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Fabrication of shape-controlled Au nanoparticle arrays for SERS substrates

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Abstract. Surface enhanced Raman Scattering (SERS) has attracted attention because the technique enables detection of various chemicals, even down to single molecular scale. Among the diverse candidates for SERS substrates, Au nanoparticles are considered promising due to their fine optical properties, chemical stability and ease of surface modification. Therefore, the fabrication and optical characterization of gold particles on solid supports is highly desirable. Such structures have potential as SERS substrates because the localized surface plasmon resonance of gold nanoparticles is very sensitive to combined molecules and environments. In addition, it is well-known that the properties of Au nanoparticles are strongly dependent on their shape. In this work, arrays of shape-controlled Au nanoparticles were fabricated to exploit their enhanced and reproducible optical properties. First, shape-controlled Au nanoparticles were prepared via seed mediated solution-phase synthesis, including spheres, octahedra, and rhombic dodecahedra. Then, these shape-controlled Au nanoparticles were arranged on a PDMS substrate, which was nanopatterned using soft lithography of poly styrene particles. The Au nanoparticles were selectively located in a pattern of hexagonal spheres. In addition, the shape-controlled Au nanoparticles were arranged in various sizes of PDMS nanopatterns, which can be easily controlled by manipulating the size of polystyrene particles. Finally, the optical properties of the fabricated Au nanoparticle arrays were characterized by measuring surface enhanced Raman spectra with 4-nitrobenezenethiol.

Keywords: gold; polystyrene particle; PDMS; nanoparticle array; SERS

1. Introduction

Gold (Au) nanoparticles have received increasing attention in recent decades due to their unique and fascinating properties, including chemical stability, bio-compatibility, easy surface modification and remarkable optical properties, known as localized surface plasmon resonance (LSPR) (Daniel *et al*. 2004, Xia *et al*. 2009). Thanks to their superior properties, Au nanoparticles

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have been applied to chemical and biological sensing, (Saha *et al*. 2012) drug delivery, (Cheng *et al*. 2008) cell imaging, (Kim *et al*. 2009) optoelectronics (Wang *et al*. 2011) and catalysts. (Ma *et al*. 2011) Notably, because of their interesting LSPR properties, Au nanoparticles have been actively examined as surface enhanced Raman scattering (SERS) substrates in recent years (Wu *et al*. 2011, Ikeda *et al*. 2011, Schwartzberg *et al*. 2004, Joseph *et al*. 2011).

SERS is Raman spectroscopic technique that provides an enormously enhanced Raman signal from Raman-active analyte molecules adsorbed onto substrates which usually have metal surfaces such as silver, gold or copper (Singh *et al*. 2008). The strongest Raman signal enhancement has been observed on rough metal surfaces with nanoscale sized (10 - 100 nm) features (Campion *et al*. 1998). In addition, SERS activity is particularly strong at spots exhibiting large localized field enhancement, such as protrusions and crevices in sharp particles (Xu *et al*. 2000). For this reason, control over the shape of Au nanoparticles is one of the most important factors affecting the degree of Raman signal enhancement.

Although the shape of the Au nanoparticles affect SERS activity significantly, it is hard to achieve a stable, uniform, reliable and reproducible SERS signal by just spraying a suspension of shape controlled Au nanoparticles onto a substrate. Consequently, the fabrication of metal nanoparticle arrays has been a focus of research with the goal of enhancing SERS activity, uniformity and reproducibility (Wang *et al*. 2006). Various methods, such as nanosphere lithography (Haynes *et al*. 2003), electron beam lithography (Hatab *et al*. 2008), electrostatic self-assembly (Yap *et al*. 2012), and capillary methods (Que *et al*. 2011) have been researched. However, high costs, complexity and the difficulties of large scale fabrication of metal nanoparticle arrays with high SERS activity and reproducibility remain as challenging problems.

In this study, an array of shape-controlled Au nanoparticles was fabricated on a nanopatterned PDMS substrate by a simple and reproducible method. Three different shapes of Au nanoparticles, Au spheres, Au rhombic dodecahedra and Au octahedra were synthesized via seed mediated solution-phase synthesis using 11 nm spherical Au seeds. Then, these synthesized shape-controlled Au nanoparticles were arranged on a nanopatterned PDMS substrate by drop casting a Au nanoparticle suspension, followed by evaporation.

The PDMS substrates were prepared by soft lithography of polystyrene (PS) particles. The morphology-dependent SERS activities of the fabricated shape-controlled Au nanoparticles arrays were investigated with 4-nitrobenezenthiol (4-NBT). The experimental results showed that the Au rhombic dodecahedra nanoparticle array exhibited a higher SERS activity and enhancement factor than arrays fabricated with Au nanospheres or Au octahedra nanoparticles. Finally, the influence of the pattern size of the PDMS substrates on SERS activity was also investigated, using 60 nm Au rhombic dodecahedra arrays with different pattern sizes.

2. Experimental

2.1 Chemicals and materials

Gold chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, ≥99%), hexadecyltrimetylammonium bromide (CTAB, ≥99%), hexadecyltrimetylammonium chloride (CTAC, ≥ 98%), sodium citrate tribasic dehydrate (≥ 99%), poly(vinylpyrrolidone) (PVP, $M_w \fallingdotseq$ 55,000), sodium borohydride ($NaBH_4$, 99%), L-ascorbic acid (AA, > 99%), and *N*,*N*-dimetylformamide (DMF, 99%) were all purchased from Sigma-Aldrich and used to synthesize three different gold nanoparticles. Sodium styrene sulfonate, hydrogen carbonate, styrene monomer, potassium persulfate were also obtained from Sigma-Aldrich and used to prepare PS colloidal nanoparticles. Slide glasses (76 mm × 26 mm, Waldemar Knittel Inc. (Germany)) and chlorotrimetylsilane (Aldrich), Sylgard 184TM (Dow corning) were used for preparing a 3D colloidal master mold and PDMS replica mold. 4-nitrobenzenthiol (4-NBT, Aldrich) was used as an analyte for the SERS measurement, and high-purity deionized water with a resistivity of 18.3 MΩ was used and produced by Pure Power water purification system (Human, Korea) in all experiments.

2.2 Synthesis of Au seeds

Single-crystal spherical Au seeds were produced using a two-step procedure (Kim *et al*. 2011, Ma *et al*. 2010). Firstly, 3 nm Au nanoparticles were synthesized by adding 0.6 ml of 0.01 M ice-cold $NaBH_4$ aqueous solution to an aqueous solution containing 5 ml of 0.5 mM $HAuCl_4$ and 5 ml of 0.2 M CTAB. The seed solution was left undisturbed at 28℃ for 3 h to decompose the excess of $NaBH_4$ remaining in the solution. Synthesized 3 nm Au seeds were grown into 11 nm Au seeds by adding 3 ml of the as-prepared suspension of 3 nm Au seed into a transparent mixture of 6 ml of 0.5 mM $HAuCl_4$, 6 ml of 0.2 M CTAC and 4.5 ml of 0.1 M AA aqueous solution. This solution was also kept undisturbed at 28℃ for 1 h. The color of the final mixture changed from transparent to red within a minute, indicating the formation of larger Au nanoparticles. After completion of the reaction, the reaction solution was centrifuged at 15000 rpm for 20 min. and washed with deionized water once.

2.3 Synthesis of Au rhombic dodecahedra, sphere, octahedra nanoparticles

Three different shapes of Au nanoparticles (rhombic dodecahedra, spheres, octahedra) were prepared by adjusting the previously reported method. All three different shapes of Au nanoparticles were synthesized by the seed-mediated synthesis method using as-prepared 11 nm spherical Au seeds. In a typical synthesis of 60 nm Au rhombic dodecahedra nanoparticles, 0.3 ml of the 11 nm Au seed solution was injected into a mixture of 0.3 ml of 0.5 M sodium citrate tribasic in 0.14 ml of de-ionized water, 1.0 ml of 9.42 mM $HAuCl_4$, 0.8 ml of 0.0025 mM PVP and 9.6 ml DMF in a 50 ml glass vial (Choi *et al*. 2013). The vial was then capped and heated to 80 ℃ in an oil bath with a magnetic stir bar for 2 h.

100 nm Au sphere nanoparticles were also synthesized using a procedure similar to that used for the Au rhombic dodecahedra nanoparticles, except that 0.16 ml of the 11 nm Au seed solution was added into the reaction solution, in a 120℃ oil bath (Choi *et al*. 2013).

In a typical synthesis of 50 nm Au octahedra nanoparticle, 0.1 ml of 11 nm Au seed solution was added to a mixture of 0.1 ml of 9.42 mM $HAuCl_4$ aqueous solution, 0.6 ml of 0.00025 mM PVP and 5.18 ml DMF in a 50 ml vial and heated to 70℃ in an oil bath with a magnetic stir bar for 1 h (Kim *et al*. 2011).

After each reaction was finished, all three different Au nanoparticle reaction solutions were centrifuged at 12000 rpm for 5 min. and washed with deionized water and ethanol several times. The final product was re-dispersed in ethanol for further characterization.

2.4 Fabrication of 3D colloidal crystal master mold and PDMS replica mold

A 3D colloidal crystal master mold was fabricated by assembling synthesized polystyrene (PS) particles. 330 nm and 480 nm PS particles were prepared using emulsifier-free emulsion polymerization (Kim *et al*. 1992, Yi *et al*. 2001). 770 nm and 880 nm PS particles were synthesized using the dispersion polymerization method (Ha *et al*. 2010).

To assemble 3-D colloidal crystals, the vertical deposition method was used (Im *et al*. 2003, Kim *et al*. 2005). At first, a small amount of poly(vinylpyrrolidone) was added to 0.1 wt % PS colloidal suspension (40 ml) to increase the assembly quality. The glass substrate was cleaned with ethanol and treated by oxygen plasma to make hydrophilic surfaces, and then were vertically dipped into the PS colloidal suspension. The colloidal suspensions were placed in a furnace at a temperature of 60 ℃ and water was evaporated at a rate of 0.7 ml/h.

A PDMS replica mold was fabricated using the prepared 3D colloidal crystal master mold. The prepared 3D colloidal master mold was passivated with chlorotrimetylsilane through vapor deposition in a vacuum chamber, and a PDMS prepolymer solution containing 10% curing agent (Sylgard 184TM) was poured onto the master mold. The cast prepolymer was cured in a 60℃ vacuum oven for 3 h. After completion of the curing reaction, the PDMS mold was peeled off from the master mold (Choi *et al*. 2009).

2.5 Preparation of Au nanoparticles array on PDMS mold and SERS sample

Three different shapes of synthesized Au nanoparticles were dispersed in ethanol with 2.14 $\times 10^{-6}$ M. Before fabricating the Au nanoparticle array on the PDMS mold, the surface of the prepared PDMS mold was treated by oxygen plasma to make a hydrophilic surface. After that, each type of Au nanoparticle dispersed solution was drop cast onto the PDMS mold and the solvent was evaporated in a 60℃ drying oven for 2 h.

For preparing SERS samples of the Au nanoparticle array on PDMS, 0.2 ml of 4-NBT (1×10^{-4} M) in an ethanol and water mixture solution was dropped and evaporated in a 60℃ drying oven.

2.6 Characterization

Transmission electron microscopy (TEM) images of the products were obtained using a JEM-3011 (JEOL) transmission electron microscope, operating at an accelerating voltage of 300 kV. Scanning electron microscopy (SEM) images of the products were recorded with a field-emission scanning microscope (Sirion, FEI) operated at an accelerating voltage of 20 kV. The samples were prepared by dropping a few drops of the colloidal suspension in ethanol either on a silicon substrate for SEM or 300 mesh carbon-coated copper grids for TEM, and then drying at room temperature. The optical properties of the synthesized Au nanoparticles were recorded with a UV-vis spectrometer (Cary 100, Varian) using synthesized Au nanoparticles suspended in ethanol. The SERS spectra were measured using a high resolution dispersive Raman spectroscope (Horiba Jobin Yvon, France) with D1 filter. The concentration of the Au suspension was determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES, OPTIMA 3300 DV).

3. Results and discussion

Three different shapes of Au nanoparticles (spheres, rhombic dodecahedra, octahedra) were synthesized by seed-mediated growth method. In all cases, approximately 11 nm spherical Au nanoparticles were used as seeds for preparing the various shapes by modifying the protocol reported in the literature. In the first step, 3 nm Au nanocrystallites were obtained by the reduction of $HAuCl_4$ with $NaBH_4$ in water containing CTAB at room temperature without stirring. Then, these nanocrystallites were grown into 11 nm Au nanospheres with more uniform size, in the presence of additional $HAuCl_4$, AA and CTAC. In the second step, synthesized 11 nm spherical Au nanoparticles were used as seeds to grow the Au nanosphere, rhombic dodecahedra, and octahedra. Briefly, Au nanospheres were synthesized by injecting the as-prepared 11 nm Au seed (0.16 ml) solution into a mixture of 0.5 M sodium citrate tribasic (0.3 ml) in de-ionized water (0.14 ml), 9.42 mM $HAuCl_4$ (1.0 ml), 0.0025 mM PVP (0.8 ml) and DMF (9.6 ml) in a 50 ml glass vial. The mixed solution was heated to 80℃ in an oil bath with a magnetic stir bar for 2 h. The shape of the Au nanoparticles changed from sphere to rhombic dodecahedra when the volume of Au seed solution was increased from 0.16 ml to 0.3 ml in a 120°C oil bath. To produce Au octahedra, 11 nm of spherical Au nanoparticles (0.1 ml) were injected into a mixture of 9.42 mM $HAuCl_4$ aqueous solution (0.1 ml), 0.00025 mM PVP (0.6 ml) and DMF (5.18 ml) and heated to 70°C in an oil bath with a magnetic stir bar for 1 h.

Figs. 1A-C show the typical TEM images of the three different shapes of Au nanoparticles. As shown in the TEM images, each Au nanoparticle has a well-defined morphology with a narrow size distribution. Au nanospheres (Fig. 1A) enclosed with a mixture of various facets with an approximate diameter of 100 nm, and Au rhombic dodecahedra (Fig. 1B) enclosed with only {110} faces with size of 60 nm, were synthesized. Similarly, Au octahedra (Fig. 1C) enclosed exclusively by {111} faces with size of 50 nm were also synthesized. Fig. 1D shows the UV-Vis spectra of the three different shapes of Au nanoparticles. The LSPR peaks of Au nanospheres, Au rhombic dodecahedra and Au octahedra were centered at 569 nm, 539 nm and 558 nm, respectively. All LSPR peaks were very sharp and narrow, which can be attributed to the uniform size and shape of the three different Au nanoparticles.

To investigate the effect of the shape of the Au nanoparticles, the synthesized Au nanoparticles having three different shapes were arrayed in a PDMS replica mold through a simple drop casting method. The PDMS replica molds were prepared by using soft lithography of PS colloidal particles. Before preparing the PDMS replica molds, 3D colloidal master molds were fabricated by assembling synthesized PS colloidal particles through the vertical deposition method.

In this study, we used PVP, which is a water soluble polymer, to fabricate a high quality 3D colloidal master mold. Thanks to the characteristics of PVP, crack and line-dislocations of the 3D colloidal assembly were reduced while stability was improved; hence more uniform and regular sized PDMS replica patterns were obtained (Fig. 2). The surface of the fabricated PDMS replica mold was treated with oxygen plasma to induce a hydrophilic surface. Then, the three different shapes of as-prepared Au nanoparticles dispersed in ethanol solutions were dropped onto the PDMS mold. Fig. 2 shows the SEM images of Au nanoparticle arrays on the PDMS replica mold a pattern

size of 260 nm. As shown in the SEM images, all shapes of Au nanoparticles were well arrayed and distributed regularly in the center of nanohole patterns over a large area.

Raman signals of 4-nitrobenzenthiol (4-NBT) absorbed on three different shapes of Au

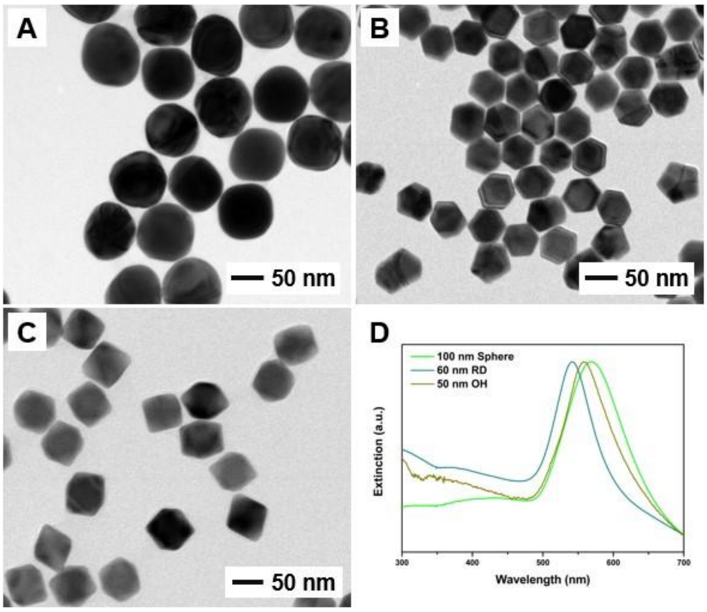

Fig. 1 TEM images of three different shapes of Au nanoparticles (A) 100 nm sphere, (B) 60 nm rhombic dodecahedra (RD) and (C) 50 nm octahedra (OH). (D) UV-vis extinction spectra of three different shapes of Au nanoparticles

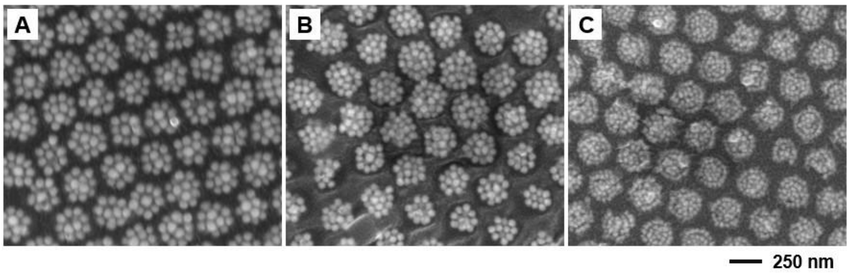

Fig. 2 SEM images of three different shapes of Au nanoparticles arrays on a PDMS replica mold with a pattern size of 260 nm. The arrayed Au nanoparticles on PDMS replica mold are (A) 100 nm Au sphere, (B) 60 nm Au rhombic dodecahedra, and (C) 50 nm Au octahedra, respectively

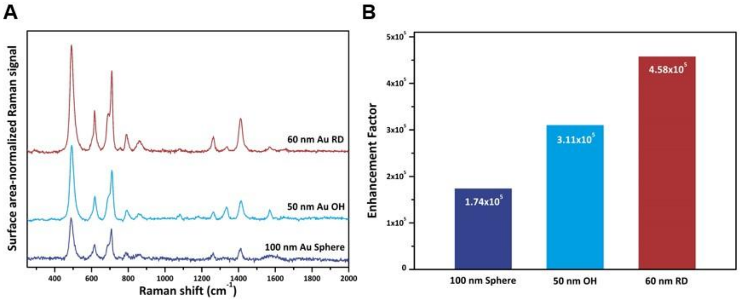

Fig. 3 (A) Surface area-normalized SERS spectra and (B) calculated enhancement factor of 1 × 10^{-4} M 4-nitrobenzentiol (4-NBT) absorbed on three different shapes of Au nanoparticle (RD, OH, Sphere) arrays on PDMS mold with pattern size of 260 nm.

nanoparticle arrays (Fig. 2) were measured to compare how the shape of each Au nanoparticle affected SERS activity. SERS samples were prepared by dropping the same amount of 4-NBT solutions onto each Au nanoparticle array and then drying in a 60℃ oven. Fig. 3A shows the relative surface area-normalized Raman signal intensity of 4-NBT on three different shapes of Au nanoparticle arrays. Au rhombic dodecahedra nanoparticle arrays exhibited higher surface area-normalized Raman signal intensity compared to Au octahedra nanoparticle arrays and Au nanosphere arrays. In addition, enhancement factors (EF), which are among the most important factors for characterizing the SERS effect, were also calculated to investigate a more accurate comparison of SERS activities. The most widely used definition for the SERS EFs is Eq. (1):

$$\mathrm{EF} = \frac{\mathrm{I_{SERS}}}{\mathrm{N_{SERS}}} \times \frac{\mathrm{N_{OR}}}{\mathrm{I_{OR}}} \tag{1}$$

where N_{OR}, N_{SERS} means the number of molecules probed for a normal Raman setting and SERS in appropriate excitation volume which was defined by the size of the focused laser spot (1μm). I_{SERS} and I_{OR} are the intensities of the same band for the SERS and the original normal Raman spectra obtained from 4-NBT, respectively (Camargo *et al.* 2010). Fig. 3B shows the calculated SERS enhancement factors for three different shapes of Au nanoparticle array. As a result of this calculation, Au rhombic dodecahedra nanoparticle arrays were found to exhibit the highest enhancement factor, 4.58×10^5. The Au octahedra nanoparticle array and Au nanosphere array showed 3.11×10^4 and 1.74×10^4, respectively. These results demonstrated the same tendency with the intensity of surface area-normalized SERS spectra (Fig. 3A).This means that the shape of the Au nanoparticle array affects the degree of SERS signal enhancement significantly and Au rhombic dodecahedra nanoparticle array is best substrate for 4-NBT detection among three different shape of Au nanoparticle arrays. One of the important factors contributing to the large Raman signal intensity and the EF of the Au rhombic dodecahdra nanoparticle array is that the binding energy of 4-NBT with the {110} plane of Au rhombic dodecahedra appears to be much higher than with the {111} and {100} plane of Au nanoparticles (Wu *et al.* 2011). Moreover, the relatively large number of corners, edges and faces of rhombic dodecahedra can also influence the SERS enhancement activity. When a lot of corners, edges, and faces exist, it is easy for face-to-face, and face-to-edge contact places to occur, which are known as SERS hot-spot regions (Camargo *et al.* 2010), between the Au nanoparticles in our fabricated Au nanoparticle array. In contrast, the Au nanosphere arrays showed the lowest Raman signal intensity and EF value because of the low binding energy with 4-NBT, and the lack of hot spot regions such as sharp tips. Moreover, even if the size of the Au nanospheres were decreased to 50 nm which are similar with the size of Au rhombic dodecahedra and Au octahedra nanoparticles, it would still show poor Raman signal intensity and SERS enhancement factor.

We further investigated the influence of the pattern size of the PDMS mold on the SERS spectra. Since the calculated enhancement factor of the Au rhombic dodecahedra nanoparticle arrays showed the strongest Raman signal enhancement, as compared to Au nanospheres and Au octahedra, Au rhombic dodecahedra nanoparticle arrays were used to investigate the effect.

Various pattern sizes of PDMS molds were fabricated using different sizes of PS colloidal particles. 480 nm, 774 nm and 880 nm of PS colloidal particles were used to prepare PDMS replica molds, and well-ordered PDMS replica patterns (Fig. 4) with sizes of 440 nm, 700 nm and 810 nm were fabricated. Compared to the size of PS colloidal particles, the pattern size of the PDMS replica mold was smaller, which can be attributed to the etching of PS by oxygen plasma

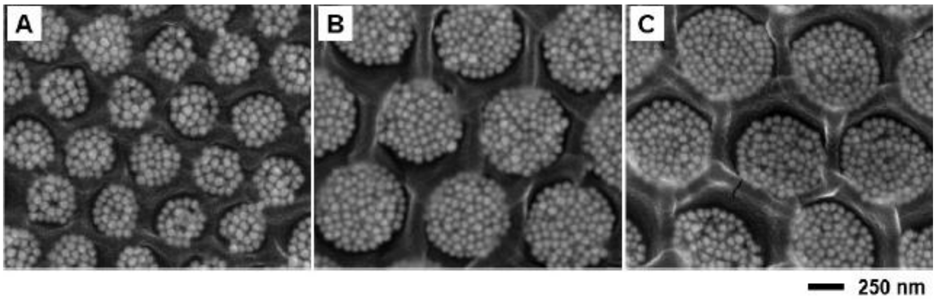

Fig. 4 SEM images of 60 nm Au rhombic dodecahedron arrays on PDMS replica mold. The diameter of patterns are (A) 440 nm, (B) 700 nm, and (C) 810 nm, respectively

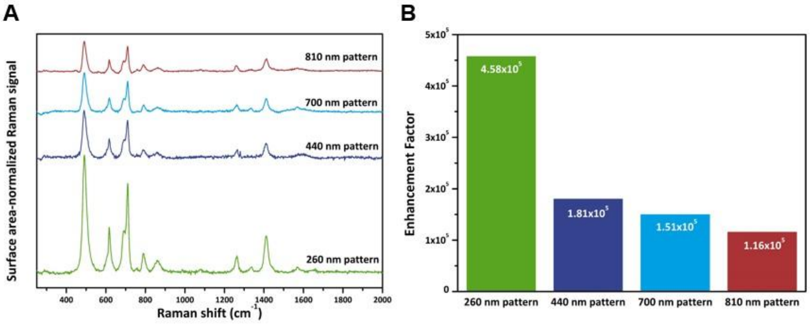

Fig. 5 (A) Surface area-normalized SERS spectra and (B) calculated enhancement factor of 1×10^{-4} M 4-nitrobenzentiol (4-NBT) absorbed on 60 nm Au rhombic dodecahedra nanoparticle arrays on PDMS molds with different pattern sizes; 260 nm, 440 nm, 700 nm and 810 nm

surface treatment. Au rhombic dodecahedra nanoparticle arrays were also prepared on PDMS replica molds with different pattern sizes by the same method as mentioned earlier. Fig. 4 shows the SEM images of fabricated Au rhombic dodecahedra nanoparticles arrays on PDMS replica molds with different pattern sizes. Au rhombic dodecahedra nanoparticles were regularly and exquisitely arrayed in various sizes of nanohole patterns. Therefore, well-ordered Au nanoparticle arrays could be fabricated on a patterned PDMS mold easily by a simple drop casting method, regardless of pattern size.

Fig. 5A shows the surface area-normalized SERS spectra of 60 nm Au rhombic dodecahedra nanoparticle arrays with different PDMS mold pattern sizes, with 260 nm, 440 nm, 700 nm and 810 nm. When the pattern size was 260 nm (Fig. 2B), the surface area-normalized Raman signal exhibited the highest intensity. As the pattern size of PDMS mold was increased, the surface area-normalized Raman signal intensity decreased. Fig. 5B exhibits the calculated SERS EFs of 60 nm Au rhombic dodecahedra nanoparticle arrays with different PDMS mold pattern sizes. As a result of the EF calculation, 60 nm Au rhombic dodecahedra nanoparticle arrays with 260 nm, 440 nm, 700 nm and 810 nm show values of 4.58×10^5, 1.81×10^5, 1.51×10^5 and 1.16×10^5, respectively. Calculated EFs also showed a tendency similar to the surface area-normalized Raman signal intensities. Therefore, the pattern size of the PDMS mold affects the SERS activity, and the small pattern size of the PDMS mold is more favorable as a SERS substrate of 4-NBT than a larger one. In general, the number of Au nanoparticles in the same confocal area decreased as the pattern size of the PDMS mold was increased. Consequently, the surface area of Au nanoparticles in a pattern array mold was reduced and that influenced the number of analyte absorbed on the Au nanoparticles in the confocal area.

4. Conclusions

In summary, Au nanospheres, Au rhombic dodecahedra, and Au octahedra were synthesized by a seed mediated solution-phase synthesis and arrayed regularly on a 260 nm pattern on PDMS substrates by a simple drop casting and evaporation method. Among the three different shapes of Au nanoparticle arrays, the Au rhombic dodecahedra nanoparticle array exhibited the strongest Raman signal intensity and had the largest enhancement factors for 4-NBT because of their shape (relatively large numbers of faces, edges, corners) and large binding energy between the {110} surface and 4-NBT. Furthermore, various pattern sizes of Au rhombic dodecahedra nanoparticle arrays, with pattern sizes of 260 nm, 400 nm, 700 nm and 810 nm were fabricated and also investigated for their comparative SERS activity. The Au rhombic dodecahedra nanoparticle array with a pattern size of 260 nm showed the strongest Raman signal intensity and highest enhancement factor due to the increased number of analyte absorbed on Au nanoparticles surface. Based on these results it can be suggested that shape and size controlled Au rhombic dodecahedra nanoparticle arrays on nanopatterned PDMS can be good substrates for the detection of various analytes with enhanced and reliable SERS activity.

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