

Preparation and Performance Testing of a SERS-enhanced Substrate

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Abstract

This study proposes a fabrication strategy for a surface-enhanced Raman scattering (SERS) substrate based on a noble-metal nanoshell array structure. First, a silicon wafer is used as the substrate, and a uniform and dense gold (Au) film is deposited on its surface by magnetron sputtering to provide a stable conductive layer and favorable optical response. Subsequently, a monolayer of polystyrene (PS) microspheres is self-assembled on the Au film to form a regularly ordered template structure. A silver (Ag) layer is then sputtered onto the surface of the PS microspheres, enabling the Ag film to uniformly coat the outer surface of the PS spheres. Finally, the PS microsphere template is removed through physical or chemical methods, resulting in the formation of a periodically arranged Au-substrate/Ag nanoshell array on the gold film surface. This structure exploits the interfacial coupling between Au and Ag, as well as the localized surface plasmon resonance (LSPR) generated by the Ag nanoshells under external laser irradiation. As a result, numerous high-intensity electromagnetic “hot spots” are produced in the inter-shell gaps and at the Au-Ag contact regions. These hot spots can significantly amplify the Raman scattering signals of molecules, thereby effectively improving detection sensitivity. In addition, the nanoshell array exhibits good structural uniformity, which contributes to excellent stability and reproducibility of the SERS signals. Experimental results demonstrate that the fabricated substrate produces pronounced Raman signal enhancement for typical probe molecules and exhibits good signal uniformity and detection reliability. Compared with conventional SERS substrates based on randomly distributed nanostructures, this method offers clear advantages in terms of structural controllability and enhancement performance. Furthermore, the fabrication process, which combines PS microsphere self-assembly with magnetron sputtering, is not only simple and relatively low-cost but also suitable for large-area preparation. Therefore, this approach provides a simple and effective strategy for constructing highly sensitive and stable SERS substrates, showing promising application prospects in chemical detection, biosensing, and environmental monitoring.

Keywords

Surface-enhanced Raman scattering, Nanoshell array structure, Localized surface plasmon resonance, Hot spots

Introduction

Surface-enhanced Raman scattering (SERS) is an ultrasensitive molecular detection technique capable of significantly amplifying the Raman signals of target molecules [1,2]. Owing to its remarkable sensitivity and molecular fingerprinting capability, SERS has attracted extensive attention and shows broad application prospects in fields such as environmental monitoring, bioanalysis, and food safety detection [3-6]. The SERS enhancement effect mainly originates from two mechanisms: electromagnetic (EM) enhancement and chemical enhancement. Among them, electromagnetic enhancement usually plays the dominant role and arises from the localized surface plasmon resonance (LSPR) generated in noble metal nanostructures under light

excitation. When nanoscale gaps exist between adjacent metallic nanostructures, the localized electromagnetic field can be highly concentrated within these regions, leading to the formation of intense electromagnetic “hot spots”. These hot spots can dramatically amplify the Raman scattering signals of molecules adsorbed in these regions, thereby significantly improving the sensitivity of Raman detection [7,8]. However, the fabrication of SERS substrates that simultaneously possess structural stability, high hot-spot density, and excellent signal reproducibility remains a key challenge and an important research focus in this field.

The structural morphology and material composition of SERS substrates play a decisive role in determining

their enhancement performance. At present, gold (Au) and silver (Ag) are the most widely used materials for SERS substrates due to their excellent plasmonic properties and strong light-matter interaction capabilities [9,10]. Among them, silver generally exhibits stronger plasmon resonance and higher enhancement factors, whereas gold offers superior chemical stability and resistance to oxidation. Therefore, constructing bimetallic Au/Ag composite nanostructures has been considered an effective strategy to simultaneously achieve high SERS enhancement and good structural stability [11]. In addition, designing ordered nanostructure arrays is an effective way to improve both the density and uniform distribution of electromagnetic hot spots, thereby enhancing the sensitivity and reproducibility of SERS substrates. Periodically arranged nanostructures can also provide better control over plasmonic coupling effects, which further contributes to stronger electromagnetic field localization and improved analytical performance.

Based on these considerations, in this study a gold (Au) film was first deposited onto a silicon wafer substrate using magnetron sputtering. Subsequently, an ordered monolayer array of polystyrene (PS) microspheres was self-assembled on the Au surface to serve as a sacrificial template. A silver (Ag) layer was then further deposited onto the PS microsphere array by sputtering. Finally, the PS microsphere template was removed through physical or chemical treatment, resulting in a periodic Au-film-supported Ag nanoshell array structure. The resulting nanostructure can generate numerous nanoscale gaps between adjacent metallic features, which act as highly active electromagnetic hot spots under laser excitation. These hot spots effectively concentrate the local electromagnetic field and significantly enhance the Raman scattering signals of molecules adsorbed on the substrate.

Furthermore, the combination of PS microsphere self-assembly and magnetron sputtering offers several advantages, including a relatively simple fabrication process, good structural controllability, and compatibility with large-area preparation. The ordered nanoshell array not only improves the density and uniformity of plasmonic hot spots but also contributes to enhanced signal stability and reproducibility. Therefore, the proposed fabrication strategy provides a feasible approach for constructing high-performance

SERS substrates with high sensitivity, structural stability, and good reproducibility. It may be beneficial for practical applications in chemical sensing, biological detection, and environmental monitoring.

Materials

The following materials were used in this study: silicon substrates with dimensions of 1 cm × 1 cm, gold (Au) and silver (Ag) sputtering targets of high purity, ethanol (99.5%) as a solvent and cleaning agent, and polystyrene (PS) microsphere solution as the template for self-assembly. All materials were used as received without further purification.

Fabrication of SERS substrates

Single-crystal silicon wafers were selected as the substrate material. To remove organic contaminants and particulate impurities from the silicon surface, the substrates were sequentially ultrasonicated in absolute ethanol and deionized water for 10-15 minutes each, followed by drying under a high-purity nitrogen stream. The pretreated silicon substrates were then placed in a magnetron sputtering system for the deposition of a gold (Au) layer. Monodisperse polystyrene (PS) microsphere solution was used as a template material. The PS microspheres were assembled onto the Au-coated silicon substrates to form a dense, two-dimensional, ordered array. The samples with the assembled PS microsphere arrays were subsequently returned to the magnetron sputtering system for the deposition of a silver (Ag) layer, which coated the surface of the PS microspheres to a controlled thickness. This template-assisted sputtering approach enables precise control over structural parameters, supporting reliable and repeatable manufacturing [12]. After the silver deposition, the PS microsphere template was removed using physical or chemical methods.

Common approaches include immersion of the samples in organic solvents such as toluene or tetrahydrofuran to dissolve the PS microspheres, or applying ultrasonic assistance to facilitate template removal. Following template removal, a periodic nanostructure array was formed at the original positions of the PS microspheres, resulting in a gold layer-silver shell (Au-Ag) nanostructure array. The resulting structure contains numerous nanoscale gaps between adjacent metal nanostructures, generating a high density of localized

electromagnetic hot spots, which are beneficial for significantly enhancing the SERS signal.

SEM characterization

The surface morphology and structural features of the fabricated SERS substrates were examined using scanning electron microscopy (SEM). After optimizing multiple sets of fabrication parameters, the samples were prepared under selected conditions: a sputtering current of 5 mA, a gold (Au) deposition time of 10 s, and a silver (Ag) shell deposition time of 10 s. Under these conditions, the resulting samples exhibited well-defined and uniform structural morphology, indicating that the chosen fabrication parameters were effective in producing consistent and high-quality Au-layer/Ag-shell array SERS substrates. Figure 1 shows the SEM images of the samples at different magnifications. Figures 1(a), 1(b), and 1(c) correspond to 30 \times , 40 \times , and 50 \times magnification, respectively. The images clearly reveal that the substrate surface consists of regularly arranged array structures with uniform distribution and pronounced periodic features. The Au-layer/Ag-shell array SERS substrates, templated by the PS microspheres, are well-ordered on the substrate surface, with clearly defined array contours and consistent nanoscale gaps between adjacent structures.

The ordered arrangement not only ensures uniformity across the substrate but also minimizes structural defects such as aggregation or collapse, which can adversely affect the formation of electromagnetic hot spots.

Such a highly ordered nanostructure array is favorable for forming numerous nanoscale gaps between metal elements, which can generate localized electromagnetic hot spots under light excitation. These hot spots are critical for enhancing the Raman scattering signals of molecules adsorbed on the substrate, as they concentrate the electromagnetic field into nanoscale volumes, effectively amplifying the local field intensity. In addition, the uniformity and periodicity of the array are expected to provide consistent SERS performance across the substrate, reducing signal variability and improving reproducibility. The SEM results indicate that the employed fabrication method successfully produces well-ordered Au-layer/Ag-shell array SERS substrates. These substrates possess clear nanoscale gaps and high structural integrity, laying a solid foundation for subsequent performance evaluation of the SERS substrates and their potential applications in chemical sensing, biosensing, and environmental monitoring.

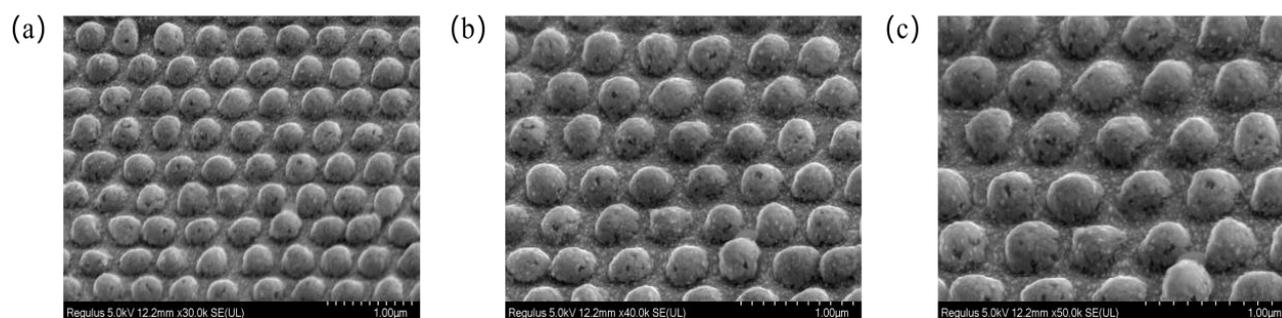


Figure 1. SEM images of the Au-layer/Ag-shell array substrates at different magnifications: (a) 30 \times , (b) 40 \times , and (c) 50 \times .

SERS performance evaluation

To evaluate the enhancement performance of the fabricated Au-layer/Ag-shell array SERS substrates, Rhodamine 6G (R6G) was used as a probe molecule. R6G solutions of different concentrations were prepared to investigate the substrate's detection sensitivity, signal reproducibility, and quantitative analytical capability. Figure 2(a) presents the SERS spectra obtained from the substrate for R6G solutions at various concentrations. As the R6G concentration decreased from 10^{-6} to 10^{-8} mol/L, the characteristic Raman peaks of R6G remained

clearly detectable, with their spectral positions largely unchanged, while the peak intensities gradually decreased with decreasing concentration.

Among these peaks, the one at approximately 612 cm^{-1} corresponds to a typical vibrational mode of the R6G molecular backbone. Notably, this peak could still be clearly observed even at the lowest tested concentration of 10^{-8} mol/L, indicating that the fabricated SERS substrate provides strong signal enhancement and an ultralow detection limit. To further analyze the quantitative performance of the substrate, the intensity

of the 612 cm^{-1} peak was plotted against the logarithm of R6G concentration and fitted using linear regression, as shown in Figure 2(b). The results exhibit a good linear relationship over the tested concentration range, with a correlation coefficient (R^2) above 0.99, indicating a high degree of fit between the measured Raman intensity and the analyte concentration. This linearity demonstrates that the substrate not only possesses high sensitivity but is also suitable for quantitative SERS analysis across a broad concentration range.

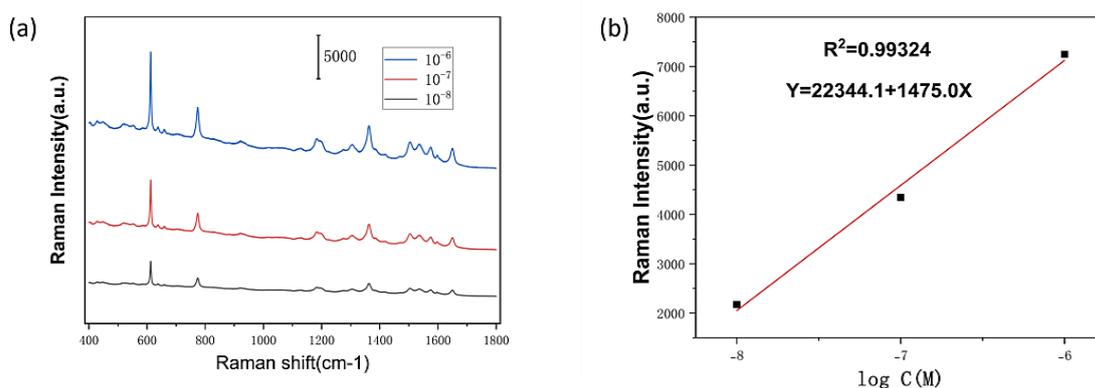


Figure 2. (a) SERS spectra of Rhodamine 6G (R6G) at different concentrations (10^{-6} - 10^{-8} M) measured on the Au layer-Ag shell array substrate. (b) Linear relationship between the SERS intensity of the 612 cm^{-1} peak and the logarithm of R6G concentration.

Conclusion

In this study, a gold layer-silver shell (Au-Ag) array SERS substrate is successfully fabricated using a combination of magnetron sputtering and a microsphere template method. SEM characterization demonstrates that this approach can produce well-ordered and uniformly distributed array structures on the substrate surface, with clearly defined nanoscale gaps between adjacent structures. The SERS performance of the substrate is evaluated using Rhodamine 6G (R6G) as a probe molecule. The results show that the substrate enables effective detection of R6G, with the characteristic Raman peak at 612 cm^{-1} clearly observable even at very low concentrations, achieving a detection limit as low as 10^{-8} mol/L.

Moreover, the Raman intensity exhibits a strong and consistent linear relationship with the logarithm of R6G concentration, indicating that the substrate possesses significant potential for quantitative analysis over a wide concentration range. The excellent enhancement is attributed to the high density of electromagnetic hot spots generated within the nanoscale gaps and the

The strong signal enhancement observed is mainly due to the dense nanoscale gaps and the well-organized periodic structure of the Au-layer/Ag-shell array. These features create many localized electromagnetic “hot spots” on the surface, which greatly boost the local electromagnetic field and, in turn, strengthen the Raman signals of molecules attached to the substrate. Moreover, the substrate’s uniformity and consistent structure ensure that signal intensities remain stable across different measurement points, which is essential for accurate and reliable analysis.

uniform periodic arrangement of the Au-Ag nanostructures. Overall, this fabrication strategy provides a simple, reproducible, and effective route for constructing high-sensitivity SERS detection platforms, holding promising applications in chemical analysis, biosensing, environmental monitoring, and other related fields.

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Conflicts of Interest

The authors declare no conflict of interest.

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