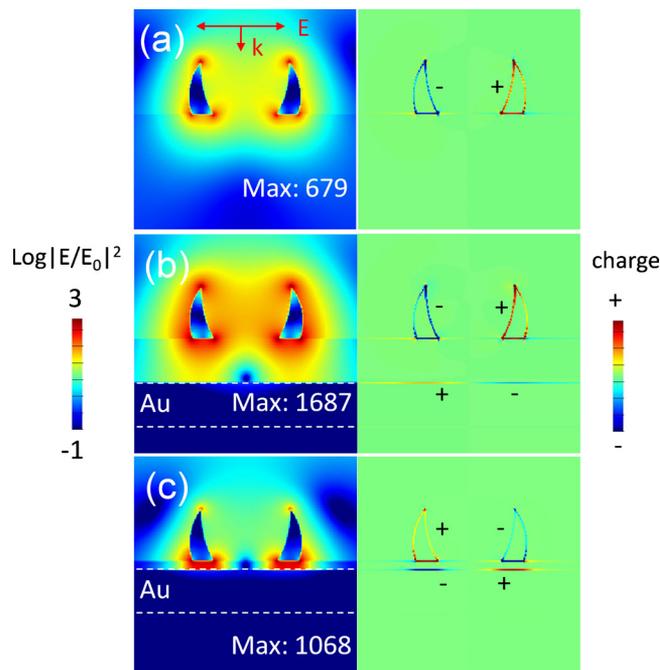


FIG. 3. (Color online) (Left) EFE ($\log|E/E_0|^2$) and (right) charge distribution of (a) Au nanorings and Au nanorings-SiO₂-Au film with (b) 50 and (c) 10 nm SiO₂ layer at resonance wavelengths of 872 nm, 932 nm, and 1138 nm, respectively. Dashed lines in (b) and (c) panels indicate the position of the 50 nm thick Au film. The maximum value of EFE ($|E/E_0|^2$) of each structure is shown in [(a)-(c)].

for comparison, where only a LSP peak of nanorings at a shorter wavelength (872 nm) is observed. To better understand the nature of the dip's shift and narrowing, the electric field enhancement (EFE, $\log|E/E_0|^2$) and charge distribution were simulated and are depicted in Fig. 3. It is apparent that a bonding dipolar LSP is excited in bare nanorings [Fig. 3(a)].¹⁰ When the nanorings and the Au film are separated with 50 nm [Fig. 3(b)], the dipolar LSPR of nanorings strongly couples to its own image charges on the Au film, which generates a quadrupolelike resonance. The coupling leads to a maximum EFE that is almost three times larger compared to the bare nanorings. More importantly, this enhancement is spread over the nanoring's surface, which is particularly useful for SERS-based molecular detection. When the separation is reduced to 10 nm [Fig. 3(c)], the coupling becomes much stronger and the EFE is mostly confined in the gap between the nanoring and the Au film, resulting in a reduction of the total dipole moment and consequently significant reduction of radiative scattering of the nanostructure. By doing so, a higher quality factor and a better confinement of optical energy in the nanostructure can be obtained. This also explains the reasons of the redshift and the linewidth narrowing of the reflectance dip.¹⁷ The latter is potentially helpful to improve the figure of merit for LSP resonance biosensing.¹⁸ The enhanced tunability of the resonance by changing the spacer thickness also helps us to match the wavelength of the nanostructure's resonance to the laser excitation. In addition, we have observed some small dips in the range of 600-800 nm for the Au nanorings-SiO₂-Au film structure, which is caused by the grating-induced excitation of DSPs at the Au film.¹⁹ All experimental spectra qualitatively reproduce the simulated spectra except for a broader linewidth of the plasmon reso-

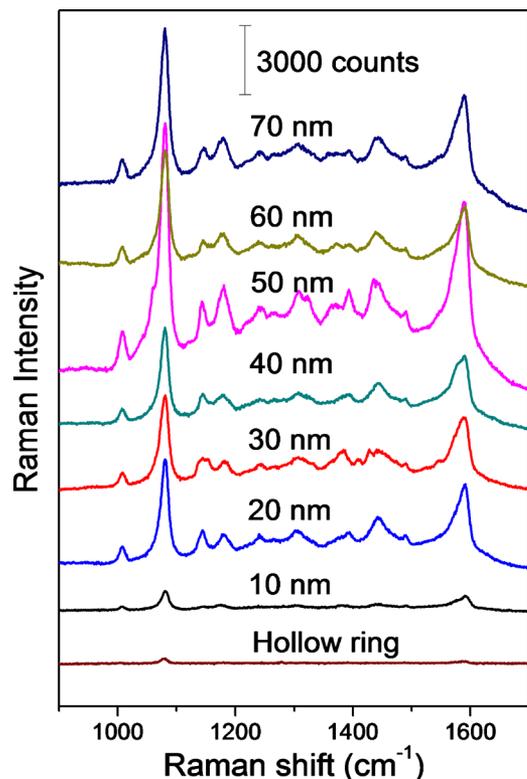


FIG. 4. (Color online) SERS spectra of 4-ATP molecules on Au nanorings (bottom) and Au nanorings-SiO₂-Au film with the thickness of SiO₂ layer from 10 to 70 nm.

nance probably induced by inhomogeneous broadening in the sample and the absence of small grating-induced dips in the visible range due to the disordered structure [Fig. 2(b)].

We employed 4-aminothiophenol (4-ATP) as a Raman probe to evaluate the SERS performance of the Au nanorings-SiO₂-Au film structure. Raman spectra were recorded on a Horiba Jobin Yvon LabRam HR 800 system with a 100× objective and a 785 nm diode laser (0.8 mW). A monolayer of 4-ATP molecules was adsorbed onto the nanorings surface by soaking in a 0.3 mM ethanol solution overnight. Figure 4 shows the SERS spectra of 4-ATP on the Au nanorings and on the Au nanorings-SiO₂-Au film with different thicknesses of the SiO₂ layer. Although the Raman signal amplitudes vary, all spectra have the same shape with the Raman shifts at 1080, 1143, 1179, 1436, and 1589 cm⁻¹, which correspond to the vibration modes of ν CS(a1), δ CH(b2), δ CH(a1), ν CC(b2), and ν CC(a1), respectively.²⁰ The average EF of 4-ATP on the Au nanorings was calculated to be 2.6×10^5 by using the Raman peak at 1080 cm⁻¹ according to the method of Wang.²¹ Obviously, the EF gets improved when the 4-ATP molecules are absorbed on the Au nanorings-SiO₂-Au film structure. In particular, the EF is increased when the 4-ATP molecules are absorbed on the Au nanorings-SiO₂-Au film structure. In particular, the EF is increased when the SiO₂ spacer becomes thicker and reaches the maximum value of 1.4×10^7 with a 50 nm in thickness then decreases again when the thickness is larger than 50 nm. We strongly believe that the improved SERS effect on the Au nanorings-SiO₂-Au film structure is caused by the EM mechanism due to the strong coupling of the LSP of the Au nanorings and the DSP of the Au film. When the Au nanorings and the Au film are separated with a small gap, e.g., 10 nm, the SERS EF is only slightly in-

creased because the structural resonance wavelength (1070 nm) is far away from the laser excitation wavelength (785 nm) and the enhanced electric field is extremely confined in the gap, which is difficult to access by the molecules. When the gap becomes larger, e.g., 50 nm, the EF is further improved because the electric field is less confined and becomes much easily accessible by the molecules. More importantly, the largely blueshifted structural resonance wavelength (914 nm) is closer to the laser excitation wavelength, which leads to a stronger electric field. However, the EF will decrease when the gap is larger than 50 nm due to a weaker plasmon coupling effect.

In conclusion, we have demonstrated the fabrication of the Au nanorings-SiO₂-Au film structures by using nanosphere lithography technique. An enhanced tunability and linewidth narrowing of plasmon resonances of the structures have been realized by controlling the thickness of the SiO₂ spacer. Moreover, we can tune the plasmonic coupling between the Au nanorings and the Au film and we have achieved a maximum NIR SERS EF as large as 1.4×10^7 . We believe the Au nanorings-SiO₂-Au film structure has a promising commercial prospect for SERS substrates due to a simple, low cost and high throughput manufacturing method, and a large EF.

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- ¹E. C. Le Ru and P. G. Etchegoin, *Principles of Surface-Enhanced Raman Spectroscopy and Related Plasmonic Effects* (Elsevier, Amsterdam, 2009).
- ²A. M. Smith, M. C. Mancini, and S. Nie, *Nat. Nanotechnol.* **4**, 710 (2009).
- ³M. G. Banaee and K. B. Crozier, *Opt. Lett.* **35**, 760 (2010).
- ⁴J. Aizpurua, P. Hanarp, D. S. Sutherland, M. Käll, G. W. Bryant, and F. J. García de Abajo, *Phys. Rev. Lett.* **90**, 057401 (2003).
- ⁵E. M. Larsson, J. Alegret, M. Käll, and D. S. Sutherland, *Nano Lett.* **7**, 1256 (2007).
- ⁶S. Kim, J.-M. Jung, D.-G. Choi, H.-T. Jung, and S.-M. Yang, *Langmuir* **22**, 7109 (2006).
- ⁷K.-Y. Jung, F. L. Teixeira, and R. M. Reano, *J. Lightwave Technol.* **25**, 2757 (2007).
- ⁸F. Hao, P. Nordlander, M. T. Burnett, and S. A. Maier, *Phys. Rev. B* **76**, 245417 (2007).
- ⁹F. Hao, Y. Sonnefraud, P. Van Dorpe, S. A. Maier, N. J. Halas, and P. Nordlander, *Nano Lett.* **8**, 3983 (2008).
- ¹⁰J. Ye, P. Van Dorpe, L. Lagae, G. Maes, and G. Borghs, *Nanotechnology* **20**, 465203 (2009).
- ¹¹F. Le, N. Z. Lwin, N. J. Halas, and P. Nordlander, *Phys. Rev. B* **76**, 165410 (2007).
- ¹²G. Lévêque and O. J. F. Martin, *Opt. Lett.* **31**, 2750 (2006).
- ¹³Y. Chu and K. B. Crozier, *Opt. Lett.* **34**, 244 (2009).
- ¹⁴J. Ye, P. Van Dorpe, W. Van Roy, G. Borghs, and G. Maes, *Langmuir* **25**, 1822 (2009).
- ¹⁵J. Ye, P. Van Dorpe, W. Van Roy, K. Lodewijks, I. De Vlamincq, G. Maes, and G. Borghs, *J. Phys. Chem. C* **113**, 3110 (2009).
- ¹⁶J. Ye, N. Verellen, W. Van Roy, L. Lagae, G. Maes, G. Borghs, and P. Van Dorpe, *ACS Nano* **4**, 1457 (2010).
- ¹⁷See supplementary material at <http://dx.doi.org/10.1063/1.3504187> for resonances position and quality factor.
- ¹⁸L. J. Sherry, S. H. Chang, G. C. Schatz, R. P. van Duyne, B. J. Wiley, and Y. Xia, *Nano Lett.* **5**, 2034 (2005).
- ¹⁹J. Cesarino, R. Quidant, G. Badenes, and S. Enoch, *Opt. Lett.* **30**, 3404 (2005).
- ²⁰M. Osawa, N. Matsuda, K. Yoshii, and I. Uchida, *J. Phys. Chem.* **98**, 12702 (1994).
- ²¹Y. Wang, H. Chen, S. Dong, and E. Wang, *J. Chem. Phys.* **124**, 074709 (2006).