Fabrication of Tunable Plasmonic 3D Nanostructures for SERS Applications

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ABSTRACT

Surface-enhanced Raman scattering (SERS) is a powerful technique used for characterization of biological and non-biological molecules and structures. Since plasmonic properties of the nanomaterials is one of the most important factor influencing SERS activity, tunable plasmonic properties (wavelength of the surface plasmons and magnitude of the electromagnetic field generated on the surface) of SERS substrates are crucial in SERS studies. SERS enhancement can be maximized by controlling of plasmonic properties of the nanomaterials. In this study, a novel approach to fabricate tunable plasmonic 3D nanostructures based on combination of soft lithography and nanosphere lithography is studied. Spherical latex particles having different diameters are uniformly deposited on glass slides with convective assembly method. The experimental parameters for the convective assembly are optimized by changing of latex spheres concentration, stage velocity and latex particles volume placed between to two glass slides that staying with a certain angle to each other. Afterwards, polydimethylsiloxane (PDMS) elastomer is poured on the deposited latex particles and cured to obtain nanovoids on the PDMS surfaces. The diameter and depth of the nanovoids on the PDMS surface are controlled by the size of the latex particles. Finally, fabricated nanovoid template on the PDMS surfaces are filled with the silver coating to obtain plasmonic 3D nanostructures. Characterization of the fabricated surfaces is performed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). SERS performance of fabricated 3D plasmonic nanostructures will be evaluated using Raman reporter molecules.

Keywords: SERS, Plasmonic, Convective assembly, PDMS, Latex particles, 3D nanostructures

1. INTRODUCTION

Surface plasmons (Surface Plasmons; SPs) are the coherent oscillation of free electrons in noble metal film or nanoparticle surface induced by electromagnetic radiation in the metal-dielectric interface1. The emerging field of research on the light-metal interactions is known as ‘plasmonics’, which is the branch of the nanophotonics2-4. Understanding of the interactions between adsorbed molecules and plasmonic nanostructures (i.e., molecular plasmonics)5 are vital phenomena for several applications such as, surface-enhanced Raman spectroscopy (SERS)6, localized surface plasmon resonance (LSPR)7 and surface plasmon resonance (SPR)8-9 spectroscopy. Plasmonic nanostructures have also been used in biomedical applications due to their tunable response (absorption and scattering) to the incident light10. Plasmonic properties (wavelength of the surface plasmons and magnitude of the electromagnetic field generated on the surface) of thin films are dependent on the type of metal, film thicknesses, and surface roughness of thin film11. However, plasmonic properties of metallic nanoparticles are strongly dependent on their type, size, shape, and composition, as well as the dielectric environment12.

Fabrication of tunable plasmonic nanostructures is the focal point for the design of novel SERS substrates due to their major contribution of electromagnetic enhancement to the SERS enhancement mechanism. Electromagnetic enhancement is directly related with surface plasmons generating on the nanostructures. Thus, higher SERS enhancement factors are obtained when the wavelength of the LSPR of the nanostructure (λSPR) is located between the excitation wavelength (λexc) and the wavelength of Raman signal (λRS)13. Several advanced methods have been used to fabricate 3D nanostructures to control and manipulate the plasmonic properties in order to maximize the enhancement factor for SERS experiments14-15.
In this study, a novel approach for the fabrication of 3D nanostructures having tunable plasmonic properties by combining of soft lithography and nanosphere lithography was reported. First, nanosphere lithography was used for the uniform deposition of the latex particles having different diameters on a glass slide using convective-assembly method to obtain template for the PDMS surfaces. After the latex particles regularly assembled to the surface, PDMS was poured on the latex thin film to obtain nanovoids on the PDMS surfaces having different diameters and depths depending on the size of used latex particles. Soft lithography offers three important advantages: parallelism, simplicity and flexibility. Finally, the nanovoids on the PDMS surfaces were filled with the silver nanoparticles to obtain 3D nanostructures having different plasmonic properties depending on the used PDMS templates. When the deeper PDMS surfaces (larger diameter) were used for the fabrication of 3D plasmonic nanostructures as template, the 3D nanostructures with more height were obtained (larger diameter). In this way, the plasmonic properties of the nanostructures were tuned by changing of the diameters and heights of the fabricated 3D nanostructures. Structural characterization of the surfaces is performed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). SERS performance of fabricated 3D plasmonic nanostructures will be evaluated using Raman reporter molecules.

2. EXPERIMENTAL SECTION

2.1 Materials
Dichloromethane was purchased from Sigma-Aldrich (USA), PDMS elastomer kit was purchased from Dow Corning (USA), Sulfate latex particles (8% w/v) were purchased from Invitrogen (USA).

2.2 Fabrication of plasmonic nanostructures
There are three main steps for the fabrication of 3D plasmonic nanostructures. Step 1: Spherical latex particles of 1600, 1400, 1200, 1000, 800, 600, 400 nm in diameters were assembled on a glass slide separately by convective-assembly method\(^{16-17}\). Experimental parameters of convective assembly were optimized by changing of the latex spheres concentration, stage velocity and the latex particles volume dropped between to glass slides. The optimum conditions to obtain uniform assembled latex thin film on a glass slide were found to be 0.8 %, 1 µm s\(^{-1}\), and 40 µL, respectively. Step 2: PDMS surfaces were prepared on the top of the latex thin film by curing the polymer mixture at 70°C for 1h. The cured PDMS was peeled off and washed with dichloromethane to remove the latex residues on the surface to obtain nanovoids on the PDMS surfaces. Step 3: PDMS nanovoids were filled with silver to obtain 3D nanostructures having different diameters and heights. SEM and AFM were used for the characterization of the latex thin films, PDMS surfaces and 3D nanostructures. All SEM images were obtained using a JEOL 6510 instrument, and AFM images were obtained with a Park Systems XE-100E instrument in noncontact mode.

3. RESULTS AND DISCUSSION

Tunable plasmonic 3D nanostructures were fabricated by using nanosphere and soft lithographies. First, colloidal latex particles (1600 nm, 1400 nm, 1200 nm, 1000 nm, 800 nm, 600 nm, 400 nm in diameter) were assembled uniformly on glass surfaces with convective-assembly method. After the latex particles assembled, PDMS elastomer was poured on the deposited latex particles and cured in an oven for 1 hour at 70°C to obtain bowl-shaped nanovoids on the PDMS surfaces. The PDMS was then peeled off from the surface to obtain bowl-shaped nanovoids with different diameters and depths at the bottom surface of PDMS depending on size of used the latex particles. SEM was used to characterize the self-assembly of latex particles and nanovoid on PDMS surfaces. Figure 1 shows the SEM images of latex particles with three different sizes (1600 nm, 1000 nm, and 400 nm) assembled on the glass slides and nanovoids obtained on the PDMS surfaces using these latex particles.

The assembled latex particles having different diameters are uniformly and closely packed on the glass slides as seen in the Figure 1 (Top). Bowl-shaped nanovoids on the PDMS surfaces with different diameters and depths can easily be prepared by using different size of latex particles as seen in the Figure 1 (Bottom). Further, AFM was used to determine the diameter and depth of the nanovoids on the PDMS surfaces. AFM images of the PDMS surfaces obtained by using 1000 nm latex particles were shown in the Figure 2.
The size of nanovoids was measured to be around 1000 nm, which is also consistent with SEM images. The nanovoids can easily be seen on 3D AFM image (Figure 2B). The line analysis was performed to demonstrate the uniformity and measure the depths of the voids. The depth of PDMS was around 300 nm when the 1000 nm latex particles were used, and it appears to be very uniform across many voids (Figure 2C). We demonstrated a simple and novel method to
fabricate nanovoids on the PDMS surfaces which will be used as template for the fabrication of 3D plasmonic structures based on the combination of nanosphere lithography and soft lithography. We also presented a systematic and comprehensive characterization of the structures. As shown in Figure 1 and 2 structural characterization was performed using SEM and AFM, demonstrating that the diameters of the nanovoids on the PDMS were approximately same size with the latex particles. Furthermore, the size of the nanovoid was tunable both in depth and diameter depending on the size of latex particles. The advantages of this approach are the simplicity of the method, uniformity, larger area, and flexibility of the structures. The prepared nanovoids having different diameters and depths were filled with Ag layer (4 µm) to obtain 3D Ag plasmonic nanostructures (Nanodomes-AgNDs). To peel off the AgNDs from the PDMS surfaces, increased the film thickness by electrochemical nickel (Ni) coating. Figure 3 shows the SEM images of latex particles (1000 nm) assembled on the glass slide, nanovoids on the PDMS surface, and 3D Ag nanostructures.

Figure 3. SEM images of the assembled latex particles (1000 nm) on the glass slide, PDMS nanovoids and 3D Ag nanostructures.

The assembled latex particles having different diameters are uniformly and closely packed on the glass slides as seen in the Figure 3. Bowl-shaped nanovoids on the PDMS surfaces with different diameters and depths can easily be prepared by using different size of latex particles as seen in the Figure 3. Afterwards, AFM was used to characterize the surface topography such as the diameter and height of AgNDs that shown in the Figure 4.

Figure 4. AFM 2D image (A), 3D image (B), and line scan obtained across the red and green line shown in B (C), of AgNDs fabricated using 1000 nm latex particles.
The size of AgNDs was measured to be around 1000 nm, which is also consistent with SEM images. The AgNDs can easily be seen on 3D AFM image (Figure 4B). The line analysis was performed to demonstrate the uniformity and measure the heights of the AgNDs. The height and diameter of AgNDs was around 300 nm and 1000 nm, respectively when the 1000 nm latex particles were used, and it appears to be very uniform across many NDs (Figure 4C). The summary results of structural characterization can be found on the Table 1.

<table>
<thead>
<tr>
<th>Diameter of Latex (nm)</th>
<th>400</th>
<th>600</th>
<th>800</th>
<th>1000</th>
<th>1200</th>
<th>1400</th>
<th>1600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter of AgNDs (nm)</td>
<td>370±21</td>
<td>519±24</td>
<td>730±46</td>
<td>965±15</td>
<td>1150±24</td>
<td>1362±24</td>
<td>1405±31</td>
</tr>
<tr>
<td>Depth of AgNDs (nm)</td>
<td>69±13</td>
<td>102±22</td>
<td>140±18</td>
<td>280±12</td>
<td>348±25</td>
<td>434±36</td>
<td>452±40</td>
</tr>
</tbody>
</table>

4. CONCLUSION

Tunable plasmonic 3D nanostructures were fabricated by combining of nanosphere and soft lithographies. Latex nanospheres having different diameters were deposited uniformly on a glass slide using convective-assembly method to obtain nanovoids with different depths and diameters on the PDMS surfaces. To obtain tunable plasmonic AgNDs, the nanovoids were filled with Ag. SERS performance of fabricated 3D plasmonic nanostructures will be evaluated using Raman reporter molecules.

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