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Raman-Active Two-Tiered Ag Nanoparticles with a Concentric Cavity

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Since the seminal discovery of surface-enhanced Raman scattering (SERS) in the 1970s^[1–3] and the first demonstration of single-molecule detection by Nie et al. and Kneipp and co-workers in 1997,^[4,5] SERS has been widely investigated for use in highly sensitive, real-time, nondestructive, and multiplexed molecular detection.^[6–11] Reliable and straightforward formation of “Raman hot spots,” where a local electromagnetic field enhanced by surface plasmon resonance reaches its maximum value, is an essential prerequisite for practical applications of SERS. In many reports, Raman hot spots generated from aggregates or assemblies of nanoparticles have been used. However, a recent paper on the site distribution of SERS enhancement from Ag thin films on self-assembled nanoparticles shows that the hottest sites (enhancement factor > 10⁹) account for only 0.006% of the total.^[12] Even though high-end electron beam lithographic methods enable patterning to form more uniform and reproducible nanoscale hot spots,^[13–15] these methods are not currently viable for large-scale fabrication of SERS substrates. Herein, we present an inexpensive and highly reliable SERS substrate where arrays of two-tiered Ag nanoparticles, each of which contains a cavity at the center, are generated by two simple steps of nano-imprinting and metal vacuum deposition. Because the individual Ag nanoparticles have their own hot spots, in the form of a nanoscale concentric cavity, it is possible to generate Raman hot spots reproducibly and without further reliance on nanoparticle aggregation or fortuitous interparticle distances. Using the fabricated two-tiered Ag nanoparticle array, highly sensitive detection of organic molecules with a wide dynamic sensing window was demonstrated.

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Thin film deposition on an uneven surface has been extensively studied for semiconductor devices, and it is well-known that the morphology of metal films deposited on a T-gate structure have a deep and narrow valley on the top of the gate-foot.^[16,17] In this report, a central truncated conical depression in a Ag film deposited onto the patterned surface is intentionally designed to create Raman hot spots. To do so, a nano-imprint mold with two-tiered Si posts, by which is meant a cylindrical pillar with two stepped diameters, was created by using spin-coated polystyrene (PS) bead arrays as masks for etching the underlying Si substrates. Two sets of PS and Si etches with O₂ and SF₆-Cl₂ plasmas, as illustrated in Figure 1, were used to create the two tiers. Plasma etching conditions were optimized for lateral and vertical etching of PS and Si, respectively, by maximizing isotropic and anisotropic characteristic of O₂ and SF₆-Cl₂ plasma, respectively (see Supporting Information (SI), Figure S1). Figure 2a and b show the sample surfaces after the first set of PS/Si etches and after a subsequent second PS etch, respectively. Through the two PS etching steps, the radial size of PS beads was reduced to define the diameters of the first and second Si tiers, and the heights of the each Si tier could be adjusted by the Si etching steps. Thus, we controlled the lateral and vertical dimensions of two tiers independently within the experimental window, which is determined by the etch selectivity between PS and Si. Figure S1 in the SI shows that for SF₆-Cl₂ plasma the etch rate ratio for Si relative to PS is ~1.8, while for O₂ plasma the ratio for Si relative to PS ~0. For example, the diameter of the second tier is varied from 150 to 70 nm in Figure 2c and d, which show tilted scanning electron microscopy (SEM) images of two-tiered Si patterns with residual PS beads on the top. As shown in the insets of Figure 2c,d, the shape of the PS bead was changed from a sphere to a spheroid with an etched top and an un-etched spherical bottom during the series of etching steps. The evolving shape of etched PS beads causes a tapered sidewall of the second Si tier, near the pillar tip, due to the high curvature at the etched PS bead edges, because the Si etch also removes some PS and thus continuously erodes the bead diameter and thickness. After the formation of two-tiered Si patterns, the residue of the etched PS beads was removed by dipping in toluene. The SEM images from plan view (Figure 2e) and cross-sectional view (Figure 2f) present the results for the fabricated nano-imprint molds. Steps and terraces of the concentric two-tiered patterns are well defined by our proposed process. It should be also noted that the central axis of the first and second tier are self-aligned, in contrast to electron-beam lithography, which requires fastidious steps for pattern alignment for each and every substrate.

After the thermal nano-imprinting (described in the Experimental Section) using the two-tiered mold presented in Figure 2e,f, a 50 nm thick Ag film was evaporated on the patterned poly(methyl methacrylate) (PMMA) surface. Figure 3a and its inset clearly show the fabricated two-tiered Ag nanoparticle array, where a Ag film was deposited on the ring-shaped terrace and inside the central hole. Due to the sloped sidewall of the second tier, which includes the pillar tip region, and the metal deposits on that sidewall, the diameter of the central depression is reduced to 40 nm at the nanoparticle surface from the initial diameter of the nano-imprint mold, which has a diameter of 70 nm at the corresponding location. For Raman measurements, the surfaces were treated with Rhodamine 6G (R6G) by depositing a drop of this Raman dye dissolved in methanol, which then evaporated to leave nonvolatile dye molecules on the surface. More details are given in the Experimental Section. Although this method cannot guarantee the uniformity of molecular coverage, which would be virtually impossible to measure at the lower limit, it does provide a reliable average value, and we do not observe large uniformity variations over 2 mm × 2 mm samples. SERS signals were then analyzed using a scanning confocal microscope with a 532 nm excitation laser and a monochromator for detection. Figure 3 b shows representative spectra from different R6G concentrations. Peak positions in these spectra were accurately assigned to the reported vibrational bands of R6G molecules.^[18–20] The intensity change produced by varying the concentration of R6G is summarized in Figure 3c. For plotting this

graph, we measured 100 different spectra at each concentration and averaged the intensity of the peak with a Raman shift of 615 cm^{-1} , which originates from in-plane bending of the R6G molecule.^[18–20] We obtained over five orders of the dynamic sensing range (Figure 3c) and detected the signal from 10 nM solutions, which corresponds to approximately 80 molecules (0.13 zeptomole) per single nanoparticle (see SI). Above the concentration level of 1 mM , SERS intensities were slightly reduced, while background signals and noise from surface-enhanced fluorescence continued to increase (see SI, Figure S2).

For the purpose of comparison, Ag nanodisks with 140 nm diameter and 50 nm height, whose dimensions were chosen for an efficient extinction of the excitation laser with a 532 nm wavelength,^[21–24] were fabricated on Si substrates (see SI, Figure S3). It is regrettable that we do not have access to tunable sources to verify the predicted frequency dependence of the SERS enhancement. Faced with this limitation, we have instead used the 2D finite-difference time-domain (FDTD) simulations, which include the substrate and resist dielectric functions to calculate the nanoparticle responses at multiple wavelengths, and to illustrate that the arrays of Ag nanodisks and two-tiered nanoparticles are both highly responsive near the 530 nm excitation laser (see SI; Figure S4). SERS characteristics were analyzed with the identical procedure for both nanodisks and two-tiered nanoparticles. As indicated by the grey line in Figure 3b, the tenfold-multiplied SERS signal from the Ag nanodisk is still very weak compared to the signal from the two-tiered Ag nanoparticle treated with the same concentration ($100\text{ }\mu\text{M}$) of R6G. Averaged peak intensities in Figure 3c demonstrate that the artificially designed two-tiered Ag nanoparticles perform better by two orders of magnitude than the Ag nanodisks for both the minimum detection level of R6G and the maximum intensity of SERS signal at dye saturation levels. The high SERS intensity for R6G-saturated two-tiered nanoparticles is particularly important to increase the signal strength for cases where Raman dyes are used to heavily label nanoparticles for SERS-based multiplex molecular imaging,^[10, 11, 25] as opposed to the most sensitive detection of rare molecules. As demonstrated in our previous reports,^[26–28] nanoparticle release from such substrates is possible simply by including a dissolvable sacrificial polymer layer underneath the nanoparticles so that the released nanoparticles can be gathered by centrifugation. If the nanoparticles are used after detachment from the dielectric substrate and suspension in water, for example, optimal dimensions of the nanoparticle could be recalculated for the resonance shifts from the new dielectric environment, although we expect that enhancements would remain qualitatively similar.

The Ag film on the ring-shaped terrace and the 40 nm diameter central cavity could be expected to serve as sources for improved sensitivity and signal intensity because the polarized outer ring can induce an enhanced electric field throughout most of the cavity volume.^[29–31] Demonstrating the effect of the central cavity, the 2D FDTD simulation in Figure 4a shows the calculated electromagnetic contribution to the SERS enhancement. The contour of $|E/E_0|^2$ in Figure 4a, where E_0 and E represent the amplitude of the incident and enhanced electrical fields, respectively, shows that the local electric field amplitude at the central hole of the two-tiered nanoparticle is significantly higher than at the corners of Ag nanodisks, or at other edges and corners of the two-tiered nanoparticles, which is also confirmed for arrayed nanostructures (see SI, Figure S4). Histograms showing the frequency of each $|E/E_0|^4$ value from both of those field contours are displayed in Figure 4b, and their statistics are summarized in Figure 4c. A sum of more than a 100-fold increase and a maximum of $|E/E_0|^4$ values, which should correlate with the maximum of the SERS intensity and the minimum of the molecular detection sensitivity, respectively, are reasonably matched with the results of the experimental comparison in Figure 3c. The right image in Figure 4a shows that SERS enhancements from Ag films on non-imprinted regions of the PMMA surface, which were left intact to simplify the fabrication process of the two-tiered

nanoparticle array, are smaller than the values observed when central cavities are present, indicating that the central cavity provides significant enhancement.

Here, we have presented a method for fabricating multi-tiered nano-imprint molds by using colloidal PS bead arrays and successive plasma etching of PS and Si. This enables self-alignment of each tier and allows a low-cost batch-type process. A two-tiered nano-imprint mold was successfully prepared, and the resulting pattern—a two-tiered Ag nanoparticle array with a 40 nm diameter hole at the center of each individual nanoparticle—was consistently produced. Compared to simple disk-shaped nanoparticles, the two-tiered nanoparticles with concentric cavities provide a highly sensitive detection limit with a wide dynamic sensing range. Therefore, the proposed nanoparticle arrays could be used for a sensitive, rapid, reliable, and inexpensive molecular detection platform. In addition, the bright SERS signal of the two-tiered nano-particle suggests considerable potential for using the released nanoparticles as in-vitro or in-vivo imaging reagents.

Experimental Section

Preparation of Nano-imprint Mold and Two-Tiered Ag Nano-particle Array

To make a nano-imprint mold, a solution of 240 nm diameter PS beads (Invitrogen) was spin-coated onto a Si substrate. Next, dry etching was performed using an electron cyclotron resonance (ECR) plasma (Plasma Quest ECR plasma etcher). At first, self-assembled PS bead arrays were etched by O₂ plasma (gas flow rate; 50 SCCM, process pressure; 50 mTorr, ECR power; 50 W, RF power; 10 W). Then, the Si substrate was etched by SF₆-Cl₂ plasma (gas flow rate for both SF₆ and Cl₂ was 20 SCCM, process pressure; 3 mTorr, ECR power; 50 W, RF power; 50 W). A second set of PS and Si etches were repeated to define the narrow pillar tip. After the final dry etching, the residual PS beads were removed by dipping in toluene. After rinsing with isopropyl alcohol and blow drying with N₂, the nano-imprint mold surface was coated with tridecafluoro(1H,1H,2H,2H-tetrahydrooctyl)-trichlorosilane (Sigma-Aldrich) to reduce contact adhesion forces during nano-imprinting. Using the completed nano-imprint mold, Si wafers coated with 200 nm thick PMMA were subjected to thermal nano-imprinting at 180 °C under a pressure of 40 bar for 60 s, by a commercial nano-imprint tool (NIL 2.5, Obducat). After separation of the mold from the wafer surface, the Ag film was deposited, to a thickness of 50 nm, using an electron-beam evaporator (ES26C, Innotec) at a base pressure of 2.5×10^{-7} Torr. Synthesized Raman-active nanoparticle arrays were examined by scanning electron microscopy (FEI XL30, Sirion).

Analysis of SERS Characteristics

A 2 μ L droplet of R6G in methanol solution was spread on 2 mm $\times$ 2 mm square samples and dried on a hot plate at 90 °C. Due to the low surface tension (~ 23 dyne cm⁻¹) and rapid evaporation of methanol, the R6G solution dried quite uniformly over the whole sample surface. Afterwards, SERS measurements were carried out using a confocal Raman microscope (alpha500, WITec). R6G treated sample surfaces were scanned over 25 μ m wide square frames, with a unit pixel size of 250 nm $\times$ 250 nm and an accumulation time of 0.036 s/pixel. To avoid photochemical damage, the power of the 532 nm excitation laser was adjusted to 1.4 mW. The power of laser was measured without objective aperture and lens.

Electromagnetic Simulation

Electromagnetic simulations were performed using Lumerical 2D FDTD software. The grid was set to a 0.5 nm square and perfectly matched layers (PML) were used as a boundary condition. The simulated structures were drawn to match the shape of the experimentally

realized particles. The particles were illuminated from the top with a linearly polarized plane wave of 530 nm wavelength.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

Schematic illustration of the overall process for making two-tiered nano-imprint molds and two-tiered Ag nanoparticles: spin-coating of polystyrene (PS) beads, two sets of PS and Si etching using O_2 and SF_6-Cl_2 plasma, residual PS removal using toluene, thermal nano-imprint lithography, and Ag film deposition. PMMA represents poly(methyl methacrylate).

Figure 2.

SEM images of a) PS array (initial diameter; 240 nm) with first Si tier after (first PS etch for 300 s)\(first Si etch for 60 s); b) PS array with first Si tier after (first PS etch for 300 s)\(first Si etch for 150 s)\(second PS etch for 120 s); c,d) two-tiered Si patterns with residual PS on the top, after (first PS etch for 300 s)\(first Si etch for 150 s)\(second PS etch for 300 (c) or 420 s (d))\ (second Si etch for 75 s); e,f) a two-tiered nano-imprint mold after residual PS removal. Images were captured from the view angles of 45° (a,c,d), 90° (b,e), and 3° (f); inset is at 0°. The scale bars in a–f and the insets represent 200 nm.

Figure 3.

a) Plan-view SEM image of two-tiered Ag nanoparticles where a cavity is at the center of each individual nanoparticle. The scale bar for the inset represents 200 nm. b) Representative SERS spectra from two-tiered Ag nanoparticle arrays treated with different concentrations of R6G: 10^{-8} (bottom), 10^{-6} (middle), and 10^{-4} M (top). Gray lines in the top graph shows the tenfold-multiplied signal from a plain Ag nanodisk array. Baseline signals were corrected. CCD cts represents charge-coupled device counts. c) Averaged SERS intensities of the peak of 615 cm^{-1} from two-tiered Ag nanoparticles (square) and Ag disks (circle).

Figure 4.

a) The squared magnitude of the local electrical field amplitude of the Ag nanodisk (left) and two-tiered nanoparticle (right). E_0 and E represent the amplitude of the incident and enhanced electrical field, respectively. The direction of incident light is from top to bottom and is polarized in the x -direction. b) A histogram showing the frequency of each $|E/E_0|^4$ value from the field contours of two-tiered nanoparticle (black squares) and nanodisk (red circles). c) Table for a comparison of maximum value and pixel-weighted sum of $|E/E_0|^4$ values from both types of nanostructures. The sum of $|E/E_0|^4$ values was calculated from the whole area of the field contours in (a), and the maximum $|E/E_0|^4$ values were obtained from the upper corner of the Ag nanodisk and the entrance of the central hole of two-tiered nanoparticle, as noted by the white arrows in (a).