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Supplementary Information

Flexible SERS-active film for studying the effect of non-metallic nanostructures on Raman enhancement

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Calculation of enhancement factor (EF)

The EF was calculated by using the equation, EF=(I_{SERS}/I_{bulk})·(N_{bulk}/N_{SERS}), where N_{bulk} and N_{SERS} represent the number of molecules in the excitation volume in conventional Raman and SERS measurement conditions, respectively, I_{bulk} and I_{SERS} represent the intensities of the collected Raman signals in conventional Raman and SERS conditions, respectively. The details of the EF calculation was described in our previous reports.[1, 2] To measure the Raman intensity in bulk condition, bulk PATP was deposited on solid substrate, and then excited with a focused laser beam. The excitation volume can be calculated from the Abbe's equation, $d_{xy} = \frac{1.22\lambda}{NA}$, $d_z = \frac{4\lambda \cdot \eta}{NA^2}$, where d_{xy} represents the spot size in *xy* direction and d_z represents the spot size in *z* direction. NA is the numerical aperture of the objective, which is 0.6 for the objective used in this work. Note that the penetration depth of the laser in bulk PATP is bigger than d_z. So the excitation volume here is equal to the volume in which the probe molecules were excited in bulk measurement. This volume can be calculated by the equation $V = \pi {d_{xy}}^2 d_z$ and the density of bulk PATP is known as ~1.18 g cm^3. Then it is easy to calculate the number of molecules in this excitation volume. For the SERS measurement condition, we assumed that the flexible PDMS film was covered with a monolayer of PATP molecules, resulting in a monolayer with a height of roughly 0.5 nm. The spot size of excitation can be obtained from the Abbe's equation, $d_x = \frac{1.22\lambda}{NA}$. Then the volume of the excited molecules can be calculated. Therefore, the number of the molecules in this volume can be calculated accordingly. Afterwards, the EF of the system can be easily calculated.

FDTD simulation procedure

Three-dimensional finite-difference time-domain (3D-FDTD) simulations were carried out using Lumerical FDTD solution. In all simulations, a mesh size of 0.5 nm × 0.5 nm × 0.5 nm was used for the structure and 0.25 nm × 0.25 nm × 0.25 nm for the interfaces. A plane wave light source with a beam size of 500 nm × 500 nm was used to illuminate the structure. During the FDTD simulation, the diameter of the AgNP was set as 40 nm, and the silicon pore size was set as 30-110 nm in diameters.

Supplementary References:

1. G. Lu, H. Li and H. Zhang, *Chem. Commun.*, 2011, **47**, 8560-8562.

2. G. Lu, H. Li, S. X. Wu, P. Chen and H. Zhang, *Nanoscale*, 2012, **4**, 860-863.

Supplementary Figures

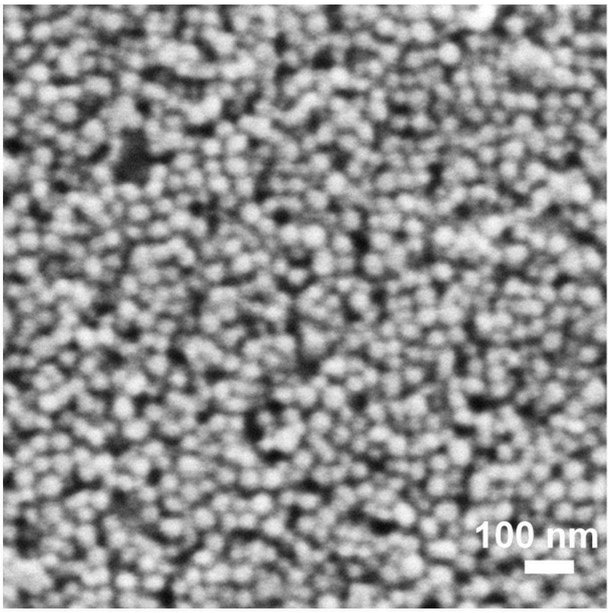

Figure S1. SEM image of the AgNPs that were used for fabrication of the SERS-active PDMS film.

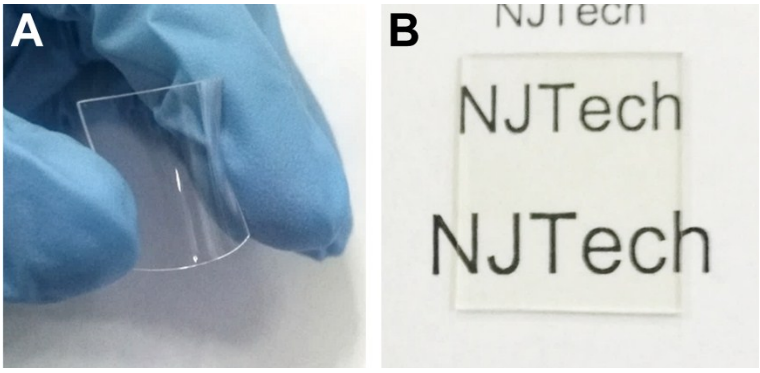

Figure S2. Photos of the AgNP-coated PDMS film. (A) The flexibility of the film. (B) The transparency of the film. The film is slightly yellowish, which is the colour from the AgNPs.

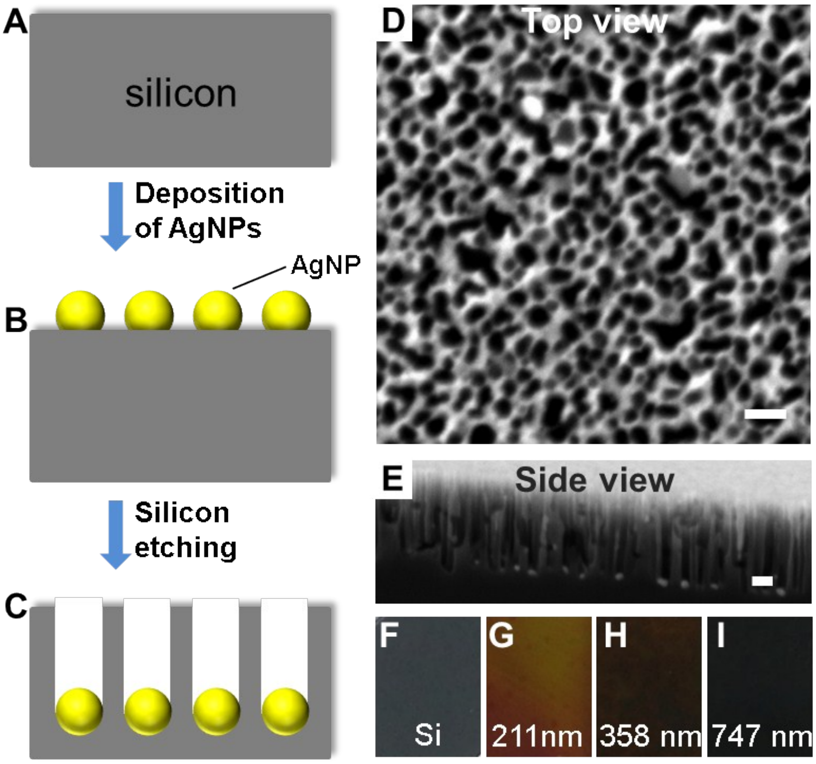

Figure S3. (A-C) Schematic illustratoin of nanoporous silicon fabrication. (D-E) Typical top and side view SEM images of the fabricated nanoporous silicon. Scale bar = 100 nm. (F-I) Photos showing the color of the bare silicon (F), nanoporous silicon with pore depth of 211 (G), 358 (H) and 747 (I) nm, respectively.

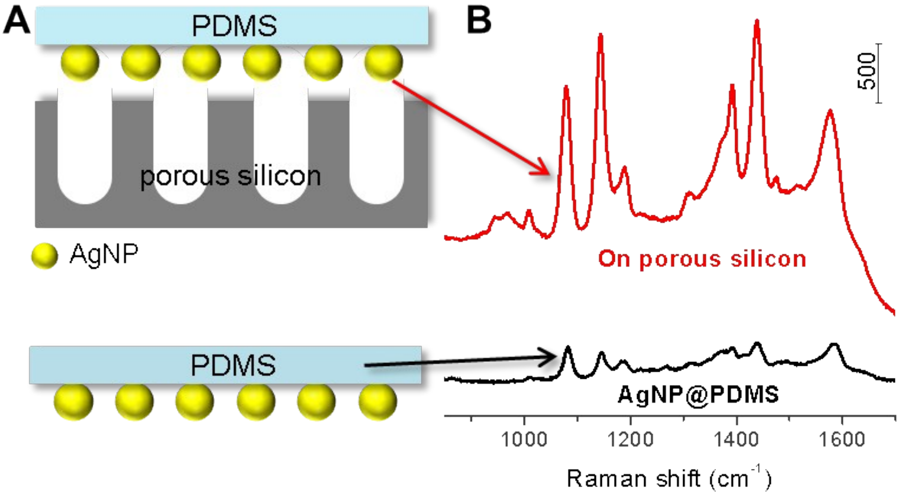

Figure S4. SERS enhancement from the AgNP-coated PDMS film (scheme shown as bottom part in (A) and spectrum shown as black curve in (B)) and the one attached onto nanoporous silicon (scheme shown as top part in (A) and shown as red curve in (B)).

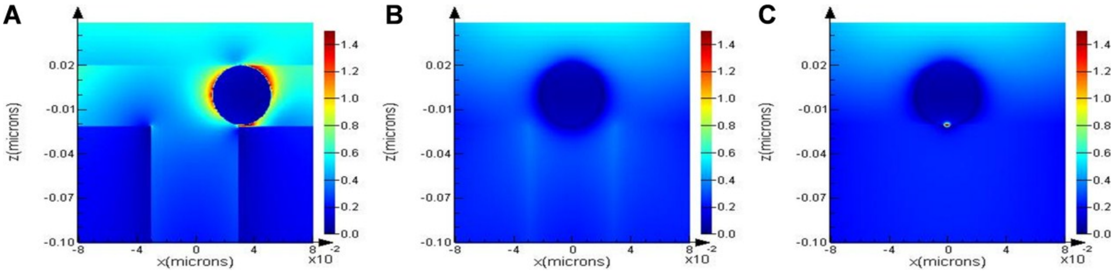

Figure S5. The electromagnetic field distribution when the adsorbed AgNP on PDMS was positioned at the edge of a silicon nanopore (A), hanging over a silicon nanopore (B) and on flat silicon surface (C). The structures were illuminated with 633 nm laser beam.

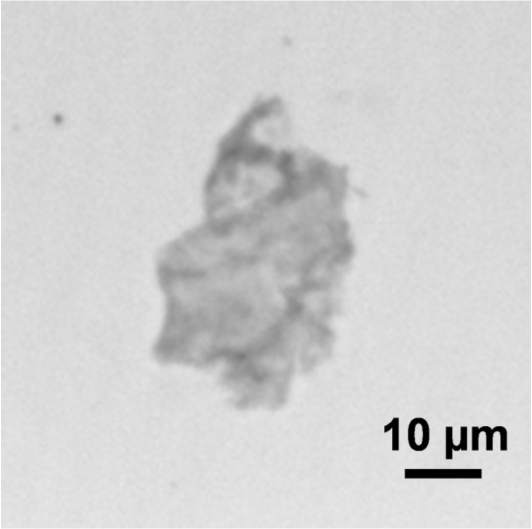

Figure S6. Optical image of GO that was spin-coated on PDMS surface.

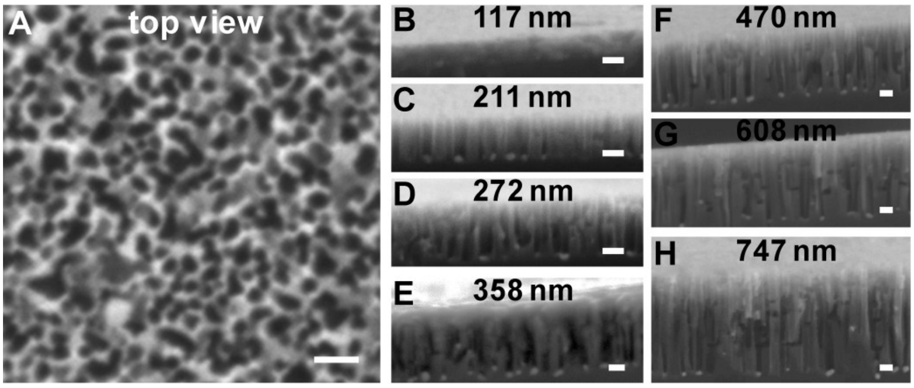

Figure S7. Top (A) and side view (B-H) SEM images of nanoporous silicon with pore depth of 117 (B), 211 (C), 272 (D), 358 (E), 470 (F), 608 (G) and 747 nm (H), respectively. Scale bars = 100 nm.

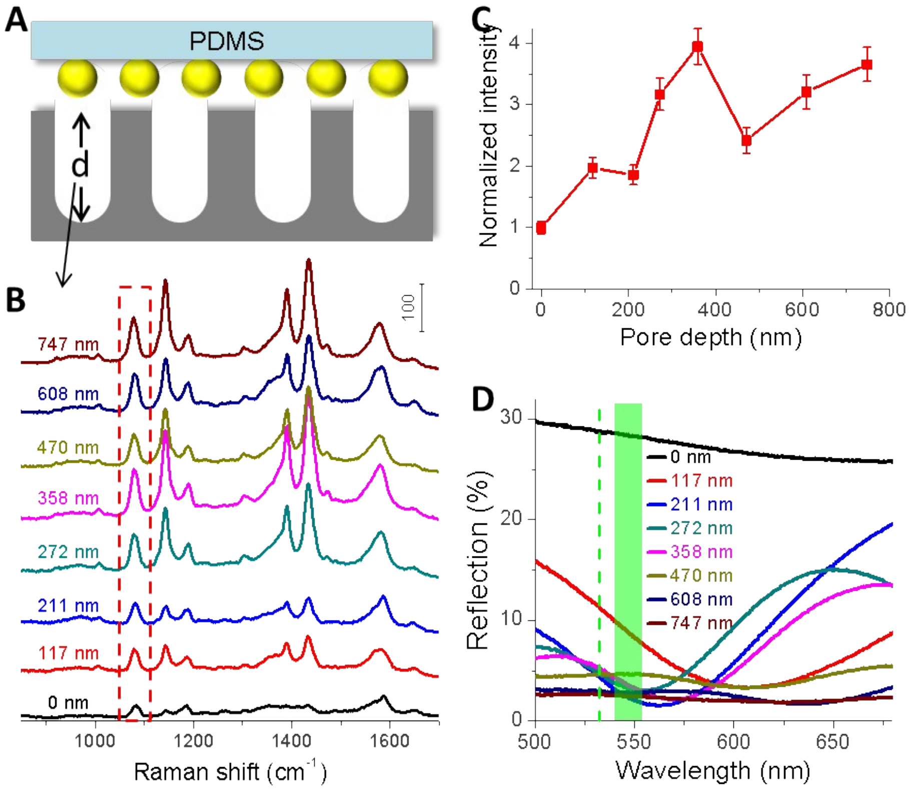

Figure S8. The effect of silicon nanopore depth on SERS enhancement (excited with 532 nm laser). (A-B) Scheme and SERS spectra from the SERS-active PDMS film when it was attached onto nanoporous silicon with various pore depths. The laser power was set as 200 kW·cm^{-2} at sample plane. (C) The Raman intensity (for the peak at 1076 cm^{-1}) changes while increasing the pore depth (normalized to the Raman intensity on flat silicon surface). (D) Reflection spectra of the nanoporous silicon surfaces, the green dotted line indicates the excitation wavelength at 532 nm and the green rectangle represents the wavelength of interested Raman scattering.

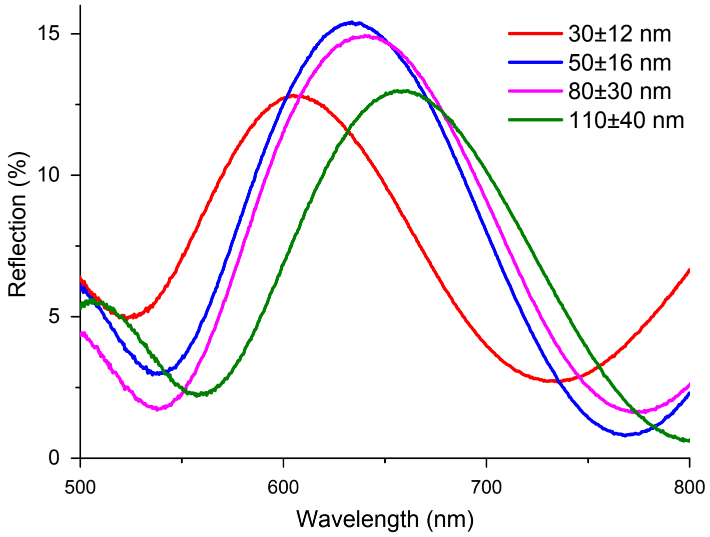

Figure S9. Reflection spectra of nanoporous silicon with pore size of 30±12, 50±16, 80±30 and 110±40 nm in diameters.

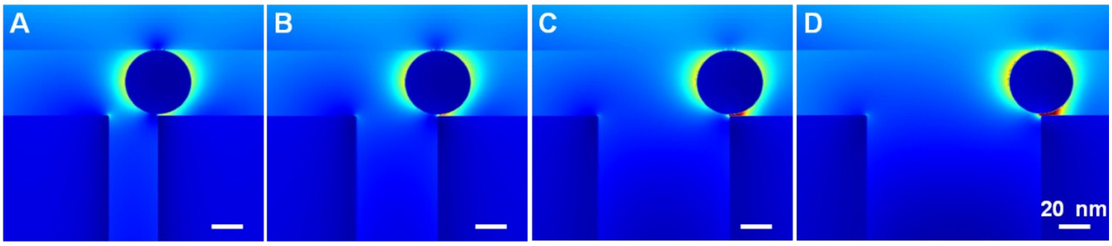

Figure S10. The electromagnetic field distribution when the adsorbed AgNP on PDMS was positioned at the edge of a silicon nanopore with pore sizes of 30 (A), 50 (B), 80 (C) and 110 (D) nm in diameters. The structures were illuminated with 633 nm laser beam.

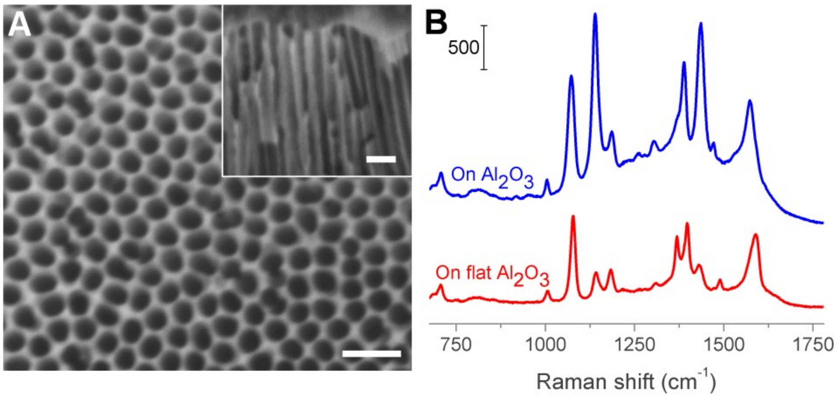

Figure S11. (A) SEM image of anodic aluminium oxide (AAO). Inset shows the side view of AAO. Scale bars = 200 nm. (B) SERS spectra of the AgNP-coated PDMS film when it was attached onto flat Al_2O_3 (red curve) and AAO (blue curve), respectively.