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Amplification of Surface-Enhanced Raman Scattering Due to Substrate-Mediated Localized Surface Plasmons in Gold Nanodimers

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Abstract: Surface-enhanced Raman scattering (SERS) is ubiquitous in chemical and biochemical sensing, imaging and identification. Maximizing SERS enhancement is a continuous effort focused on the design of appropriate SERS substrates. Here we show that significant improvement in a SERS signal can be achieved with substrates combining localized surface plasmon resonances and a nonresonant plasmonic substrate. By introducing a continuous gold (Au) film underneath Au nanodimers antenna arrays, an over 10-fold

increase in SERS enhancement is demonstrated. Triangular, rectangle and disc dimers were studied, with bowtie antenna providing highest SERS enhancement. Simulations of electromagnetic field distributions of the Au nanodimers on the Au film support the observed enhancement dependences. The hybridization of localized plasmonic modes with the image modes in a metal film provides a straightforward way to improve SERS enhancement in designer SERS substrate.

Keywords: Surface-enhanced Raman scattering (SERS), nanoantennas, localized surface plasmon (LSP), electron-beam lithography.

1. Introduction

Surface enhanced Raman scattering (SERS) continue to attract research interest due to its capabilities in ultra-high sensitivity analysis of bio- and chemical molecules.^{1,2} The SERS enhancement factors as high as 10^{11} have been demonstrated enabling single-molecule detection^{3,4} and are typically associated with the excitation of localized surface plasmon (LSP) modes in metallic nanostructures.⁵ The local charge oscillations at the structure edges lead to an enhancement of local electromagnetic field at the metal-dielectric interfaces which in turn enhances SERS in superlinear manner.⁶ As the LSP resonances crucially depends on the size and shape of and interaction between of metallic nanostructures,⁷⁻⁹ the design of nanostructures to achieve high field enhancement is one of the important factors in SERS research.

The modern nanofabrication technique, such as electron-beam lithography (EBL), focused ion-beam lithography and interference lithography promote the numerous designs of SERS substrates¹⁰ allowing for a precise control over the shape and spatial arrangement of nanostructures.¹¹ Various types of nanostructures, including nanodiscs, nanoholes, and different types of optical nanoantennas have been fabricated and tested as SERS substrate.^{12,13}

Among these designs, nanodimers, like a bowtie (two triangles facing each other) and disc dimers separated by nano-gaps, are the most preferred since they provide strong field enhancement in the gap.¹⁴⁻¹⁶ Single-DNA detection has been demonstrated with SERS by using nano-gaps of Au dimers.¹⁷ The SERS enhancement increases significantly with the decrease of gap size in nanodimers due to the significant localization of electromagnetic fields caused by the coupling between the adjacent nanoparticles. Sub-10 nm have been demonstrated for SERS enhancement,^{14-16,18-19} however, further reduction of the gap size is both extremely difficult due to the proximity effects in the EBL process and deteriorate field enhancement due to nonlocal effects.^{20,21}

Majority of the designs of SERS substrates have been focused on the optimization of LSP resonances. For example, Grand *et al.* and Féridj *et al.* studied optimization of SERS enhancement by tuning LSP resonances of controlled nanostructures and revealed important relationship between SERS enhancement and LSP resonance wavelength.^{22,23} The role of surface plasmon polaritons (SPPs: propagating surface waves along the interfaces²⁴) in SERS enhancement has been studied but provides lower enhancement factors.²⁵ In Ref.26 it has been shown that the metallic substrate has a strong influence on the optical extinction of Au nanoparticles compared to a dielectric substrate due to coupling of Au nanoparticles with the underlying Au substrate. When additional plasmonic nanostructures are placed on a smooth Au film, the LSPs of the gold nanostructures may result in a significant enhancement of the field around the Au nanostructures due to coupling between the antennas in the array via SPPs on the underlying Au film^{27,28} or LSP hybridization with the image modes in a plasmonic substrate.²⁹ This additional field enhancement, compared to LSPs on dielectric substrates, can be explored to enhance spectroscopic processes.

In this work, we investigate the role of a Au-film substrate on SERS from Au nanodimers and show that the enhancement factor is significantly improved compared to

nanoantennas on dielectric substrate. Three types of Au nanodimers such as bowtie, rectangle and disc dimers are fabricated and investigated. The 10-fold improved SERS enhancement was observed for the dimers deposited on a plasmonic film compared to a Si substrate with both types of molecules investigated (Rhodamine 6G (R6G) and 4-mercaptopyriding (4-MPy)) and for 2 excitation wavelengths. Numerical simulations of the electromagnetic properties are performed to understand the observed SERS amplification which can be attributed to hybridization of the localized plasmonic modes of the dimers due to image effects in a metallic substrate.

2. Experimental

Nanofabrication of arrays of Au nanodimers

The arrays of Au nanodimer nanostructures were fabricated with EBL in combination of lift-off process. Fabrication details can be found in our previous publications.^{30,31} The major process steps are shown in Fig. 1: (a) substrate preparation- a 5 nm-thick titanium and then a 50 nm-thick Au layer were sputtered on the silicon (Si) wafer surface; (b) spin-coating- 40 nm polymethyl methacrylate (PMMA) 495 and then 80 nm PMMA 950 layers were spin-coated onto the Au surface; (c) EBL exposure- accelerating voltage was 50 kV and beam current was 100 pA; (d) Development- the nano patterns was developed with IPA-DI water developer (IPA:DI)=7:3; (e) electron-beam evaporation- the samples were coated with a 40-nm Au layer via an electron beam evaporator; (f) lift-off- lift-off of the gold nanodimers was performed with acetone. The overall size of the structured area was $30 \times 30 \mu\text{m}^2$.

Fig. 1 Schematics of the fabrication process of nanodimers on a Au film: (a) Au sputtering; (b) PMMA spin-coating; (c) EBL exposure; (d) development; (e) electron-beam evaporation of Au; (f) lift-off; (g) illustration and SEM image of the final disc dimer array.

Raman measurements

The R6G and 4-MPy were chosen as molecular probes for Raman spectroscopy. The concentration of R6G is 5×10^{-5} M and the concentration of the 4-MPy (Sigma-Aldrich) solution is 2×10^{-3} M. The patterned substrate was cleaned with DI water, dried with nitrogen flow and cleaned with oxygen plasma. The SERS substrate was functionalized with respective R6G and 4-MPy molecules by immersion the substrate into the R6G and 4-MPy solutions, respectively. Then the samples were taken out and rinsed with DI water and dried with nitrogen blower. Raman spectra were acquired in a backscattering geometry using micro-Raman spectrometer LabRAM ARAMIS (Horiba Jobin Yvon). The laser source was focused on the sample surface using a 100 $\times$ objective (NA=0.9) to obtain a spot size of approximately 1 μ m. Excitation laser wavelength is 532 nm for the measurements on R6G

and 785 nm on 4-MPy. The laser power at the sample position was set as low as 0.6 mW to avoid burning and surface carbonization of the adsorbed molecules. The acquisition time for each SERS spectrum was 5 s, unless indicated differently.

Numerical simulation methods

Numerical simulations were performed to calculate the spectra and near-field distribution of the antennas. The simulation is based on finite integration technique (FIT) with commercial software CST Microwave Studio.³² The nanostructure dimensions of the models were used as those measured from SEM images. The sharp tips of the bowties and corners of the rectangle dimers are rounded in the simulation to the curvatures estimated from the SEM images and is 5 nm. The periodic boundary conditions were applied to simulate an array of the nanoantennas. The individual nanodimers were simulated by applying perfectly absorbing boundary conditions. In both cases Floquet ports were applied in the propagation direction. The structure was excited by normally incident light with its polarization along the direction of the dimers. The permittivity of Au used for simulations are the experimental values of Johnson and Christy.³³

3. Results and discussion

SERS Spectroscopy

Fig. 2 shows the SEM images of the fabricated Au bowtie, disc and rectangle dimer arrays. These nanodimers are deposited on continuous Au film, with their axis oriented in x-direction (Fig. 2a). The side-length of the bowtie, the diameter of the discs and the long side of the rectangles in the dimers are all 140 nm (the short-side length of the rectangle dimer is

80 nm). The gap size between the particles in all the dimers is 20 nm. The array periods in x- and y-directions are $P_x=500\text{nm}$ and $P_y=300\text{nm}$, respectively.

Fig. 2 (a) Schematic of a plasmonic nanostructure placed on a Au film and SEM images of (b) bowtie, (c) disc dimer and (d) rectangle dimer array. In all cases the gap in the dimer is 20 nm.

The SERS spectra for 532 nm and 785 nm Raman excitation wavelengths were investigated (Fig. 3). We first investigated the SERS spectra of the R6G molecules under the excitation with a wavelength of 532 nm for which these molecules have a maximum Raman

cross-section. The measured SERS spectra from arrays of bowtie, rectangle dimer and disc dimer deposited on a continuous Au film are shown in Fig. 3a. The polarization of the laser source is along the long axis direction of the dimer nanoantennas (x– direction). Four dominant peaks at 1195, 1359, 1506 and 1647 cm^{-1} are observed and attributed to aromatic stretching vibrations.^{34,35} The SERS intensity at the band at 1647 cm^{-1} is the highest among the peaks and was used as a measure of the enhancement (Fig. 3a). The bowtie antennas show the highest SERS intensity, followed by the rectangle dimers and disc dimers. This observation bodes well with the bowtie's sharp tips. In designing SERS substrates, sharp tips are preferred because their ability to concentrate electromagnetic fields via both plasmonic and “lightening-rod” effects.³⁶ The adjacent edges forming the nano-gap of the disc dimers are round and blunt and, therefore, produce lowest SERS enhancement, while the rectangles have the most extended nanogap. The SERS measurements from the molecules on unpatterned part of the Au film was not able to identify Raman peaks as a low roughness and electrically continuous film does not provide significant electromagnetic field enhancement.

For comparison, a set of counterpart nanodimers were fabricated on a silicon substrate. The SERS measurements under the same conditions as in the previous case, show much weaker enhancements than for the nanoantennas placed on Au film (Fig. 3b). This demonstrates a significant contribution of the underlying Au film to the SERS enhancement on nanoantennas. For the SERS intensity at the peak 1647 cm^{-1} , the enhancement improvement for the bowties on the gold film is more than one order of magnitude, 13 times, compared to the same antennas on a Si substrate, $I_{\text{Au}}/I_{\text{Si}}=13$.

Molecules 4-MPy have a large Raman cross section for the excitation wavelength of 785 nm. These molecules form a self-assembled monolayer on Au surfaces.³⁷ Fig. 3c shows the SERS spectra of 4-MPy molecule acquired from arrays of bowties, rectangle dimers and disc dimers deposited on a Au film. The strongest Raman intensity peak at 997 cm^{-1}

corresponds to the variation of hydrogen bonds when the Au atoms are in the same plane with the 4-MPy molecules. This mode is observed for bulk 4-MPy at 988 cm^{-1} and is blue-shifted 997 cm^{-1} in the SERS spectra of the monolayers on a Au surface due to the variation of hydrogen bonds when the Au atoms are in the same plane with the 4-MPy molecules.^{38,39} The band at 1096 cm^{-1} originates from the ring-breathing mode with C-S. This peak is red-shifted from a 1105 cm^{-1} peak of bulk 4-MPy to 1096 cm^{-1} in the SERS spectra due to coupling of the ring-breathing mode with the C-S stretching when the sulfur is bonded to gold surface.³⁹ For the nanoantennas on a Si substrate (Fig. 3d), the SERS intensity is much weaker than for a Au film, despite 10 times longer acquisition time. Except for a weak peak at band 998 cm^{-1} , other Raman peaks hardly distinguishable. The improvement of the SERS intensity due to a plasmonic film compared to Si-substrate is very significant and reaches 30 fold, much larger than that of the R6G molecules.

Fig. 3 SERS spectra of (a,b)R6G (the excitation wavelength of 532 nm) and (c,d) 4-MPy molecules (the excitation wavelength of 785 nm) measured on arrays of bowtie, rectangle dimer and disc dimers placed on (a,c) Au film and (b,d) Si substrate. The polarization of the excitation light is along the dimer direction. The numbers in the panels indicate the Raman shift. The acquisition time is normalized to 1 s for the measurements in (a-c) and 10 s in (d). The spectra are shifted with respect of each other in vertical direction for visualisation.

To better understand the SERS performance of the substrates, a SERS enhancement factor (EF) has been estimated as^{15,40}

$$EF = \frac{I_{SERS} N_{bulk}}{I_{bulk} N_{SERS}}, \quad (1)$$

where I_{SERS} is the intensity of a peak in the SERS spectra, I_{bulk} is the intensity of the same peak in the conventional Raman spectrum measured with a bulk substance, N_{SERS} is the number of molecules probed in the SERS measurements and N_{bulk} is the number of molecules within the excitation volume of the laser spot for the solid samples. The reference Raman spectra were obtained by measuring R6G and 4-MPy solid samples, respectively. The N_{bulk} was estimated by considering the laser spot of 1 μm in diameter, the laser penetration depth in the bulk sample (2 μm in R6G for the 532 nm and 10 μm in 4-MPy for the 785 nm laser, obtained from literatures^{41,42}) and densities of the bulk samples (1.26 g/cm³ for the R6G and 1.2 g/cm³ for the 4-MPy). The N_{SERS} was calculated by taking the surface coverage of R6G with concentration of the order 10⁻³ M is 10 monolayers and the area of the single R6G molecule is 4 nm² in a densely packed R6G monolayer.^{43,44} The number of 4-MPy molecules adsorbed on the substrate was calculated by assuming monolayer coverage on the surface of SERS substrate. A packing density of 6.8×10¹⁴ molecules/cm² reported for benzenethiol was

used for the calculation of N_{SERS} .^{45,46} The peak at 1647 cm^{-1} for the R6G molecules and the peak at 998 cm^{-1} for the 4-MPy molecules were used for the estimates of the enhancement factor.

Shown in Fig. 4 are the calculated EFs for the R6G molecules and 4-MPy molecules adsorbed onto the Au nanodimers fabricated on Au film and Si substrate, respectively. The calculated EFs were on the order of 10^5 for the all the nanodimers on Au film and on the order of 10^4 for the nanodimers on Si. For both the molecules, the EFs of the molecules adsorbed on the Au dimers supported on Au film are approximately one order magnitude higher than that for those on Si substrate. Comparing to the enhancement factors reported in the literatures, the EFs obtained in this work are among the highest EFs obtained from nanofabricated SERS substrates like nanorings, nanodots and nano-SRRs (10^4 - 10^6).^{34,47,48} Although the EFs are generally lower than that achieved with chemically synthesized nanoparticles or nanoparticle aggregates,^{17,49} the nanodimers fabricated with EBL have uniform features which are reproducible and robust. The EFs of the dimer nanostructures on Au film are much higher than that on the silicon surface. This suggests that the SERS enhancement can be improved by using a continuous Au-film underneath Au nanostructures.

Fig. 4 The measured enhancement factors for the dimer nanoantennas on Au film and Si substrate for (a) 532 nm and (b) 785 nm excitation wavelengths for the polarization of the excitation along the dimer direction.

Discussion

The above experimental results have shown the introduction of Au film can significantly enhance the SERS performance. To further understand the amplification of SERS of the Au nanodimers on Au film, numerical simulation of reflection spectra and electromagnetic distribution of in the near-field of the Au nanodimers were performed on different substrates (Fig.5). The resonances in reflection spectrum correspond to the excitation of LSP resonances which is origin of SERS enhancement.²² In Fig. 5a, narrow resonances are observed in the wavelength range 550-600 nm for the nanodimers on a Au film, which are shifted in the wavelength range of 800-900 nm for the same dimers on a Si substrate (Fig. 5b). This shift is due to both the change of the refractive index of the substrate and hybridization of the resonances due to the interaction with the image modes in a Au substrate which are absent for a Si substrate. The variation of the geometrical shape of the nanodimers alters the resonance wavelengths, reflecting the contribution of LSPs.

Shown in Fig. 5(c) and (d) are the spectra dependencies of the intensity enhancement $(E/E_0)^2$ at the nanogaps for the nanodimers on Au film and on Si substrate, respectively. For the nanodimers on Au film, the highest enhancement is observed in the wavelength range 550-600 nm, which is in agreement with the resonance wavelengths shown in Fig. 5(a). For the nanodimers on Si substrate, the field intensity peaks in wavelength range 800-900 nm, which corresponds to the resonance at 800-900 nm in the reflection spectra shown in Fig. 5(b). The field intensity of nanodimers on Au film is much higher compared to the same nanodimers on a Si substrate, in agreement with the our experimental observations.

Fig. 5 Simulated far-field reflection spectra from Au nanodimer array on Au film (a) and (b) Si substrate. The polarization of the incident light is along the dimer direction. The green and pink bars indicate the excitation of SERS wavelength range for 532 nm and 785 nm laser source, respectively. (c) and (d) Spectral dependence of the intensity enhancement $(E/E_0)^2$ measured at the gaps as indicted in the insert.

Fig. 6 shows the distributions of electric field, current density and power flow of the nanodimers. In the former case, high field intensity (a1-c1, a2-c2) is confined to the tips of the triangle, the edges of the rectangles and the edges of the disc dimers. The distributions are symmetrical with respect to the dimer axes. The field distributions around the top and the bottom of the nanodimers indicate to the strong interaction with a Au substrate and hybridization of the excitations which influence the field distribution, which is significantly different around the nanodimers on the Au and Si substrates. The absolute electric field

enhancement is much higher for the Au nanodimers on the Au film compared to the nanodimers on a silicon substrate, with the magnitudes corresponding well to the enhancement factors observed in the experiment. Comparison of the simulated reflection spectra and field distributions for the periodic arrays of the nanodimers and isolated nanodimers show very small difference which indicate that the SPP excitation and coupling between the nanoantennas in the array due to SPP modes can be neglected in the studied experimental conditions and the determining factor is the image modes in the Au film. The cross-sectional distribution of current density (a3-c3 and a7-c7) and the power flow (Fig. 6 (a4-c4) and (a8-c8)) correspond to the same picture of the LSP excitations. The field distributions are closely related to the geometrical design of the nanostructures and similar in shape for the nanostructures placed on both Au and Si substrates. At the same time, the power flow distributions across the substrates are very different. The reflection from a Au substrate cannot, however, explain the 10-fold enhancement of the SERS signal even if all the SERS signal is reflected. In reality, the SERS signal generated by point sources (molecules) in the vicinity of Au film may also be partially coupled to SPP modes on Au film even in the absence of nanoantennas. The latter has a significant role in a possible additional coupling to SPP modes. These SPP modes are then partially absorbed in Au film due to Ohmic losses, thus, introducing partial decrease of SERS signal observed in the far-field. The modeled field distribution point out that SERS is driven by the field enhancement originating from a nanoantenna coupled to its image in a Au film. The hybridization of the localized surface plasmon resonances of the Au nanodimers and their images further enhances the SERS signal (Fig. 7).

Fig. 6 Simulated electric near-field distribution ($|E|/|E_0|$) at the distance 45 nm from the

substrate, current density, and power flow around the Au nanodimers monitored at a wavelength of 532 nm for the Au nanodimers on (a1-c1, a2-c2, a3-c3, a4-c4) Au film and (a5-c5, a6-c6, a7-c7, a8-c8) Si substrate. The polarization of the excitation light is along the dimer direction.

Fig. 7 Schematic of hybridization of localized surface plasmon resonances of Au nanoantennas with their image mode in a Au film.

Similar observations can be made for the excitation wavelength of 785 nm (Fig. 8). In this case, despite the LSP modes are observed near the excitation wavelengths for the dimers on a Si substrate, the SERS enhancement is suppressed due to strong radiation in the substrate and weak reflection of the signal from the nanoantennas on a Si substrate. Again, the simulated absolute magnitude of the field enhancement is in agreement with the experimental observation of the relative SERS intensities between different substrates and different excitation wavelengths.

Fig. 8 Simulated electric near-field distribution ($|E|/|E_0|$) at the distance 45 nm from the substrate, current density and power flow around the Au nanodimers monitored at a wavelength of 785 nm for the Au nanodimers on (a1-c1, a2-c2, a3-c3, a4-c4) Au film and (a5-c5, a6-c6, a7-c7, a8-c8) Si substrate. The polarization of the excitation light is along the dimer direction.

It is interesting to compare the SERS enhancement from the nanoantennas for different polarizations: along the axis of between particles in the dimer discussed above and normal to it shown in Fig. 9. In the latter case, the SERS intensity is much lower than that for the orthogonal polarization for all cases considered for different molecules and excitation wavelengths. The SERS enhancement factors of the R6G molecules with 532 nm excitation for the bowtie, rectangle and disc dimers on Au film are 2.1×10^5 , 1.7×10^5 and 1.2×10^5 , respectively. The SERS enhancement factors of the 4-MPy molecules with 785 nm excitation for the bowtie, rectangle and disc dimers on Au film are 1.2×10^5 , 1.4×10^5 and 1.2×10^5 , respectively. This is consistent with the expected behavior of dimer's LSPs which lack the coupling effect between individual particles forming a dimer in this case. It is also noted that the geometrical shape doesn't significantly influence the SERS enhancement of the nanodimers for this excitation conditions. Fig. 9(c) is the simulated reflection spectra of the bowtie, rectangle and disc nanodimers for y-polarized excitation light. The resonance is further blue-shifted as compared to that for the x-polarized incident light as shown in Fig. 5, indicating the absence of coupling effect between the adjacent particles. The SERS spectra from the nanostructures on Si substrate are not presented for this polarization as the Raman signal is much smaller than for a Au substrate.

Fig. 9 SERS spectra of (a) R6G (the excitation wavelength of 532 nm) and (b) 4-MPy molecules (the excitation wavelength of 785 nm) measured on arrays of bowtie, rectangle dimer and disc dimers placed on Au. The numbers in the panels indicate the Raman shift. The acquisition time is normalized to 1 s. (c) Simulated far-field reflection spectra from Au nanodimer array on Au film. (d) Plots of field intensity $(E/E_0)^2$ as function of wavelength of the nanodimers on Au film. The polarization of the excitation light is normal to the dimer axis.

Fig.10 shows the electric field distribution on the top of the nanodimers (45 nm above substrate surface) with polarization of the excitation light along vertical direction (y-axis). These distributions are related to LSP of individual particles as seen by their shapes, and the field enhancement in the gap is practically absent. Nevertheless, the effect of the individual particles' LSP hybridization with the image modes in a Au substrate is clearly visible leading to stronger field enhancement (and SERS signal) compared to a Si substrate.

Fig. 10 Simulated electric near-field distribution ($|E|/|E_0|$) at the distance 45 nm from the substrate for different nanodimers and excitation wavelength for the polarization of the excitation light normal to the dimer axis.

4. Conclusions

We have demonstrated significant improvement of SERS enhancement from dimer nanoantennas placed on plasmonic substrate. The Au-film-supported nanodimers of different shapes exhibit the enhancement factors of more than 10-fold higher than that placed on a Si substrates, with the absolute SERS enhancement factors of the order 10^5 achieved. The enhancement is explained by the hybridization of localized surface plasmon resonances of the nanoantennas with their image modes in a Au film. Comparison of the SERS enhancement for different polarizations of the excitation light addressing either dimer's or individual nanoparticle's LSP modes shows the imaging coupling leads to the field enhancement in all configurations. This strategy of SERS enhancement circumvents the challenges in fabrication of extremely small nanotips or nanogaps that are conventionally pursued and provides a

simple way to design advanced SERS substrates with large areas, high sensitivity and reliability.

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Table of contents entry:

Surface-enhanced Raman scattering (SERS) is significantly enhanced by placing plasmonic nanoantennas on a plasmonic substrate.