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COMMUNICATION

Tunable SERS from aluminium nanohole arrays in the ultraviolet region†‡Zhi-Lin Yang,^{*a} Qian-Hong Li,^a Bin Ren^b and Zhong-Qun Tian^b

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Ordered Al nanohole arrays for tunable UV-SERS are theoretically proposed and simulated by using FDTD method. The properly designed Al nanohole arrays produce stable and predictable Raman enhancement under the deep UV laser illumination. The SERS enhancement factor as high as 5 to 6 orders of magnitude is attained in the optimal geometry. The correlation between the SERS and EOT is studied in detail.

Since the first observation of the Surface-enhanced Raman scattering (SERS) by Fleischmann and coworkers,¹ this technique has been extensively investigated and widely used in chemistry, physics, biology, surface science, material science and nanoscience. Hitherto, most SERS investigations and applications have been limited to the visible and near-infrared ranges since the widely used Au, Ag, and Cu substrates do not exhibit strong surface plasmon resonance (SPR) in the shorter wavelength regime where their interband transitions become prominent. Recently, the investigation on the near and deep ultraviolet excited SERS (UV-SERS) and UV-TERS are rapidly evolving because of its great advantages and application in bioscience and material sciences.^{2,3}

Aluminium, whose permittivity holds a large negative real and a small positive imaginary components in the UV region, supports a collective excitation of the conduction electrons known as surface plasmon excitation, being potentially served as an active UV-SERS substrate. Although Zeman and Schatz predicted that Al ellipsoids enable strong Raman scattering enhancement up to 5 orders of magnitude in the UV region two decades ago,⁴ only a limited number of experimental reports exploring plasmonic effects of Al in this region can be found. Recently, Dörfer and coworkers reported an encouraging experimental result, wherein they observed surface-enhanced Raman signal from a 50 nm-thick aluminium surface immersed in aqueous solution containing crystal violet with 244 nm laser excitation.⁵ Chan and coworkers,⁶

Langhammer and coworkers,⁷ reported the localized surface plasmon resonance (LSPR) spectra of triangular aluminium nanoparticle arrays and nanodisk arrays, respectively. Both of them showed that the LSPR of the precisely fabricated Al nanoparticle arrays can be easily extended to the UV, even deep UV, region.

In this communication, particular efforts are made to address the plasmonic properties of ordered Al nanohole arrays, which is stimulated by the more stable and reproducible SERS than nanoparticle based structures that have been confirmed experimentally.^{8–11} Ekinci and coworkers have successfully observed the extraordinary optical transmission (EOT) in the ultraviolet region of Al nanohole arrays.¹² The transmission peaks in the UV region strongly confirmed the resonant excitation of surface plasmons (SPs) and imply the possibility to utilize Al nanohole arrays as potential substrates with tunable UV-SERS.

The geometry of Al nanohole arrays considered in this work is illustrated in Fig. 1, where the parameters p , d , and t denote the hole periodicity, hole diameter and film thickness, respectively. All calculations were performed by using Lumerical FDTD solutions software (Version 6.5). The incident plane wave propagated along the negative z -axis direction with polarization along x direction. Periodic boundary conditions in the x and y directions were used in the simulation. Simulation time was set to be 1000 fs, which was long enough to ensure calculation convergence. The frequency dependent optical constant of Al was taken from ref. 13.

Fig. 2a shows that the transmission spectra from Al nanohole arrays are quite different from that of a single nanohole.

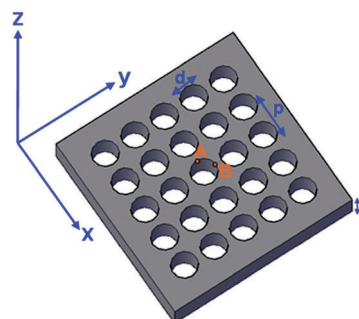


Fig. 1 Schematics of nanohole arrays in the Al film with diameter d , thickness t and periodicity p .

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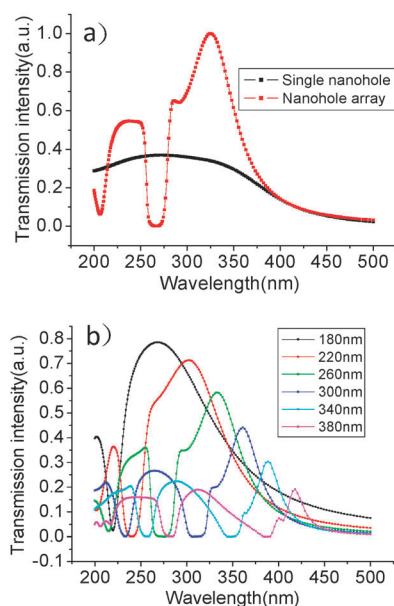


Fig. 2 calculated transmission spectra through single Al nanohole and nanohole arrays. (a) Calculated transmission spectra for a single nanohole with $d = 150$ nm, $t = 90$ nm and nanohole arrays with fixed periodicity $p = 256$ nm (b) Calculated transmission spectra for nanohole arrays with different periodicities (from 180 nm to 380 nm) as listed in the legend at $d = 150$ nm, $t = 90$ nm.

For a single nanohole with $d = 150$ nm, $t = 90$ nm, there is only a broad and relatively weak LSPR band located at the UV region. For nanohole arrays with the hole periodicity $p = 256$ nm, the SPR modes are dramatically changed. There are four distinct SPR peaks that all distributed within the UV region. These peaks clearly showed the occurrence of the surface plasmon resonance in this frequency region.¹⁴ As the holes periodicity changes in the range of 180 to 340 nm, the peak positions of transmission remain in the UV region, as shown in Fig. 2b. The peak position keeps a monotonous red-shift tendency with the increasing of holes periodicity and it finally turns into the visible region when the periodicity is larger than about 360 nm. This tunable SPR in the UV region is quite different from those of gold and silver, which just show good plasmonic properties in the visible and near infrared region. The reason is that Au and Ag exhibit interband absorptions below the wavelength of about 590 nm and 350 nm, respectively, whereas Al has low absorption down to wavelength of 200 nm due to its free electron like character and high bulk plasmon frequency. The accessibility of the SPR in the 200–500 nm range makes Al an excellent candidate for SERS and other potential plasmonic applications in the UV region.

We have demonstrated that the peak position of the transmission spectra can be easily tailored through changing the hole periodicity in Fig. 2. The tunable peak position of EOT means tunable SPR in the UV region for Al nanohole arrays. So, for a given excitation laser with constant wavelength, for example, 325 nm He–Cd laser or 244 nm deep UV laser, one may get strong UV-SERS signal from Al nanoholes substrate through changing the hole periodicity to an appropriate value. Brolo *et al.* have experimentally investigated the correlation of EOT with SERS in Au nanohole arrays,⁸ indicating that SERS

enhancement factor usually reaches the maximum at certain wavelength where the largest transmission can be detected also. This is understandable since SPR is responsible for both EOT and SERS from the nanohole arrays in most of cases, and we have confirmed this in our previous theoretical works.¹⁵ However, the frequency for the maximum SERS signal is not always at the EOT peak because of the complex mechanism of EOT phenomenon, which cannot be explained by the SPR theory thoroughly.¹⁶ In order to quantitatively understand the relationship between EOT and SERS in the subwavelength Al nanohole arrays, a theoretical comparison is given in Fig. 3. Two points (marked as A and B in Fig. 1) on the surface are selected to calculate their local electric field intensity enhancement (defined as $|E_{\text{loc}}/E_{\text{in}}|^2$) in the range of 200–500 nm. The geometric parameters are the same as Fig. 2a. Obviously, field intensity enhancement at point A is higher than that at point B, which can be easily understood since the polarization is along the x direction. Although the electric field intensity enhancement at points A and B are different, both of which can reach the maximum at 211 nm, 282 nm and 336 nm. It is well known that SERS enhancement is approximately proportional to the fourth power of the local field enhancement, so the maximum SERS enhancement at point A is about 4×10^5 when a 211 nm laser is applied. However, our calculation results show that the profile of the electric field intensity enhancement is clearly different from that of the transmission spectra, regarding the relative values or positions of their peaks, as shown in Fig. 3.

Exploring the physical origin of SPR may help us understand the aforementioned wavelength deviation between the EOT peak and the maximum SERS. In the case of normal incidence, the wavelength of propagating surface plasmons (PSPs) resonance (λ_{sp}) from nanohole arrays can be roughly estimated using the following equation:¹⁷

$$\lambda_{\text{sp}}(i, j) = \frac{P}{\sqrt{i^2 + j^2}} \sqrt{\frac{\epsilon_d \epsilon_m}{\epsilon_d + \epsilon_m}}$$

where P is the lattice constant (periodicity) of the array, i and j are integers that are related to the scattering orders of the array, ϵ_d and ϵ_m are the real part of dielectric constants of the adjacent medium and the metal, respectively. According to the equation, the 285 nm peak in the transmission spectrum is the (1, 0) PSPs mode, and the one at 225 nm is the (1, 1) mode.

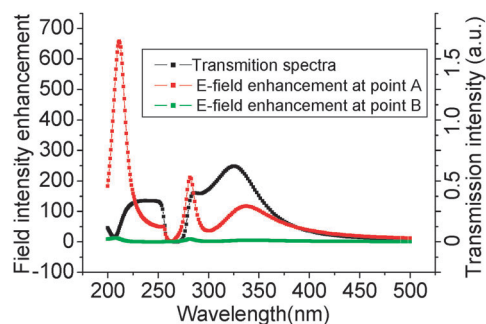


Fig. 3 Calculated electric field intensity enhancement of two points (A, B, marked in Fig. 1) at the reflected surface and transmission intensity over the spectral range of 200 nm to 500 nm from nanohole arrays with $p = 256$ nm, $d = 150$ nm and $t = 90$ nm.

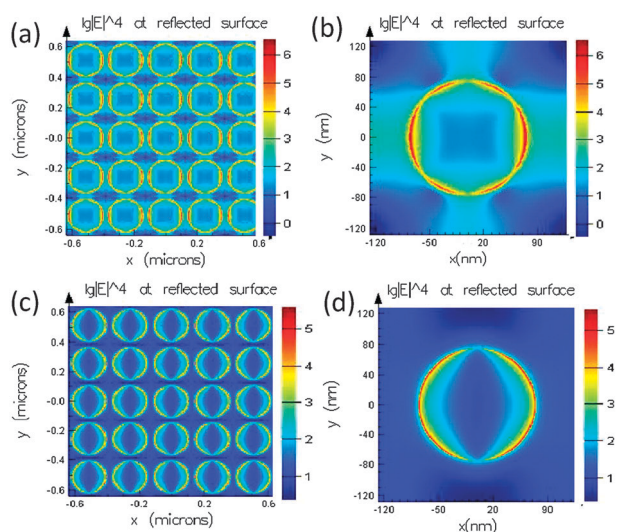


Fig. 4 Calculated SERS electromagnetic enhancement distribution at a reflected surface of Al nanohole arrays with $p = 256$ nm, $d = 150$ nm, $t = 90$ nm at 211 nm excitation (a), (b) and at 282 nm excitation (c), (d).

The other two peaks located at 250 nm (quadrupole mode) and 325 nm (dipole mode) can be attributed to the resonance of localized surface plasmon (LSP) modes, which can be clearly identified by the calculated electric field intensity enhancement distribution on the surface of nanohole arrays, as shown in Fig. 4. The interactions between PSPs on both surfaces and LSPs in the hole make the overall transmission spectra and SERS properties very complex.^{18,19} In general, the PSPs due to the interaction of the light with the ordered nanoholes play a dominant role in the enhanced transmission, however, the LSPs contribution cannot be negligible. From Fig. 3 and 4, we can infer that the relative contribution of both PSPs and LSPs to EOT and SERS are not exactly identical. So, one should keep in mind that the nanohole array gives resonant transmission at the excitation wavelength that probably does not correspond to the maximum surface-enhanced Raman scattering signal. SPs modes and UV-SERS properties at the transmission surface can be found in Fig. S1 and Fig. S2 in the supporting information.†

From Fig. 4, one can see the highest SERS enhancement is always located near the aperture edge at the air/Al interface, and the maximum SERS enhancement at the edge is about 6 orders of magnitude. These small regions with very high SERS enhancement factor are usually called “hot spots”, which play a key role in SERS especially in single molecular SERS. The hot spots are always located at the hole edge and is of great importance in attaining reproducible spectra, without which quantitative analysis is very difficult even impossible.

The main disadvantage of using the Al substrate in SERS is the existence of the natural 2–3 nm oxide layer. In order to quantitatively estimate the effect of the oxide layer on EOT and SERS, a detailed calculation is presented in the supporting information. The oxide layer with distinct thickness (1–4 nm)

makes all SPR peaks slightly red-shifted (Fig. S3†) and the maximum SERS enhancement shows about one order of magnitude decrease when 2 nm Al_2O_3 layer forms on the pure Al surface (Fig. S4†). However, the SPR modes keeps unchanged (Fig. S5†). This is particularly useful sometimes because a natural born oxide layer provides an isolated layer to prevent the direct interaction between Al and the probe molecules, similar to that of shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS).²⁰

In summary, Al nanohole arrays are proposed to be utilized as efficient SERS substrates with high reproducibility in the UV Region. The non-identical wavelength dependence of maximum field enhancement and of maximum optical transmission for Al nanohole arrays with subwavelength geometries imply the discriminating contributions of PSPs and LSPs to EOT and SERS. These results offer abundant opportunities to understand the underlying physical mechanism of EOT and SERS and design a promising platform for UV-SERS studies and applications.

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