Growth of Nanostructured Silver Flowers by Metal-Mediated Catalysis for Surface-Enhanced Raman Spectroscopy Application

Min Liu*

ABSTRACT: Metallic flowers with nanoscale surface roughness can provide a platform for highly sensitive and reproducible surface-enhanced Raman spectroscopy (SERS). Here, we present a method to grow a nanostructured silver flower (NSF) at the apex of a plasmonic tip based on metal-mediated catalysis, where the NSF was rapidly generated in no more than 1 min. The NSF was used as the SERS substrate under linear polarization beam (LPB) excitation to achieve a $10^{-9}$ M detection sensitivity for the malachite green analyte. The reproducibility for SERS is examined to have been guaranteed by comparing Raman intensity enhanced by different NSFs. Compared with the LPB, the azimuthal vector beam (AVB) excitation can further improve the SERS activity of the NSF, which is consistent with the simulation result that the gap mode can be effectively generated between two adjacent Ag nanoparticles (NPs) and between the NPs and the Ag pyramids on the surface of the NSF under AVB illumination. This work makes it promising for plasmonic tip-mediated catalysis to be applied in nanofabrication, the products of which can be further exploited in nanoscale-based ultrasensitive detection.

1. INTRODUCTION

Surface-enhanced Raman spectroscopy (SERS) is an important tool for ultrasensitive detection by "fingerprint" Raman peaks to recognize molecules.1−5 Substrate optimization is the key to improving the SERS sensitivity.6−9 To date, many kinds of noble metal nanostructures, i.e., nanoparticles,10 nanorods,11 and nanotriangles,12 have been commonly used as SERS substrates. However, it is challenging to guarantee the sensitivity and reproducibility simultaneously.13 It is thus worth noting that the mesoscopic particles with a rough surface and nanostructured silver flowers (NSFs) have demonstrated their superiority in this aspect.13−15 Chemical synthesis is usually used to fabricate NSFs,16,17 but the NSF products randomly produced in the reaction solution need to be transferred and assembled on carriers for sensing application. Fabrication of NSFs directly assembled on carriers may bring advantages to practical application, such as avoiding the tedious transferring and assembling process of NSFs on carriers and immobilizing NSFs at designated sites on purpose, while a new mechanism of NSF fabrication has to be sought for achieving that.

Metal-mediated catalysis (MMC) has been raised to accelerate chemical reaction and is explained by the joint effects of electromagnetic (EM) field enhancement, hot electron transfer, and heating.18−22 Metallic nanostructures such as nanobowties,23 nanospheres,24 nanorods,25 and nanotips26−29 were adopted to perform MMC. Up to now, MMC has been applied in CO oxidation,30 hydrogen evolution,31 water reduction,32 etc. However, the platform of MMC-induced fabrication for a solid and physical object like NSFs remains to be explored. It is thus our interest to look for a new process to grow NSFs directly on carriers with an MMC mechanism.

Considering the EM field enhancement characteristics of a fiber-based plasmonic tip,33−35 it may be a good candidate for performing MMC while not demanding expansive nanofabrication processes such as e-beam lithography and a focused ion beam. The synergy of MMC and plasmonic tips can bring a new platform for efficient and cost-effective fabrication of NSFs at designated sites, i.e., tip apexes in a controlled manner.

In this work, we develop a method to fabricate NSFs at metalized fiber tips. The plasmonic tip-mediated catalysis (PTMC) is enabled by the enhanced EM field at the apex of a plasmonic tip illuminated internally via in-fiber light. NSFs with different diameters were prepared by controlling the reaction time, denoting a good reproducibility. The SERS performance of the products was experimentally examined. A $10^{-9}$ M detection sensitivity for the malachite green (MG) analyte is achieved. The reproducibility for SERS is examined to have been guaranteed by comparing Raman intensity enhanced by different NSFs. The azimuthal vector beam (AVB) excitation was theoretically and experimentally verified to further improve the SERS performance of the NSF compared with the linear polarization beam (LPB) excitation.

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2. METHODS AND EXPERIMENT

2.1. Fabrication of NSF Based on Plasmonic Tip-Mediated Chemical Reaction. Plasmonic tip-based MMC was developed to fabricate NSFs at the tip apex. A plasmonic tip-mediated chemical reaction was applied to prepare the NSF, which contains two steps, i.e., fabrication of a silver-coated fiber tip and silver-coated fiber tip-mediated photocatalysis.

A fiber taper was first prepared by a chemical etching method. The light-induced chemical deposition method was used to deposit a Ag film on the surface of the fiber tip. As shown in Figure 1a, a silver film was formed on the surface within 4 min and a Ag-coated fiber tip was prepared. A continuous wave laser beam with a power of 10 mW at 1550 nm was coupled into the single mode fiber (SMF) by a fiber adapter, as shown in Figure 2b. Mix silver ammonia solution (0.01 g/mL AgNO₃ solution and a moderate amount of ammonia) and potassium sodium (0.05 g/mL) tartrate with a volume ratio of 1:1 together. When the Ag-coated fiber tip was internally illuminated by the laser beam, the hot spot was generated at the tip apex and accelerated the chemical reaction near the tip apex, resulting in rapid growth and formation of an NSF at the tip apex within 1 min, as shown in Figure 1c. The scale of the NSF can be controlled by adjusting the reaction time, as shown in Figure 1c–g. Note that the growth rate of the NSF decreased after the NSF generation, and the diameter of the NSF became almost invariable after 20 min, as shown in Figure 1g.

2.2. Experimental Verification of Plasmonic Tip-Based MMC. To verify that the above fabrication of the NSF was based on the plasmonic-tip induced MMC, as shown in Figure 2a, a gold-coated fiber tip was adopted to prepare NSFs at the tip apex by using the experimental setup shown in Figure 2b. Here, the gold-coated fiber tip was prepared by an ion sputtering method, the surface topography of which was characterized by scanning electron microscopy (SEM) and is depicted in Figure 2c. It can be seen that the coating was compact and consisted of the nanoscale particles with the diameter of the subwavelength. Figure 2d shows an NSF at the apex of the gold-coated fiber tip prepared with the process exhibited in Figure 2b. It demonstrated that the NSF had been achieved at the tip apex based on MMC, as shown in Figure 2d. The diameter of the NSF is 20.4 μm under conditions of a 15 min reaction time. The corresponding energy-dispersive spectroscopy (EDS) results, as exhibited in Figure 2e,f, indicates that the chemical element at the apex of the fiber tip is gold, and the generated nano-structured flower is silver. In other words, the silver nano-
structured flower can be fabricated under the conditions that the silver mirror reaction is induced by a gold-coated fiber nanotip illuminated by the laser. The nanostructured flower occurs because the chemical reaction rate near the apex is quite bigger than that in the other position of the tip surface, revealing that MMC based on the plasmonic tip arises. The plasmonic tip illuminated by the laser can generate considerable electric field enhancement and hot electron emission in the vicinity of the apex, which is the possible reason of why the chemical reaction rate near the apex is much bigger.

3. RESULTS AND DISCUSSIONS

3.1. SERS Examination Using NSF. The surface topography of the NSF used as the SERS substrate is shown in Figure 3a, which demonstrates that the diameter of the NSF is about 8 μm. It can be seen from the partial enlargement image that Ag nanoparticles (NPs) with a radius of ~25 nm are distributed on the pyramid surface of the NSF. In the Raman detection experiment, a He–Ne laser, with a power of 20 mW at 632.8 nm, was used to externally excite the NSF. A laser line filter was used to eliminate the side modes. A polarizer was used to control the power of excitation light. A half-wave plate was put after P to adjust the polarization direction of the LPB. The LPB was illuminated on the surface of the NSF through a 100X micro-objective (MO). The SERS signal was collected via a 20X micro-objective (MO) and then coupled into a spectrometer. The NSF was dipped in malachite green (MG) solution at a specific molar concentration and taken out for natural drying. Raman spectra of MG with different concentrations (10⁻⁶, 10⁻⁷, 10⁻⁸, and 10⁻⁹ M) detected by the NSF under linear polarization beam (LPB) excitation are shown in Figure 3b, revealing that the Raman detection sensitivity of MG is 10⁻⁹ M with the NSF as the substrate. Compared with similar silver flower-shaped nanostructures, the detection sensitivity is high and comparative. Raman spectra of MG (10⁻⁵ M) excited with the LPB on eight NSFs are exhibited in Figure 3c. The corresponding Raman intensity at 1613 cm⁻¹ is shown in Figure 3d. Note that the SERS signal is strong and relatively stable for different NSFs. The relative standard deviation (RSD) is calculated to be 15.1%, demonstrating a high reproducibility.

Figure 4. (a) Experimental setup for SERS improvement with AVM excitation: MO: micro-objective; NSF: nanostructured silver flower. (b) Intensity distribution of the AVB with an azimuthal polarization output and the polarization examination results (b₁−b₅). (c) Raman spectra of MG (10⁻⁵ M) detected by the NSF excited with the LPB and AVB.

Figure 5. (a) Sketch map of the NSF on the cross section of R = 1 μm. Electric field intensity distributions of the AVB (b) and LPB (c) illuminated on the nanostructured silver flower. (d–f) Electric field intensity distributions of the local surface plasmon modes under excitation of the AVB and the LPB with a polarization direction vertical and parallel to the center line of the pyramid, respectively.
3.2. SERS Examination under AVB Illumination. The AVB was used to improve the SERS performance, the experimental sketch of which is shown in Figure 4a. A zero-order vortex waveplate was used to generate the azimuthal vector beam in free space. The AVB was externally illuminated on the NSF through a micro-objective (MO1), and the Raman signal was collected by MO2. Figure 4b1−b5 shows the intensity distribution of the AVB with an azimuthal polarization output and the corresponding polarization examination results. Figure 4c shows the Raman examination result with two excitation methods, and note that the Raman intensity excited via the AVB is 1.5 times stronger than that of the LPB.

To compare the electric field enhancement characteristic of the local surface plasmon modes excited by the LPB and AVB, the cross-sectional model of the NSF with nanoparticles on the pyramid surface is selected to simulate the EF characteristic. As shown in Figure 5a, the radii of the NSF and the Ag NPs are set as \( R = 1 \, \mu m \) and \( r = 25 \, nm \), respectively, and the gap between two adjacent NPs is \( g = 2 \, nm \). The local surface plasmon mode distribution is simulated at a wavelength of 632.8 nm under excitation of the AVB and LPB. The corresponding simulated results are shown in Figure 5b,c,d, indicating a more uniform distribution under illumination of the AVB than the LPB excitation. Figure 5e,f shows the electric field enhancement characteristics of the local surface plasmonic modes on the surface of the Ag NP-coated pyramid under excitation of the LPB and AVB, respectively. In the case of AVB excitation, the gap mode can be effectively excited between two adjacent Ag-NPs and between the NPs and the Ag pyramids, as shown in Figure 5d. As shown in Figure 5e, the gap modes between two adjacent Ag-NPs and between the NPs and the Ag pyramids can also be excited with the linear polarization direction of the LPB vertical to the center line of the pyramid, but the electric field enhancement factor is smaller than that of AVB excitation. When the linear polarization direction of the LPB is parallel to the center line of the pyramid, as shown in Figure 5f, only the gap modes between two adjacent Ag-NPs can be excited. Based on the simulation results shown in Figure 5e,f, note that the gap mode only possesses a large electric field enhancement factor when the LPB has a polarization direction parallel to the center line of the pyramids. In other words, the gap mode with an optimized electric field enhancement factor cannot be effectively excited by the LPB at any position of the cross section of the NSF, but the AVB can realize a uniformly electric field enhancement on the surface of the NSF with a large electric field enhancement factor.

4. CONCLUSIONS

In summary, we present a method to fabricate the NSF at the apex of a plasmonic tip based on MMC, where the NSF was prepared in no more than 1 min. The NSF was used as the SERS substrate under LPB excitation to achieve a detection sensitivity of \(10^{-9}\) M for MG. The reproducibility for SERS is examined to have been guaranteed by comparing Raman intensity enhanced by different NSFs. Compared with LPB excitation, the AVB excitation can further improve the SERS activity of the NSF. The Raman intensity excited via the AVB is 1.5 times stronger than that of the LPB, which is consistent with the simulation result. This work may provide a new way for rapid nanofabrication by MMC, the products of which can be further applied in fields of ultrasensitive detection, in-situ detection, chemical identification, optical sensing, etc.

■ AUTHOR INFORMATION

Corresponding Author

Min Liu — School of Physics and Optoelectronic Engineering, Xidian University, Xi’an 710071, China; MOE Key Laboratory of Material Physics and Chemistry under Extraordinary Conditions and Shaanxi Key Laboratory of Optical Information Technology, School of Physical Science and Technology, Northwestern Polytechnical University, Xi’an 710072, China; orcid.org/0000-0001-5681-4407; Email: lium@xidian.edu.cn

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c05021

Notes

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