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Gold Surface Plasmon Crystal Structure Based-on Polystyrene Template for Biosensor Application

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Abbreviations: **PS**, Polystyrene; **SEM**, Scanning Electron Microscope; **SPR**, Surface Plasmon Resonance; **UV-VIS**, Ultraviolet-Visible

Abstract

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In this communication, we assembled ordered polystyrene (PS) microsphere array as a template with the drop-coating method, and the oxygen plasma was used to etch the template to adjust the spacing between the PS microspheres. Nano-triangular gold array and silver Nano-pyramid array were obtained by ion beam sputtering to deposit precious metal gold and silver. We observed the surface morphology of Au and Au/Ag composite films by scanning electron microscope and characterized the films by X-ray diffraction and Ultraviolet/visible light spectrophotometer. The results show that the etching time of oxygen plasma has an obvious effect in adjusting the spacing between PSs and has a significant effect on the morphology of Au structure.

Keywords: Polystyrene microspheres / self-assembly / oxygen plasma / metal nanostructures

1. Introduction

In recent years, with the development of nanophotonic, precious metal nanoparticles have been widely used in bio-sensing [1, 2], nonlinear optics [3, 4], solar cells [5, 6] and other fields. Because it has many excellent characteristics, especially the characteristic that its surface plasmon resonance (SPR) wavelength is adjustable in the visible and near-infrared bands when the precious metal nanoparticle realizes a periodic arrangement structure, it has attracted much research attention [7- 15]. With the rapid development of the preparation technology, it is used to prepare a wide variety of metal nanostructures, including nanorods [16], nanospheres [17], Nano-crescents [18], Nano-cups [19], Nano-disks [20], and etc. Since the SPR wavelength is closely related to the shape and size of the precious metal nanoparticles and the refractive index of the surrounding medium, the surface plasma (SP) resonance band can be broadened from the visible light region to the infrared region, and the continuous adjustment of the resonance band of the SP can be achieved by accurate controlling of the size, which also greatly enhances the application value of the metal nanostructure.

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At present, there are many methods for preparing surface plasma metal nanostructures, including electron beam lithography [21], focused ion beam [22], metal deposition via porous alumina template [23], femtosecond laser etching [24], and nanosphere etching [25, 26]. Among these methods, nanosphere etching is a simple, inexpensive and effective method for preparing an ordered two-dimensional metal array structure using a polystyrene microsphere colloidal crystal as a template. In this paper, we proposed an innovative method to employ the plasma etching with PS microsphere array as a template to control the structure of golden triangle array, so as to regulate the surface plasmon resonance properties of the array. Similar studies are not reported in other literatures. The basic principle is: firstly, the monodisperse colloidal microspheres are specially arranged to form a two-dimensionally ordered crystal-like structure; then using this array of colloidal crystals as a template, we can sputter precious metal materials between the microspheres by ion beam sputtering or magnetron sputtering; finally, the microspheres are removed to obtain a porous and long-range ordered new precious metal nanostructure material.

2. Material and methods

2.1. Raw materials and reagents

The preparation steps are shown in Fig. 1. The following raw materials and reagents are required: A quartz substrate, a PS microsphere solution (microsphere's diameter of 500 nm and a mass percentage of 2.5 wt.%), an oxygen plasma etching machine, deionized water, alcohol, chloroform, a liquid gun, and an ultrasonic cleaner.

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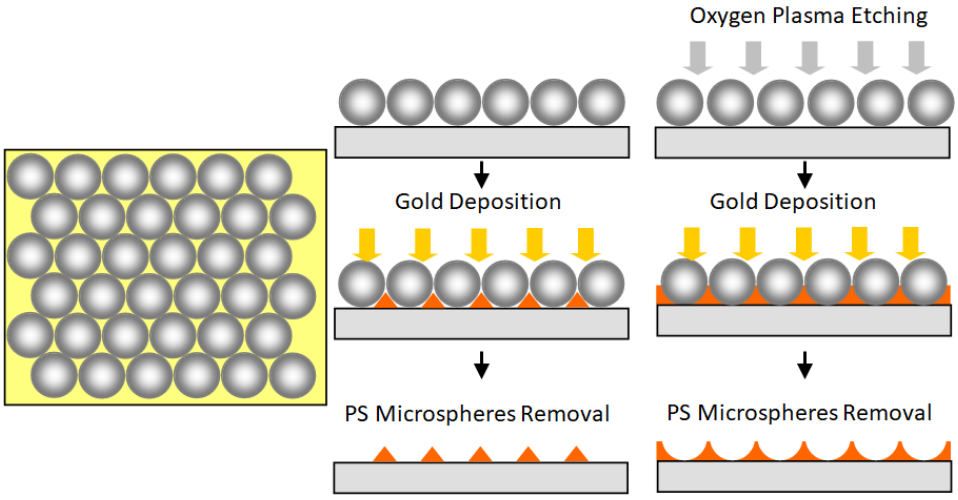

Figure 1. Preparation Steps

2.2. Preparation of monolayer polystyrene template

The 2.5 wt.% PS microsphere solution was placed in an ultrasonic cleaner for 20 minutes to allow the PS microspheres to better disperse in the aqueous solution. At the same time, the quartz substrate is cleaned with deionized water and alcohol. When the quartz substrate is dry, it is etched in an oxygen plasma etching machine for 3 minutes with the oxygen flow rate of 5 ml/min and the power of 50 W. After the quartz substrate is etched, 10 µL PS microsphere solution is dropped onto the surface of the quartz substrate by the liquid gun. The water of the PS microsphere solution is evaporated under natural conditions to form an array structure of PS microspheres on the quartz surface. Finally, the prepared PS microsphere array was bombarded with oxygen plasma to form a PS array template with a large gap, as shown in Figure 2.

2.3. Ion sputtering Deposition of Gold

A 50-nm-thick gold film was deposited on the surface of the PS array by ion sputtering, and then the quartz substrate on which the gold film was deposited was ultrasonically cleaned in a chloroform solution for 1 minute to remove the PS microspheres, and eventually form a silver Nano-cones array

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structure on the surface as shown in Figure 3(a-c). The bright parts are the gold nanostructure and the dart parts are the location of PS microspheres.

2.4. Test and Characterization

The surface morphology of the film was observed with a scanning electron microscope (SEM). X-ray diffraction was used to analyze the crystal form of the Au thin film. The ultraviolet-visible (UV-VIS) transmission spectrum of the film was measured with an UV-VIS spectrophotometer.

3. Results and discussion

3.1. PS colloidal array template

Fig. 2 shows a SEM image of a single-layer PS template surface. It can be seen from Fig. 2a that on surfaces that are not etched with oxygen plasma, the PS is arranged in an orderly, close-packed fashion. Fig. 2b is the surface after etching for 20 s by oxygen plasma. After PS is oxygen plasma etched, the inter-ball space is slightly widened, but overall it shows an arrangement of a hexagonal lattice structure. In other words, during the self-assembly process of the PS microspheres, the arrangement of a hexagonal lattice structure is in the lowest energy state, therefore this arrangement is the most compact arrangement.

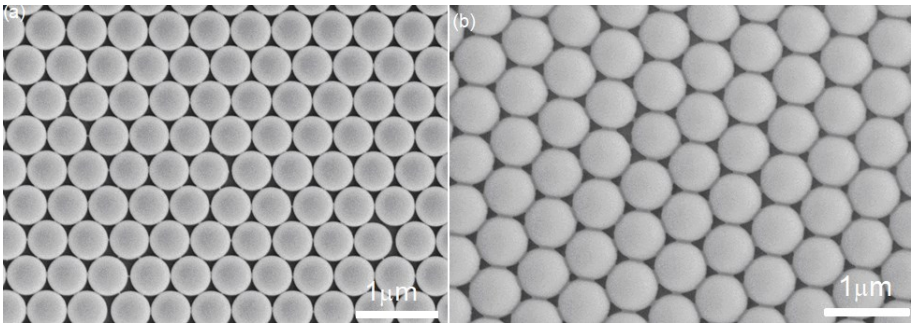

Fig. 2. SEM of single-layer PS microsphere array structure: (a) without oxygen plasma etching, (b) with oxygen plasma etching for 20s.

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3.2 Surface morphology of precious metal gold pyramid array structure films

During the process of preparing an ordered gold triangular array structure by a colloidal template method, from the perspective of possession ratio, approximately 74% of the space is occupied by PS microspheres and only 26% of the space is occupied by deposited gold. Therefore, we use PS microspheres with a diameter of 500 nm. The space occupied by a gold triangle structure is 0.215 μm.

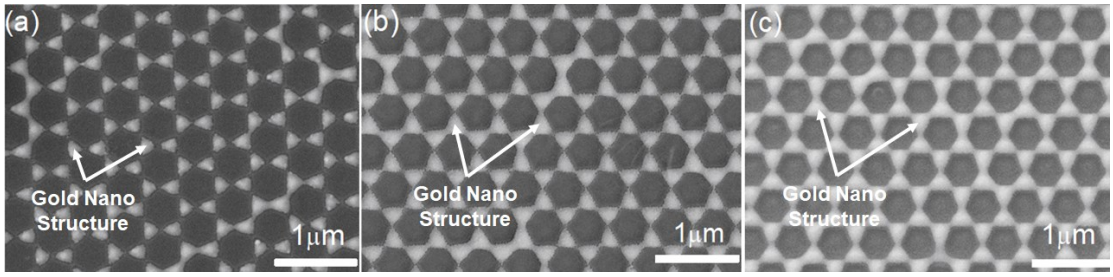

Fig. 3. SEM image of gold triangle array structure: (a) without oxygen plasma etching, (b) with oxygen plasma etching for 20s, (c) with oxygen plasma etching for 50s.

3.3 Performance of Au pyramid array structure and silver cone array structure film

It can be seen from Figure 4 that the diffraction peak at 38.43° is very obvious, corresponding to the (111) crystal planes of the Au thin film, the Au triangular array structure and the silver Nano-pyramid array structure, respectively. A diffraction peak at 38.43°does not destroy the crystal structure of gold. For gold, (111) crystal plane is a low energy surface. As the exposed surface of the gold triangle array is (111), therefore in XRD only peaks corresponding to (111) crystal plane can be seen. But for the other crystal planes (222) (100) (110), the peak doesn't appear, indicating that the PS microspheres on the surface of the substrate are completely processed, and the crystal faces of the surface gold structure all follow the same direction. The difference in intensity comes from the changes brought by the Au triangular array structure.

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The UV-VIS transmission spectrum of a film sample of gold-triangular array structure was performed in the wavelength range of 200-1200 nm and the wavelength spacing of 10 nm. The results are shown in Figure 5(a), (b). It can be seen from Figure 5b that under the conditions of different oxygen plasma bombardment, due to the significant change in the spacing of the triangular array structure, the absorption peaks of different structures produce a slight red shift. It can be seen from Figure 5(c) that in the absence of oxygen plasma bombardment, the resonance peak is located at 511 nm. After oxygen plasma bombardment for 50 s, the resonance peak redshifted to 524 nm.

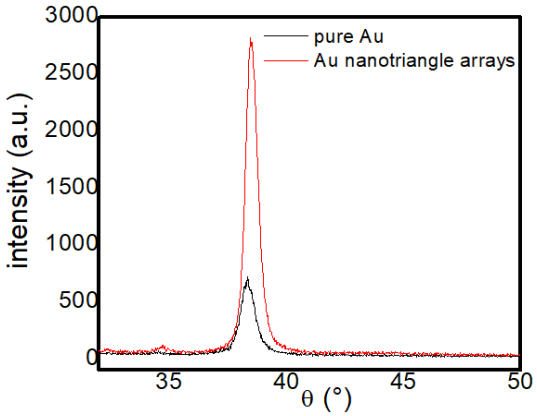

Figure 4. XRD spectrum of Au thin film and Au triangular array structure.

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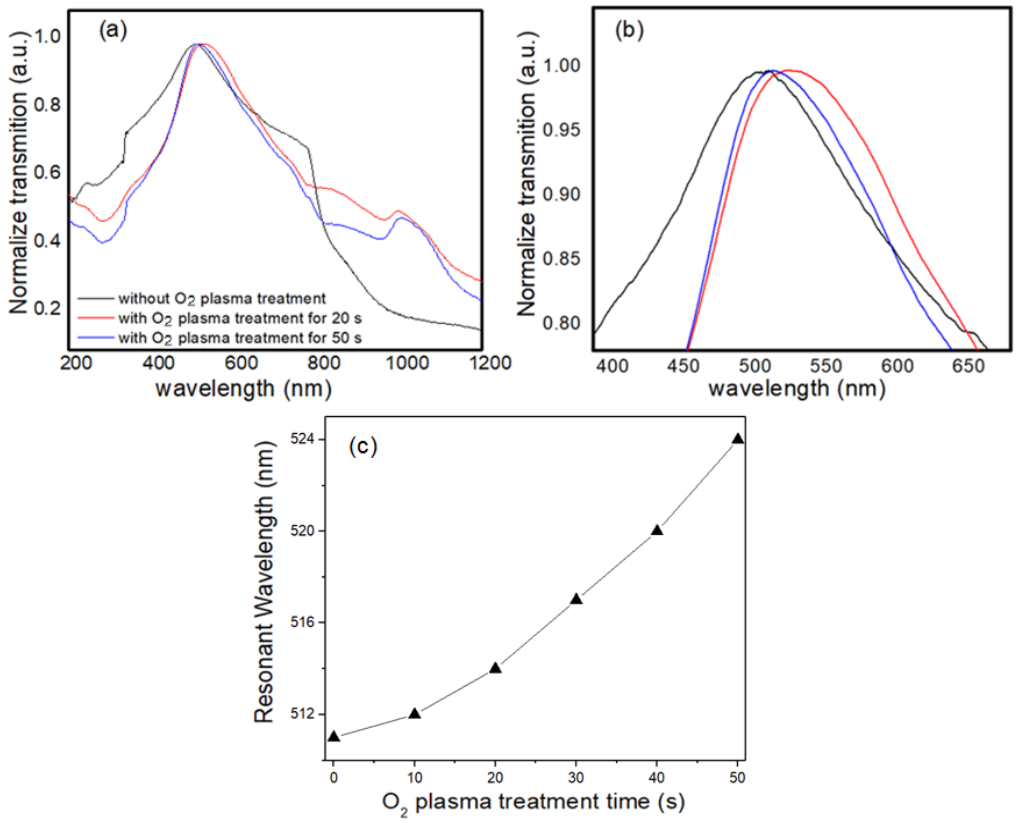

Figure 5. UV-VIS transmission spectrum of gold triangle array: (a) 200-1200 nm transmission peak, (b) 400-600 nm partial enlargement (c) Relationship between resonance wavelength and oxygen plasma bombardment time

4. Conclusion

Using the PS microsphere array as a template prepared by the drop-coating method and controlling the time of oxygen plasma bombardment to adjust the spacing between PS microspheres, we realized the assembly of a single golden triangle nanoparticle into the hexagonal array. Furthermore, we effectively control the position of the surface plasmon resonance transmission peak of the gold array structure so that the resonance wavelength changed from 518 nm to 540 nm. This gold nanostructure has important applications in surface-enhanced Raman spectroscopy, solar cells, and bio-sensing.

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Conflict of Interest

There is no conflict of interest to declare.

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