An efficient nanopatterning strategy for controllably fabricating ultra-small gaps as a highly sensitive surface-enhanced Raman scattering platform

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Received 26 June 2019, revised 26 August 2019
Accepted for publication 1 October 2019
Published 22 October 2019

Abstract
The realization of large-scale and high-density gaps with sizes as small as possible is crucial for designing ultra-sensitive surface-enhanced Raman scattering (SERS) substrates. As known, the ultrathin alumina mask (UTAM) surface nanopatterning technique allows the fabrication of periodic nanoparticle (NP) arrays with 5 nm gaps among the NPs, however, it still faces a significant challenge in realizing the reliable distribution of nanogaps over a large area, because of the unavoidable collapse of the UTAM pore wall during the traditional one-step homothermal pore-widening process. Herein, an efficient two-step poikilothermal pore-widening process was developed to precisely control the pore wall etching of a UTAM, enabling effectively avoiding the fragmentation of the UTAM and finally obtaining a large-scale UTAM with a pore wall thickness of about 5 nm. As a result, large-scale NP arrays with high-density sub-5 nm and even smaller gaps between the neighboring NPs have been realized through applying the as-prepared UTAM as the nanopatterning template. These NP arrays with sub-5 nm gaps show ultrahigh SERS sensitivity (signal enhancement improved by an order of magnitude compared with NP arrays with 5 nm gaps) and good reproducibility, which demonstrates the practical feasibility of this promising two-step pore-widening UTAM technique for the fabrication of high-performance active SERS substrates with large-scale ultra-small nanogaps.

Supplementary material for this article is available online

Keywords: ultra-small gaps, two-step poikilothermal pore-widening method, ultrathin alumina mask, SERS, nanoparticle arrays

(Some figures may appear in colour only in the online journal)

1. Introduction

It is crucial to realize large-scale high-density gaps with sizes as small as possible between neighboring nanostructures for periodic nanoarray systems, especially ultra-sensitive surface-enhanced Raman scattering (SERS) substrates [1–4]. The large enhancement of the Raman signal is primarily attributed...
to the condensed electromagnetic field associated with local surface plasmon resonance (LSPR) on the several nanometer gap, i.e., hot spot [5–8]. Both theoretical [5] and experimental [9] studies have demonstrated that the electric field enhancement increases sharply with the decreasing of gap size. And the high SERS enhancement factor (EF) can be up to $10^{12}$ at the ‘hot spot’ [10, 11]. So far, various methods [4, 12–28] have focused on the fabrication of very small gaps (sub-10 nm), including lithographic methods (such as electron-beam lithography, nanosphere lithography, focused ion-beam patterning, and soft-lithography), and scanning probe microscopy writing techniques. However, intrinsic limitations hinder their further application for these traditional techniques [29–32]. How to fabricate high-density gaps with sizes as small as possible is still a great challenge. Undoubtedly, the properties of nanostructures are closely related to their preparation methods [33–37], therefore, an appropriate fabrication method is essential to optimize structural performance.

In recent years, the ultrathin alumina mask (UTAM) surface nanopatterning technique has shown the unique superiority of structural parameters controllability, ultrahigh density ($10^{10}$–$10^{12}$ cm$^{-2}$) of patterns, and easy fabrication on a large scale (>1 cm$^2$). So it has been regarded as an effective alternative method for fabricating nanoarrays with a controllable and tunable spacing size in a time-saving and low-cost way. By adjusting the pore size of the UTAM, the flexible control of the pore wall thickness can be easily achieved. For our prepared UTAMs, the distance of the pore center to center is certain, about 100 nm, so the larger the pore diameter, the smaller the interpore distance (i.e. pore wall thickness). Hence the gaps between the neighboring nanostructures in the arrays can be adjusted to be as small as possible by decreasing the UTAM pore wall thickness during the UTAM-based fabrication. We have obtained [32] ultra-high-density 5 nm nanogaps in ordered periodic nanoparticle (NP) arrays using the traditional UTAM technique (a homothermal one-step pore-widening process at 30 °C) and the prepared samples have shown excellent SERS performance with high Raman enhancement up to $10^9$ and ideal reproducibility (relative standard deviation as low as 2%). However, it is almost impossible to realize reliable sub-5 and even much smaller gap distribution on a large area with good uniformity only by using the traditional homothermal pore-widening UTAM technique, because of the unavoidable collapse of the pore wall during a very long duration wet-chemical etching process. Although it is possible to get a UTAM with a pore diameter larger than 95 nm by reducing the temperature during the pore-widening process (<30 °C, such as 15 °C or 20 °C), it would be very time consuming and also might add more difficulties in realizing an ideal UTAM with a pore diameter as large as possible. This is the obvious limitation of the conventional homothermal pore-widening procedure.

Herein, an efficient two-step poikilothermal pore-widening process was developed to precisely control the pore wall etching of a UTAM, enabling effectively avoiding the fragmentation of the UTAM and finally obtaining a large-scale UTAM with a pore wall thickness of about 5 nm. As a result, large-scale NP arrays with high-density sub-5 nm and even smaller gaps between the neighboring NPs have been realized by applying the as-prepared UTAM as the nano-patterning template. These NP arrays with sub-5 nm gaps show ultrahigh SERS sensitivity (signal enhancement improved by an order of magnitude compared with NP arrays with 5 nm gaps) and good reproducibility, which demonstrates the practical feasibility of this promising two-step pore-widening UTAM technique for the fabrication of high-performance active SERS substrates with large-scale ultra-small nanogaps.

2. Experimental

2.1. Fabrication of UTAMs based on the two-step poikilothermal pore-widening method

The UTAMs were prepared using a two-step anodization method [38–41] and an improved two-step poikilothermal pore-widening process. Briefly, the high-purity (99.999%) aluminum foil with 0.22 mm thickness was first anodized in 0.3 M of oxalic acid aqueous solution at 2 °C and 40 V DC for 12 h. Then, the anodic oxide layer was removed in a mixture of H$_3$PO$_4$ (6 wt%) and H$_2$CrO$_4$ (1.8 wt%) at 60 °C. Secondary anodization was carried out using the same condition as the first step for 5 min, and finally an alumina membrane with a certain thickness on the Al layer was obtained. Subsequently a photore sist layer was dropped on the top of the alumina as a supporting layer with a heat treatment process in an oven at 80 °C for about 30 min, followed by the removal of the Al back layer in a solution of CuCl$_2$ and HCl. After that, a two-step poikilothermal pore-widening process was conducted, different from the one-step homothermal enlargement process at 30 °C used in the traditional method [32, 38]. In the first step, the pore-widening process was carried out in a phosphoric acid solution (5 wt%) at 30 °C for about 65 min to get a stable sample with an average pore diameter of about 80 nm, which has a large enough pore size and is easy to transfer. Then the sample was rinsed with deionized water and acetone, respectively, followed by the transfer onto the Si wafer (hydrophilic pretreatment and dried). To avoid the sample from drifting away during the subsequent broadening process, it was attached to the wafer by using a tape. Then in the second step, the UTAM continued to be etched at a relatively lower temperature (5 °C, 10 °C, 15 °C, 20 °C, and 25 °C, respectively, for screening optimum temperature) by being immersed in the 5 wt% phosphoric solution for a certain time (different durations for different etching temperatures) to get the samples with pore diameters as large as possible before collapse. Finally, the UTAMs with ideal pore diameters as large as possible were obtained after being rinsed with deionized water and removing the tape.

2.2. Fabrication of NP arrays

The NP arrays were prepared by thermally depositing Ag on the top surface of the UTAM/Si substrate at the rate of
2.4. Characterization and SERS Measurement

The samples for the SERS measurements were prepared by immersion of the Ag/Si substrate in a solution for 30 min as the reference. Subsequently, all the samples were rinsed with deionized water and dried by nitrogen gas flow.

2.3. Preparation of samples for SERS measurement

The samples for the SERS measurements were prepared by immersion of the Ag/Si substrate in 1 × 10⁻⁷ M of Rhodamine 6G (R6G) aqueous solution (30 ml) for 30 min to make sure the surface, especially the ‘hot spots’, adsorbed a monolayer of R6G molecules. To determine the EFs, an Ag film/Si substrate was immersed in 10⁻³ M of R6G aqueous solution for 30 min as the reference. Subsequently, all the samples were rinsed with deionized water and dried by nitrogen gas flow.

2.4. Characterization and SERS Measurement

Scanning electron microscopy (SEM) images were obtained on an field-emission SEM (JSM-6700 F, JEOL Company). SERS spectra were collected by a 100 × (N.A. 0.9) objective Renishaw InVia plus Raman spectrometer with a 514.5 nm wavelength argon ion laser excitation in a cumulative exposure time of 50 s. All the SERS spectra were acquired from five to six different locations of the same sample, and the typical spectrum was reported. Baseline correction of the measured spectra was performed to remove the broad background and fluorescence band. All the experiments were performed in duplicate or triplicate to check the repeatability of the whole process.

0.4 nm s⁻¹ under a vacuum of 8.4 × 10⁻⁴ Pa in a physical vapor deposition process (PVD). After depositing 60 nm thick Ag, the UTAMs were stripped away, leaving the ordered Ag NP arrays on the surface of the Si substrate. By changing the UTAM structural parameters, a series of Ag NP arrays/Si with different particle diameters and separations were achieved. For comparison, a sample Ag film/Si with the same Ag deposition thickness was fabricated by PVD.

3. Results and discussion

Figure 1 illustrates the fabrication of Ag NP arrays with ultra-small gaps (the average particle diameter is larger than 95 nm) based on a two-step poikilothermal pore-widening UTAM technique. As detailed in the experimental section, after the first step of the etching process at 30 °C for 65 min, an alumina membrane with average pore diameter (D) of about 80 nm was obtained (as shown in figure 2(a)). The condition of t₁ = 65 min and D = 80 nm is to enable membranes with a large pore diameter and that are easy to transfer. In the traditional one-step homothermal method, if the etching continues to produce a pore diameter larger than 95 nm, the etching duration will be longer than 75 min (a pore diameter of 95 nm can be realized for about 75 min during the wet-etching process at 30 °C [32]). However, it is quite difficult to control the reliable sub-5 nm pore wall in such a long-duration wet-etching process at 30 °C, because of the avoidable collapse of the pore wall at the rapid etching rate at 30 °C. Figure 2(b) demonstrates a broken UTAM after one-step 80 min pore-widening at 30 °C, and the whole structure completely fell into pieces. According to our experience, the lower the temperature used, the slower the etching rate is maintained, and the easier the pore-widening process is controlled and an intact UTAM with a large diameter is obtained. (As shown in figures S1 and S2, available online at stacks.iop.org/NANO/31/045301/mmedia in the supporting information, the pore diameter of the UTAM varies obviously with the etching temperature under the same condition of etching duration and treatment.) Thus, it is possible to get a UTAM with a pore diameter larger than 95 nm by reducing the temperature during the pore-widening process (<30 °C, such as 15 °C or 20 °C, and an even much lower temperature of 10 °C or 5 °C), however, it will be a long-duration process and very time-consuming. Therefore, an ingenious two-step
Therefore, the slow etching rate at lower temperature fi
the pore wall starts cracking, as shown in
with varying the etching time
UTAM with a large enough average pore diameter
(duration for the second-step etching process to realize a
small as possible. To screen out the right temperature and
for realizing ideal UTAMs with the interpore distance as
later, about 18 min later for the second enlargement at 25
Details are found in Table S2. Nevertheless, for the two-step
enlargement process, the final pore size of the UTAM strictly
depends on the second pore-widening temperature \( T_2 \) and
etching duration \( t_2 \). In our current experimental data, the
largest average pore diameters of the UTAM are 97.8, 94.6,
95.8, 95.2, and 97.6 nm at 5 \(^\circ\)C, 10 \(^\circ\)C, 15 \(^\circ\)C, 20 \(^\circ\)C, and
25 \(^\circ\)C, and the corresponding second enlargement time is 150,
75, 30, 20, and 15 min, respectively.

The experimental results at different second-widening
temperatures present a good linear relationship between the
final pore diameter \( D_f \) and second-widening time \( t_2 \), (as shown
in figures 4(a)–(e)) which means that the large pore diameter

**Figure 2.** SEM images of the UTAMs after the one-step homothermal pore-widening process at 30 °C for 65 min (a) and 80 min (b); after the first-step pore-broadening at 30 °C for 65 min, then the second-step etching at 25 °C for 15 min (c) and 18 min (d), respectively. All the scale bars are 100 nm.
can be precisely controlled by carefully adjusting the duration of the second-step etching at an appropriate temperature condition until achieving the ideal pore size as large as possible. As mentioned before, the lower the pore-widening temperature, the lower the etching rate during the second-widening process, and hence the easier the controllability of a pore diameter that is as large as possible, however, the whole experiment is more time-consuming. All the data including $D_{\text{ave max}}$, pore-widening temperatures, and times are listed in Table S1 to screen out the optimal experimental conditions. Obviously, the temperatures of 15 °C and 20 °C have a greater advantage than the other temperatures (5 °C, 10 °C, and 25 °C) for second pore-widening and it can be predicted that the ideal UTAM with a pore size larger than 95 nm and even much larger can be realized by precise adjustment and manipulation during the whole process. By

![Figure 3. SEM images of the UTAMs with different average pore diameters after the second pore-widening treatment for different etching times ($t_2$) at different temperatures ($T_2 = 5 \degree C$, 10 \degree C, 15 \degree C, 20 \degree C, and 25 \degree C, respectively). All the scale bars are 100 nm.](image)

![Figure 4. The linear relationship between the UTAM pore diameter and the second pore-widening duration at different temperatures: (a) 5 °C, (b) 10 °C, (c) 15 °C, (d) 20 °C, (e) 25 °C and (f) between the UTAM pore diameter and the one-step homothermal pore-widening time at 30 °C.](image)
contrast, the linear relationship is not very good between the pore diameter and widening time \( t_1 \) in the traditional one-step homothermal etching process at 30 \(^\circ\)C (as displayed in figure 4(f)), because the high etching rate makes it hard to precisely control the pore-broadening process. Due to the easy collapse, the pore-etching process only lasted 70 min (as shown in figure S5). All these results show the unique advantage of this kind of ingenious two-step poikilothermal pore-widening strategy again.

Using the two UTAMs with an average pore diameter of 95 nm (the largest diameter obtained by the one-step homothermal pore-widening method at 30 \(^\circ\)C) and about 97.8 nm (obtained by the two-step poikilothermal pore-widening technique) as templates, two Ag NP arrays with ultra-small nanogaps of about 5 and sub-5 nm were fabricated with PVD. SEM images and SERS spectra of these two Ag NP SERS substrates are shown in figure 5. Obviously, both NP arrays have a high sensitive response to \( 10^{-7} \) M of R6G molecules, but it is worth noting that the Raman signal enhancement of the 97.8 nm sample (depicted as S97.8) is much stronger than that of the 95 nm sample (depicted as S95). The calculation results of the SERS signal EFs for both S97.8 and S95 relative to the Ag film/Si (shown in table S2) quantitatively show that S97.8 has improved signal enhancement by ten times compared with S95. That is because the gap size of S97.8 is much smaller than S95 (\( G \approx 5 \) nm), hence the SERS intensity increases sharply with the decreased gap size because of the strong coupling effect associated with the localized plasmon at the ultra-small gap between the adjacent NPs. This increase in EF value demonstrated that this effective method can realize more sensitive detection to trace materials, which is meaningful and helpful both in theoretical research and practical application for SERS-based sensing in many fields.

Besides the high sensitive response of probe molecule R6G, the Ag NP array of S97.8 also shows large-scale structural uniformity and good reproducibility in the Raman signal which is important to a practical SERS substrate. Raman mappings taken on an area of 20 \( \times \) 20 \( \mu \)m\(^2\) for S97.8 absorbed on \( 10^{-7} \) M of R6G and the particle size distribution diagram are shown in figure 6. Figure 6(a) displays six of the spot-to-spot SERS maps for different areas (20 \( \times \) 20 \( \mu \)m\(^2\)) of the substrate, which were recorded with a 2 \( \mu \)m step using the integrated area of the baseline-corrected peaks at 1650 cm\(^{-1}\). The regular color distribution of each map shows that the Raman signal intensities tend to be reproducible. Moreover, the average intensities of SERS mapping shown from six different areas of the substrate are very close, also indicating that the fabricated Ag NP arrays are highly uniform and have good reproducible SERS enhancement in a large area. The diagram of particle size distribution (figure 6(b)) also shows the good uniformity and regularity of S97.8.

**Figure 5.** SEM images of the Ag NP arrays with average particle diameters of \( \sim \)95 nm (a) and \( \sim \)97.8 nm (b), and SERS spectra ((a') and (b')) of \( 1 \times 10^{-7} \) M of R6G absorbed on these two arrays.
4. Conclusions

In summary, an efficient two-step poikilothermal pore-widening process was developed, and with the precise control over the pore wall etching of the UTAM, large-scale UTAMs with a pore wall thicknesses of about 5 nm were obtained, avoiding the fragmentation of the UTAM effectively. As a result, large-scale NP arrays with high-density sub-5 nm and even smaller gaps between the neighboring NPs have been realized based on these as-prepared UTAMs. The excellent SERS performance, such as ultrahigh sensitivity and good reproducibility, of the NP arrays with sub-5 nm gaps demonstrates the practical feasibility of this promising two-step pore-widening UTAM technique for the fabrication of high-performance active SERS substrates with large-scale ultra-small nanogaps.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Nos. 21577086, 21671131, 11875185 and11605111), State Scholarship Fund (File No. 201806895008), the Program for Changjiang Scholars and Innovative Research Team in University (No. IRT_17R71), and the German Research Foundation (DFG: LE 2249/4-1 and LE 2249/5-1).

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