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Research paper

Large-scale Ag-nanoparticles/Al₂O₃/Au-nanograting hybrid nanostructure for surface-enhanced Raman scattering



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ABSTRACT

There has been increasing interest in surface-enhanced Raman scattering (SERS) due to its ability in nondestructive and efficient detection of molecules. However, the fabrication of ideal SERS substrates with large-scale, strong and uniform 'hot spots' was always the challenge for the commercial use of SERS. Here, we designed an Ag-nanoparticles/Al₂O₃/Au-nanograting hybrid nanostructure as SERS substrate, in which the deep Au nanograting was formed by nanoimprint lithography (NIL) and metal deposition process, and the isolating layer of Al₂O₃ was deposited by atomic layer deposition (ALD) to form the large area precisely-controlled nanograps between nanoparticles and nanograting. This hybrid nanostructure utilized the deep metal grating and further the strong local field from multiple coupling systems to realize large-scale and uniform "hot spots". The optimized hybrid structure substrates showed a highly uniform field enhancement, with the enhancement factor of ~5.2 × 10⁷ and the sensitivity of ~10⁻⁹ M, which manifested their potential and promising application in commercial use of SERS.

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1. Introduction

Raman spectroscopy is a technology used to detect the vibrational, rotational and other low frequency modes, which are specific to certain chemical bonds and symmetry of molecules, and thus can provide fingerprint information and be applied to the analysis in biological and medical science [1–3]. Nevertheless, the intensity was usually too weak to be detected until the enhancement methods were applied. Since discovered over 40 years ago [4], surface-enhanced Raman scattering (SERS) has been more and more widespread in the field of chemical and biological analysis with the development of nano-fabrication technologies. The SERS process is observed for molecules adsorbed on the surface of noble metal substrates with nanoparticles [5–6] or other nanometer scale structures [7], which could trap the light as surface plasmons and form the so-called 'hot spots'. An electromagnetic "hot spot" is a point with a strongly enhanced local field. The interaction between the enhanced local electromagnetic field near the 'hot spots' and the molecules will result in the enhancement of characteristic Raman signal. In recent years, single-molecule detection has been achieved with different kinds of substrates [5-6,8-9], and the tip-enhanced Raman scattering technology is also improved [9-12]. However, the fabrication of the SERS substrates with high-density, uniform and largearea 'hot spots' is still a challenge [13–17].

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The nanogap is an ideal nanostructure to produce "hot spots", and thus some methods to fabricate the nanogaps were recently reported, in which electron beam lithography (EBL) was mostly used [16,18-20], but it is high cost and low yield. Compared with EBL, the nanoimprinting lithography (NIL) has shown its advantage in largearea fabrication of period patterns [21-23]. The atomic layer deposition (ALD) technology, which is famous for the precise control of the film thickness, can be used to fabricate the sub-10 nm gaps between the metallic structures (mostly in vertical position), and thus provide an efficient approach to obtain 'hot spots' in large area with high density. Recently, the system composed of metallic nanoparticles and film has been studied intensively because of its strong near-field enhancement, which can be applied to plasmonic detection [20,24–26]. The strong electromagnetic enhancement is closely related to the interplay between the particles and the film, and further, the coupling between localized surface plasmon (LSP) and surface plasmon-polarization (SPP). Therefore, in this hybrid system, the nanogaps between metallic nanoparticles and film are important to obtain an extremely strong nearfield induced by high-density "hot spots" from the nanogaps, and ALD technology is an appropriate approach to produce the nanogaps. The nanograting structure, which itself can be excited SPP effectively, has been widely used as SERS substrate [14,18], and it has more optical contact area with the nanoparticles than the flat film. Additionally, the nanograting structure is easy to be formed by large-area fabrication using nanoimprinting lithography (NIL). Based on the favorable factors above, a hybrid structure of metallic nanoparticles/nanogap/metallic nanograting may be more ideal plasmonic nanostructure for SERS substrate compared with the reported hybrid system composed of metallic nanoparticles and film.

In this work, we designed a metallic nanoparticles/Al₂O₃/metallic nanograting hybrid structure as SERS substrate, which can be fabricated by nanoimprinting, ALD and metal deposition technology. Among them, ALD technology can precisely control the deposition of Al₂O₃ thin film, and easily tune the nanospacing between metallic nanoparticles and nanograting from 1 nm to 9 nm to obtain an optimal nanogap for field enhancement. In addition, it has been demonstrated that a heterogeneous metal hybrid system can increases greatly the electromagnetic field intensity in the nanospacing region compared with homogeneous metal system [27-29], this is because the heterogeneous metal structure combined the effect of two resonances from different metals that is more favorable to near field enhancement in the optical responses. Therefore, Ag nanoparticles and Au nanograting are chosen to compose the heterogeneous metal hybrid system as SERS substrate. The results indicated that the hybrid substrate produced large-area and uniform "hot spots", and showed a good performance in the signal enhancement and repeatability, and the high sensitivity.

2. Experimental section

2.1. Fabrication of hybrid nanostructure.

The fabrication consists of four kinds of processes: the nanoimprinting, the dry etching, the metal deposition and atomic layer deposition. Firstly, the 2-inches Ni parent template (purchased from Obducat Company), patterned with linear rectangular grating with period of 180 nm, line-width of 60 nm and groove depth of 120 nm, was used to copy an intermediate polymer stamp (IPS) film by a Nanoimprint Lithography system (Eitre-3, from Obducat Company) in the thermal imprinting mode (160 °C, 40 bars; 1 min). After demolding, the IPS film was ready as the new template for the next ultraviolet nanoimprint process. The 1 cm \times 1 cm piece samples are chosen for measurement convenience. The imprint resist TU2 (purchased from Obducat Company) was spin-coated onto a silicon substrates, which formed the resist layer with thickness of 120 nm, then the samples were baked on a hotplate (95 °C, 3 min) to remove the solvent in resist, imprinted (65 °C, 30 bars, 1 min) under the radiation of UV lamp and then separated with the IPS molds. The residual TU2 resist (nearly 10 nm thick) was removed with O_2 plasma (10 sccm O_2 , 50 mTorr Pressure, 100 W power), and the underneath Si substrate was etched by using ICP (55 sccm HBr, 8 mTorr, 50 W RIE power, 750 W ICP power, 20 °C) to obtain the Si-nanograting, and the Si etching depth during this process was nearly 80 nm. After remove of residual resist, metal deposition was performed by using customized Magnetron Sputter system. The Au film (50-120 nm thick) was deposited on the Si-nanograting, in which the sample holder kept rotating at 10 rmp to ensure the uniformity of deposition. The sub-10 nm (1-9 nm) thick isolating Al₂O₃ layer was deposited by ALD system (Savannah-100 from Cambridge NanoTech, Inc.) with the precursors of trimethylaluminium (TMA) and H₂O gas under temperature of 80 °C, and the low temperature avoid the thermal effect on the Au film. Finally, Ag-nanoparticles (Ag-NPs) were deposited by electron beam evaporator (Peva-600E Ebeam evaporator from Taiwan) with a low deposition rate of 0.2 Å/s. The thickness of Ag thin film is changed from 3 nm to 9 nm, respectively the average diameter of the nanoparticles varied from ~18 nm to ~65 nm, while the gaps between the adjacent Ag nanoparticles on the top of the hybrid nanostructure were maintained at sub-10 nm.

2.2. Raman scattering measurement.

The *p*-thiocresol was used as the Raman probe, and the samples were immersed in its ethanol solution with concentration of 10^{-5} M for 4 h, repeatedly washed with ethanol and dried with nitrogen. As

for the sensitivity measurement, the solution concentrations should be diluted down to 0.1 nM (or 10^{-10} M). The SERS spectra measurements were carried out by using a confocal Raman spectroscopy (LabRAM HR800) equipped with a piezo-stage which moves along x- and y-directions. The excitation laser with the wavelength of 532 nm and the power of 0.65 mW was focused by a × 100 objective lens on the samples, and the emitted scattering signals were collected with the same lens, which has a laser spot with the diameter of 1 µm. The excitation laser was polarized perpendicular to the lines of grating. All the samples were measured in the same condition, and spectra were collected from several randomly selected positions on the substrates.

2.3. Numerical simulation

Numerical simulation of the near-field distribution was performed with commercial software FDTD Solution based on finite-difference time-domain method. The geometrical parameters of the nanostructure were set as close as possible to the practical situation, and the refractive indices or dispersion laws of the materials were all from the material database in software. A single unit of the periodic hybrid nanostructure was chosen to be simulated. The boundary condition was set as periodic in x direction and perfect absorption layers in y and z direction. The incidence light was set as a plane wave propagating in z direction from the top of the substrate, and its polarization was perpendicular to the lines of grating (*p*-polarized).

3. Results and discussion

A schematic of fabrication process of hybrid nanostructure is shown in Fig. 1. Here the low-cost IPS was used as the new template instead of hard molds, showing some advantages such as free-adhesion-layer, clean and protection for the parent template. The grating patterns were transferred from the Ni molds to the immediate IPS template via the thermal imprinting process, and subsequently formed on the TU2 resist via the UV nanoimprint process. The residual TU2 resist was removed by O₂ plasma, and the underneath Si substrate generate the Sinanograting after the ICP etching process. The Au grating was obtained with the Au film deposition. The sub-10 nm isolating Al₂O₃ layer deposited by ALD system under low temperature of 80 °C was uniform and served as a isolating layer between the Au grating and Ag-nanoparticles (Ag-NPs) deposited finally. According to this process, a hybrid



Fig. 1. Schematic of fabrication process of Ag-nanoparticles/Al₂O₃/Au-nanograting hybrid nanostructure.

nanostructure can be smoothly obtained, and the surface morphological images of the structure fabricated at each process were showed in Fig. 2. The resist TU2 on Si substrates cured to the nanograting after imprinted, and then was utilized as mask during etching process to make the underneath silicon form nanograting, as shown in Fig. 2(a). Subsequently, gold film and sub-10-nm Al₂O₃ layer were deposited onto Si-grating to obtain Au-nanograting and the isolating layer above. Because of the Au deposition on sidewall by sputtering, the nanograting was widened from 75 nm to 120 nm when the thickness of Au film was 70 nm, displayed in Fig. 2(b), while the influence of the Al_2O_3 layer on the width was negligible. After ALD process for Al₂O₃ isolated nanolayer, Ag-nanoparticles were uniformly deposited by electron beam evaporation, which can be seen in Fig. 2(c). Fig. 2d displayed a cross-sectional view of the structure, in which Si nanograting was totally coated by the film above. In addition, Fig. 2e gives the change of the diameter of the nanoparticles with the 'thickness' of deposited Ag film, the average diameter of the nanoparticles varied from ~18 nm to ~65 nm when the thickness of Ag thin film is changed from 3 nm to 9 nm. The methods applied to obtain the hybrid nanostructure, such as the nanoimprint and atomic layer deposition, were all compatible with the large-area fabrication, which was favorable to detect the reproducible and uniform Raman signal. Actually, the 2 in. hybrid substrate can be easily fabricated, but the small-sized piece samples with an area of $1 \text{ cm} \times 1 \text{ cm}$ were prepared for the convenience of measurement and further optimization.

By measuring Raman spectra, the ability of the hybrid nanostructure to enhance the Raman signals was demonstrated and compared with various substrates in Fig. 3(a). Comparing of a little enhancement from the single-layer substrates, such as Ag NPs and the Ag NPs on Si nanograting, the enhancement of Raman signals was more significant on the hybrid structure. Furthermore, Au-nanograting showed a better improvement of SERS performance than the flat film in hybrid nanostructure, which was also proved by several literatures [30–31]. The two characteristic peaks at 1075 cm^{-1} (S—C stretching vibration) and 1590 cm⁻¹ (C =C stretching vibration of benzene ring) were both sharp and suitable to calculate the enhancement factor (EF) and to evaluate the uniformity in the following experiments. For the single-layer substrates, the enhancement of Raman signals was mainly attributed to the localized surface plasmon resonance (LSPR) among the adjacent Ag NPs, which was limited even when the particles was deposited on the grating. However, the situation would make a big difference if the hybrid nanostructure, the multiple coupling systems were exactly introduced. The intensity of two main Raman shift peaks was more than one order of magnitude than that of the single-layer Ag NPs. In the hybrid system, the LSPs excited near the Ag-NPs interplay with the SPs of the Au film and LSPs of the surface roughness of the Au film. As the metallic grating has more optical contact, able to be excited SPs more efficiently than the film, generate "hot spots" with higher density, and thus the Ag NPs/Al₂O₃/Au nanograting structure deserve the better performance. Additionally, the isolated nanolayer of Al₂O₃ in this hybrid structure plays a very important role in the Raman enhancement, which can tune precisely the spacing between nanoparticles and the film to form high-density "hot-spots" for producing strong local electromagnetic field. The existence of the isolating nanolayer Al₂O₃ makes it possible to produce more opportunity for the LSPPs to couple in the vertical direction, which improve the limitation of the coupling in horizontal direction.

In order to further tune the plasmonic coupling among the hybrid nanostructure and achieve the maximum Raman signal enhancement, the thickness of the isolating layer (Al₂O₃ layer), the thickness of Au film deposited on nanograting and the size of Ag NPs were optimized, respectively. As the isolating layer between the particles and nanograting, the thickness of Al₂O₃ layer is extremely important to the coupling in the hybrid nanostructure, and thus the influence of it on the SERS performance was firstly studied, as displayed in Fig. 3(b). In this hybrid nanostructure, the thickness of deposited Au and Ag were



Fig. 2. SEM images of a) Si nanograting with width of 75 nm, b) Au grating with width of 120 nm, c) Hybrid nanostructure consist of 5 nm Ag thin film, 5 nm Al₂O₃ layer and 50 nm thick Au, d) Cross section view of the same hybrid structure, e) Ag thin film with thickness from 3 nm to 9 nm and dependence of average diameter of Ag nanoparticles in hybrid nanostructure on the Ag thickness. Scale bar, 100 nm in a)–d) and 50 nm in e).



Fig. 3. SERS spectra of *p*-thiocresol absorbed on various substrates: a) two kinds of single-layer and two kinds of hybrid structure, b) the hybrid nanostructure substrates with different Al_2O_3 layers (from 1 nm to 9 nm), c) the hybrid nanostructure substrates with different Au thicknesses, d) the hybrid nanostructure substrates with different from 3 nm to 9 nm). The inserted figures in (b), (c), (d) are showing the dependence of Raman shift intensity at 1075 cm⁻¹ on the thickness of Al_2O_3 layer, Au and Ag particles, respectively.

50 nm and 5 nm, respectively. The SERS signals from the substrate with 3 nm-thick Al₂O₃ layer exhibits the most obvious enhancement, which means a 3 nm spacer is the optimized distance for the interaction between the LSPs from Ag NPs and the SPs from Au nanograting. Neither more than 3 nm nor less than 3 nm was beneficial to the interaction. The former will weaken the coupling, and the latter will lead to the overlap of electronic density of the double-layer metallic structure and even the electron tunneling across the spacer that reduces the coupling and field enhancement. Refer to the Au grating in our configuration, the period of grating was constant (~180 nm), while the line-width and the depth could be tuned by the thickness of Au film deposited. To further elucidate the impact on final Raman signal enhancement, the thickness of Al₂O₃ and Ag thin film were fixed at 3 nm and 5 nm. It is apparent that the width and the depth of the obtained Au grating are changed as the thickness of the Au film deposited on the Si grating is increased. The increased width of the Au grating lines at fixed period have little influence on the excitation of the surface plasmon resonance induced in grating. However, the optimized depth of the groove on the grating could achieve desirable enhanced SERS signals, which has been investigated theoretically and experimentally [32]. One the one hand, the deep grating could provide increasing resonance width and thus large SERS signals without the complex angular adjustment, which is adaptable to the actual measurement in which the scattering signals are collected with an lens. One the other hand, there is an optimized depth of the grating, which was 80 nm, slightly larger than the thickness of Au, corresponding with the highest SERS enhancement factor according to the previous literature [32]. Specifically, the narrow resonance width in the shallow grating is an unfavorable factor. The deeper grating will not further improve SERS performance, and it's not beneficial to the following deposition process for hybrid nanostructure. The SERS spectrum in Fig. 3(c) indicates that distinguished SERS signals resulted from the hybrid nanostructure, especially in the substrate with a 70 nm thick Au layer, the case in which the grating depth is near to 80 nm. Our SERS measurement results further verified the conclusion above. Considering that the LSPs depend on the shapes and sizes of Ag particles, the thickness of Al₂O₃ and Au were fixed at 3 nm and 70 nm, and hybrid nanostructure with different thicknesses of Ag thin film are prepared for optimization. In Fig. 3(d), the substrate with 5 nm 'thickness' Ag particles (almost 30 nm in diameter) have the best performance in SERS, which shows the excited localized surface plasmons had the strong interplay with the surface plasmons from Au-grating. To summarize, the optimal hybrid nanostructure with the highest Raman enhancement should be fabricated based on the following parameters in this work: 70 nm Aunanograting, 3 nm Al₂O₃ layer and 5-nm-thick Ag thin film. With the final optimized sample, the SERS enhancement factor was estimated to 5×10^7 by comparing the Raman intensity at 1075 cm⁻¹ and 1590 cm^{-1} according to the method described in the literature [33].

To further evaluate the SERS properties of the hybrid nanostructure, the uniformity and repeatability of SERS signals need to be verified. Fig. 4(a) and (b) show Raman maps across a random 10 μ m × 10 μ m area of the hybrid nanostructure. The integration time and the step-size were 5 s and 1 μ m, respectively. It can be seen that except for the individual



Fig. 4. a) and b) Raman maps showing the uniformity of SERS signal across a 10 μ m × 10 μ m area of the hybrid nanostructure. Two main peaks at 1078 cm⁻¹ and 1590 cm⁻¹ are mapped. c) Repeatability measurement of SRES signals in the same sample, including five processes with 2 h intervals. d) Sensitivity measurement using the change of SERS signals of *p*-thiocresol with different concentrations on the same substrate.



Fig. 5. FDTD simulations showing the x-z view of electromagnetic field distribution around different nanostructural modes a) Ag nanoparticles on Si substrate, b) hybrid nanostructure of Ag-nanoparticles/Al₂O₃/Au film, c) hybrid nanostructure of Ag-nanoparticles/Al₂O₃/Au film, in which the Ag nanoparticle is placed at the corner.

area with higher or weaker signals, the most part of mapping area shows acceptable uniformity. Considering the limitation of the laser spot diameter (1 μ m), these mapping results were references for the uniformity evaluation. Fig. 4(c) shows the repeated collection of the SERS signal on the same samples with 2 h intervals, and the consistency of the data demonstrates the good repeatability of the substrate. The sensitivity measurement results with different concentrations of *p*thiocresol molecules are displayed in Fig. 4(d). As the concentration decreases, the peaks of the characteristic Raman gradually become weak but still distinguishable near to the 1 nM concentration. This quantitative analysis manifest the strong detection ability of the hybrid substrate, make it possible to be applied on the trace analysis of molecules.

The results of SERS measurement for this hybrid nanostructure are desirable, but related theoretical simulations are very necessary. The electromagnetic field distribution near the hybrid nanostructure was simulated to figure out the origin of the enhanced Raman signal by FDTD method, as shown Fig. 5. The localized field enhancement from the surface plasmons impacts both the incident and scatter light, so the Raman scattering intensity is approximately scales as |E| [4], where the E is the magnitude of incident electromagnetic field. Thus, the SERS enhancement can be inferred according to the localized field intensity near the metal structure.

In Fig. 5, the near field distribution of the nanostructure in three kinds of condition was simulated with FDTD methods. During the simulation, the Ag particles on substrates were treated as oblate ellipsoid shape particles and the thickness of Al₂O₃ was fixed on 3 nm for simplification. We can find that as for the Ag nanoparticles on Si substrate shown in Fig. 5(a), the localized electrical field shows limited enhancement, and the corresponding 'hot spots' are located at the position where the particle contacts to the substrate. Compared with the situation with simple flat substrate, the hybrid nanostructure of Ag-NPs/ Al₂O₃/Au film presents the hot spots with a significantly enhanced field intensity, as the interaction between the LSPs from the Ag-nanoparticles surface and the SPs on the Au film, which is illustrated in Fig. 5(b). As the Au film was further replaced with Au grating, the Ag nanoparticles have two characteristic positions, one is similar to that in Fig. 5(b), the other is at the corner of the groove of Au grating or near the side wall of the grating shown in Fig. 5(c). In the second condition, the number of the hot spots and the intensity of the local field are evidently increased, which indicated the advantage of the Au grating compared with the Au flat film as the substrate. In general, the performance of the hybrid nanostructure of the Ag NPs/Al₂O₃/Au grating is resulted from a combination of the two situation in Fig. 5(b) and (c).

The simulation results above were well consistent with measured SERS spectra, verifying the good SERS property of hybrid nanostructure due to great advantages on the numbers of hot spots and the intensity of the localized field. Additionally, for the practical hybrid nanostructure, the Ag nanoparticles distribution was rather complex, which might locate on the top, bottom and the sidewall of Au nanograting. Here we only focus on the interaction between nanoparticle and nanograting and thus take the characteristic condition shown in Fig. 5(b) and (c) as typical examples. Actually if the Ag-nanoparticles are closely enough to each other, the gaps between the adjacent nanoparticles will also act as 'hot spots', which has contributed to the enhancement of local electromagnetic field.

4. Conclusions

We design and fabricate a hybrid nanostructure of Ag-nanoparticles/ Al₂O₃/Au-nanograting nanostructure as a promising SERS substrate. By a series of the structural optimization, this hybrid nanostructure shows great SERS properties, including desirable Raman enhancement with enhancement factor of 10^7 , high sensitivity down to 10^{-9} M and good uniformity. The measured results demonstrate that this heterogeneous hybrid mode of two kinds of metal nanostructures can produce large-scale strongly 'hot spots' with high density that benefit from the multiple coupling in the hybrid structure, which are also proven by FDTD simulations. Considering of the low-cost and high reproduction during the fabrication process, this hybrid nanostructure SERS substrate has the growth potential for commercial use in the chemical, biological and even single molecule detection.

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