Preparation of metallic triangular nanoparticle array with controllable interparticle distance and its application in surface-enhanced Raman spectroscopy

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This paper reports a facile method for fabricating metallic triangular nanoparticle array with controllable interparticle distance, based on a combination of nanosphere lithography, reactive ion etching and physical sputtering technique. Light transmission spectra of the metallic triangular nanoparticle arrays with a series of interparticle distances are measured, which show a surface plasmon resonance whose position is observed to shift to longer wavelength for the polarization direction parallel to the long particle pair axis with decreasing the interparticle distance. With this structure as surface-enhanced Raman scattering substrate, the Raman signal is strongly enhanced and shows high dependence on the interparticle distance. The controllable interparticle distance and large-area ordered array of the substrate suggest its promising application in surface-enhanced Raman spectroscopy.

1. Introduction

Recently, there have been growing interests in the design and fabrication of novel metallic nanostructures because of their unique optical properties [1–7], which in most cases are associated with surface plasmon (SP) resonances [8]. By properly engineering metallic nanostructures, plasmons can be locally trapped at specific locations of the nanostructure surfaces [9], producing significantly enhanced optical fields, which can be utilized for applications such as surface-enhanced Raman scattering (SERS) [10–13], plasmonic nanolasers [14], sensing [15], optical antennas [16], and optical tweezers [17].

Among various metallic nanostructures, ordered metallic nanoparticle array structures have received tremendous interest in recent years due to their distinct properties of plasmon resonances [18]. It is shown that when metallic nanoparticles are patterned into one- or two-dimensional (2D) ordered arrays, plasmon coupling between individual metallic nanoparticles may dramatically modify the optical responses [19–22]. For potential applications, great efforts have been devoted to develop low-cost and highly efficient fabrication methods to produce large-area ordered arrays of metallic nanoparticles so far [23]. However, these metallic nanoparticle arrays often show difficult to control in terms of the interparticle distance. Meanwhile, it is well established that the local optical fields in the interstitial space between two nanoparticles can be strongly enhanced by several orders of magnitude with decreasing the interparticle distance, which is responsible for enhanced Raman and fluorescence signals as well as many other phenomena [24–26]. Therefore, it is highly desirable to develop a novel and simple route to obtain large-area ordered arrays of metallic nanoparticles and to allow control of their separation on a nanometer scale.

In this paper, we discuss the fabrication of metallic triangular nanoparticle array with controllable interparticle distance prepared by a combination of nanosphere lithography, reactive ion etching and physical sputtering technique. The optical properties of the metallic triangular nanoparticle array and its application in SERS are investigated experimentally. It is found that the Raman signal is strongly enhanced with this structure as SERS substrate, and the enhancement in the Raman signal exhibits high dependence on the interparticle distance.

2. Sample fabrication procedure

Fig. 1 schematically shows the fabrication procedure of the metallic triangular nanoparticle array with controllable interparticle distance. In brief, a large-area 2D colloidal crystal consisting of polystyrene (PS) beads (~1.58 μm in diameter) was first self-assembled following our reported method [27][Fig. 1(a)]. The PS colloidal crystal was then
etched in an ICP (CE-300L, ULVAC) system, in which a pressure of 20 mTorr (1 Torr ~ 133 Pa), a RF power of 100 W, and an O₂ flow rate of 20 sccm (standard cubic centimeter per minute) were applied. With carefully controlling the plasma etching time, the size of PS microspheres can be reduced on demand. Meanwhile, the cylinders can be formed between neighboring nanospheres and will become more and more thinner in diameter with increasing the plasma etching time [Fig. 1(b)]. Subsequently, a thin gold layer with a typical thickness of ~45 nm was plasma deposited onto the colloidal crystal mask on a silica substrate in a vacuum of 5 × 10⁻⁶ Torr at a rate of 0.55 Å s⁻¹ by an ion-beam coater (IBC Model 682, Gatan Corp.) [Fig. 1(c)]. After metal deposition, the colloidal crystal mask is peeled off and a highly ordered array of Au triangular nanoparticles is prepared [Fig. 1(d)]. As a typical example, Fig. 2 shows the scanning electron microscopy (SEM) images of two as-prepared Au triangular nanoparticle arrays, in which 0 s and 130 s plasma etching are applied on the PS colloidal crystal mask, respectively. It is seen that the 2D ordering feature is well preserved in the resultant metallic triangular nanoparticle arrays, and the interparticle distance can be decreased by increasing the plasma etching time, which can be clearly seen from the higher magnified SEM images [Fig. 2(a) and (b) insets].

3. Results and discussion

The near-infrared transmission spectra under normal incidence for the metallic triangular nanoparticle arrays are measured using a Fourier-transform infrared spectrometer with a polarizer. The incident light polarization configuration in the present studies with respect to the ordered arrays is schematically shown in Fig. 1(d).

The coordinate is chosen such that metallic triangular nanoparticle arrays lie on the xy-plane. Light is incident along z-axis with its polarization along y-axis (the long particle pair axis). Fig. 3(a) shows the measured transmission spectrum of the gold triangular nanoparticle array without plasma etching under normal incidence. For the regular periodic array, the transmission shows two transmission resonances (TRs) indicated using the arrows, which are, respectively, located at 1368 nm and 2150 nm. It has been shown that the broad band at 2150 nm is due to a dipole resonance of the gold triangular nanoparticles, and the origin of the band at the shorter wavelength is not yet clear, but it is possibly because of a collective light scattering of the particle array [28].

Fig. 3(b) shows the transmission spectra of the gold triangular nanoparticle arrays with other interparticle distances prepared by using different plasma etching time under normal incidence, in which the transmission spectrum of the triangular nanoparticle array without plasma etching is also exhibited for comparison. It can be clearly seen from Fig. 3(b) that the position of the TR for \( \lambda_2 \) indicated in Fig. 3(a) remains unchanged when the plasma etching time increases from 0 s to 130 s, which implies that the TR of \( \lambda_2 \) are independent of the interparticle distance and are related only to the array periods. Based on the above discussion and our previous work [28,29], there exists an obvious red-shift with increasing the plasma etching time, which most likely arises from increasing interparticle plasmon coupling when decreasing the interparticle distance [30].

More importantly, the Au triangular nanoparticle array after etching the colloidal crystal mask for \( t=130 \) s exhibits a strong SERS effect using R6G as a probe molecule, as shown in Fig. 4. For comparison, the results for other three triangular nanoparticle arrays, prepared after etching the colloidal crystal mask for \( t=0 \) s, 80 s and 20 s, and the smooth Au film, prepared by physical plasma deposition on the silica substrate, are also given in Fig. 4. Before Raman examination, the samples were dipped into a solution with 10⁻⁴ M R6G with stirring for 24 h, rinsed with deionized water, and dried with high-purity flowing nitrogen. It can be clearly seen from Fig. 4 that the smooth Au film hardly gives a Raman signal (black line), as for the Au triangular nanoparticle arrays, the Raman signal is significantly enhanced and shows a increasing trend with decreasing the interparticle distance, which is due to the fact that the local optical fields in the interstitial spaces between neighboring nanoparticles could be strongly enhanced with the decrease of interparticle distance [31]. It is noted here that if the interparticle distance can be further decreased by optimizing the plasma etching time or the Raman pump laser wavelength can be tuned in the vicinity of the resonant plasmonic mode of the structure, the SERS enhancement would be further enhanced [24,32].
4. Summary

In summary, the metallic triangular nanoparticle arrays with controllable interparticle distance were fabricated by a combination of nanosphere lithography, reactive ion etching and physical sputtering technique. The arrays possessed large-area ordered nanostructure and could be used as the SERS-active substrates. The correlation between interparticle distance and SERS intensity was investigated, which showed that the SERS intensity increased with the decrease of interparticle distance. It is a simple and flexible method to fabricate SERS substrates.

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References