

Tunable Fabrication of SERS-Active Noble Metal Nanoarrays

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Abstract. This work demonstrates the fabrication of uniform gold nanoarrays by utilizing self-assembled block copolymer (BCP) template, which enables us to finely tune the gold nanostructures by simply adjusting reaction time. We fabricated a series of evolutionary gold nanostructures with different reaction time, and investigated their corresponding SERS effects. Results show that the nanostructures have strong size-dependent Raman signal enhancement. This work provides a fast, simple and reproducible way to fabrication of SERS-active substrate with tunable nanostructures.

1. Introduction

Noble metal nanomaterials possess unique physical and chemical properties and have been widely utilized in catalysis[1, 2], optical sensing[3, 4], bioimaging[5, 6], SERS detection[7-10], and so on. Controllable fabrication and properties modulation of such metal nanostructures has drawn great attention. Block Copolymers (BCPs) are special polymers obtained by chemically linking two or more different polymer segments together, and different blocks possess different physical and chemical properties. BCPs can be phase separated at the nanometer scale with certain solvents. Based on its microphase separation, BCPs can be self-assembled into various ordered nanopatterns which can guide interface-confined chemical reactions to grow nanomaterials. Large-area functional nanostructures with uniform size and shape can be obtained by BCPs-template approach [11-15].

In this paper, we present a simple, low-cost and robust technique to grow high-density ordered arrays of Au nanoparticles on silicon wafer at room temperature over large areas with the assistance of BCP polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP). Confined with the nanopatterns derived from this amphiphilic diblock copolymer on silicon substrates, galvanic reduction reaction of gold was initiated in the P4VP region of BCP film and thus periodically ordered gold nanoarrays can be achieved, mimicking the morphology of the template. This approach allows for finely tuning gold nanostructures with variable size and gap, and further modulating their optoelectronic properties, such as SERS effects. Here a practical platform is developed to fabricate a series of gold nanoarrays and investigate their relative SERS activities using Nile blue A(NBA) as sensing molecule. This work paves a way to better understanding of SERS effects and to further design of SERS substrates of better performance.

2. Methods

2.1. Pretreatment of silicon wafers

The silicon wafer was cut into small square pieces with an area of about 1cm². Then they were immersed into absolute ethanol for ultrasonic treatment and washed by ultrapure water, following with



N₂ flow drying. After that, silicon wafers were treated by immersing in a piranha solution (H₂SO₄ and H₂O₂ in a 7:3, v/v) at 75°C for 15min. At last the silicon wafers were washed with ultrapure water and dried with N₂ gas flow.

2.2. Preparation of BCP template on silicon wafer

The block copolymer PS-*b*-P4VP (109-27) was dissolved in toluene, then heated and stirred to obtain a solution with a mass fraction of 0.5%. A layer of block copolymer template was formed on the surface of silicon wafer by spin coating. Samples were transferred to the dryer and kept more than 24h for follow-up operation after spin coating.

2.3. Preparation of Au nanostructures

The sample which surface coated with a BCP template was immersed in a mixture of 0.5mM HAuCl₄ /1% HF aqueous solution at room temperature for a given time. Then the sample was washed with ultrapure water and dried with N₂ gas flow.

2.4. Characterization

In our study, the morphologies of BCP template and gold nanostructures were characterized by field emission scanning electron microscopy (FE-SEM; Zeiss Ultra Plus). Surface-enhanced Raman spectra were collected by using a Renishaw Invia Reflex Raman spectrometer. NBA was used as a probe molecule. The prepared samples were firstly immersed in 5ml 10⁻⁵ M NBA aqueous solution for 30min and then dried under room temperature for SERS measurements.

3. Results and discussion

The process of block copolymer self-assembly on substrates is a versatile bottom-up approach capable of achieving nanopatterns. Block copolymer PS-*b*-P4VP forms micelle structures in toluene solvent, with the hydrophilic P4VP block as the core and hydrophobic PS block as the crown. Its nanopatterning on the silicon substrate can be achieved by simple spin-coating, P4VP nanodot arrays surrounded by PS matrix. As shown in figure 1(a), the as spin-coated PS-*b*-P4VP film on silicon forms ordered nanodot arrays with P4VP domain of 30-45nm in diameter and center-to-center spacing between two adjacent P4VP cores of around 105nm.

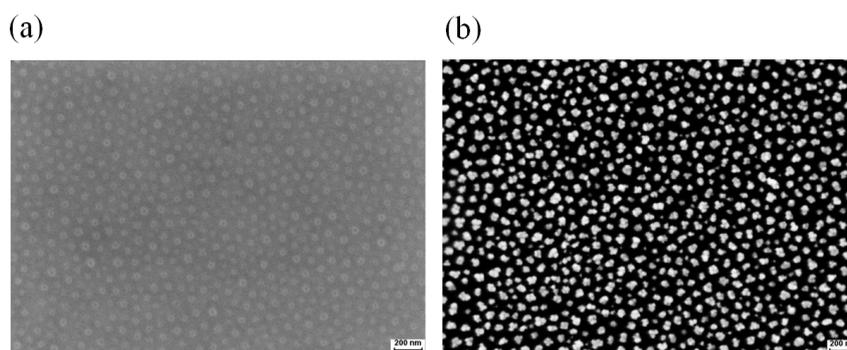
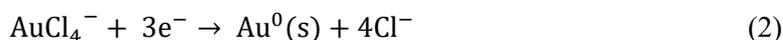


Figure 1. SEM images of (a) PS-*b*-P4VP BCP film spin-coated on silicon wafer and (b) gold nanoarrays derived from the BCP template

Synthesis of gold nanostructures on a silicon surface is carried out by immersing the silicon wafer in a HAuCl₄/HF solution. The hydrophilic P4VP region can provide a channel for the wet chemical reaction. The reaction process includes two parts: silicon oxidation etching and gold reduction deposition. The P4VP-covered surface of the silicon wafer where HF penetrates through is locally oxidized and dissolved, and thus releases free electrons, while the PS matrix-protected silicon surface remains unetched. And then, the trivalent gold ions at the interface of the P4VP domain and solution

accept the electrons are reduced to zero-valent gold atoms and selectively deposited on the etched silicon surface[16]. In this process, the following reactions occur:



Therefore, the reaction can be well-confined by the BCP nanopatterns[17], thereby resulting in metallic gold nanoarray structures, mimicking the morphology of the BCP template on the semiconductor surface, as shown in figure 1(b).

Controllable fabrication of a series of gold nanoarrays is performed by changing reaction time. It can be seen from figure 2 that the gold nanostructures with different size were obtained by the same BCP template. With the reaction time period of 3min, 5min, 8min, 10min, 13min, 15min, respectively, the average particle diameters of the gold nanoarrays increases accordingly, ranging from 43nm to 73nm. While the arrangement of gold nanoparticles keeps similar to that of the BCP templates, which indicates that the reaction takes place in the P4VP microregion in a controllable way, and further illustrates the feasibility of the BCP as a template.

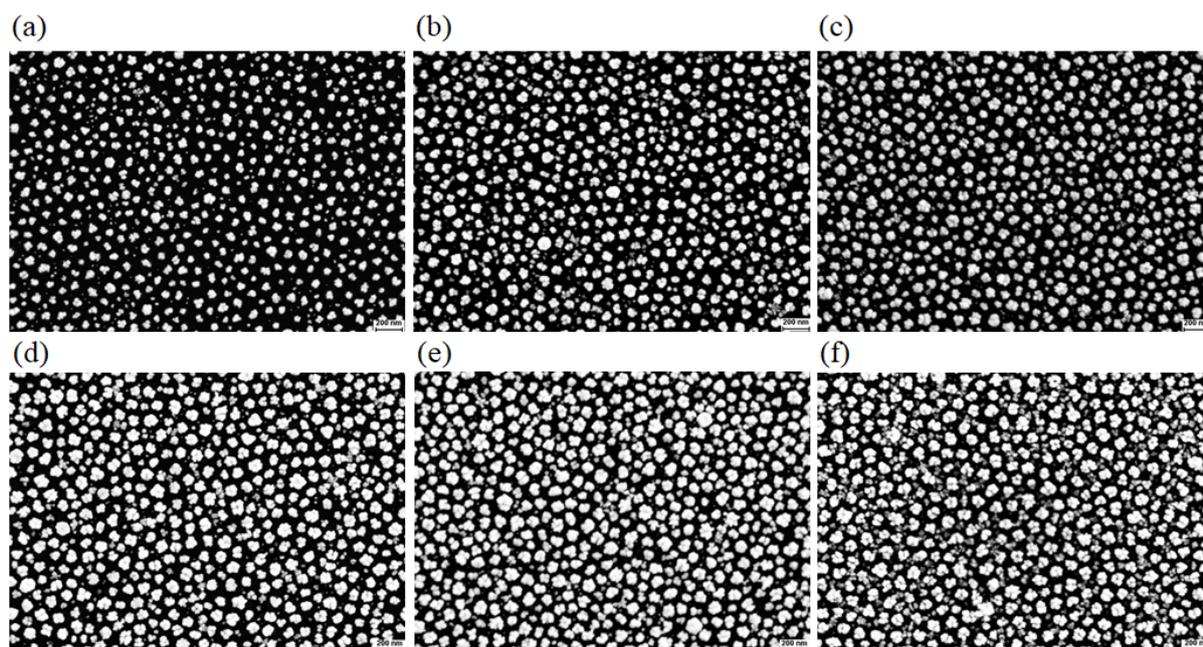


Figure 2. SEM images of Au nanostructures prepared with different reaction time of: (a) 3min; (b) 5min; (c) 8min; (d) 10min; (e) 13min; (f) 15min respectively.

The SERS performance of Au nanostructures was characterized by using NBA as sensitive molecule. Figure 3 shows the Raman spectra of NBA on the Au nanostructure prepared with various reaction time mentioned above. It can be seen that the characteristic peak intensity of the as-obtained sample is obviously higher than that of the original silicon wafer, indicating that the as-fabricated gold nanoarrays have significant SERS activities. Moreover, as the reaction time increases, their SERS intensities get stronger. This phenomenon can be explained by the widely accepted electromagnetic enhancement mechanism. SERS activity is related to surface plasmon polariton resonance occurring in the nanogaps between the nanoparticles, which induces strong electromagnetic field enhancement and thus presents strong SERS-active signals[18, 19]. As the diameter of nanoparticles of the nanoarrays with determined center-to-center spacing increases, the width of the nanogaps between adjacent particles decreases, and stronger SERS enhancement is achieved.

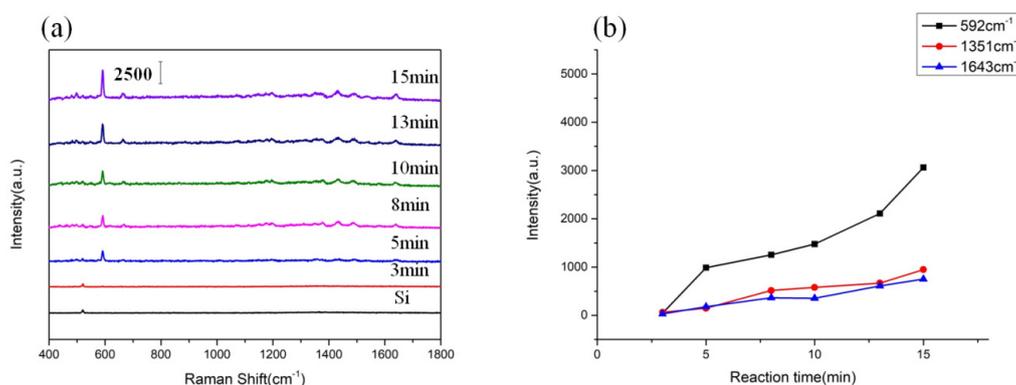


Figure 3. (a) Raman spectra of NBA on the Au nanostructures prepared with various reaction time. (b) Intensity tendency of different characteristic peaks in Raman spectra

The strongest Raman scattering intensity at 592cm^{-1} was chosen to calculate the analytical enhancement factor (AEF) of the gold nanoarrays. The AEF of samples were calculated to be 9.3×10^4 with reaction time of 15 min, according to the following equation [20]:

$$\text{AEF} = (I_{\text{SERS}}/C_{\text{SERS}})/(I_{\text{Raman}}/C_{\text{Raman}}) \quad (3)$$

Where I_{SERS} and I_{Raman} represent the integrated intensity of the measured SERS spectra and Raman spectra, respectively. C_{SERS} and C_{Raman} denote the concentration of NBA for SERS and normal Raman scattering, respectively.

4. Conclusion

In this paper, we demonstrates a BCP template-guided self-assembly process to fabricate high-density and ordered gold nanoparticle arrays on silicon wafer at room temperature over large areas without the use of any expensive equipment or clean room processing. Tunable gold nanostructures were achieved by simply adjusting the reaction time and their corresponding SERS activities were examined. The results indicate that this kind of metal nanoarrays have potential applications in optical sensing and SERS detection as SERS-active substrates.

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