

# Electronic Supplementary Material

## Trapping analyte molecules in hotspots with modified free-standing silver bowtie nanostructure for SERS detection

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### Table of Contents

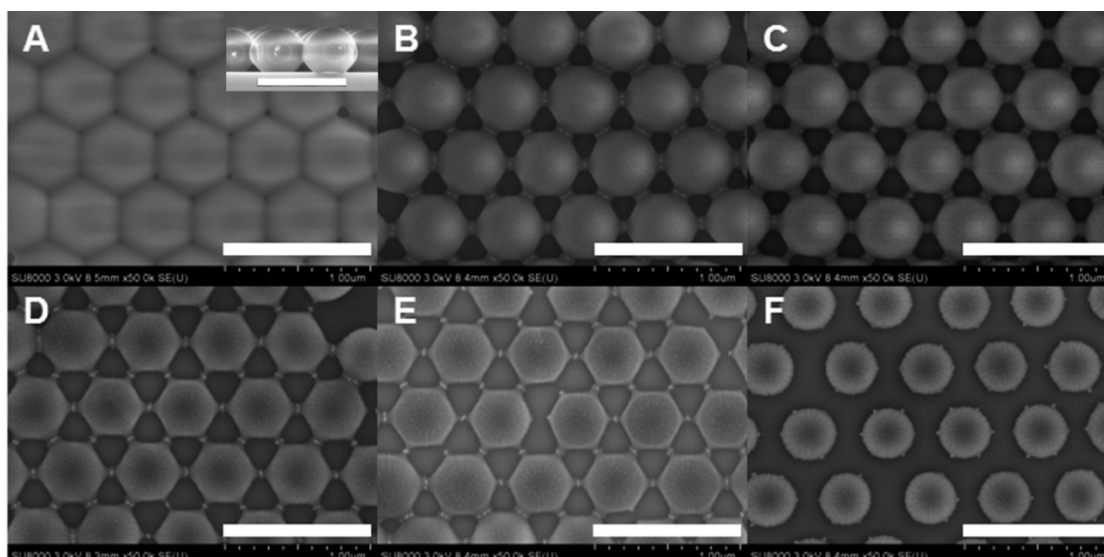
**Figure S1.** SEM images of PS spheres with different etching time.

**Figure S2.** SEM images of silver covered spheres after silver being dissolved for different durations.

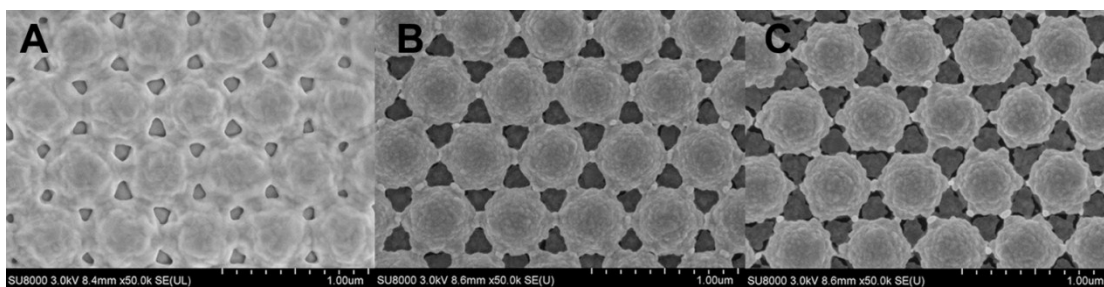
**Figure S3.** Comparison of Raman spectra collected on the substrates prepared with different dissolving time.

**Figure S4.** Correlation of Raman intensity and the dissolving time for preparing the SERS substrates.

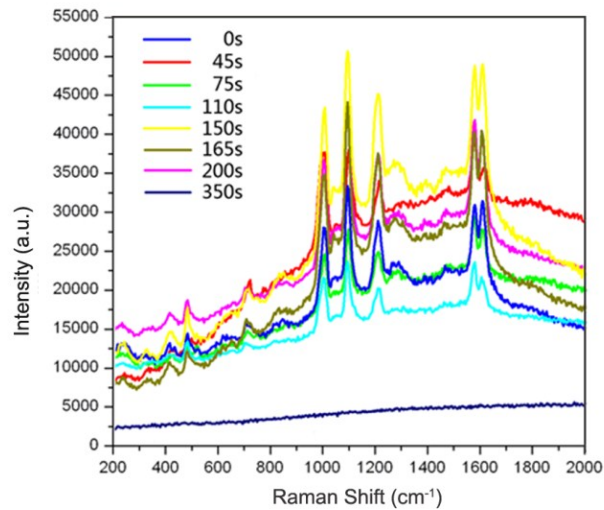
**Figure S5.** SEM images of PS spheres of disconnecting bridges before and after depositing silver film; Raman spectra collected on silver covered PS spheres with disconnecting bridges before and after being rinsed.



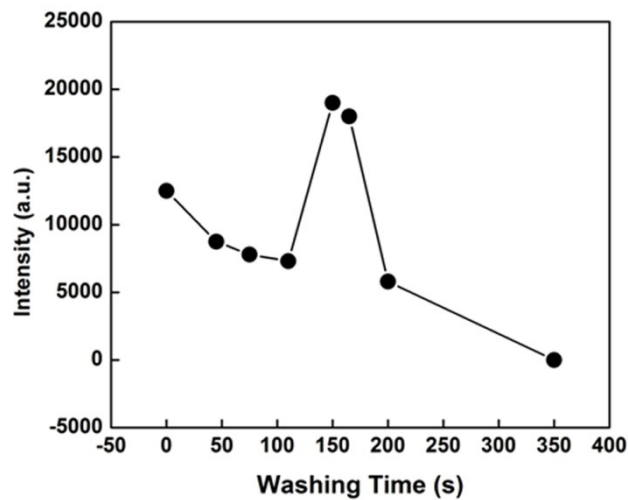
**Figure S1.** SEM images of PS spheres after etching for (A) 0 min, (B) 3 min, (C) 6 min, (D) 7.25 min, (E) 8 min, (F) 10 min , respectively. The scale bar is 1 $\mu$ m.



**Figure S2.** SEM images of silver covered spheres after silver being dissolved for (A) 0 s, (B) 75 s, (C) 150 s, respectively.



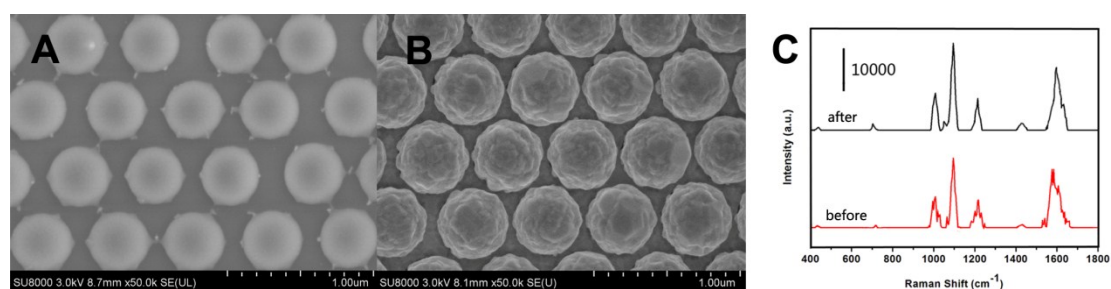
**Figure S3.** Comparison of Raman spectra collected on the substrates prepared with different dissolving time.



**Figure S4.** Correlation of Raman intensity and the dissolving time for preparing the SERS substrates.

To investigate the effect of dissolving time on the Raman intensities, we collected Raman spectra on 8 substrates prepared with different dissolving time, the spectra are shown in Figure S3. The Raman intensity decreases with extending the dissolving

time from 0 to 110 s because more silver being dissolved leads to a smaller oscillation momentum, which reduces the signal intensity. And then it greatly increases to the maximum with extending the dissolving time to 150 s because the nanogaps (less than 20 nm) are created on the bridges. After that, the intensity gradually decreases to zero with extending the dissolving time from 150 to 350 s because the nanogaps become larger and more silver is dissolved until the silver is completely dissolved. The correlation of Raman intensity and the dissolving time for preparing the SERS substrates is shown in Figure S4.



**Figure S5.** SEM images of PS spheres with disconnecting bridges (A) before and (B) after depositing silver film, (C) Raman spectra of  $10^{-5}$  M ( $10 \mu\text{L}$ ) 4-MPY collected on sample (B) before and after being rinsed. The laser of 532 nm is 7.92 mW. The

integration time is 1000 ms.

The detail of the SERS measurement:

We drop 10  $\mu\text{L}$  4-MPY aqueous solution on the substrate, after drying in atmosphere, SERS spectrum was collected as the one before rinsing process; after that, the sample was rinsed with water and dried in atmosphere and then a spectrum was collected as the one after rinsing process. The concentration of 4-MPY molecules is  $10^{-5}$  M. The laser of 532 nm is 7.92 mW. The integration time is 200 ms.