Different number of silver nanoparticles layers for surface enhanced raman spectroscopy analysis

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ABSTRACT

For application in practice, reducing the cost and simplifying the steps in fabrication of SERS substrates with excellent property are still the important factors. Here, a three-dimensional (3D) Ag nanoparticles (NPs) obtained by facile thermal evaporation is obtained for SERS. The Raman enhancement effect gradually become strong as the number of Ag NPs layers increase and attain the best until four layers Ag NPs deposited for the finite penetration depth of incident laser. The intensity of Raman signal collected from the four-layer Ag NPs substrate is around 11.3 times stronger than that from one-layer Ag NPs. Besides, the reproducibility of the SERS substrate was also significantly promoted as the layers of Ag NPs increases. The SERS substrate exhibits temporal stability and its enhancement factor attains 6.8×10^8. Furthermore, the SERS substrate can easily combine with some other blocks with superior SERS property and show better SERS ability. Additionally, the in-situ trace analyses in aquatic products were realized by flexible Ag NPs/PET substrate.

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1. Introduction

Surface enhanced Raman spectroscopy (SERS) has been proved to be one of the most practical and powerful techniques for label-free and sensitive detection of trace molecules [1–12]. The SERS technology is determined by the localized surface plasmon resonances (LSPR) on the surface of metallic nanostructures which localize the incident light as near-field evanescent waves. The LSPR produces a large electromagnetic field enhancement, called "hot spots", at the nanoscale gaps area in a metallic nanostructure. It is reported that the Raman signal can be intensified to 10^{15} times for some metal nanostructures with highly effective hot spots, realizing the single-molecule detection [4,13–15]. One of the most effective metal nanostructures for SERS are based on a sub–10 nm gap and the SERS effect increases exponentially as the gap further decreases [16,17]. However, the current techniques used to obtain the effective metal structures, such as the lithographic methods, atomic layer deposition and Langmuir–Blodgett film transfer rely heavily on specialised equipment, which is difficult to satisfy the requirements of time-saving, low cost and sufficient throughput [18–20].

Yoon et al. have fabricated an effective vertical stacking SERS substrate which positioned a single metallic nanowire on the continuous metallic film [21]. The vertical stacking nanostructure provides effective SERS hot spots at the contact region between the nanowire and the metal film. This results exhibit the potential of the vertical stacking metal nanostructure used for highly effective SERS substrate. However, it is still challenging to realize the practical use for the uncontrollable synthesis of 3D plasmonic nanostructures using solution-based methods. Furthermore, Choy et al. introduced a kind of Ag NPs/Graphene/Ag film structure which offered tremendous Raman signal enhancement [22]. Sun et al. developed Au NPs/Graphene/Au NPs sandwiched structure and this structure exhibit excellent SERS effect [23]. Long et al. deposit multilayered Ag nanoparticles generated by sodium citrate reduction for SERS [24]. However, these 3D plasmonic nanostructures also accompany relative poor reproducibility problem for the random distribution of metal nanostructures. A uniform 3D cross-point metal nanostructure designed by Jung et al. can obtain homogeneous SERS signal by a method of solvent-assisted high-resolution nanotransfer printing [25]. Nevertheless, the method is over complicated when the SERS substrate applied to practice. In this regard, developing a facile way to get a plasmonic nanostructure possessing high reproducibility and excellent SERS ability is still of potential application requirements and great scientific interest.

Here, a three-dimensional Ag nanoparticles obtained by facile thermal evaporation is obtained for SERS. The Raman enhancement effect is increasing as the increasing number of Ag NPs layers. This is because the Ag NPs vertical stacking brings the additional hot spots and the synergistic effect of the vertical and in-plane coupling effect. The Raman signal collected from the four-layer Ag NPs substrates attain the best and is around 11.3 times stronger than that from one-layer Ag NPs. Interestingly, the reproducibility was also significantly promoted as the layers of Ag NPs increases with the relative standard deviation (RSD%) $5.54 \sim 7.57\%$ which is obtained from 30 successive measurements. Besides, the SERS substrate also exhibits temporal stability and its enhancement factor attains 6.8×10^8. Furthermore, the SERS substrates composite with graphene are realized and show better Raman signal enhancement ability. Additionally, the in-situ trace analyses in aquatic products were also realized by flexible Ag NPs/PET substrate.

2. Experimental

2.1. Preparation of different number of metal NPs

To obtain the uniform layer-by-layer Ag NPs 3D structure, we used a thermal evaporator to deposit around 15 nm sizes of Ag NPs onto SiO2, PET and graphene. The substrates were fixed on the sample platform and placed directly right above the evaporant. The 4 mg silver wire was used as the evaporator source at distance of 40 cm under the sample platform. Evaporator current was kept 120 A until all of the silver wire were evaporated. The pressure of chamber was kept at 6×10^{-3} Pa during evaporation. The quantity of silver wire is the most critical factor to determine the final morphology of the Ag NPs. After the one-layer Ag NPs obtained, the PMMA solution was spin coated on the surface of one-layer Ag NPs to form a PMMA/Ag NPs composites. Then, the second Ag NPs layer was deposited on the PMMA/Ag NPs. The two-layer Ag NPs was obtained after removing the PMMA layer in the acetone solution. Spinning coating a PMMA layer on the Ag NPs/PMMA/Ag NPs, evaporating the third Ag NPs layer and removing the PMMA, the three-Ag NPs nanostructure was obtained. Repeating the steps, the four-layer Ag NPs, five-layer Ag NPs and six-layer Ag NPs can be also fabricated.

2.1.1. SERS experiments

To test the SERS effect of different Ag NPs layers, two probe molecules (Rhodamine 6G (R6G) and crystal violet (CV)) were used. The R6G and CV were dissolved in water to obtain the solution from 10^{-6} to 10^{-12} M. 2 μL R6G and CV with the concentration from 10^{-6} to 10^{-12} M were drop directly on the prepared substrates, respectively. The samples were totally dried before carrying out the SERS characterization. Raman signal were collected using a Raman spectrometer under the same condition (532 nm laser, 1 mW laser power, gratings with 1800 grooves per 1 mm, $\times$ 50 objective lens, 1 μm laser spot, 4 s acquisition time).

2.1.2. Characterization

The morphologies of the Ag NPs with different layers were obtained using scanning electron micros-copy (SEM, Zeiss Gemini Ultra-55). The Raman spectroscopy was performed using a Raman spectrometer (Horiba HR Evolution 800). For the UV–visible absorption and transmission measurement, the 3D structures with different Ag NPs structures were fabricated on PET. The transmittances and absorbance spectra of the 3D structure with different Ag NPs layers were obtained on a spectrophotometer (Hitachi, U-4000) using the transmission mode and absorbance mode respectively. The blank PET substrate was used as a reference to remove the background and the spectrum range was typically from 300 to 800 nm.

2.2. Results and discussion

For further application in practice, reducing the cost and simplifying the steps in fabrication of SERS substrates are still the important factors on basis of ensuring high Raman signal enhancement ratios. Thermal evaporation is one of the most facile ways to obtain metal NPs array with excellent SERS effect. Different morphology and distribution of metal NPs can be obtained by carefully controlling the amount of metals. For example, Fig. 1(a) illustrates schematically the fabrication of four kinds of SERS substrate with different Ag NPs morphology by controlling the amount of silver wire. With 2 mg, 4 mg, 8 mg and 12 mg silver wire evaporated respectively, four kinds of Ag NPs with different morphology and distributions were formed as shown in Fig. 1(b). The average gap of Ag NPs in Fig. 1(b) obtained with 2 mg silver wire evaporated is around 20 nm, which is relatively sparse. When we increase the quantity of silver wire to 4 mg, the Ag NPs distribute densely and the gaps among Ag NPs narrow to 5 nm as shown in Fig. 1(b) II. However, the Ag NPs become cluster without any gap as the evaporated silver wire increase to 8 mg as shown in Fig. 1 (b) III. To further increase the quantity of the silver wire, Ag film was obtained as shown in Fig. 1(b) IV.

To test the SERS performance of the four substrates with different Ag NPs morphology, the R6G were deposited as the probe molecules. 2 μL R6G solutions with the concentration of 10^{-5} M was deposited on the four different SERS substrates, dried naturally and carried out the Raman detection. The Raman signal of R6G collected from the four SERS substrates is shown in Fig. 1(c). The SERS signal obtained from the substrate evaporated 4 mg silver wire present 5.2 times higher than that evaporated 2 mg silver wire, 1.5 times higher than that evaporated 8 mg silver wire and 7.5 times higher than that evaporated 12 mg silver wire. It clearly indicate that the Ag NPs nanostructure with 5 nm nanogap get the best SERS performance compared with the 20 nm nanogap Ag NPs, excessively dense Ag NPs cluster and Ag film.

While the excellent SERS effect of one-layer Ag NPs have been obtained for the narrow nanogap among Ag NPs, the additional vertical coupling effect at the contact region and the synergistic effect of the vertical and in-plane coupling effect would further enhance the Raman signal for 3D SERS substrate. Fig. 2(a) illustrates schematically the fabrication of 3D metal NPs of SERS substrate with various Ag NPs layers by controlling the number of evaporation times. With 4 mg silver wire firstly deposited with nearly vertical evaporation angle ($>80°$), uniform Ag NPs with average gap around 5 nm were formed in the first thermal evaporation as shown in Fig. 2(b). The size distribution of the Ag NPs is mostly located around 15 nm as shown in Fig. S1. To obtain the two-layer Ag NPs nanostructure, a PMMA layer was spin coated on the one-layer Ag NPs. The same quantity silver wire was deposited to obtain a layer of Ag NPs on top of the PMMA/Ag NPs. Then put the Ag NPs/PMMA/Ag NPs composite in the acetone solution to remove the PMMA layer, and two-layer Ag NPs nanostructure was obtained. Similarly, Spinning coating a PMMA layer on the Ag NPs/PMMA/Ag NPs composites, evaporating the third Ag NPs layer and removing the PMMA, the three-Ag NPs nanostructure would be obtained. Repeating the steps, 3D Ag NPs nanostructure with different layers was obtained. Fig. 2(b) exhibits the morphology of the Ag NPs nanostructures with different layers. It is observed visually that the change of the morphology of the Ag NPs with the increasing number of layers. The absorbance spectrum of Ag NPs with various layers in the range from 300 to 1000 nm was also collected as shown in Fig. 3(a). The peaks of plasmonic resonance were located at the wavelength of 448.2 nm, 505 nm, 524.5 nm, 567.1 nm and 610.2 nm