Controlled Assembly of Highly Raman-Enhancing Silver Nanocap Arrays Templated by Porous Anodic Alumina Membranes

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A convenient nanoscale technique is reported for the fabrication of highly ordered hemispherical silver nanocap arrays templated by porous anodic alumina (PAA) membranes as robust and cost-efficient surface-enhanced Raman scattering (SERS) substrates. This geometry produces a high Raman signal due to its periodic hexagonal arrangements and control of the gap between the nanostructures in the sub-10-nm regime. The surface structure can be tuned further to optimize the enhancement factor according to optional PAA fabrication and silver deposition parameters. Finite-difference time-domain calculations indicate that the structure may possess excellent SERS characteristics due to the high density and abundance of hot spots.

1. Introduction

Surface-enhanced Raman scattering (SERS) is recognized as one of the most sensitive spectroscopic tools offering highly sensitive chemical and biological detection. The fact that particle plasmons allow the direct coupling of light to resonant electron plasmon oscillations has spurred tremendous research activities in the design and fabrication of highly SERS-active substrates in nanostructured films and metallic nanoparticles. The most established substrates are those sprayed with Ag or Au colloids that yield intense SERS signals at certain local junctions. These interstitial sites, so-called SERS “hot spots” or “hot junctions” in the nanostructures, consist of two or more coupled nanoparticles or nanostructured surfaces with closely spaced features. They are believed to have highly concentrated electromagnetic (EM) fields associated with strong localized surface plasmon resonance. In routine, online trace analysis, SERS substrates must be stable with a high concentration of giant Raman cross-section hot spots, and also be reproducibly prepared, inexpensive, and easy to make. Although spraying Ag or Au colloids onto a substrate leads to an extremely high SERS signal at some local hot spots, due to particle aggregation, it is not easy to achieve a reliable, stable, and uniform SERS signal spanning a wide dynamic range. Popular approaches to remedy the problems of poor control over the particle aggregation states include immobilization at surfaces, entrapment within stable matrices, or fabrication of complex surface structures (e.g., with microfabrication), but these processes can be demanding in terms of labor and cost, and it is sometimes impossible to extend them to large dimensions. Although these efforts illustrate the great potential of using SERS as a sensitive molecular sensing tool, precise control of the gaps between the nanostructures on a SERS-active substrate, with interparticle gap dimensions in the sub-10-nm regime necessary for intense SERS enhancement, is...
still extremely difficult to obtain by existing nanoscale fabrication methods.

In this Full Paper, we report the fabrication of highly ordered hemispherical silver nanocaps arrays templated by porous anodic alumina (PAA) membranes as robust and cost-efficient SERS substrates with significant SERS enhancement. The use of PAA membranes as templates for the fabrication of SERS substrates is especially promising considering their easy fabrication, excellent reproducibility, modest cost, and large-area production, thereby boding well for applications in sensing. For example, it is well known that metal nanowires grown in highly ordered PAA membranes using electrodeposition can be partially exposed to form regular nanowire and nanoelectrode arrays from a broad range of metals such as Cu, Ag, Au, Ni, Co, Pd, and Pt. Researchers have found that the SERS probe intensity depends critically on the aspect ratio of the protruding field of the nanowires and this may afford excellent opportunities to gain deeper insight into the details of the SERS mechanism. In a later study, Wang and colleagues adopted a similar approach to produce PAA-templated silver nanoparticle arrays with a precisely controlled variation of interparticle gaps of between 5 and 25 nm. Their work represented the first quantitative observation of the SERS effect on a substrate with controlled hot junctions in the sub-10-nm regime, and confirmed the theoretical prediction of interparticle-coupling-induced Raman enhancement. Very recently, Ko and Tsukruk introduced three-dimensional (3D) SERS substrates using PAA membranes with inner walls decorated with gold nanoparticles. These works have a similar feature. That is, they all utilize uniformly aligned, vertical cylindrical pores of PAA to fabricate SERS-active nanostructures. It should be noted that, with the exception of vertical cylindrical pores of PAA to fabricate SERS-active nanometer-sized platforms, in which the areas exhibiting large gap-related enhancement are organized in a regular pattern. The surface structure can further be tuned to optimize the enhancement factor (EF) according to optimal PAA fabrication and silver deposition parameters.

2. Results and Discussion

In the procedure for fabricating arrays of hemispherical silver nanocaps separated by tunable gaps on the PAA substrates, we first obtained PAA templates with different nanopore diameters, which could be controlled by adjusting the anode voltage, and subsequently via nanopore-enlarged processing. A two-step anodic process was also utilized to improve the nanopore periodicity of the PAA membranes. Afterwards, silver was deposited onto the surface of the PAA substrates in a conventional direct-current magnetron-sputtering system. Figure 2 shows a series of scanning electron microscopy (SEM) images of the silver-coated PAA membranes formed using different anodic voltages. The sputtering time of the silver was ten minutes. The typical small-angle X-ray diffraction (SAXD) spectrum was obtained from the sample exhibited in Figure 2c. The diffraction peak can be indexed to the (111) plane of face centered cubic (fcc) silver (JCPDS 04-0783; see Figure S1). As shown in the SEM images in Figure 2, these silver nanocaps cover the alumina protrusions and exhibit periodic hexagonal arrangements. Their sizes \(D = 50 \pm 5 \text{ nm}\) are almost equal to each other due to the similarly shaped alumina protrusions and equal sputtering times. Their gaps \((G1, G2)\) can be determined approximately by measuring \(G3\), assuming that the array of six silver nanocaps is arranged by perfectly hexagonal disks. The corresponding average values of \(G3\) are shown in Figure 2f. Thus, by varying the anodic voltage of the PAA templates, the nanopore expands or contracts while moving the deposited silver nanocaps closer or further together. The spacing can be tailored from less than 10 nm to 90 nm. Since the spacing between the nanocaps can be controlled by adjusting the anodic voltage, the hot spot is actively tuned during a given SERS experiment to achieve the strongest coupling between adjacent nanocaps. It should be noted here that perfect self-organized growth, which controls the nanopore arrangement, only occurs under a certain anodic voltage. This is shown to be 40 V by our experiments (see Figure 2c).

Figure 1. a) A 3D AFM image of the PAA surface. b) Section analysis along the white line in (a). The two arrows correspond to those in (a). c) Schematic representation of a planar PAA surface with dimensional parameters \(D, G1, G2,\) and \(G3\), where \(D\) is the island diameter and \(G1, G2,\) and \(G3\) are the ortho-, meta-, and para-island gap, respectively. 

A small protrusion along the surface of the pore wall, and a dent occurs at each corner of each hexagonal cell. A concave shape can be observed between two neighboring protrusions. To depict this feature more clearly, we conduct a section analysis along the white line in Figure 1a and present the corresponding result in Figure 1b. Top-to-bottom fluctuations of the cell boundary between the two protrusions are obvious. The planar geometry of the PAA substrate is shown schematically in Figure 1c, in which \(D\) is the island (protrusion) diameter and \(G1, G2,\) and \(G3\) are the ortho-, meta-, and para-island gap, respectively. Such opening features of the pores, as caused by volume expansion when aluminum is converted into alumina, can be used as templates to design and fabricate 3D SERS-active nanometer-sized platforms, in which the areas exhibiting large gap-related enhancement are organized in a regular pattern. The surface structure can further be tuned to optimize the enhancement factor (EF) according to optimal PAA fabrication and silver deposition parameters.
To evaluate the Raman-enhancing capability of the silver nanocap arrays displayed in Figure 2, a water solution (10⁻⁵ M) of rhodamine 6G (R6G) is applied to the substrates. Figure 3 shows a collection of spectra illustrating the efficiency of the SERS. In this study, we use a He–Ne laser (λ = 633 nm) as the excitation source because its wavelength is close to the expected coupled surface plasmon resonance arising from a hybrid mode at the air–silver interface. It reflects a coupled particle-plasmon-plasmon-wave system and has higher transmission through the gaps.[11,22–24] Many salient peaks can be observed, and the more pronounced ones at 1313, 1362, and 1510 cm⁻¹ can be assigned to the totally symmetric modes of in-plane C–C stretching vibrations.[25] The excessive Raman enhancement can, at first glance, be associated with the effect of resonance coupling between neighboring nanocaps (hot spots), while the fluorescence quenching suggests that some of these molecules spontaneously adsorb onto the surface of the nanocaps causing Förster resonance energy transfer from the R6G dyes to silver nanocaps.[26] Comparisons among the spectra reveal the existence of different SERS enhancements, especially the quantitative intensity comparison from the selected band (1510 cm⁻¹) in the inset. It can be observed that the Raman enhancement observed from the sample in Figure 2c is larger than that from the others. Such strong enhancement in sample c can be attributed to the fact that the nanocap arrays are assembled with a favorable gap configuration (G3 ≈ 35 nm, G2 ≈ 25 nm, G1 < 10 nm) and a highly ordered arrangement. This, as well as a high density of both Ag nanocaps (≈1 × 10¹⁰ cm⁻²) and hot spots (≈1 × 10¹¹ cm⁻²), is necessary for intense SERS enhancement.

It is notable that, although mass particle aggregation can be observed in samples a and b (Figure 2a and b), the values of G2 and G3 decrease, thus not reducing the SERS enhancement significantly. It can be further concluded that the larger interstitial sites in samples d and e (Figure 2d and e) are not favorable to SERS.

Apart from finding that the gaps between neighboring silver nanocaps can be tuned by varying the anodic voltage to optimize the SERS, we also increased the sputtering time of silver from 10 min to 15 and 20 min to tailor the sizes of the silver nanocaps. Figure 4 shows SEM images of the silver-coated PAA membranes formed by using different Ag sputtering times (15 and 20 min), and the corresponding SERS spectra. Both the PAA membranes were formed under a constant DC voltage of 40 V. Together with the 10-min-sputtered sample shown in Figure 2c, the geometries of the three samples show two main features: 1) The silver nanocap arrays are assembled with a highly ordered arrangement (see Figure S2), which is critical for the fabrication of substrates with uniform SERS enhancement, and 2) although the sizes of the nanocaps are increased by increasing the sputtering time, the D + G1 value is almost fixed at ≈55 nm, thereby moving the deposited silver nanocaps closer for further aggregation. The variation in the SERS signal intensity at 1510 cm⁻¹ is shown in Figure 4c. The intensity of the R6G Raman signal decreases when the sputtering time goes from 15 min to 20 min. This is due to mass particle aggregation between adjacent silver nanocaps when the caps are brought together as the size becomes larger. It is worth mentioning that, as the nanocaps approach each other physically (when the sputtering time of silver goes from 10 min to 15 min), the SERS signal intensity increases by a factor of more than 2 at 1510 cm⁻¹ (see Figures 3 and 4c). This result has good correlation with the calculation, which shows that the coupling between particles is quite short range.[27]
In order to assess the relative contributions of different geometries to the above experimentally observed SERS intensities, the local EM fields were calculated using commercial finite-difference time-domain (FDTD) software (CST MWS 2009), which has recently been demonstrated to be highly useful in the study of the EM properties of metallic nanostructures for almost arbitrary complexity. The array of silver nanocaps is approximated by six hexagonally arranged hemispheres using dimensional parameters (\(D, G_1, G_2, G_3\), shown in Table S1) equal to the mean values of the samples produced experimentally. The light at 633 nm is assumed to be incident normal to the sample (see the inset of Figure 5a). Aside from the obvious approximation that a large 2D array is mimicked by a six-element cluster, the approximation that the silver nanocaps covering the alumina nanoislands can be approximated using hemispheres is a significant approximation because we show that the field strengths depend significantly on the hemisphere sizes as well as the gaps between them. Figure 5a–c mimics the situation of the samples fabricated at different constant DC voltages (the value of \(D\) is fixed at 50 nm, whereas \(G_1\) increases from 2 nm to 30 nm). Figure 5d–f shows the situation of the samples fabricated using different Ag sputtering times (the value of \(D + G_1\) is fixed at 55 nm, whereas \(G_1\) increases from 2 nm to 25 nm). In the color contour plots of the near EM-field distributions shown in Figure S3, one can find that higher enhancement is achieved from the smaller intercap gap size. It is notable that the enhancement increases with reduction in the value of the gap-to-diameter ratio (see Figure 5a and d). The largest enhancement is achieved in the case shown in Figure 5d (EF \(\approx 10^4\)), which is simplified as the fourth power of the local electric-field enhancement: EF = \((E_{loc}/E_0)^4\). The simulation is in agreement with the studies reported by Wei et al. and also our experiments.

3. Conclusions

In summary, we report a simple technique to fabricate highly ordered hemispherical silver nanocap arrays templated by PAA membranes. This geometry exhibits a high Raman signal due to periodic hexagonal arrangements and gap control between the nanostructures in the sub-10-nm regime. FDTD calculations further indicate that the structure may possess excellent SERS characteristics due to the high density and abundance of hot spots. This design of the silver nanocap array with uniform and highly reproducible SERS-active properties may open a new framework for the fabrication of robust, cost-effective, large-area SERS-based sensors.

4. Experimental Section

Sample preparation: High-purity Al foils (99.99%) with 0.2-mm thickness were cleaned by acetone to degrease the surfaces, followed by electropolishing for 3 min in a mixture of ethanol and perchloric acid with a volume ratio of 5:1, under a constant DC voltage of 15 V, to further remove surface impurities. After rinsing in distilled water and drying, the Al foils were anodized separately in a 0.5 m oxalic acid solution under a constant DC voltage of 20 V (30 V, 40 V, 50 V, 60 V) at 10 °C. In order to obtain an ordered nanopore array, we used a two-step anodization process [18, 19]. The Al foils were first anodized for 2 h, followed by immersion in a mixture of chromic acid (1.8 wt%) and phosphoric acid (6 wt%) at 100 °C for 1 h, and then cleaned with acetone, ethanol, and distilled water.

4.1. PAA Coating

The PAA coating was performed at room temperature and a constant DC voltage of 20 V. The PAA solution was prepared by diluting a 20 wt% PAA solution in water to a concentration of 10 wt%.

4.2. Silver Electrodeposition

Silver electrodeposition was performed at a constant DC voltage of 20 V. The Ag seed layer was deposited on the PAA-coated Al foils using an Ag metal bath with a constant DC voltage of 20 V.

4.3. SEM Imaging

The SEM images were obtained using a JEOL JSM-7000F field emission scanning electron microscope. The samples were coated with a thin layer of gold before imaging.

Figure 4. SEM images obtained from the silver-coated PAA membranes formed using different Ag sputtering times of a) 15 and b) 20 min. The scale bar is 100 nm. Both the PAA membranes are formed at a constant DC voltage of 40 V. c) SERS spectra of R6G-adsorbed silver-coated PAA membranes corresponding to those in (a) and (b), demonstrating the intensity variation of the SERS signal at 1510 cm\(^{-1}\).

Figure 5. Simulated EM-field distribution maps of the silver nanocap arrays with different parameters. a) \(D = 50\) nm, \(G_1 = 2\) nm; b) \(D = 50\) nm, \(G_1 = 5\) nm; c) \(D = 50\) nm, \(G_1 = 30\) nm; d) \(D = 53\) nm, \(G_1 = 2\) nm; e) \(D = 65\) nm, \(G_1 = 10\) nm; f) \(D = 30\) nm, \(G_1 = 25\) nm. The k vector and polarization of the incident light in the simulation are shown in (a).
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75 °C (1:1 by volume). After 2 h, the alumina layer, which grew at the first step, was removed and the surface of the foil became bright. The anodization time in the second step was 2 h. Afterwards, the PAA templates were obtained. Silver nanocap films were prepared on the PAA membranes at room temperature under argon (20 sccm) in a conventional direct-current magnetron-sputtering system. A 50-mm-diameter high-purity silver plate (>99.99%) was used as a target. The sputtering chamber was initially evacuated to a base pressure below 2.5 × 10⁻³ Pa, and then pre-sputtering was carried out for 5 min at an argon gas pressure of 1.0 Pa in order to clean the target surface. The power of the magnetron in each run was 0.04 mW. The signal collection time was 50 s. For evaluation of the sample was 0.04 mW. The signal collection time was 50 s. For evaluation of the substrate Raman-enhancing capability, a 10⁻⁵ M water solution of R6G was used. In order to allow molecule adsorption, the substrates were maintained for 30 min in the R6G solution, and then taken out and rinsed thoroughly. It should be noted that the acquisition time and the laser power were the same for all the Raman spectra. The SERS spectra were recorded from multiple sites on the substrate surface to confirm reproducibility. Similar SERS spectral characteristics, such as enhancement, position, and relative intensity of the bands, were determined from various locations due to large-area production of uniform geometries (see Figure S2).

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