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# Fabrication and optical properties of controlled Ag nanostructures for plasmonic applications

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Noble metal nanoparticles exhibit unique plasmon resonances compared to bulk metal that depends on the nanoparticle size, shape, and interparticle distance. Towards this goal, the paper describes a simple and low-cost method for producing large area arrays of ordered silver nanoparticles with morphologies such as dots, rings, and bowls, based on the nanosphere lithography by combining evaporation and sputtering techniques. Pronounced, we demonstrate here a facile fabrication strategy that nanosphere monolayer could serve as a sacrificial mask access to generate silver nanobowl arrays. The experimental and simulated results show that the Ag nanodot arrays exhibit a satisfactory surface-enhanced Raman spectroscopy effect and adjustable frequency. These approaches will surely facilitate further exploration of metal nanostructures for applications in nanoscale optical sensors. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4820270>]

## I. INTRODUCTION

Nanoparticles (NPs) array are of great interest due to its potential application in chemical and biological sensors,<sup>1</sup> high-density data storage,<sup>2</sup> optoelectronics devices,<sup>3</sup> and chemical catalysts for the growth of aligned one-dimensional nanostructure.<sup>4</sup> Among these applications, noble metal array, especially Ag and Au NPs have been widely investigated in recent years because of their unique optical properties, depending mainly on the phenomenon of localized surface plasmon resonance (LSPR).<sup>5</sup> The LSPR of metal nanoarray can be used as sensors since local dielectric environment variation would induce LSPR peak shift.<sup>6</sup> The LSPR of nanoarray structures can also be exploited as surface-enhanced Raman spectroscopy (SERS) substrates to achieve sensing with a detection limit of a single molecule by enhancing the electromagnetic field at the surface by enhancement factors as large as  $10^{14}$ – $10^{15}$ .<sup>7,8</sup>

An essential component for all of those applications is the ability to tailor the particle plasmon resonances according to the desired application. And the optical properties depend on and can be tuned by adjusting the size, shape, interparticle distance, and dielectric environment.<sup>9–12</sup> More recent calculations<sup>13,14</sup> proved that for increasing complex structures, several distinct and strong resonances may exist and the resonance wavelengths can be modulated by varying the nanoparticle geometry. The increasing diversity of metal NPs reported in the literature is well matched by numerous prospective applications of LSPR-active particles.<sup>15</sup> Thus,

the ability to control the LSPR of nanoparticles will provide unprecedented levels of insight into their surface-enhancing properties.

Among the great variety of methods able to fabricate nanostructure array, nanosphere lithography (NSL) is an inexpensive, simple to implement nanofabrication technique capable of producing well-ordered nanoparticle arrays with tailored properties in size, shape, and material, as compared to conventional photolithographic methods.<sup>16</sup> Using a perpendicular evaporation on the polystyrene (PS) template, honeycomb arrays of nanodots are synthesized on substrates after removing the PS template, which is a typical process of NSL. This method has been significantly refined and extended in recent years.<sup>17,18</sup>

In this paper, we demonstrate a novel and efficient strategy for fabricating large-area ordered arrays of silver (Ag) nanoparticles with morphologies such as dots, rings, and bowls, expected to have as required plasmon resonances through control of the geometrical shape of nanometer-sized metal. This method is based on the nanosphere lithography by combining evaporation and sputtering techniques. The method comprises two steps, namely mask preparation and subsequent metal deposition. Our aim is to investigate the influence of the array structure and deposition method on the nanoparticle morphologies and LSPR properties, in realizing the further exploration of metal nanostructures for applications in nanoscale optical sensors.

## II. MATERIALS AND METHODS

Figs. 1–3 show the schematic illustration of the experimental procedures for fabricating different Ag nanostructures arrays.

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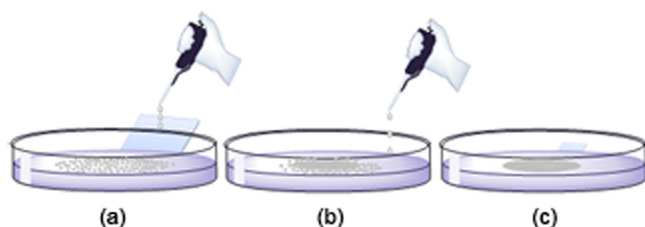


FIG. 1. The preparation process of monolayered masks consisted of PS nanospheres: application of PS nanospheres onto a water surface (a), consolidation of PS nanospheres (b), and lift off ordered monolayer (c).

### A. Nanosphere mask preparation

A hexagonal close-packed array of PS nanoparticles was prepared on quartz substrate by floating-transferring technique (Fig. 1). First, the monolayers were prepared using monodisperse PS nanoparticles with the diameter of 460 nm. Monodispersed PS seed particles were produced by dispersion polymerization according to Zhang *et al.*<sup>19</sup> The polystyrene solution was obtained as 1 wt. % suspensions and further diluted in a 1:1 ratio in ethanol, which acted as a spreading agent.

Quartz substrates were cut into small pieces of  $1\text{ cm} \times 1\text{ cm}$ . Prior to patterning, each square was treated with acetone and ethanol in an ultrasonic bath for 10 min to remove organic contaminants from the quartz substrate. Then, the specimens were immersed in 10% sodium dodecyl sulfate (SDS) solution for 24 h to achieve a hydrophilic surface. Following steps as described above, the substrates were rinsed repeatedly with water and then used immediately or stored in water until use.

After this pretreatment, the nanospheres solution was introduced to the water surface via microscope slide placed at one end of the watch glass at an angle of  $\sim 45^\circ$  with respect to the water surface. Prepared polystyrene solution mentioned above was migrated onto the oblique microscope slide and droplets flowed slowly into water surface along

microscope slide path and PS particles started to form an unordered loose monolayer on the water surface (Fig. 1(a)). To consolidate the particles, the water surface tension was changed by the addition of 2% SDS and a large monolayer with highly ordered areas was obtained (Fig. 1(b)). Such monolayers were then lifted from the water surface using previously mentioned substrates (Fig. 1(c)) and allowed to dry in a closed Petri dish to stabilize the rate of evaporation, and to be kept away from dust in air.

### B. Metal nanostructure preparation

Metal nanostructures were prepared by the electron beam evaporation and DC magnetron sputtering. The evaporation system uses the perpendicular evaporation, while the sputtering system uses tilted-angle-rotation sputtering method.

Fig. 2 shows the diagram of the experimental apparatus: (1) sample holder; (2) template coated with PS monolayer; (3) DC sputtering; (4) silver target; (5) evaporation source (Ag); and (6) electron beam source. The value of the substrate-target distance was 150 mm. Sputtering was performed at a constant power of 120 W for 2 h. The Ag films were deposited at room temperature. The thickness of Ag thin film is about 100 nm.

Fig. 3 shows the representation of the PS surface patterning. Starting from monolayer PS nanospheres on quartz substrates (Fig. 1), different kinds of surface nanostructures are prepared by three fabrication processes (processes I–III). (I) Using a perpendicular evaporation on the PS nanosphere template, honeycomb arrays of Ag nanodots are synthesized on substrates after removing the PS template (process I: A1–A2), which is a typical process of NSL. (II) At the same time, nanosphere monolayer could serve as sacrificial masks, the purified Ag nanobowls are obtained after the polymer cores were dissolved in  $\text{CHCl}_3$  (process II: A1–A3). (III) When the sputtering is carried out with a certain angle and the PS template is rotating at a certain rate, Ag nanoring arrays are fabricated (process III: B1–B2).

### C. Characterization

The samples were characterized by scanning electron microscopy (SEM, FEI Sirion FEG) and ultraviolet–visible (UV–vis) absorption spectra (Varian Cary 5000). The investigation of crystallinity of the Ag nanobowl arrays was performed by a JEOL 2010 (HT) transmission electron microscope operating at 200 kV.

## III. RESULTS AND DISCUSSION

Fig. 4 presents the SEM images of a self-assembled monolayer of PS nanospheres with a diameter of 460 nm at different magnifications. In this process, hexagonal ordered monolayers of monodisperse PS nanosphere are prepared by a modified floating-transferring technique, and subsequently the individual PS nanosphere is used as a shadow mask for the preparation of different Ag nanostructures. The specimens are successfully coated with large domains of defect-free packing over the entire substrate surface. It shows the uniformity and high coverage of the fabrication method.

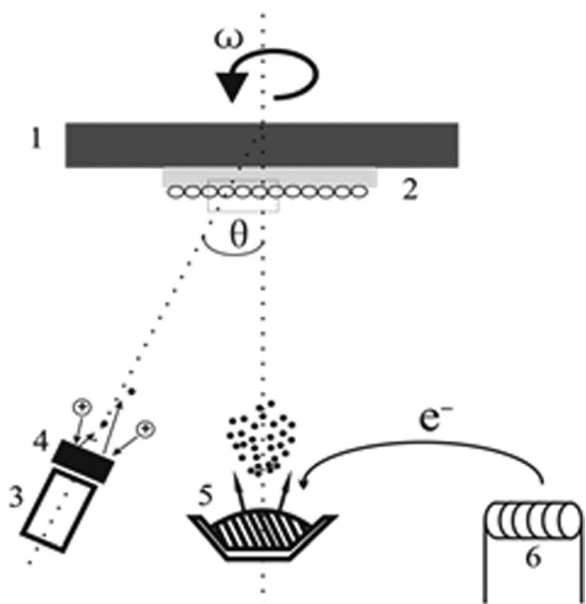


FIG. 2. The diagram of the evaporation and sputtering system.



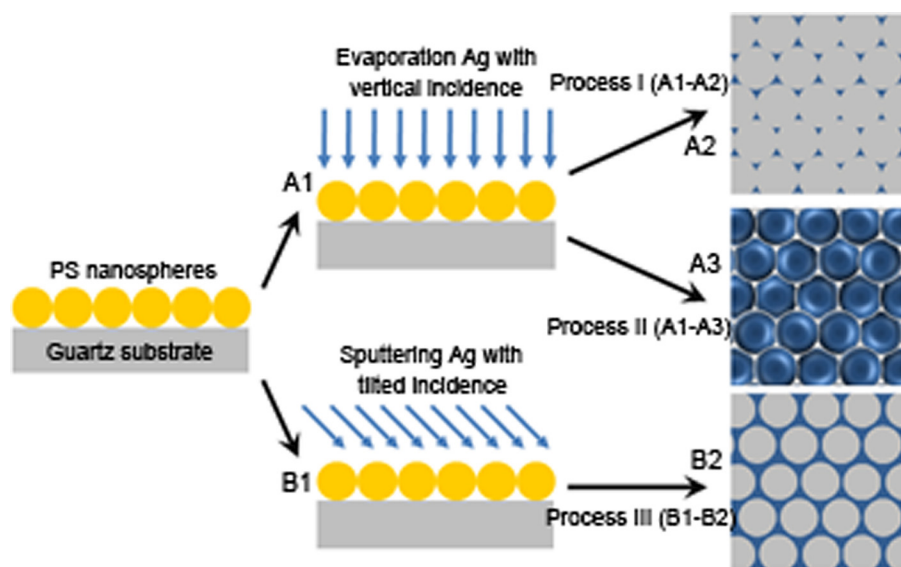


FIG. 3. Schematic representation of the experimental procedures for fabricating various ordered Ag nanostructures arrays using three fabrication processes (processes I–III): (I) honeycomb arrays of nanodots (A1–A2), A1: perpendicular evaporation on the PS sphere template; A2: removing PS template; (II) nanobowl arrays are obtained after the polymer cores were dissolved in  $\text{CHCl}_3$  (A1–A3). (III) nanoring arrays (B1–B2), B1: sputtering is carried out with a certain angle and the PS template is rotating at a certain rate, B2: removing PS template.

The topography images of Ag thin layers over PS nanospheres prepared by evaporation and sputtering methods are provided in Figs. 5(a) and 5(b), respectively, for comparison. The insets (top right) is the corresponding high magnification plane view of Ag capped PS nanospheres. As it can be seen, the arrangement of PS nanospheres becomes much more closely packed after deposition process. It is due to the kinetic energy produced by the heat effect on PS nanospheres when incident particles reach the template, and this heat effect could lead to the deformation of PS nanospheres to some extent. While the deformation induced by sputtering is more seriously compared with the evaporation, which is due to the incident particle energy of sputtering is much larger than that of the evaporation, and it is thought to be dynamically significant in edge regions. It also can be seen from Fig. 5(a) that the PS nanospheres around vacancy site suffered more serious deformation compared with other close packed site. This effect could be ascribed to the oblique incidence of Ag particles, which predominantly attacks the vacancy site; another factor could be the negatively charged nanospheres that attract the  $\text{Ag}^+$  ions near their underside.<sup>20</sup> Thus, the colloids are reduced in size by exposure to plasma

and these size-reduced colloids are then used as shadow masks for the preparation of nanorings.

In addition, the high mobility of the Ag atoms during the deposition process enabled the Ag to cover the interspaces and the top surfaces of PS nanospheres. But the capped Ag thin layers on the top surface of PS nanospheres by sputtering are rough than that by the evaporation, we put this interesting phenomenon owing to the oblique incidence of Ag particles during sputtering process.<sup>21</sup> As the sputtering time increases, the apertures among PS nanospheres become smaller and smaller, and a less amount of Ag particles with such an oblique incident angle can enter the apertures. Accordingly, excessive Ag is accumulated on the surface of PS nanospheres in the inhomogeneous distribution leading to crude surface. Nevertheless, Ag particles can be uniformly distributed on the PS nanospheres surface and vertically enter the apertures sufficiently owing to the perpendicular evaporation.

The hexagonal patterned Ag nanodot arrays prepared by evaporation method are shown in Fig. 6. There is an aperture among every three adjacent PS nanospheres within the PS nanosphere arrays. These apertures form periodic honeycomb arrays. Therefore, with a monolayer PS nanosphere template as a mask during evaporation processes, honeycomb arrays of periodic nanodots can be fabricated on substrates after removing the PS templates (Fig. 3—process I).

Fig. 7 shows the SEM image of Ag nanoring arrays prepared by sputtering method (Fig. 3—process III). It can be seen that the large area ordered Ag nanoring arrays can be produced under our experimental conditions. Detailed study of high magnification (the inset in Fig. 7) reveals that Ag nanoring arrays are formed in the shadow regions of the PS nanospheres. The size of single domain of nanoring arrays is determined by the size of PS nanospheres and the incident angle of the Ag particle flux.

In the sputtering process, sputtering is carried out with a  $45^\circ$  angle and the PS template is rotating at a certain speed, the high mobility of the Ag particles during the sputtering process enabled the Ag to cover the entire substrate surface even beneath the PS nanospheres except where the PS

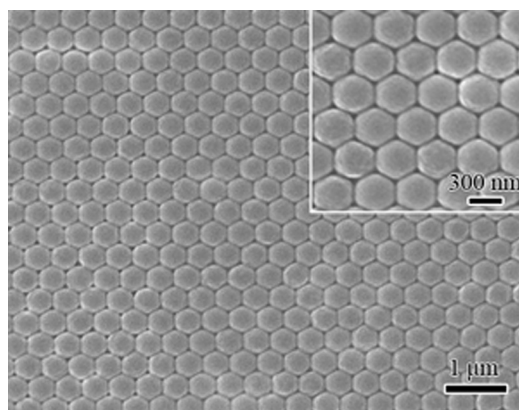


FIG. 4. SEM image of a self-assembled monolayer of PS nanospheres with a diameter of 460 nm. Inset is the corresponding high magnification SEM image.

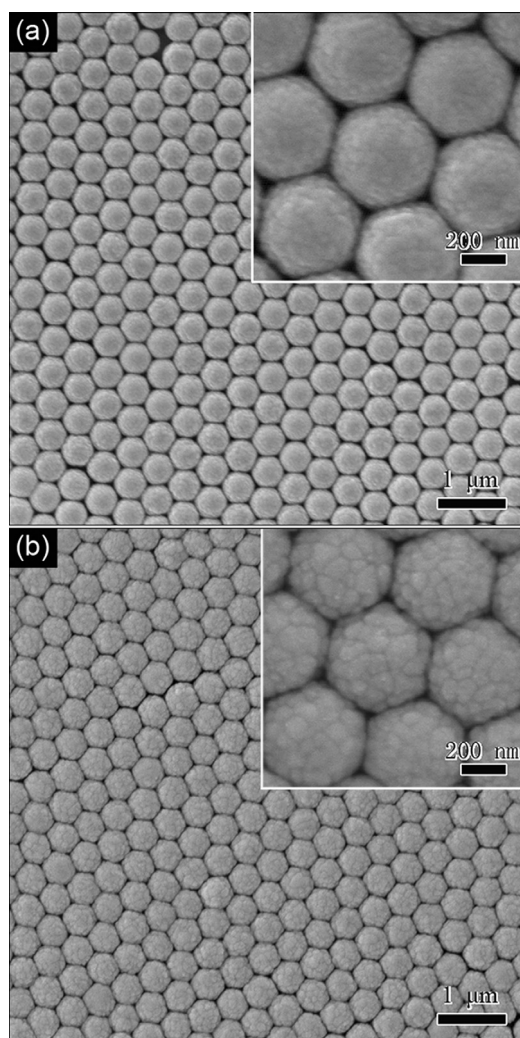


FIG. 5. SEM images of Ag thin layers over PS nanospheres prepared by evaporation (a) and sputtering (b) methods. Inset is the corresponding high magnification plane view respectively.

nanospheres actually contacted the quartz substrates.<sup>22</sup> Besides, the monolayer PS nanospheres were slightly reduced in size under plasma as to effectively enlarge the dimensions of the aperture between PS nanospheres, resulted in a significantly higher probability of Ag particles to be injected around the vacancy site. Thus, Ag particles aggregate around the falling edge site of the PS nanospheres where the incoming trajectory of incident Ag particles flux through the apertures is not blocked, and the ordered Ag nanoring arrays are acquired after removing the PS spheres. Different from sputtering deposition, Ag particles enter the apertures vertically and the triangular Ag nanodots arrays are left on the substrate after the lift-off process of PS mask by the evaporation technique (Fig. 3—process I).

Not only monolayer close packed PS nanosphere arrays were used as shadow mask discussed above but also they could be served as sacrificial mask access to the formation of nanobowl arrays.<sup>23</sup> Ag particles are deposited mainly on the upper side of well ordered monolayer PS nanospheres during the evaporation process, uniformly.<sup>24</sup> This arises from the close-packing nature of the microspheres, which efficiently prevent Ag coverage on the lower side of the template. As a

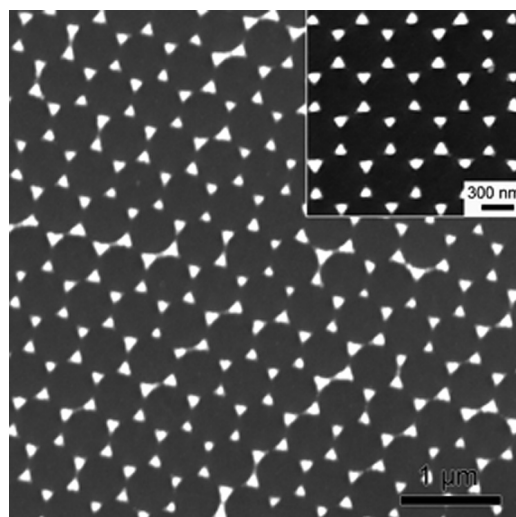


FIG. 6. SEM image of hexagonal patterned Ag nanodot arrays prepared by evaporation method. Inset is the corresponding high magnification SEM image.

result, highly ordered arrays of Ag nanobowl were fabricated by perpendicular evaporation method after the polymer cores were dissolved in  $\text{CHCl}_3$  (Fig. 3—process II), and the Ag nanobowl arrays were extracted from the  $\text{CHCl}_3$  for characterization. The diameter and thickness of the nanobowls can be adjusted by choosing the size of the sacrificial PS nanospheres and the reaction time of metal deposition. It can be seen in Fig. 8(a), the periodicity of the starting nanobowls structure remained integrity after the dissolution of polymer material.

To reveal more morphological characteristics, the profile of the reverse surface of nanobowls is presented in Fig. 8(b), in which the spherical shape and the smooth exterior surface of the bowls can be clearly seen. The walls of these nanobowls have connected to each other owing to the aggregation of Ag at the touching areas between adjacent nanospheres. The notches between the bowls are the result of the contact point between PS nanospheres.

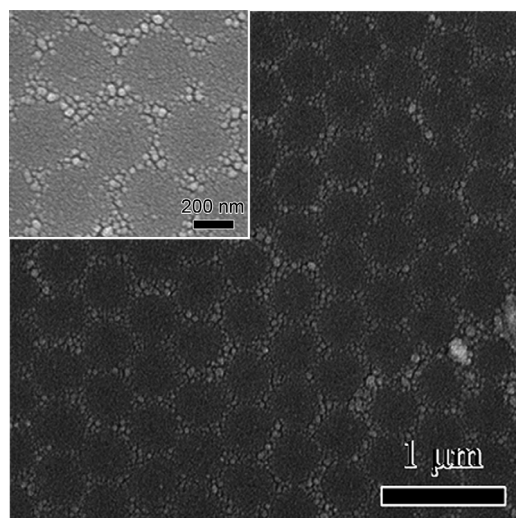


FIG. 7. SEM image of Ag nanoring arrays produced by sputtering Ag with tilted incidence angle. Inset is the corresponding high magnification SEM plane view image of the Ag nanoring array.



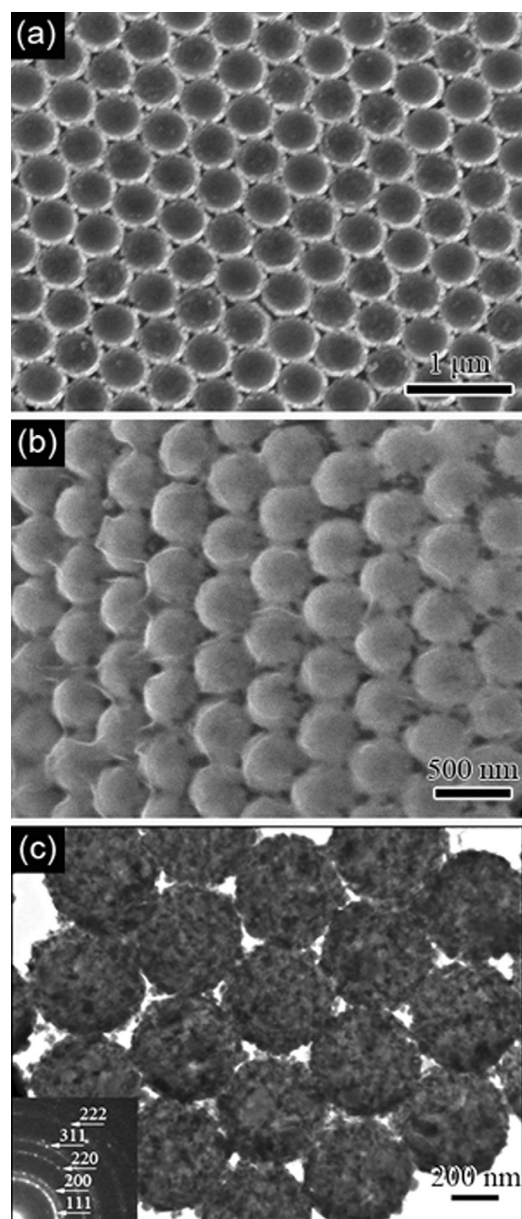


FIG. 8. (a) SEM image of an ordered Ag nanobowl arrays; (b) SEM image of profile view image of the Ag nanobowl arrays; (c) TEM image of Ag nanobowl arrays, the inset is the corresponding SAED patterns.

Moreover, it is also noted that these nanobowls have smoother outer surfaces than inner surfaces due to the restraint of the porous polymer template. And their uniformity relies on the uniform size of the polymer particles as well as the order degree of the original PS nanosphere template.<sup>25</sup> Furthermore, these nanobowls are extremely robust structurally. The dispersion of nanobowls by strong sonication in the TEM sample-prepared process did not deform, as seen in Fig. 8(c). The TEM image in Fig. 8(c) confirms that the inner surfaces of the nanobowls are not smooth, being composed of many small silver nanoparticles. The inset of Fig. 8(c) is typical selected area electron diffraction (SAED) patterns recorded on the Ag nanobowls, indicating their FCC phase of Ag and the formation of pure Ag with high crystallinity. These obtained metallic microstructures exhibit typical features such as: a high ratio of surface area to volume value, a

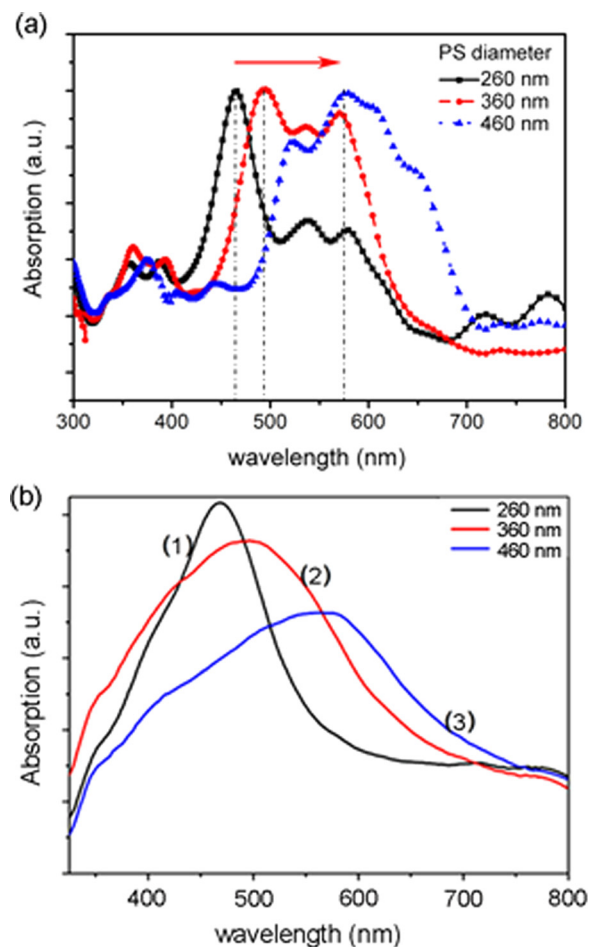


FIG. 9. (a) The simulated absorption spectra of Ag nanodot arrays on quartz substrates with various sizes; (b) UV-vis spectra of the samples.

well ordered structure, reduced symmetry of building blocks, which endow them with a variety of applications in photonic devices, photocatalysts, and biotechnology.<sup>25</sup>

To estimate the relationship between Ag nanostructure geometry and LSPR wavelength, we try to simulate the absorption spectra of Ag nanodots arrays (Fig. 3—process I) with various nanodot sizes using the finite-difference time-domain method. The simulation result is shown in Fig. 9(a). When the PS nanospheres diameter is increased from 260 to 460 nm, the simulated absorption peak shows a red-shift, such changes with the nanodot size has been confirmed experimentally. Fig. 9(b) shows the typical UV-vis spectra of the Ag nanodots arrays. The LSPR peaks for the three samples are positioned at 460, 490, and 560 nm, respectively. According to the simulated and experimental results, the Ag nanodot size can be used as a parameter to adjust the LSPR wavelength available. The ability to produce Ag nanostructure arrays with wavelength-tunable LSPRs opens up new applications in tailoring the particle plasmon resonances according to the desired application.<sup>5</sup>

#### IV. CONCLUSION

In summary, we present an effective approach for fabricating highly ordered Ag nanodots and nanoring arrays. The

process utilizes the nanosphere lithography by combining evaporation and sputtering methods. Simultaneously, PS nanospheres mask being served as a sacrificial mask access to the formation of Ag nanobowl arrays. The approach presented in this paper can be executed to other metals, since electron beam evaporation system can deposit a wide range of metals with controllable thickness and composition. Moreover, the nanostructures geometry can be controlled effectively by simply choosing the deposition time of metal nanoparticles and the size of the PS nanospheres. The obtained periodic particle arrays can be exploited as the SERS substrate for they can enhance the electric field in resonance with surface plasmons hugely. And nanobowl structures are of wide application in photonic devices and biotechnology due to their special structure.

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