

Supporting information

High performance surface-enhanced Raman scattering from dummy molecular imprinting onto silver microspheres

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EXPERIMENTAL SECTION

Materials. Silver nitrate (AgNO_3), methanol, and acetic acid were purchased from the Tianda Chemical Reagent Plant (Tianjin, China). Methacrylamide, divinylbenzene (DVB), crystal violet, and azobisisobutyronitrile (AIBN) were obtained from Guangfu Chemical Industry (Tianjin, China). 3-Methacryloxypropyltrimethoxysilane (MPS) was obtained from Aladdin. Abietic acid was obtained from Aladdin. Acetonitrile was purchased from the Third Chemical Factory of Tianjin (Tianjin, China). Ascorbic acid and polyvinyl pyrrolidone (PVP) were purchased from the Tianjin Damao Chemical Reagent Factory (Tianjin, China).

Synthesis of Ag microspheres. 0.2 mL of 1 M AgNO_3 and 2 mL of 1M PVP aqueous solution were added to 10 mL of ultrapure water under strong stirring. After dissolved, 0.2 mL of 1M ascorbic acid was fast added into the mixture under stirring for 15 min. The obtained Ag microspheres were washed with water and ethanol, and then dried in vacuum at 40°C for 24 h.

MPS modified Ag microspheres. 500 mg Ag microspheres were added into the 40 mL mixture of ultrapure water and ethanol. Then 4 mL MPS was injected under nitrogen protection, and the resulting solution was heated at 40 °C for 24 h.

Synthesis of core-shell Ag@DMIPs microspheres. 1 mmol abietic acid, 4mmol

methacrylamide, 20 mmol DVB, and 20 mg AIBN were added into 20 mL of acetonitrile. Then 200 mg of modified Ag microspheres were dispersed in solution. The reaction was stirring 4 h at 70 °C under the protection of nitrogen. The resulting microspheres were washed with methanol-acetic acid (4:1, V/V) solution until no template molecule was detected in the washing solutions. Finally, the products were dried under vacuum at 40 °C for 24 h.

Synthesis of core-shell Ag@MIPs microspheres. Ag@MIPs was prepared by Ag@DMIPs method except that abietic acid was replaced with crystal violet.

Raman detection of the Ag@DMIPs. 20 mg Ag@DMIPs was soaked in different concentration CV ethanol solution of 4.0 mL and shaken in vibrator for 2 h. A drop of mixture was dispersed to an area about 40 mm² on a piece of clear glass substrate. Raman signals were detected after the sample complete dry.

Characterization. The products were characterized by X-ray diffractometer (XRD, Shimadzu XRD-6000) with Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$), transmission electron microscope (TEM, Tecnai G20 Philip), and scanning electron microscopy (SEM, Hitachi S-8010). SERS data was recorded by a Renishaw in Via micro-Raman spectroscopy system ($\lambda = 633 \text{ nm}$). The available laser power kept at 0.1 mW, and accumulation time were 10 s.

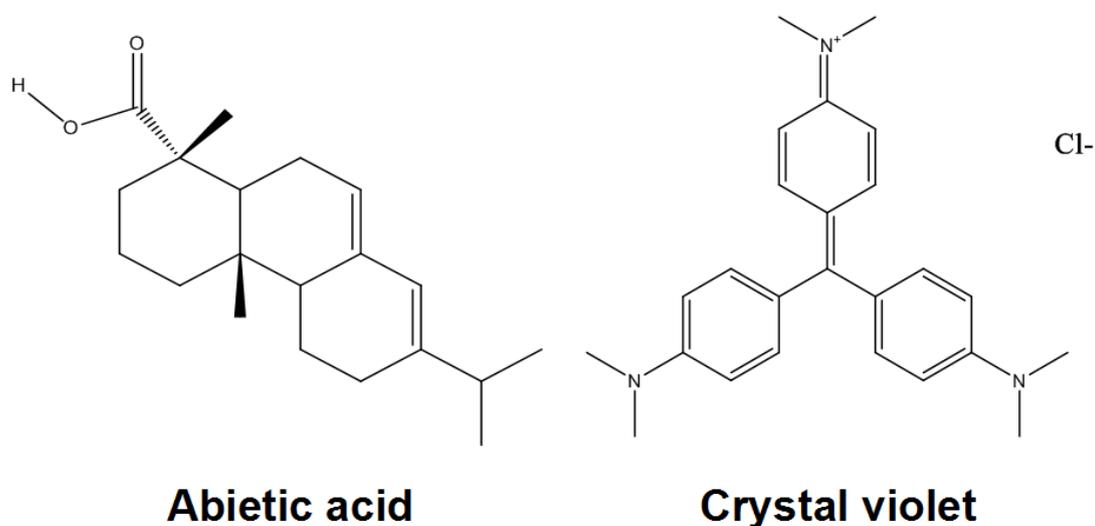


Fig. S1 Structures of abietic acid and CV.

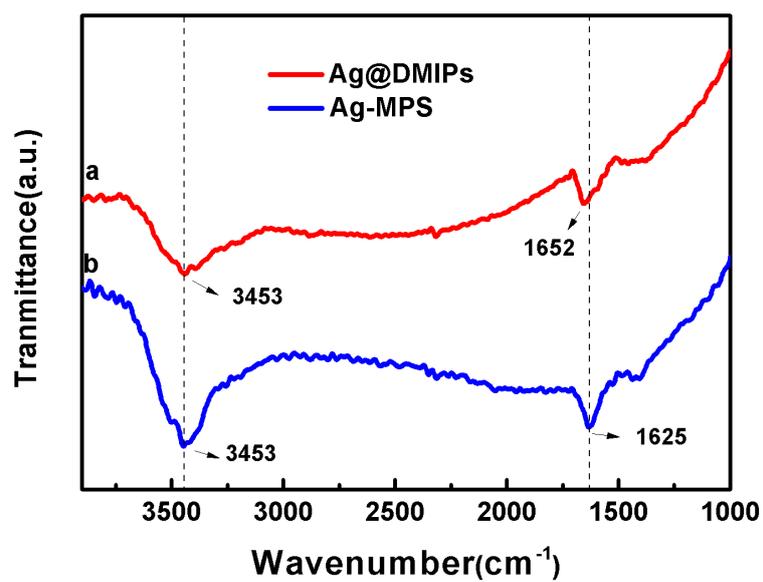


Fig. S2 FT-IR spectra of Ag@DMIPs(a) and Ag-MPS (b).

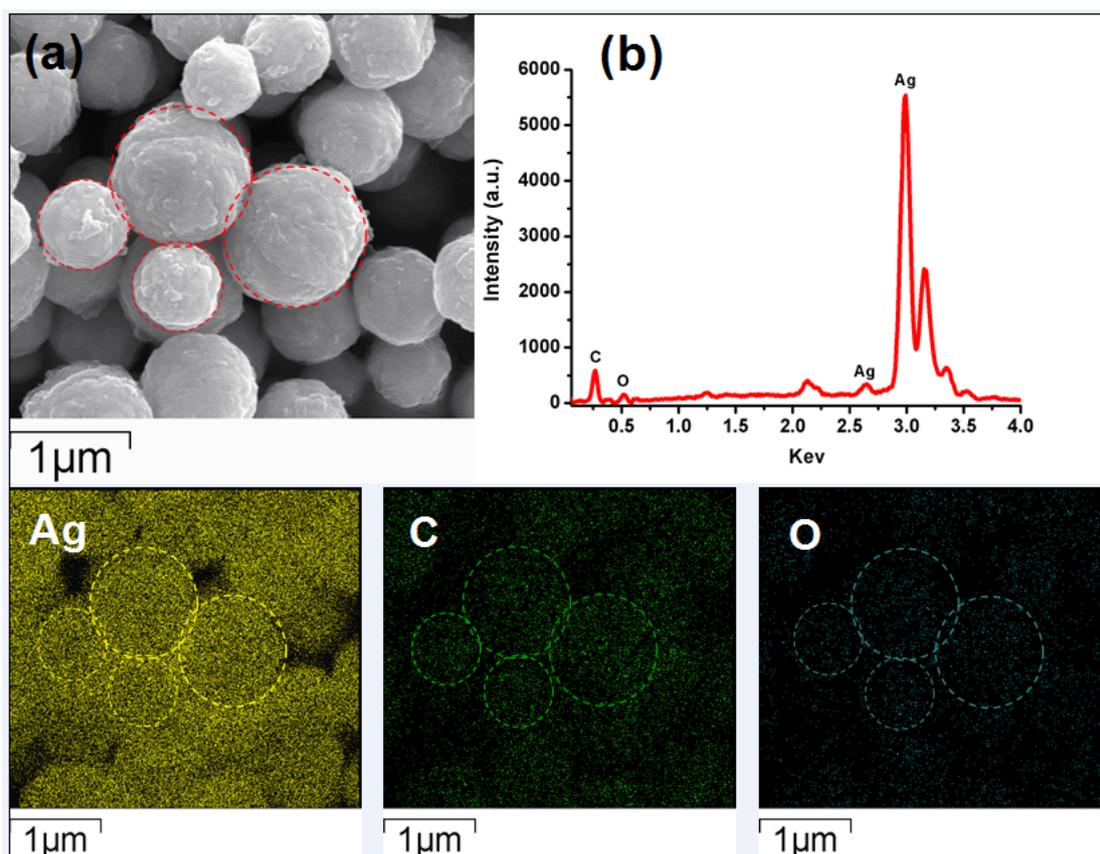


Fig. S3 SEM image (a) and EDS spectrum of Ag@DMIPs(b), and elemental mapping patterns for each element present in Ag@DMIPs.

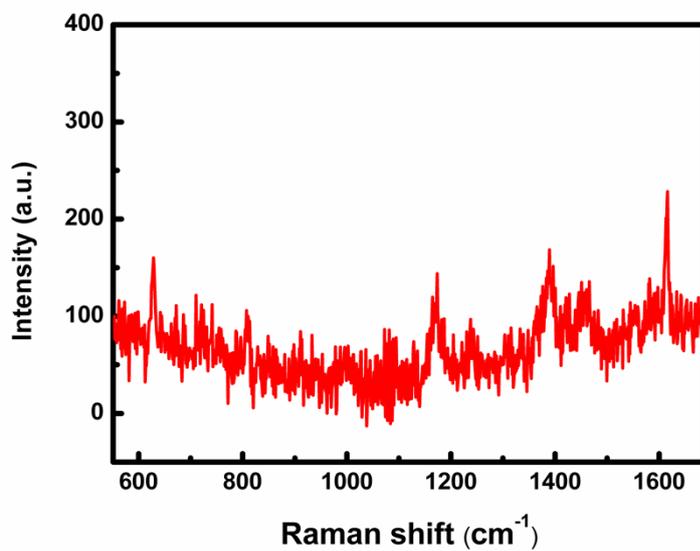


Fig.S4 SERS spectra of CV (10^{-9} M) obtained from the Ag@DMIPs.

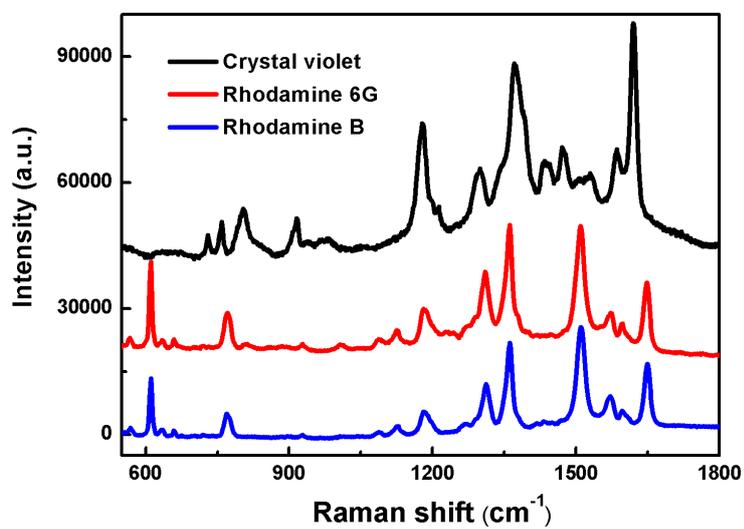


Fig.S5 Raman spectra of Ag@DMIPs in 10^{-3} Crystal violet, Rhodamine 6G and Rhodamine B ethanol solutions.

We synthesize a CV-template core-shell molecularly imprinted polymer (Ag@MIP) as a specific functional SERS substrate and detect the sensitivity of the Ag@MIPs (Fig.S6). The CV template molecules can't be totally removed from the MIPs layer, therefore the Raman spectrum of Ag@MIPs displays CV characteristic Raman peaks (Fig.S7).

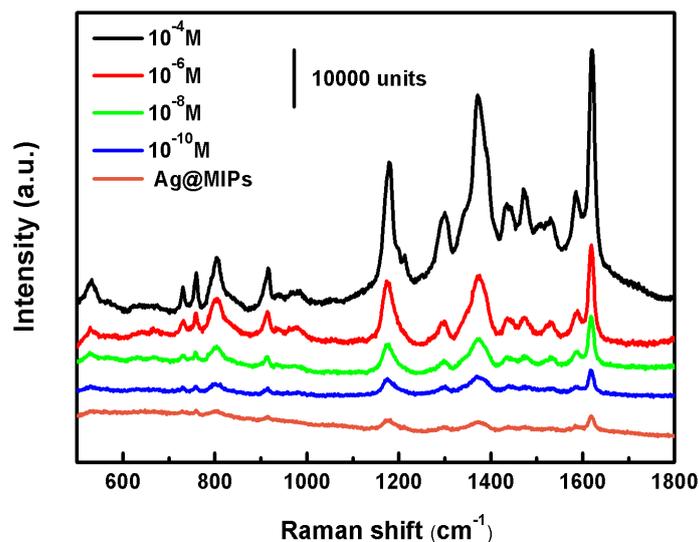


Fig.S6 SERS spectra of CV in different concentrations taken on the Ag@MIPs. Ag@MIPs represents the extracted Ag@MIP.

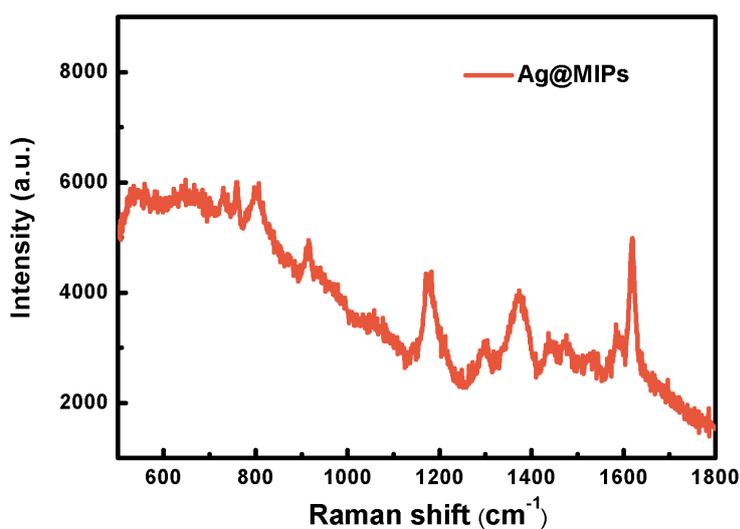


Fig.S7 Raman spectrum of Ag@MIPs SERS substrate after removing the CV template molecules.

SERS spectra of Ag@DMIPs and Ag@DMIPs in 10^{-8} M solution of CV were measured (Fig. S8), and found that SERS spectrum of Ag@DMIPs has no signals at 500-2500 cm^{-1} .

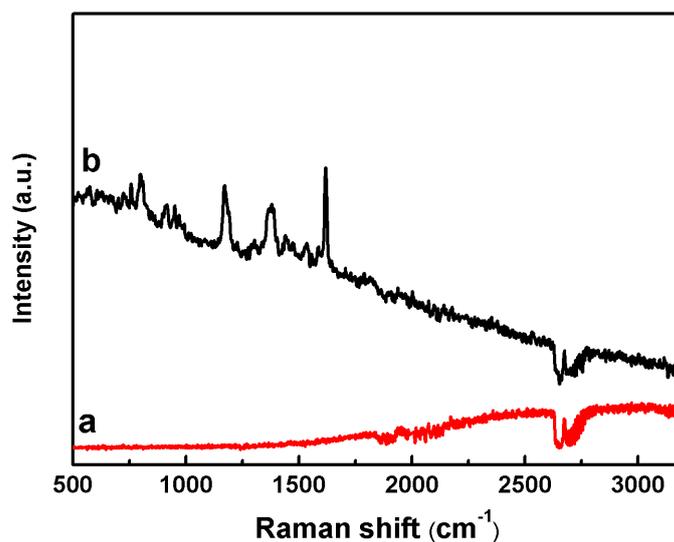


Fig.S8 SERS spectra of Ag@DMIPs (a) and Ag@DMIPs in a 10^{-8} M solution of CV (b).

Calculation of the enhancement factor (EF)

Following the reported procedure¹, and using the CV peak at 1618 cm^{-1} , we estimated enhancement factor (EF) according to the following equation:

$$EF = \frac{I_{SERS} / N_{SERS}}{I_{Nor} / N_{Nor}} \quad (1)$$

Where I_{SERS} and I_{Nor} represent the intensity of SERS spectrum and conventional Raman spectrum at the same band, N_{SERS} and N_{Nor} represent the corresponding number of CV molecules in the focused incident laser spot.

In our experiment, I_{SERS} and I_{Nor} were determined to be 12688 units (Fig.4) and 393 units (Fig.S6), respectively.

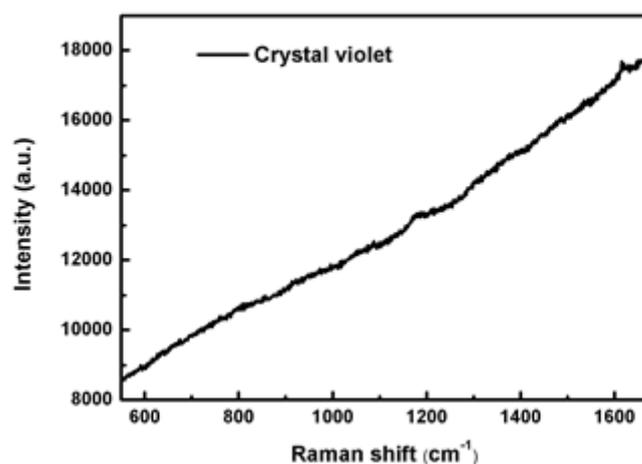


Fig. S9 The Raman spectrum of CV powder on glass slide.

According to the absorption intensity of CV solution with different concentration shown in UV-vis spectra (Fig.S7), we estimated that the effective numbers of CV molecules adsorbed on Ag@DMIPs surface in the laser spot of a dimension of 1 μm would be 4.45×10^7 .

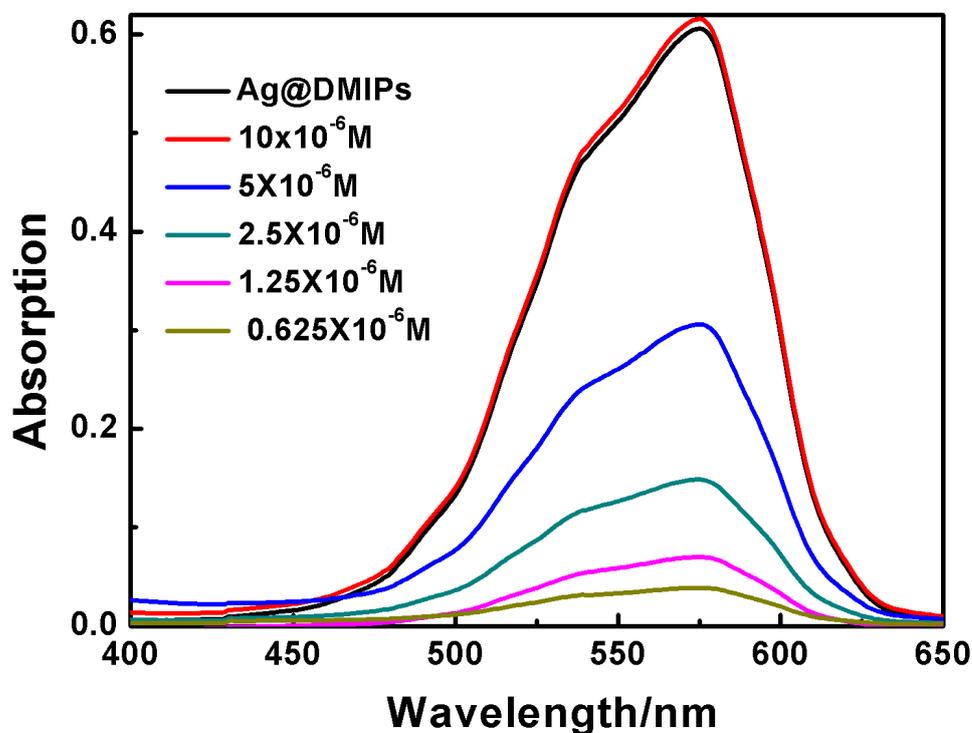


Fig. S10 UV-vis spectra of CV solution with different concentrations.

On the other hand, N_{Nor} can be estimated by the following expression:²

$$N_{Nor} = A_{obj} H_{obj} \rho_{Nor} \quad (2)$$

where A_{obj} represents the area of the laser spot of a dimension of $\sim 10 \mu\text{m}$ ($A_{obj} = \pi (5000)^2 \text{nm}^2$), H_{obj} is the height of the volume of CV contributing to the Raman signal, and ρ_{Nor} is the density of CV power (1.48×10^{21} molecules/cm³).

As shown in Fig. S8, H_{obj} can be calculated to be $77.88 \mu\text{m}$.³

Thus, we determined $N_{Nor} = 9.03 \times 10^{12}$.

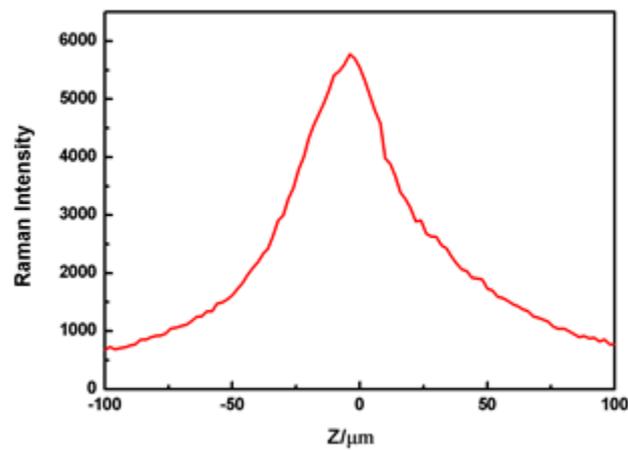


Fig. S11 Raman intensity-depth profile of the integrated intensity of 520 cm^{-1} band for a Si wafer.

Combined with the above results, this makes the EF to be 6.55×10^6 .

References

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