Fabrication of Long-range Ordered, Broccoli-like SERS Arrays and Application in Detecting Endocrine Disrupting Chemicals

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1. Field emission scanning electron microscopy (FE-SEM) images of SiO_2 colloidal crystal-assisted Ag surface-enhanced Raman spectroscopy (SERS) substrates at different deposition time.

Figure S1 reveals the corresponding FE-SEM images of Ag SERS substrates after deposition of Ag nanoparticles onto the SiO_2 colloidal crystal template for 90 s, 180 s, and 300 s, respectively. The nanostructure in Figure S1b presents a broccoli-shaped SERS array morphology. The nanoparticles with a close interparticle distance on each

"flower head", together with a greater roughness in Figure S1b suggest this broccoli-like nanostructure is an ideal SERS array. So 180 s was set as the deposition time used for the following deposition.

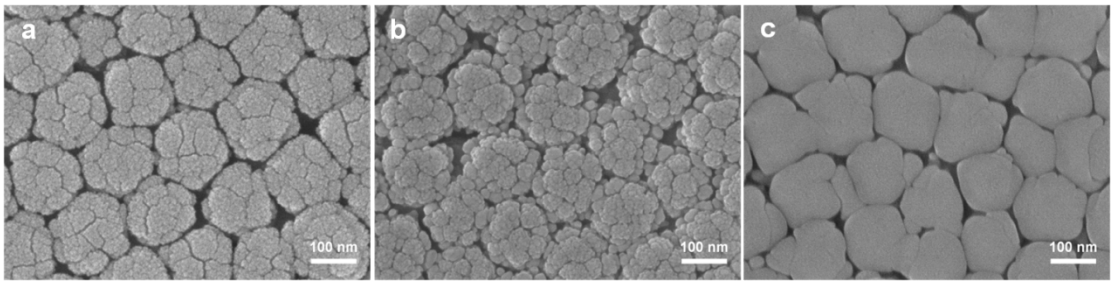

Figure S1 FE-SEM images of Ag SERS substrates after deposition of Ag nanoparticles onto the SiO_2 colloidal crystal template for (a) 90 s, (b) 180 s, and (c) 300 s, respectively.

2. Enhancement factors (EFs) calculation

The EF is one key factor to assess the performance of SERS substrates. Here, rhodamine 6G (R6G) was employed as the probe molecule. 10^{-2} M of R6G solution was used for normal Raman detection, and 10 μL of 10^{-4} M R6G solution was dripped onto SiO_2 colloidal crystal-assisted Au, Ag SERS substrates, respectively for SERS detection.

The most widely used definition for EF is[1]

$$EF = \frac{I_{surf}}{I_{bulk}} \times \frac{N_{bulk}}{N_{surf}}$$

where I_{surf} and I_{bulk} are the integrated intensities of R6G molecules adsorbed on the above Au or Ag SERS substrate and from 10^{-2} M of R6G bulk solution, respectively. N_{surf} and N_{bulk} are the corresponding numbers of R6G molecules adsorbed on the SERS substrate and in the bulk solution effectively illuminated by the laser beam, respectively.

$$N_{bulk} = Ahc_{bulk}N_A$$

where A is the area of the laser focal spot, h is the confocal depth of the laser, and h is 13 μm according to our previous work,[2] c_{bulk} is the concentration of R6G bulk solution, here c_{bulk}=10^{-2} M, N_A is the Avogadro constant.

Provided that R6G molecules were in monolayer adsorption on the Au and Ag SERS substrate:

$$N_{surf}=\frac{c_{surf}vN_AA}{\pi r^2}$$

where c_{surf} is the concentration of R6G solution for SERS, c_{surf}=10^{-4} M, v is the volume of R6G solution used for SERS detection, v=10 μL, r is the radius of 10 μL of R6G solution formed on the SERS substrate, r=3.5 mm.

Figure S2a, S2b are the normal Raman spectrum of 10^{-2} M of R6G solution and SERS spectrum of 10^{-4} M of R6G solution acquired from the above broccoli-shaped Au SERS substrate, respectively. The integrated intensities of the bands for I_{bulk} (1511 cm^{-1}) and I_{surf} (1508 cm^{-1}) are 646 and 144915 cps, respectively. Considering the different incident laser power for normal Raman spectrum and SERS spectrum acquisition, and the different number of molecules in each unit volume,[2] I_{surf} / I_{bulk}=144915×10^4 / 646.

Finally, the EF of this SiO_2 colloidal crystal-assisted Au SERS substrate can be calculated as 1.12×10^7.

The integrated intensity of the band for I_{surf} (1511 cm^{-1}) in Figure S2c is 187189 cps. Similarly, the EF of this SiO_2 colloidal crystal-assisted Ag SERS substrate can be calculated as 1.45×10^7. It should be noted that both the EFs of Au and Ag SERS arrays here refer to the spatially averaged values over the entire laser focal spot.[3]

Each SERS spectrum in Figure S2b, S2c is an average result of the five detections in Figure 2a, 2b, respectively.

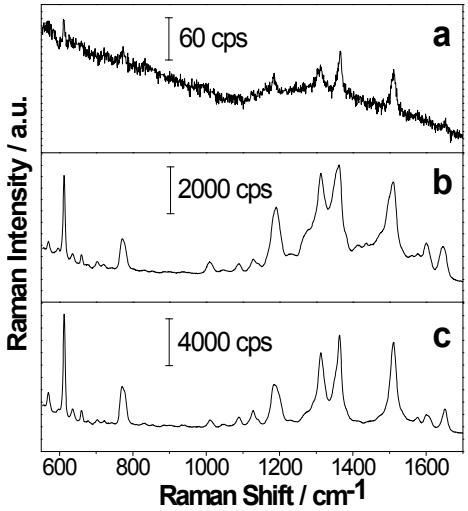

Figure S2 (a) Normal Raman spectrum of 10^{-2} M R6G solution. Laser power: 80 mW. SERS spectrum of 10^{-4} M R6G solution acquired from SiO_2 colloidal crystal-assisted (b) Au and (c) Ag SERS substrates (the deposition time were both 180 s), respectively. Laser power: 0.8 mW.

References

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