

High-density Ag nanoneedle forest array by nano-peeling technique for near-infrared SERS detection

Zhiming Chen,^{ab} Pan Zeng,^{ab} Yifan Wang,^{ab} Guofeng Zhang,^a Jie Yu,^a An Cao,^a

*Dilong Liu,^{*a} and Yue Li^{*a}*

a. Key Lab of Materials Physics, Anhui Key Lab of Nanomaterials and Nanotechnology, Institute of Solid State Physics, HFIPS, Chinese Academy of Sciences, Hefei 230031, P. R. China

b. University of Science and Technology of China, Hefei 230026, P. R. China

**Address correspondence to dlliu@issp.ac.cn, yueli@issp.ac.cn*

1. Experimental section

1.1 Materials

Monodispersed PS microspheres (diameter: 500 nm) in aqueous suspensions (2.5 wt%) were purchased from AnHui ZhongKe YuanZhen Technology Co., Ltd. Ethanol ($\geq 99.7\%$), Acetone ($\geq 99.5\%$) and 4-aminothiophenol (4-ATP, 99.0%) were obtained from Sinopharm Chemical Reagent Co., Ltd. The target of Ag (purity: 99.99%) was bought from ZhongNuo Advanced Material (Beijing) Technology Co., Ltd. Rhodamine6G (R6G, 99%), Orange II (96%) and Methylene blue (MB, $\geq 70.0\%$) were purchased from Sigma-Aldrich. Sylgard 184 silicone elastomer base (PDMS) was bought from Dow Corning Holding Co., Ltd. Norland optical adhesive 61 was purchased from Norland Products Inc. All of the chemical reagents were of analytical grade and used without any purification. Deionized water was obtained by a Milli-Q water purification system.

1.2 Preparation of PDMS cured PS array

First, the quartz substrate was firstly cleaned with acetone/ethanol (1 : 1 in volume) and DI water in an ultrasonic bath, followed by drying in an oven at 60 °C for 30 min. The dried quartz substrate was treated with a plasma cleaner for 10 min. After the above cleaning process, the surface of the substrate was sufficiently hydrophilic. Then, monolayer PS colloidal crystals as templates were fabricated on the quartz substrate through air/water interface self-assembly process. Finally, the PS monolayer assembled on the quartz substrate was placed in a petri dish, then filled with enough PDMS to ensure complete coverage.

After that, the petri dish was placed in a vacuum environment for 12 h and then transferred to an oven for 12 h at 70 °C . After the PDMS was fully cured, the upper part of the PDMS was completely stripped off from the quartz substrate to obtain the PDMS cured PS array.

1.3 Preparation of the high-density nanoneedle forest array via the nano-peeling technique

A uniform layer of optical adhesive Nor61 was spin-coated on the pretreated hydrophilic silicon (Si) substrate, under a rotation speed of 6000 r/min. Then, the PDMS cured PS array was covered on the top of the optical adhesive layer, flowed by imprinting treatment with a stress of 5 N for 5 min to ensure the air bubbles completely removed. After that, it was quickly transferred to a UV light irradiation (wavelength: 365 nm; power intensity: 40 mW/cm²) for 30 min to make the optical adhesive fully cured. With the separation of quartz substrate and PDMS from optical adhesive layer, the high-density nanoneedle forest array was obtained.

1.4 Preparation of the high-density Ag nanoneedle forest array

A certain thickness of Ag film layer was deposited on the obtained the high-density nanoneedle forest array by using a magnetron sputtering deposition device. The sputtering power was ≈ 20 W, which led to a ≈ 4 nm / min⁻¹ deposition rate. The Ag deposition time was set at 1, 2, 3, 4 and 5 min for 4, 8, 12, 16 and 20 nm Ag layer, respectively.

1.5 Investigation of the NIR-SERS Performance

Different concentrated 4-ATP solutions (10^{-7} M, 10^{-8} M, 10^{-9} M, 10^{-10} M, 10^{-11} M) were prepared by the dilution of 10^{-1} M 4-ATP ethanol solution with deionized water.

Substrates for NIR-SERS were immersed in 4-ATP solution with different concentrations for 6 h for further use. For enhancement factor (EF) investigation, 5 μL 4-ATP solution with a concentration of 10^{-1} M was added on to the surface of $0.5 \times 0.5 \text{ cm}^2$ Si wafer. For comparison, 5 μL of 10^{-7} M 4-ATP ethanol solution was dropped on the high-density Ag nanoneedle forest array.

1.6 Characterizations

All the products were characterized by field emission scanning electron microscopy (FESEM, Sirion 200), atomic force microscopy (AFM, Park NX10). A sputtering device (Quorum, Q150RS PLUS) was used to deposit the metal film. The substrates were dipped in the 4-ATP molecule solutions for overnight to conduct the SERS performance. The SERS performance was studied using a confocal microprobe Raman spectrometer (Renishaw Invia). Typically, the excitation lasers used here were 785 nm, 633 nm and 532 nm in wavelength, The laser power and the integral time was set at 1 mW and 5 s, respectively.

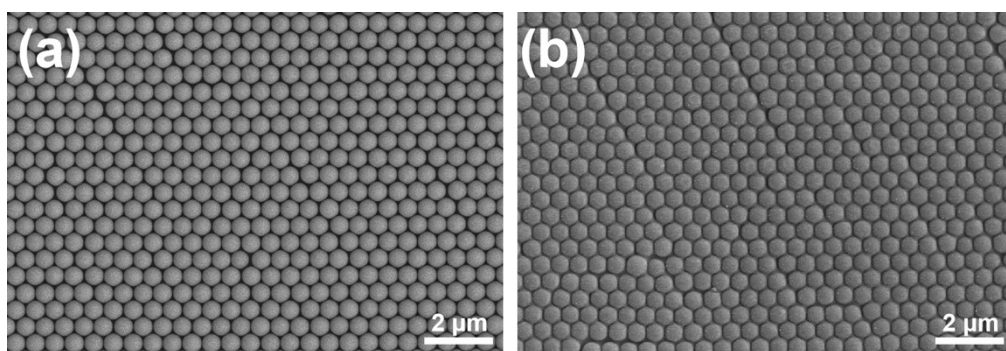


Fig. S1 SEM images of (a) the PS array and (b) the PDMS cured PS array.

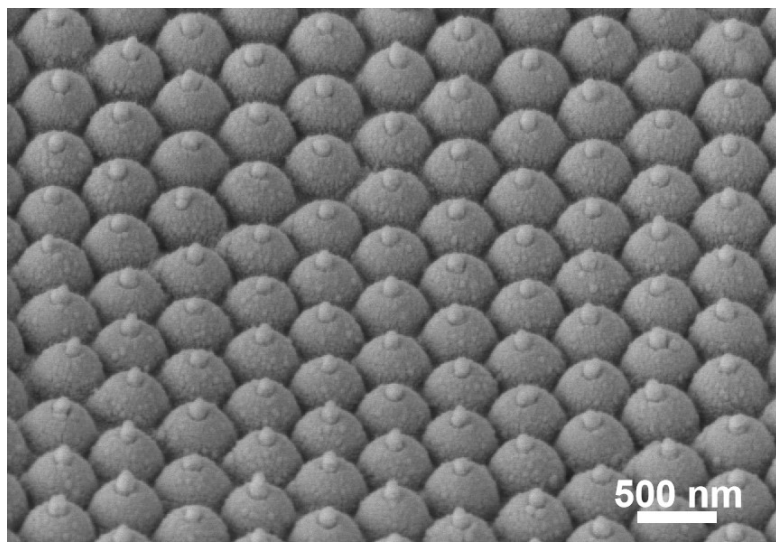


Fig. S2 SEM image of the high-density nanoneedle forest array viewed at 45°.

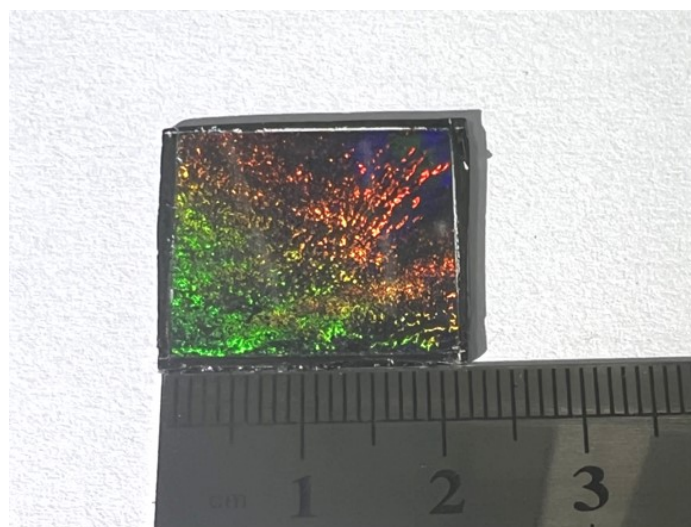


Fig. S3 Digital photograph of the high-density nanoneedle forest array on a large area (2 x 2 cm²).

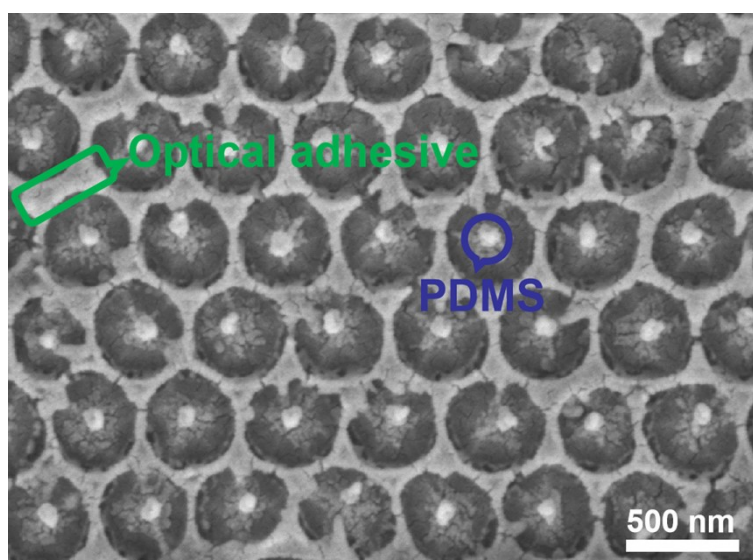


Fig. S4 SEM image of the nanoneedle forest structure obtained after 5 min of processing by an oxygen-plasma cleaner.

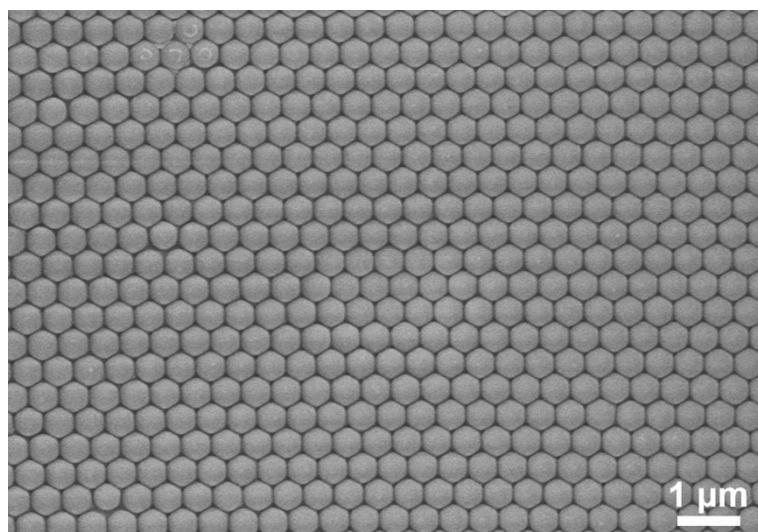


Fig. S5 SEM image of the array without nanoneedle forest structure prepared by PS array after UV irradiation.

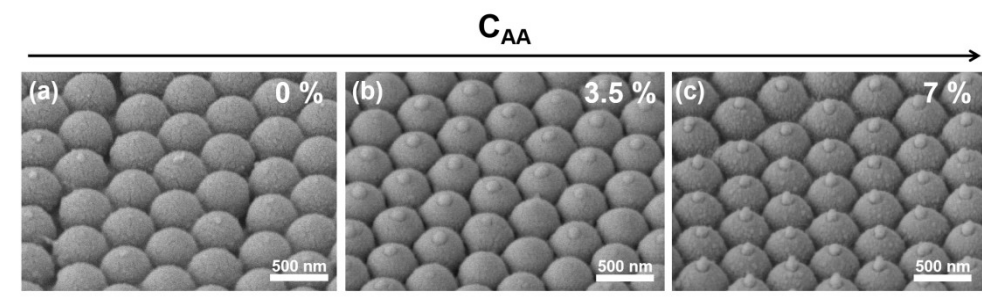


Fig. S6 SEM images viewed at 45° of the obtained arrays by using different content of AA: (a) 0 %, (b) 3.5 %, and (c) 7 %, respectively.

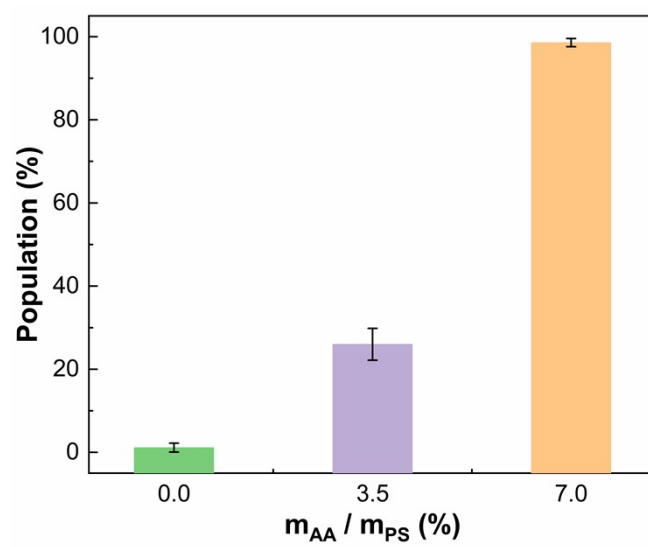


Fig. S7 The population content of the nanoneedle forest structure on PS array by using different content of AA.

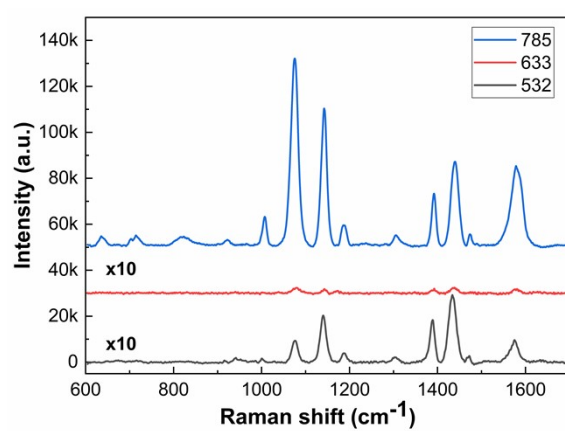


Fig. S8 The SERS spectra of of 10⁻⁷ M 4-ATP on the high-density Ag nanoneedle forest array under different wavelength laser (532 nm, 633 and 785 nm).

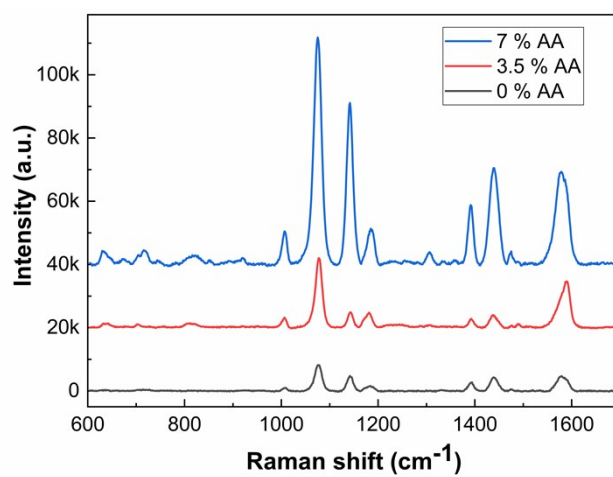


Fig. S9 SERS spectra of 10^{-7} M 4-ATP on the obtained array by using different content of AA: 0, 3.5, and 7 %, respectively.

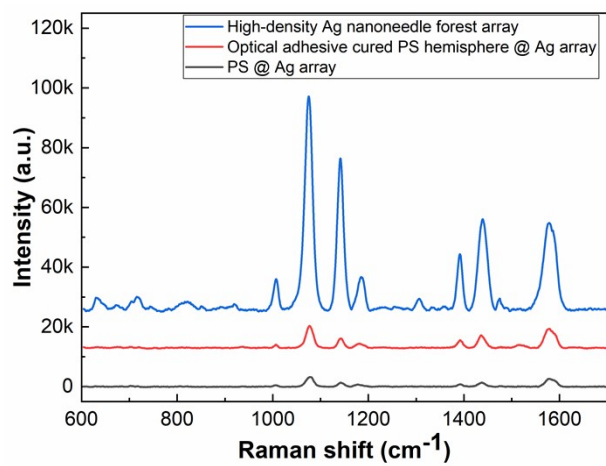


Fig. S10 The SERS spectra of 10^{-7} M 4-ATP on PS @ Ag array, optical adhesive cured PS hemisphere @ Ag array and the high-density Ag nanoneedle forest array.

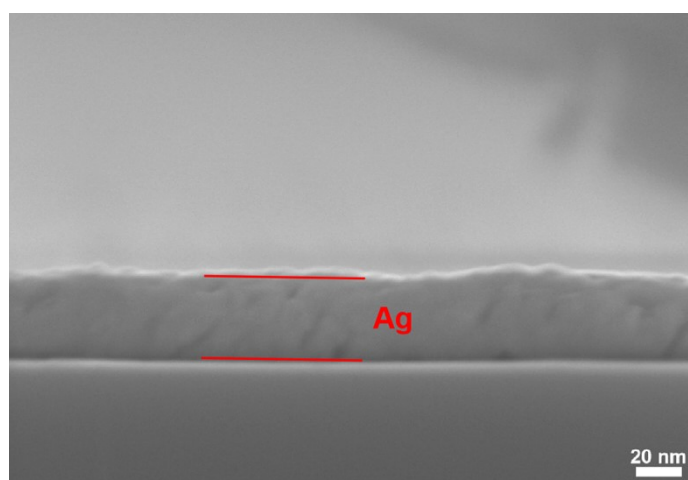


Fig. S11 Ag film with the thickness of 40 nm obtained with a deposition time of 10 mins. FESEM observation indicates that the sputtering rate of Ag was 4 nm/min.

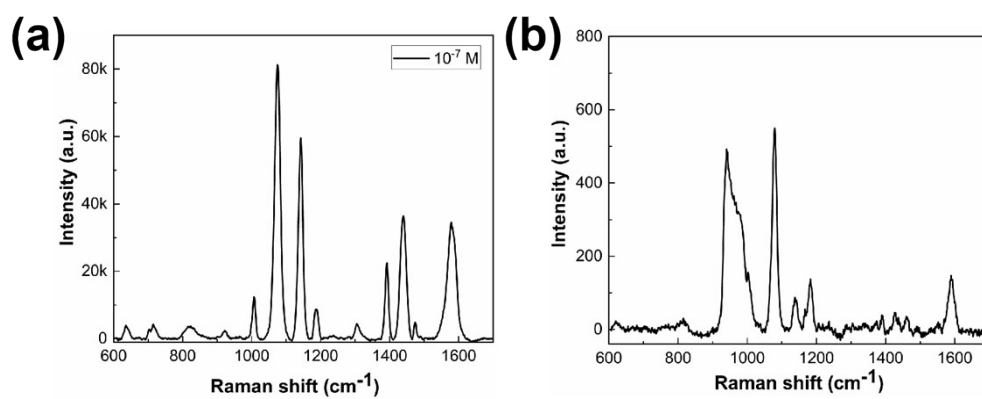


Fig. S12 (a) The NIR-SERS spectra of 5 μL 10⁻⁷ M 4-ATP on the high-density Ag nanoneedle forest array. (b) The SERS spectra of 5 μL 10⁻¹ M 4-ATP concentrations on blank silicon substrate.

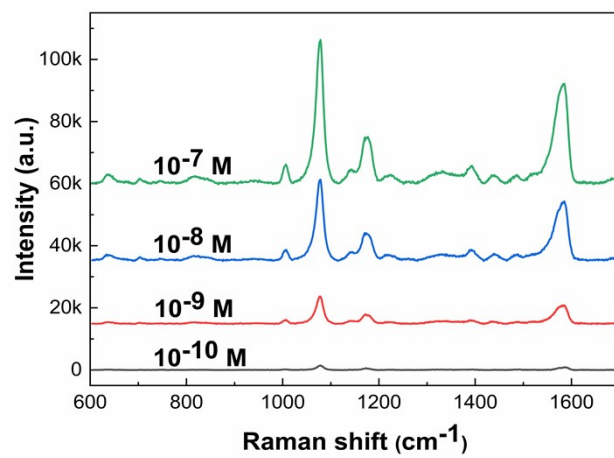


Fig. S13 SERS spectra of different 4-ATP concentrations on the high-density Au nanoneedle forest array.

Calculation of enhancement factor

The enhancement factor (EF) of the high-density Ag nanoneedle forest array was calculated by the following formula:

$$EF = (I_{SERS} / N_{SERS}) / (I_{Normal} / N_{Normal})$$

Here, I_{SERS} and N_{SERS} represent the SERS signal intensity of the major peak 1080 cm^{-1} of the high-density Ag nanoneedle forest array substrate and the number of 4-ATP molecules adsorbed on the high-density Ag nanoneedle forest array substrate, I_{Normal} and N_{Normal} represent the SERS signal intensity of the major peak 1080 cm^{-1} of the silicon wafer substrate and the number of 4-ATP molecules adsorbed on the silicon wafer substrate. The concentration of 4-ATP on the high-density Ag nanoneedle forest array substrate and the silicon wafer substrate were 10^{-7} M and 10^{-1} M , respectively, and the drop volume was $5 \text{ }\mu\text{L}$ and $5 \text{ }\mu\text{L}$ respectively. The values of I_{SERS} (81090 counts) and I_{Normal} (549 counts) were obtained by SERS test (Fig. S9a and 9b).

We assumed that the dropped 4-ATP molecules were evenly covered on the high-density Ag nanoneedle forest array and silicon wafer, the values of N_{SERS} and N_{Normal} can be estimated by the following formula:

$$N_{SERS} = 5 \times 10^{-6} \text{ L} \times 1 \times 10^{-7} \text{ mol/L} \times 6.02 \times 10^{23} \text{ mol}^{-1} \times \left(\frac{\pi d^2}{4 a^2} \right)$$
$$N_{Normal} = 5 \times 10^{-6} \text{ L} \times 1 \times 10^{-1} \text{ mol/L} \times 6.02 \times 10^{23} \text{ mol}^{-1} \times \left(\frac{\pi d^2}{4 a^2} \right)$$

Here, d represents the diameter of the laser spot, and its value is about $1 \text{ }\mu\text{m}$, a is the length of the side of the substrates, $a = 5 \text{ mm}$.

Therefore:

$$EF = 1.48 \times 10^8$$