Supporting Information

Electrostatic Self-Assembly of 2D Janus PS@Au Nanoraspberry Photonic-Crystal Array with Slow-Photon-Effect-Enhanced Near-Infrared SERS Activity

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Experimental section

Materials

Aqueous PS latex suspensions (2.5 wt.%, sulfonate ligand modification) with 500, 750 and 1000 nm in diameter were purchased from Alfa Aesar corporation. Silicon wafers and glass slides were purchased from ZhongNuo Advanced Material (Beijing) Technology Corporation. Ethanol (> 99.7%), acetone (> 99.5%), hydrogen peroxide (H_2O_2, 35%), concentrated sulfuric acid (H_2SO_4, 95%~98%), sodium chloride (NaCl, > 99.8%), hydrochloric acid (HCl, 36%~38%), sodium hydroxide (NaOH, > 96%), silver nitrate ($AgNO_3$, > 99.8%), chloroauric acid ($HAuCl_4$, 99.9%) and ethylene glycol (EG, >99.5%) were obtained from Sinopharm Chemical Reagent Corporation. Poly (diallyldimethylammonium) chloride (PDDA, M_w =100 000~200 000, 20 wt.% in water) and 4-ATP (4-Aminothiophenol) (97%) were purchased from Sigma-Aldrich. The deionized (DI) water was produced by a Milli-Q integral water purification system. All chemicals and solvents were directly used without any further purification.
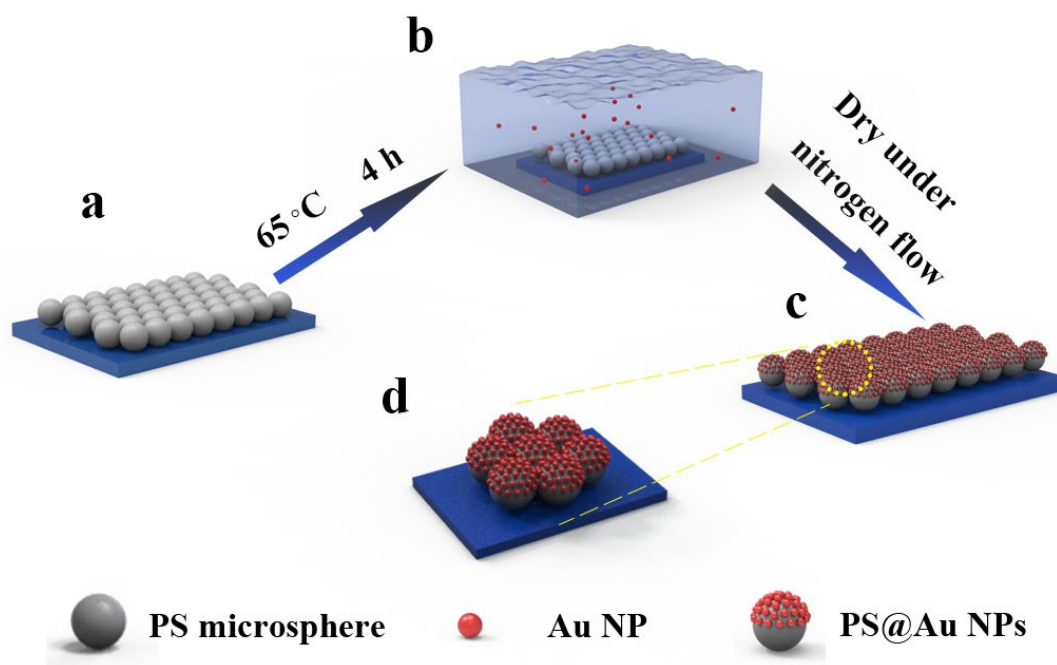
Preparation of PS photonic crystal arrays

As reported in our previous works,[1-3] the PS photonic crystal arrays with a ultra-large scale (10~100 cm^2) was obtained by an air/water interface self-assembly process. Briefly, glass slides were soaked in acetone, ethanol, piranha solution (H_2SO_4:H_2O_2=3:1), and water in sequence and sonicated for 15 min, and then dried under a nitrogen stream. After that, to obtain a super hydrophilic surface, these glass slides were treated in a UV ozone cleaner for 30 minutes. DI water was injected onto the glass surface, forming a certain thickness of water film. Then, aqueous PS latex suspension (mixed with ethanol 1:1 in volume) was gently and continuously dripped on the edge of the water film. After a while, the PS latexes were spontaneously

assembled into a close-packed monolayer array on the water surface. With the evaporation of the water, these PS monolayer arrays were transferred to a clean silicon wafer for further electrostatic attraction of Au nanoparticles.

Synthesis of Au nanoparticles

The Au nanoparticles with controllable sizes were synthesized by using an one-pot polyol-reduction method, as previously reported in our group[4-7]. Briefly, $HAuCl_4$ (1 M, 30 µL), PDDA (1.2 mL) and $AgNO_3$ aqueous solution (0.1M, 12 µL) were added into EG solution (60 mL) in a glass vial. The solution was stirred vigorously for 3 min, and then placed into an oil bath at 220 °C for 120 min without any disturbing. the color of the precursor solution was gradually changed into deep-wine red, indicating the formation of colloidal Au nanoparticles. After cooling to the room temperature, the final product was centrifuged at 10,000 rpm for 30 min and rinsed repeatedly with DI water for three times to remove the residual EG and PDDA surfactant.

Scheme. 1 Schematic illustration of the fabrication of 2D Janus PS@Au nanoraspberry photonic-crystal array. (a) 2D PS photonic-crystal array transferred on a silicon wafer. (b) The silicon wafer with PS array was immersed in the colloidal Au nanoparticle

solution at 65 ℃ for 4 h for the electrostatic self-assembly. (c, d) 2D Janus PS@Au nanoraspberry photonic-crystal array was obtained after dried under nitrogen flow.

Electrostatic self-assembly of 2D Janus PS@Au nanoraspberry photonic-crystal array

Scheme. 1 presents the schematic illustration of electrostatic self-assembly of 2D Janus PS@Au nanoraspberry photonic-crystal array. Firstly. the PS photonic crystal array transferred on the silicon wafer (about 1cm^2) was heated at 60 ℃ for 12 h to enhance the adhesion between the PS latexes and the wafer substrate. Meanwhile, Au nanoparticle suspension (50 µL), NaCl solution (0.2 M, 100 µL) and DI-water (3 mL) were added into a glass container and agitated uniformly. After that, the treated PS photonic-crystal array substrate was put into the container and then placed into a water bath (65 ℃) for 4 h, allowing the electrostatic self-assembly to take place. Since the PS latexes and Au nanoparticles have the opposite charges, the Au NPs would be spontaneously adsorbed onto the PS photonic-crystal array, forming a kind of Janus PS@Au nanoraspberry structure.[8, 9] The final assembled array was rinsed with DI water for three times to remove residual Au nanoparticles and dried under nitrogen flow.

Characterizations

The structure morphologies of the final samples were characterized by field-emission scanning electron microscopy (FE-SEM, Sirion 200). The optical absorption spectra of the products were recorded by an ultraviolet visible-near-infrared (UV−Vis−NIR) spectrophotometer (Varian, Cary 500). The optical reflection spectra of the products were recorded by the R1 angle-resolved spectroscopy system (R1-A-UV). The zeta potentials of Au nanoparticles and PS latexes were tested by a Zetasizer analyzer (NANOPLUS 3). The substrates were dipped in the 4-ATP or R6G 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 and 532 nm in wavelength, the integration time was 5 s and the laser power was set as 1.25 mW.

The influence of ionic strength on electrostatic repulsion is based on DLVO theory

According to the DLVO (Derjaguin, Landau, Verwey and Overbeek) theory,[10] the stability of colloidal solution is determined by the relative balance of two forces, namely the electrostatic repulsion of the same charge and the gravitational force generated by van der Waals force. When the repulsive force is greater than the gravitational force, the colloid is in a stable state, otherwise, a coagulation process will occur. The gravitational potential energy generated by van der Waals force between two spherical particles can be simply expressed by the following formula:[11]

$$V_A = -\frac{Aa}{12H}$$

Here, V_A is the van der Waals gravitational potential energy (the gravitational potential energy is specified as a negative value), a is the radius of the nanosphere, H is the distance between the two spheres, and A is the Hamaker constant. Since the Hamaker constant A and a are only related to the properties of the colloidal particles themselves, the gravitational potential energy V_A is a function related to the distance between particles.

The electrostatic repulsion between colloidal particles can be simply expressed as:[12]

$$V_B = \frac{64\pi a n_0 k_B T \gamma_0^2}{\kappa^2 e^{\kappa H}}$$

Here, V_B is the electrostatic repulsion energy, n_0 represents the ion concentration in the solution, k_B is Boltzmann's constant, T is the reaction temperature.

In the stern electric double layer model, the meaning of γ_0 is:[12]

$$\gamma_0 = \frac{\exp(ze\psi_\delta / 2k_B T) - 1}{\exp(ze\psi_\delta / 2k_B T) + 1}$$

Obviously, this value can be regarded as a constant.

In a given colloidal solution system, the value of κ is mainly related to the ion concentration n_0 in the solution, namely:

$$\kappa \propto \sqrt{n_0}$$

When the temperature T is constant, the electrostatic repulsion energy V_B can be simplified as the following expression:

$$V_B \propto \frac{1}{e^{\sqrt{n_0}\,H}}$$

Considering that H is always positive, as the ion concentration increases, the electrostatic repulsion energy will decrease significantly.
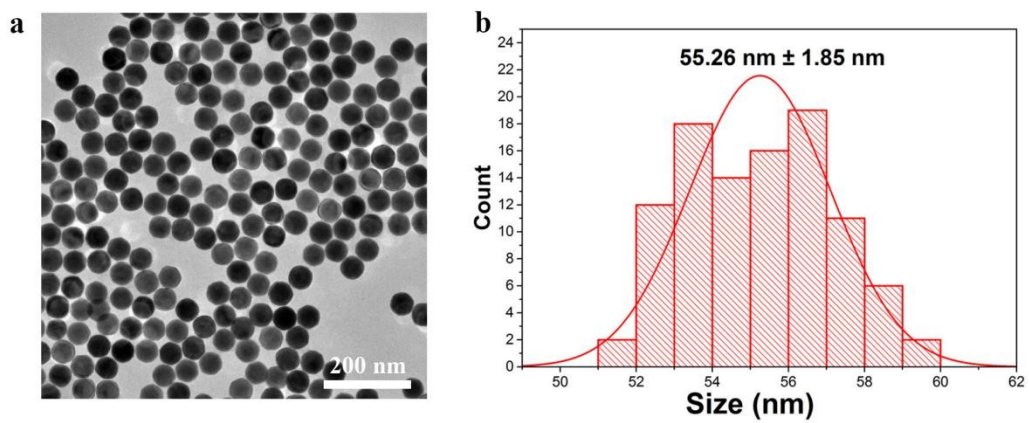
Fig. S1 (a) The TEM image of the Au nanoparticles. (b) The histogram of the size distribution of Au nanoparticles.
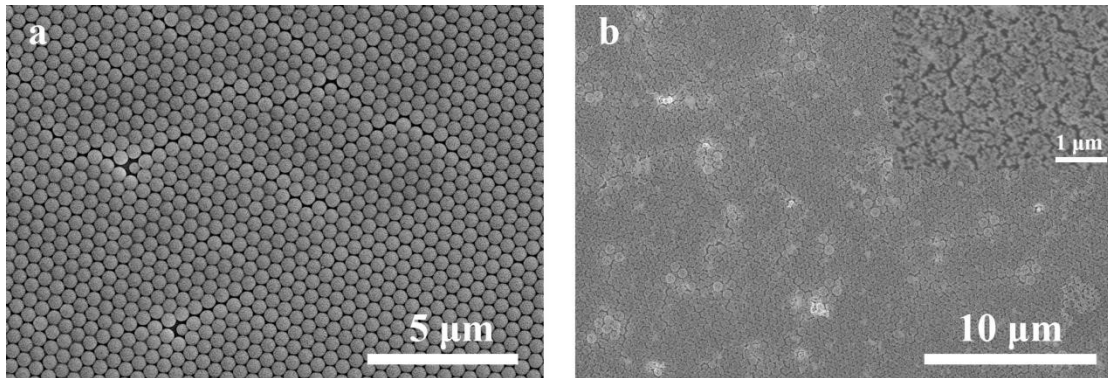
Fig. S2 (a) The low-magnification SEM images of the PS array before loading Au nanoparticles. (c) The low-magnification SEM images of the PS array after loading Au nanoparticles.
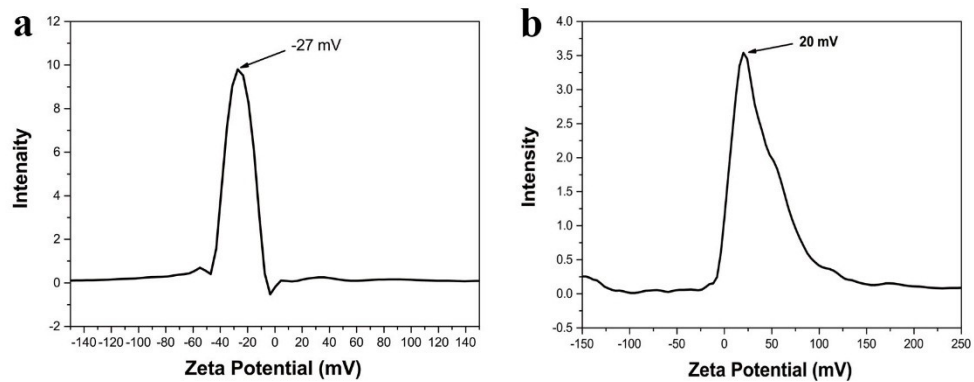
Fig. S3 The zeta potential of the aqueous Au nanoparticles (a) and the aqueous PS latexes (b).

Calculation of enhancement factor

The enhancement factor (EF) of 2D Janus PS@Au Nanoraspberry Photonic-Crystal Array was calculated by the following formula:[13]

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

Here, I_{SERS} and N_{SERS} represent the SERS signal intensity of the major peak 1078 cm^{-1} of the PS@Au NPs array substrate and the number of 4-ATP molecules adsorbed on the PS@Au NPs array substrate, I_{Normal} and N_{Normal} represent the SERS signal intensity of the major peak 1078 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 PS@Au NPs PC array substrate and the silicon wafer substrate were 10^{-8} M and 10^{-2} M, respectively, and the drop volume was 1 μL and 5 μL respectively. The values of I_{SERS} (53,103 counts) and I_{Normal} (83 counts) were obtained by SERS test (Fig. S4a and b).

Assuming that the dropped 4-ATP molecules were evenly covered on the PS@Au NPs PC array and silicon wafer, the values of N_{SERS} and N_{Normal} can be estimated by the following formula:

$$N_{sers} = 1 \times 10^{-6} L \times 1 \times 10^{-8} \, mol/L \times 6.02 \times 10^{23} \, mol^{-1} \times \left(\frac{\pi \dfrac{d^2}{4}}{S_1}\right) = 525.3$$

$$N_{Normal} = 5 \times 10^{-6} L \times 1 \times 10^{-2} \, mol/L \times 6.02 \times 10^{23} \, mol^{-1} \times \left(\frac{\pi \dfrac{d^2}{4}}{S_2}\right) = 1.182 \times 10^9$$

Here, d represents the diameter of the laser spot, and its value is about 1μm, S_1 and S_2 represent the area of the PS@Au NPs PC array and silicon wafer, assuming the area of the PS@Au NPs PC array and silicon wafer are 9 mm^2 and 20 mm^2 respectively.
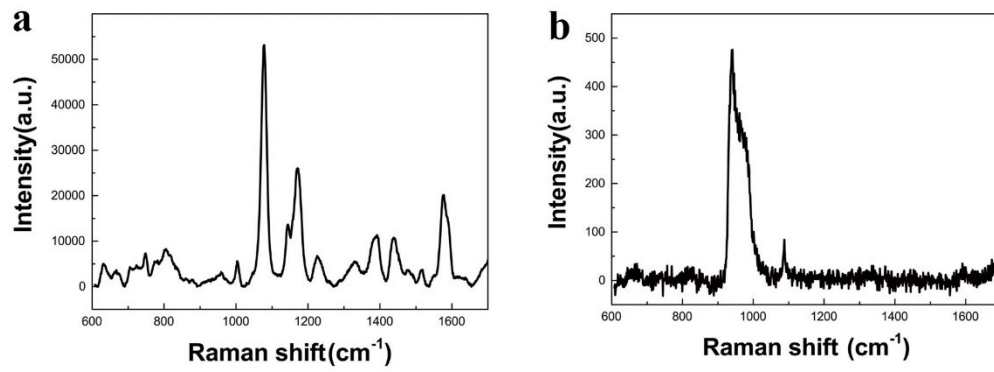
Therefore:

$$EF = 1.44 \times 10^9$$

Fig. S4 (a) The SERS spectra of 4-ATP (10^{-8}M) on the PS@Au NPs PC array substrate.

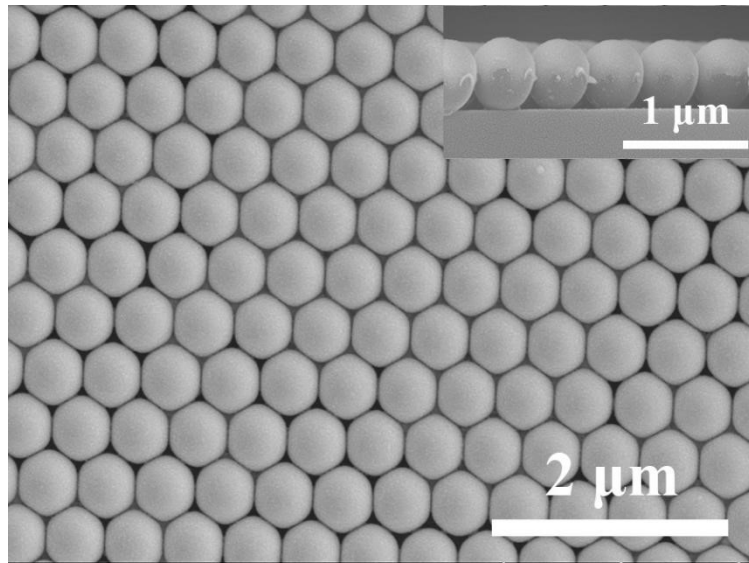(b) The SERS spectra of 4-ATP (10^{-2}M) on the silicon wafer substrate.

Fig. S5 SEM image of the PS photonic crystal array sputtered with a thin layer of gold film, and inset showing the corresponding cross-sectioned SEM image.
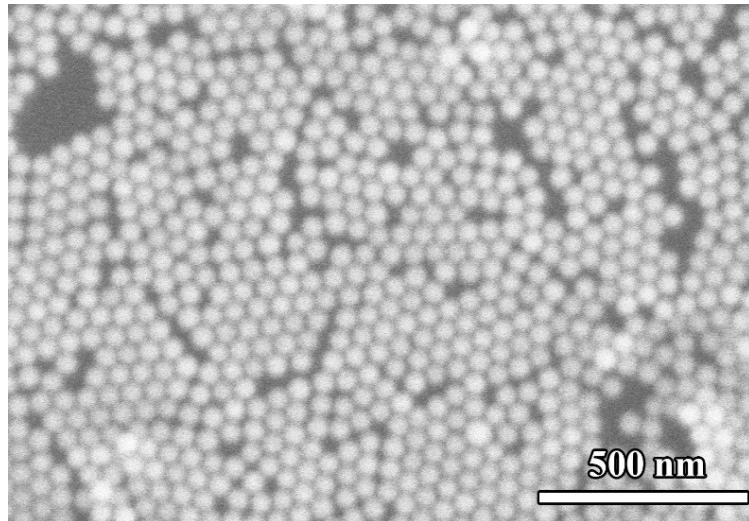
Fig. S6 SEM image of the 2D Au NPs array on the silicon wafer.

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