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Composite Structure of Ag Colloidal Particles and Au Sinusoidal Nanograting with Large-Scale Ultra-High Field Enhancement for SERS Detection

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Abstract: In this study, a novel composite Surface-Enhanced Raman Scattering (SERS) substrate is proposed for ultrasensitive detection. Consisting of gold sinusoidal nanograting and silver colloidal nanoparticles (AgNPs-AuSG), this type of SERS substrate is easy for fabrication by maskless laser interference lithography, and capable of providing large-scale ultra-high field enhancement, attributed to localized surface plasmons (LSPs) and surface plasmon polaritons (SPPs). The enhancement factor (EF) of this composite substrate is as high as up to 10 orders of magnitude in the simulation experiment. Experimental results show that this large-area, productive SERS substrate of AgNPs-AuSG has realized sensitive TNT and RDX detection with the limit of detection (LOD) of 10⁻¹⁰ M, which may be a potential candidate for trace explosives detection.

Keywords: surface plasmon polaritons; sinusoidal nanograting; ultrahigh field enhancement; enhancement factor



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). 1. Introduction

Surface-enhanced Raman spectroscopy (SERS), as a 'chemical fingerprint' of the target materials, is a sensitive and reliable detection method extensively employed in biosensors [1,2], food security [3,4], and environment safety [5,6]. Considerable efforts have been made to develop the SERS substrate, including fabricating and using a range of structures and materials [7,8]. In terms of conventional two-dimensional SERS substrates, the enhanced Raman signal usually relies on the "hot spots" generated by the LSP resonance between nanoparticles [9,10]. Qian et al. [11] proposed a hybrid nanostructure composed of nanoporous gold films and gold nanoparticles. Ardini et al. [12] designed a large area-efficient SERS substrate, a nanoporous gold decorated with silver nanoparticles. These substrates have giant enhancement due to strong near-field coupling. It has been demonstrated that the coupling of mutual polariton modes can be excited by the particlefilm complex structure [13–15]. Above the metal film, the metal nanoparticles (NPs) are periodically arranged with several nanometers apart from each other, which can act as a two-dimensional grating to excite the SPP wave, leading to the coupling of LSPs and SPPs [16]. So far, researchers have found that the SERS EF of the metal film and NPs coupling structure is sensitive to many factors, including the thickness of the dielectric layer, the size of the nanoparticle, and the distance between them [17,18]. However, it is not easy to control the interparticle at small periodicities, which is very important, because in this case strong coupling between adjacent NPs can be achieved [19–22]. In this paper, a composite SERS substrate is designed, as shown in Figure 1. The substrate is composed of two parts: one is the gold sinusoidal grating (AuSG) as a fixed substrate; the other is silver colloidal nanoparticles (AgNPs), which act as a flowing substrate.



Figure 1. Schematic diagram of the composite SERS substrate.

The composite SERS substrate has the following advantages:

- (1) High field enhancement. There are a lot of hot spots in the dimer and gaps between the nanoparticles and the grating surface.
- (2) Fabrication friendliness. The sinusoidal nanograting can be easily fabricated over a large area using the currently established dual-laser interferometric lithography method, avoiding the expensive and time-consuming electron beam-based nanofabrication method. AuSG with pattern periodicity has the advantage over the random configuration of surface structures due to its reproducibility and pattern scalability.
- (3) Continuous detection. Combining colloidal AgNPs with continuous flow microfluidics helps trap the analyte at the detection area [23], which is important for SERS detection. The flowing AgNPs also help resolve the problem of memory effects and make the composite SERS substrate reusable.

This paper delves into the EM field enhancement in the AgNPs-AuSG substrate, which could contribute to the actual detection of trace explosives.

2. Model and Theoretical Analysis

2.1. Theoretical Analysis

SiO₂

molecule

Theoretical and experimental studies have shown that when the gap between adjacent NPs reaches the order of tens of nanometers, the LSPs generated by NPs can be coupled to each other to elevate the EM fields, and the Raman intensity can be 2–4 orders of magnitude stronger than that of a single nanoparticle [24]. The concept of plasmon coupling (hybridization) was first proposed and explained from the perspective of molecular orbital hybridization by Nordlander [25].

Besides, the coupling of SPPs and LSPs can also be explained by the theory of plasmon hybridization. When NPs are close to the metal grating, the surface plasmon modes will interact with each other and produce a hybrid mode [21]. The coupling is related to the resonance frequencies of LSPs and SPPs. When their resonance frequencies are close, the coupling strength of LSPs and SPPs increases significantly, usually accompanied by Rabi splitting, that is, the energy separation between normal modes [26]. In order to avoid Rabi splitting, according to Mie's theory, small AgNPs with a radius of about 30 nm are chosen, and the resonance wavelength of LSPs is far away from that of AuSG SPPs at 785 nm in the experiment [27]. The weak coupling of LSPs and SPPs will not affect their resonance frequencies, which brings convenience to Raman detection. Therefore, under the joint enhancement of SPP and LSP, we can obtain a highly enhanced electric field.

SPPs, propagating at the metal/dielectric interface, are essentially two-dimensional electromagnetic waves, which cannot be excited directly by light beams [28,29]. For the sinusoidal grating depicted in Figure 1, the SPPs can be excited when their wavevector matches with the incident photons and grating as follows [30]:

$$\beta = k_0 \sqrt{\frac{\varepsilon_m(\omega) \times \varepsilon_d}{\varepsilon_m(\omega) + \varepsilon_d}} = k_0 n_d \sin \theta_i \pm m \frac{2\pi}{\Lambda}$$
(1)

where β is the SPP wave vector, $k_0 = \frac{\omega}{c}$ is the incident wave vector, and $2\pi/\Lambda = k_g$ is the grating wavevector. Here, Λ is the periodicity of the grating, ω and c are the frequency and speed of the incident light, $\varepsilon_m(\omega)$ and ε_d are metal and dielectric permittivity, θ_i is the angle of the incident light with respect to the normal on the grating, m is an integer and represents the grating diffractive order, n_d is the refractive index of the medium surrounding the device, namely water.

2.2. FDTD

Since the use of near-infrared (NIR) excitation can greatly reduce the interferences from fluorescence and effectively avoid the decomposition of samples induced by strong excitation energies at the shorter wavelengths, 785 nm laser has become one of the most common excitation sources for portable Raman instruments. In the actual TNT and RDX detection experiments, an excitation laser with a wavelength of 785 nm (Ocean Optics Laser-785, 100 μ m at 0.22 NA) is used. It is well known that an optimized SERS enhancement is expected when the periodicity of grating is tuned to match with the excitation source in SERS experiments. In order to excite SPPs at 785 nm, the periodicity of the AuSG has to be about 570 nm by Equation (1), with the dispersive dielectric function of Au from Ref. [31]. The optical responses of the composite substrate are computed through FDTD simulations, as defined in Figure 1. The Λ , amplitude, and thickness of AuSG are set to 570 nm, 20 nm, and 120 nm, respectively since it has a large SERS. Periodic boundary conditions (PBCs) are used in the X- and Y-direction, while perfectly matched layers (PMLs) are used in the Z-direction. The normal incidence of light (plane waves) with transverse magnetic (TM) polarization, are considered as excitations. The dispersive dielectric function of Ag and Au is extracted from the experimental data from the Ref. [31,32]. The nondispersive refractive indices of H₂O and glass (SiO₂) are considered as 1.3356 and 1.45, respectively. Relatively fine grid spacings set with 1 nm, and simulation time with 1000 fs is applied for well-converged results.

3. Results

3.1. Double Enhancement

Some scholars have studied the characteristics of SPPs formed by gold sinusoidal grating [33]. Excitation of SPPs is detected as a minimum in the reflected light. The reflection and absorbance spectra of AuSG as a function of incident light and the electric field distribution at the resonance wavelength are shown in Figure 2.



Figure 2. Reflection and absorbance spectra of AuSG as a function of excitation light wavelength. The subplot is the electric field distribution of the x–z plane (y = 0) at an SPP resonance wavelength of 786 nm. The Λ , amplitude, and thickness of AuSG are 570 nm, 20 nm, and 120 nm, respectively.

It can be seen from Figure 2 that the SPPs resonate at the excitation light wavelength of 786 nm, which corresponds to m = 1 of the grating diffractive order, according to Formula (1). In the electric field distribution subplot, the SPPs propagate along the surface of the grating, accompanied by the periodic spatial distribution of the surface electric field.

SPPs, as an evanescent wave, can enhance the electric field above the grating surface by a maximum of 16.5 times.

In turn, the surface electric field of AgNPs entering this range can be enhanced [34]. The coupling between LSPs and SPPs depends on many conditions, such as AgNP size and position. When AgNPs are located at different positions of the evanescent field, the coupling of LSPs and SPPs is different, resulting in different electric field enhancements. Due to the periodicity of the evanescent field, the electric field enhancement of AgNPs at two typical positions of the evanescent field is analyzed, as shown in Figure 3.



Figure 3. The electric field distribution in the x–z plane (y = 0) at the resonance wavelength of SPPs at 786 nm, where AgNP is located at z = 200 nm. The area enclosed by the white curve represents an electric field greater than 10 V/m. The subplots are the Energy flux.

In Figure 3A, due to the weak evanescent field near AgNPs, the electric field of the AgNP surface is mainly enhanced by LSPs, and the field intensity is small. On the contrary, in Figure 3B, the evanescent field around AgNPs located at z = 200 nm is almost 10 V/m seen from Figure 2, which enhances the field of AgNP surface greatly. It is noted that the double enhancement of LSPs and SPPs, resulting in a field enhancement of as high as 43.8 around the AgNPs, is almost 2 times that in Figure 3A. It can be found that the LSP mode in Figure 3B is a dipole mode, while the quadrupole mode appears in Figure 3A. It is well known that the field at higher LSP modes is smaller than the one at the dipole mode.

3.2. Large-Scale Field Enhancement

As an evanescent wave in the dielectric, the SPP fields fall off exponentially along the direction perpendicular to the grating surface, with the evanescent decay length of the fields calculated by Formula (2):

$$\delta_d = 1/\sqrt{\beta^2 - \varepsilon_d k_0^2} \tag{2}$$

It is evident that δ_d = 322.3 nm in the water at λ_0 = 785 nm by Formula (2). In other words, a wide area of the enhanced field is formed over the surface of the grating, which can further couple with the LSPs formed by AgNPs or Ag dimers in this region. The E_{max} and EF of x–y plane in the water away from the surface of AuSG are shown in Figure 4.

The z value of the monitoring plane (x–y plane) is continuously scanned through FDTD, and the electric field distribution of the x–y plane at different distances L is obtained. As can be seen from Figure 4, when L = 69.4 nm, the maximum electric field strength of the x–y plane can still be about 11.7 v/m. In other words, only due to the enhancement of SPPs of the AuSG, the theoretical EF reaches 10^4 in the range of L < 70 nm.

Combined with AgNPs, many hot spots can be formed in this area. Generally speaking, the stronger the evanescent field is, the greater the electric field enhancement on the AgNP surface may be. Due to the liquid flow, AgNPs do not always adhere to the AuSG surface, and the distance between them will vary randomly. The changing trend of the electric field enhancement of the composite substrate is further studied under the condition of changing the distance between AgNPs and AuSG.



Figure 4. E_{max} and EF on the x–y plane in water as a function of the distance L from AuSG. The subplot is the electric intensity distribution of x–y plane at L = 69.4 nm, that is, z = 200 nm.

In order to reduce the error caused by the simulation, the calculation method of the average EF of hot spots is first defined. It is well known that SERS EF can be approximately calculated as $EF \approx (|E_{loc}|/|E_0|)^4$. According to the characteristics of the structure, considering the numerical instability of the metal surface and the scale of adsorbed molecules, the average EF of a certain area is defined as \overline{EF} .

$$\overline{EF} = \left(\frac{\iiint(|E_{loc}|/|E_0|)dv}{V}\right)^4 \tag{3}$$

where $E_0 = 1$ V/m, is the incident electric field, $E_{loc} = (E_x, E_y, E_z)$ is the local electric field, and V is the volume of a certain area, that is, the range within 2 nm from the hot spot in the experiments.

In order to evaluate the enhancement capability of the composite substrate, a location with a large evanescent field on the different x-y plane is selected for analysis and simulation research. The E_{max} and EF as a function of the distance between AgNPs and AuSG with water medium are shown in Figure 5.



Figure 5. E_{max} and EF as a function of the distance between AgNPs and AuSG with water medium. The distance is from 5 nm to 305 nm. The subplot is the schematic of electric field enhancement.

It can be obtained from Figure 5 that when the distance between AgNPs and AuSG is 5 nm, EF can reach as high as 10^7 . Even when the distance is 95 nm, the EF reaches 10^6 . On the contrary, when there is no AgNP, the EF at this position is only 10^4 , as shown in Figure 4. This is because, in the larger evanescent field, SPPs can be used as the excitation source of the in-sphere LSPs, which greatly enhances the electric field intensity on the surface of AgNPs.

It is noted that in the range of less than 305 nm, the EF of the AgNP surface hot spot can be greater than 10⁵. This wide range of electric field enhancement characteristics can

greatly reduce the accuracy of the detection molecules on the substrate surface position in the SERS detection enhancement application.

3.3. Ultra-High Field Enhancement

When AgNPs and AuSG are close, the nanogap between them forms a hot spot with extremely high field enhancement, and their electric coupling is similar to that of a dimer. When the distance between AgNPs and AuSG is 2 nm, the electric field distribution in the x–z plane and average EF of nanogap, that is, the hot spot, is shown in Figure 6.



Figure 6. Electric field distribution and EF at resonance wavelength when the distance between AgNPs and AuSG or Au film is 2 nm; (**A**,**B**) AgNPs on AuSG; (**C**) AgNP dimer on AuSG. The gap of the dimer is also 2 nm. (**D**) AgNPs on Au film. The thickness of the film is 120 nm, and the incident light wavelength is about 573 nm.

SPPs can be coupled into LSPs to form an equivalent scattering source when encountering AgNPs, thereby elevating the electric fields. The average EF of the hot spot in Figure 6A is about 10⁷, while in Figure 6B, it reaches 10¹⁰ due to the strong SPPs. In Figure 6A, a transverse dipole is formed, and electrons are concentrated on the left and right sides of the bottom of the AgNPs, forming two hot spots between the AgNPs and AuSG. In Figure 6B, the AgNPs become a longitudinal dipole affected by the strong evanescent wave, with electrons concentrate on the top and bottom surfaces, so that the EF of both the hot spot and the top region of the AgNPs are significantly elevated. When the dimer is close to AuSG, the hot spot is not only in the nanogap of AgNPs, but also in the nanogap between the dimer and AuSG. The average EF of all hot spots is greater than 10⁸, as shown in Figure 6C. Theoretically, the composite substrate has an ultra-high electric field enhancement capability, making it possible and effective to detect trace explosives such as TNT, DNT, and RDX.

In Figure 6D, although plasmon resonance may also occur between AgNPs and Au film, and can generate hot spots with high field enhancement. But the resonance largely depends on factors such as the frequency of the incident light and the distance between AgNPs and Au film. Therefore, it is not easy to obtain a large electric field enhancement at a specific frequency, such as 785 nm. On the contrary, no matter how AgNPs flow, the composite substrate composed of AgNPs and AuSG can achieve a high electric field enhancement of 785 nm, which is close to the resonance wavelength of SPPs.

3.4. Experiment

In order to test the trace level explosives detection performance of the composite substrate and verify the simulation results, SERS detection of low concentration TNT and RDX solution samples is carried out.

The designed AuSG can be realized experimentally by the following procedures: Firstly, a positive photoresist (PR; NOA-63) is spin-coated on an SiO₂ substrate. Secondly, the AuSG with a periodicity of about 570 nm is fabricated by laser interference lithography (LIL; Coherent MBD-266, a wavelength of 266 nm and a power of 30 mW) [35]. The amplitude and periodicity of AuSG can be flexibly adjusted and controlled by changing the time and angle of LIL. Then, the Au layer (about 120 nm) is deposited through evaporation at a rate of 0.1 nm/s. The AgNPs with a diameter of about 60–110 nm are prepared by the procedure described in Ref. [36]. The Atomic Force Microscope (AFM) image of the surface morphology of the grating and the Transmission Electron Microscope (TEM) image of AgNPs colloids are shown in Figure 7.



Figure 7. (**A**) Top-view AFM image of AuSG with a periodicity of about 570 nm; (**B**) surface profile scan of the AuSG; (**C**) TEM image of AgNPs.

TNT and RDX solution samples with low concentrations are prepared, and then added to the composite substrate. In the experiment, Ocean Optics Laser-785 is used as the excitation laser, and SERS signal is measured with a Raman fiber optic probe (Inphotonics RPB, 200 μ m collection fibers) and a Raman spectrometer (Ocean Optics QE *Pro*). The spot size of the excitation laser is about 200 μ m at the focus point of the Raman probe. The SERS spectra of TNT and RDX are collected and the average values of Raman signal intensities from 600 to 2000 cm⁻¹ are shown in Figure 8.



Figure 8. Example SERS spectra of (A) TNT; (B) RDX.

It can be found that when the concentration of TNT solution is 10^{-8} M, there are some strong Raman characteristic peaks of the TNT molecule SERS spectrum, which are 824 cm^{-1} (NO₂ scissoring vibration), 1212 cm⁻¹ (C-H ring bend and in-plane rocking), 1364 cm⁻¹ (NO₂ symmetric stretching), 1536 cm⁻¹ (NO₂ asymmetric stretching), and 1619 cm⁻¹ (2,6-NO₂, asymmetric ring stretching) [37], in Figure 8A. That is to say, the main Raman vibrations of TNT at those Raman shifts, are obviously enhanced and can be easily detected. However, when the concentration of the TNT solution drops to 10^{-11} mol/L, the Raman signal intensity of TNT is so weak that Raman characteristic peaks can hardly be found. The characteristic RDX bands at 885 cm⁻¹ (C-N-C ring breathing mode), 1218 cm⁻¹ (N-C stretching), and 1310 cm⁻¹ (CH₂ twisting, N-N stretching vibration) are also present in the SERS spectra down to a solution sample as low as 10^{-10} M, as shown in Figure 8B. From Figure 8, the experimental results indicate that the limit concentration of TNT and RDX solutions for SERS detection can reach 10^{-10} M. These results also confirm that the explosives materials have very distinct and identifiable SERS bands that can be measured using the composite SERS substrates.

Under experimental conditions, the analytical enhancement factor (AEF) can be calculated by:

$$AEF = \frac{I_{SERS}/C_{SERS}}{I_{RS}/C_{RS}}$$
(4)

where I_{SERS} and C_{SERS} are the Raman signal intensity and trace explosives concentration from composite SERS substrate, while I_{RS} and C_{RS} are the Raman signal intensity and trace explosives concentration from non-SERS substrate, respectively. It can be seen from Figure 8 that the symmetrical nitro stretching at 1364 cm^{-1} is the strongest band of TNT, and the C-N-C ring breathing at 885 cm⁻¹ is the strongest band of RDX, which can be used to estimate the AEF [37]. For the non-SERS substrate, the trace explosives concentration is 0.1 M. The AEF of the composite SERS substrate is about 5.3×10^8 at 1364 cm⁻¹ for TNT with a concentration of 10^{-8} M, and is 1.2×10^{8} at 885 cm⁻¹ for RDX with a concentration of 10^{-8} M. The AEF is not as large as the maximum EF of simulation. One of the reasons may be the random distribution of explosive molecules and AgNPs in the fluid. Raman signals of not all molecules are strongly enhanced by the electromagnetic coupling effect between AgNPs and AuSG. The AEF critically depends on the availability of the number of hotspots, the analyte molecule adsorption, the orientation of molecules on the AgNP surface, and the excitation wavelength. We are investigating how to capture analytes through surfacegrafted agents (such as 4-Aminothiophenol) or metal-organic-frameworks (such as ZIF-8), and localize them on the surface of flowing AgNPs to improve SERS performance.

4. Conclusions

In this paper, a composite SERS substrate consisting of gold sinusoidal nano-grating and silver colloidal nanoparticles was proposed and studied. The substrate can be fabrication-friendly for large areas only when double laser interferometric lithography and hot evaporation are used. Due to SPPs and LSPs, the composite substrate had a large-scale ultrahigh field enhancement, with EF reaching up to 10 orders of magnitude, verified by the numerical simulations. The experiment results show that the substrate had an LOD of 10^{-10} mol/L in the detection of both explosives TNT and RDX. Combined with microfluidic technology, we are confident that the composite SERS substrate has a great potential for real-time, continuous detection of trace explosives in the future.

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