Supplementary Information

Porous Au–Ag hybrid nanoparticles array with broadband absorption and high-density hotspots for stable SERS analysis

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1. **Optimizing the reaction time of the galvanic replacement**

We investigated the Raman spectra and morphology of the porous Au-Ag hybrid NPs array with different reaction times from 0 min to 25 min. According to Fig. S1a, the SERS intensity grew up as the reaction time increased, and approached to constant for reaction time above 20 min. Fig. S1b-g displayed typical SEM images of the as-prepared porous Au-Ag hybrid NPs arrays with reaction time of 0, 5, 10, 15, 20, and 25 min. After 20 min reaction, the galvanic replacement reaction proceeded to completion and the topography of the porous Au-Ag hybrid NPs array went to stable. Therefore, we chose the reaction time of 20 min as an optimal one in the experiment.

Fig. S1 (a) The Raman spectra of the porous Au-Ag hybrid NPs array with a series reaction time from 0 min to 25min, the spectrum of sample with 0 min reaction time was multiplied by 10 folds. The SEM images of the Au-Ag hybrid NPs array with different reaction time: (b) 0 min, (c) 5 min, (d) 10 min, (e) 15 min, (f) 20 min, (g) 25 min, the scale bar is 200 nm.
2. Optimizing the thickness of the Ag film deposition

To obtain the optimal thickness of the Ag film deposition, we fabricated the porous Au-Ag hybrid NPs arrays with 70 nm, 85 nm, and 120 nm thickness of the Ag film deposition, and measured the Raman spectra, as shown in Fig. S2a. The SEM images of the three samples were presented in Fig. S2b-d. There was no distinct difference between the Raman spectra from 75 nm- and 85 nm-thick samples. However, the Raman spectrum was more enhanced for 120 nm-thick sample because the adjacent porous Au-Ag hybrid NPs were coupled and consequently more hot spots emerged. Furthermore, the coupling between the porous NPs also introduced some non-uniformity for the substrate array, which resulted in more SERS signal RSD. For example, the RSD of the porous Au-Ag hybrid NPs array increased from 7.7% to 10.9% as the thickness of Ag film deposition increased from 85 nm to 120 nm. Taking both the SERS EF and uniformity into consideration, we chose the thickness of Ag film deposition of 85 nm in the experiment.

Fig. S2 (a) The Raman spectra of the porous Au-Ag hybrid NPs array with different thickness of Ag film deposition. The SEM images of the Au-Ag hybrid NPs array with different thickness of Ag film deposition: (b) 120 nm, (c) 85 nm, (d) 70 nm, the scale bar is 200 nm.
Fig. S3 The SERS spectra of the porous Au-Ag hybrid NPs array under 633 nm laser excitation.