Supporting Information

Split-type Structure of Ag Nanoparticles and Al_2O_3@Ag@Si nanocone arrays:An Ingenious Strategy for SERS-Based Detection

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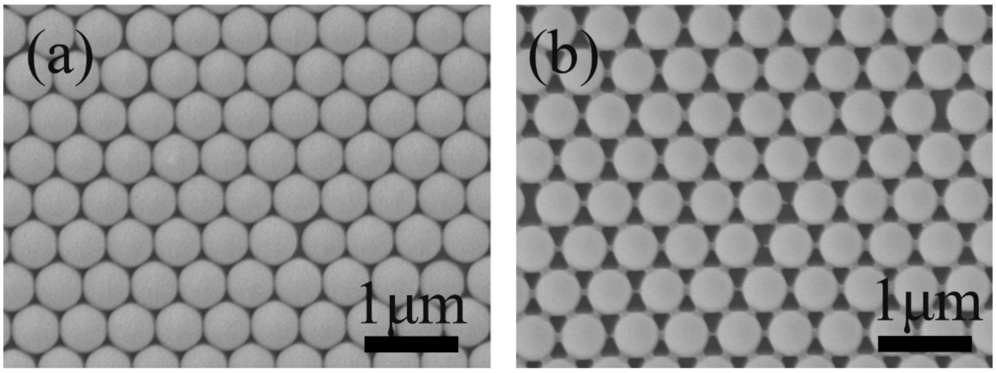

Fig. S1 (a) SEM image of the PS colloidal monolayer on a Si wafer. (b) PS monolayer after Plasma etching.

Firstly, through gas/liquid interface self-assembly, close-packed and uniform PS monolayer colloidal crystals were prepared on a cleaned glass substrate. The formed PS monolayer colloidal crystals kept in an oven at 120 ℃ for 2 min to make the PS pheres become planar and form contact with the silicon substrate. Etching was carried out using SF_6 plasma in a conventional RIE machine with a flow rate of 36 sccm, a pressure of 3.2 Pa, and a RF power of 200 W. The residual PS micro-spheres coated on the top side of the silicon nanocones were removed by immersion in methylene chloride (CH_2Cl_2) for 2 minutes. [1]

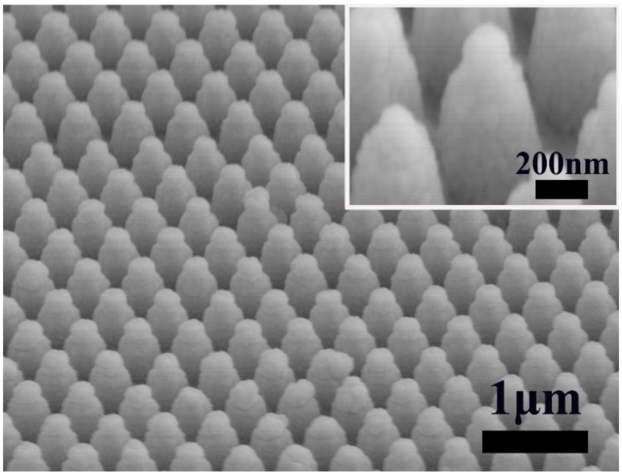

Fig. S2 SEM image of Ag@Si nanocone arrays coated with ultrathin 2 nm Al_2O_3 films by ALD.

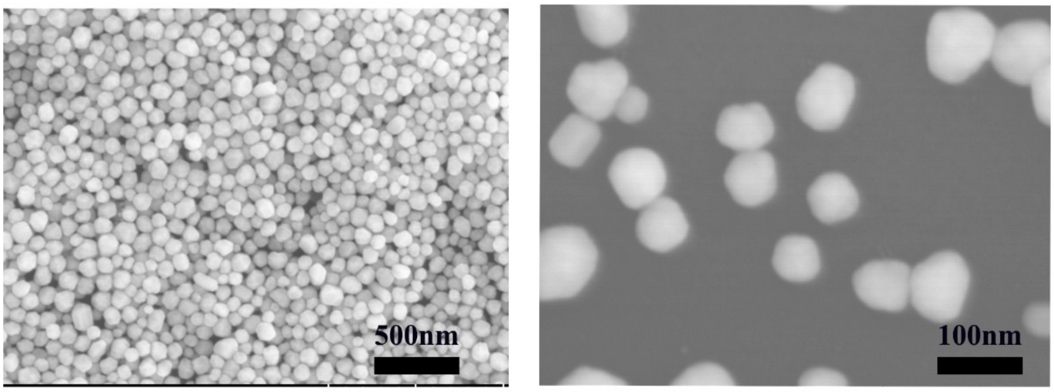

Fig. S3 SEM images of Ag- NPs prepared by liquid phase method.

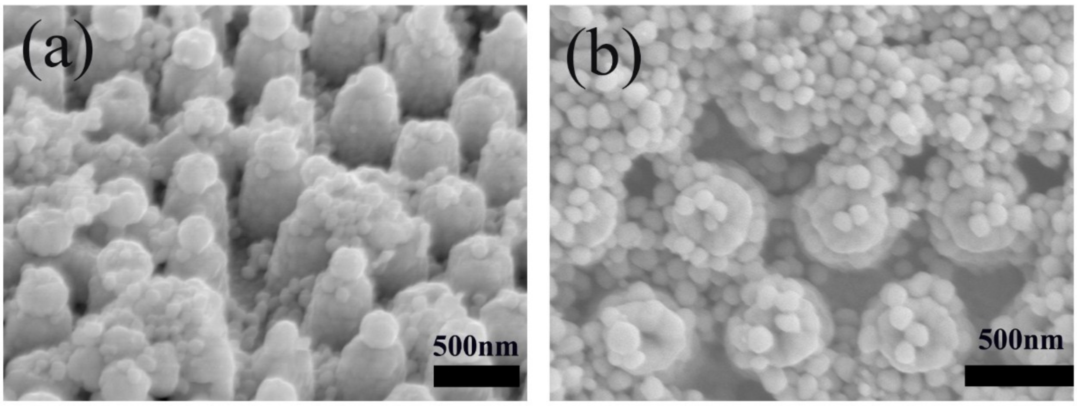

Fig. S4 SEM images of unmodified Al_2O_3@Ag@Si nanocone array combined with Ag-NPs.

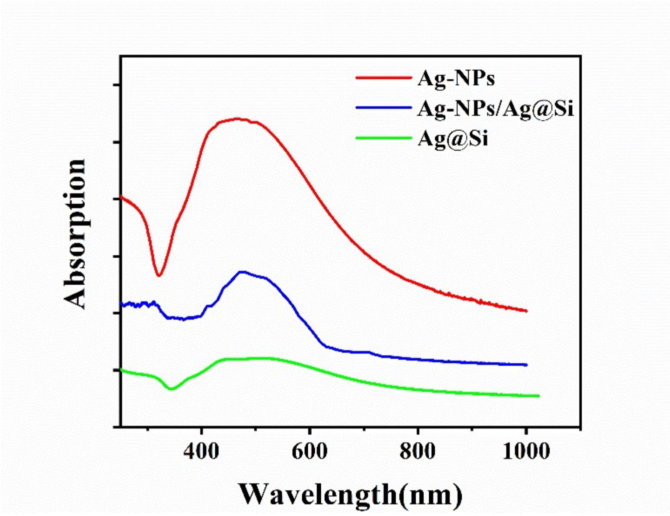

Fig. S5 UV–Vis–NIR absorption spectra of different Ag related substrates.

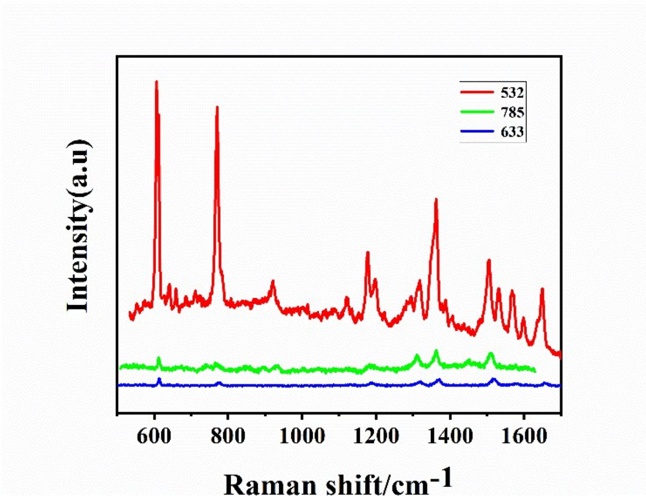

Fig. S6 SERS spectra of R6G (10^{-8} M) adsorbed on the split-type substrate examined by 532, 633, and 785 nm excitations.

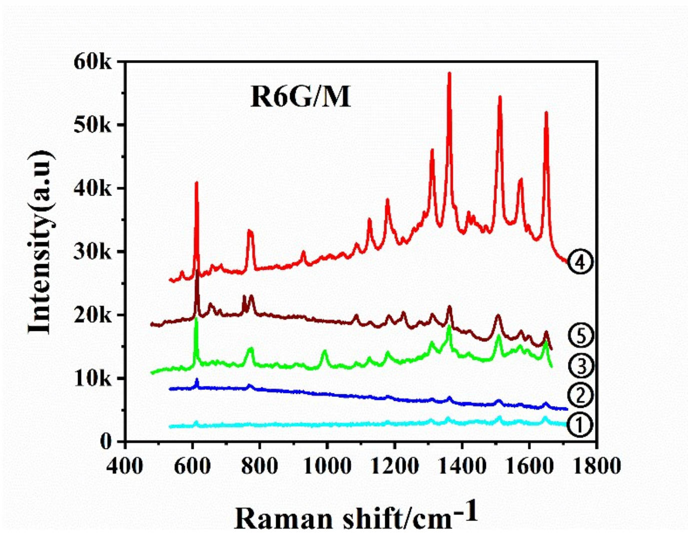

Fig. S7 Comparative SERS spectra of different Ag related substrates. ①Film of Ag NPs.②Ag@Si nanocone arrays without Ag-NPs. ③Ag-NPs@Ag@Si nanocone without Al_2O_3 shell.④ Ag-NPs@ Al_2O_3@Ag@Si array. ⑤Ag-NPs@ Al_2O_3@Ag film.

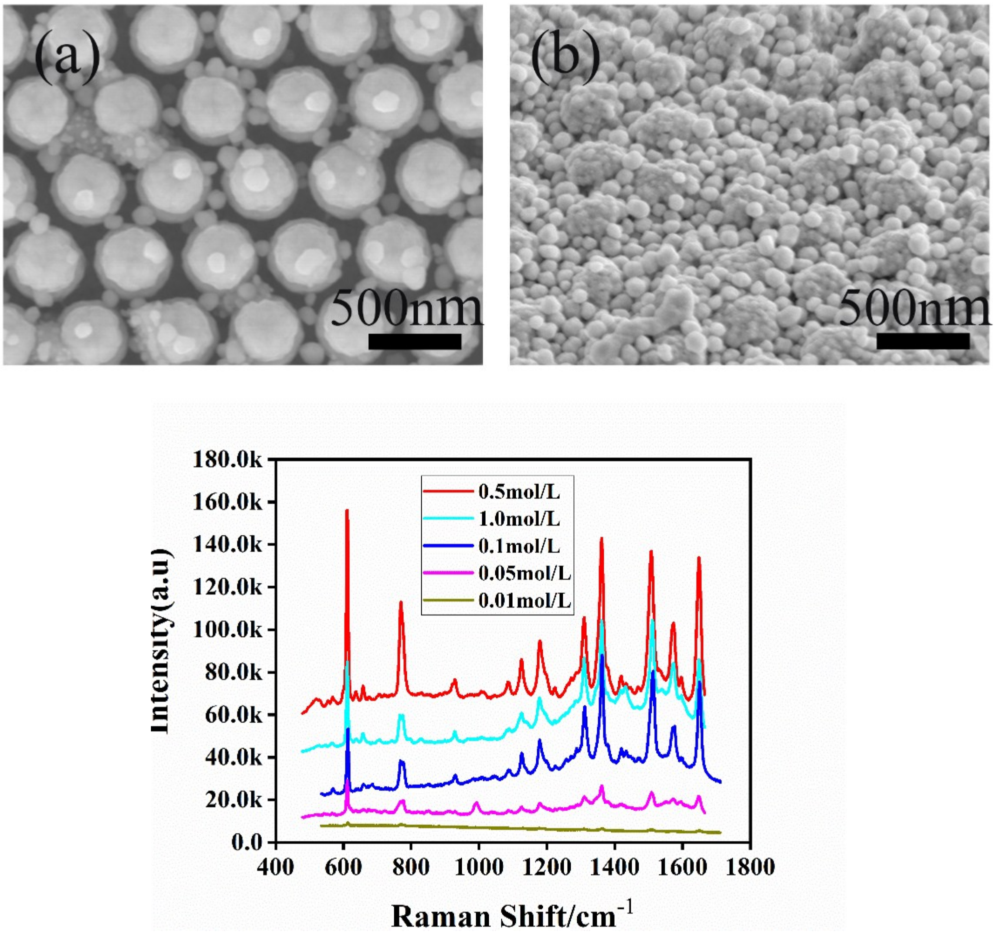

Fig. S8 SEM images of Ag-NPs@Al_2O_3@Ag@Si with low (a 0.05mol/L) and high (b 1.0mol/L) concentration. The following diagram shows raman spectra of R6G with Ag-NPs varied concentrations adsorbed on the split-type substrates.

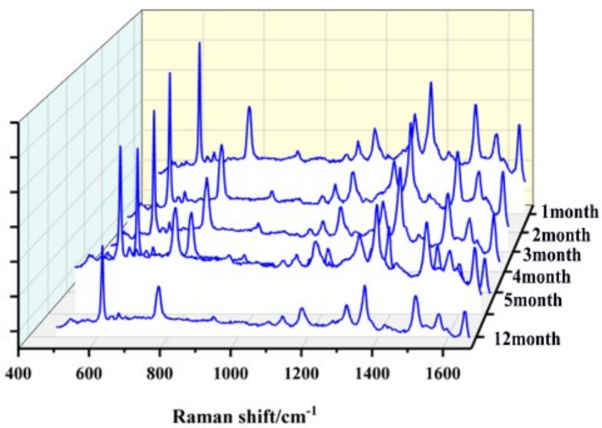

Fig. S9 Raman spectra of R6G (10^{-8} M) measured at different stock time.

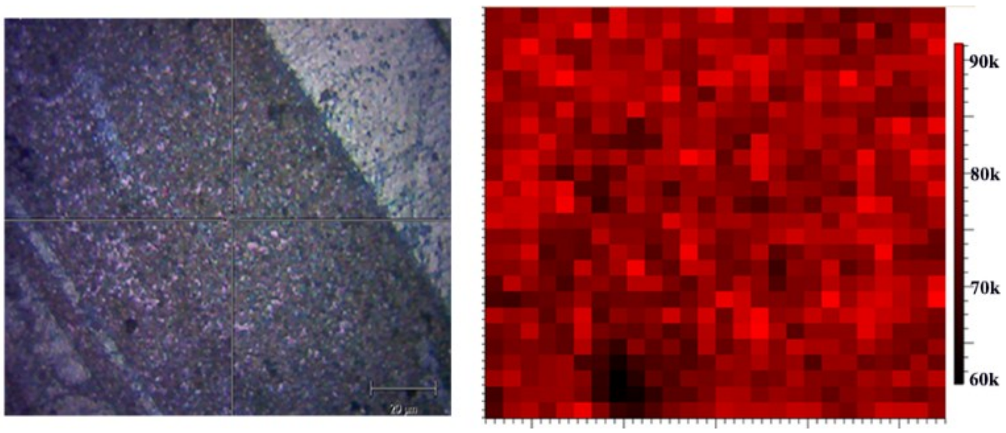

Fig. S10 Optical image of split-type substrates and SERS mapping of 4-ATP on the area.

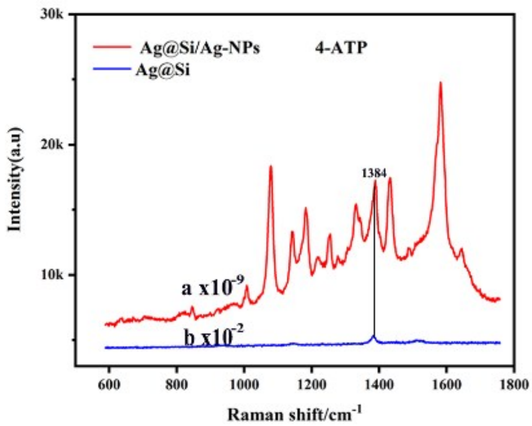

Fig. S11 SERS spectrum of the split-type substrate (upper curve) and normal Raman spectrum of 4-ATP.

$EF=(I_{SERS}/N_{SERS})(I_{RS}/N_{RS})^{-1}$ Considering the area of laser spot is the same, the foregoing equation thus simply are transformed into: $N_{SERS=}(C_{SERS*}V_{SERS}) /S_{SERS}$ SERS spectra of 5 μL 10^{-9} M 4-ATP ethanol solution dispersed on split-type substrates with area of 25 mm^2 (a) , and (b) Raman spectrum of 4-ATP obtained by dispersing 1 μL 10^{-2} M 4-ATP ethanol solution on 25 mm^2 Ag@Si wafer.

I_{SERS} and I_{NRS} correspond to the integrated SERS and NRS intensities, respectively, normalized for acquisition time and laser power. The average surface of a nanocone (with an average diameter of 200 nm and an average length of 500 nm) is $S_{SERS}500\times100^2\pi/3=$ 1.66×10^6 (nm^2) .S_{NRS} $=200\times200=$ 4×10^4 (nm^2) .So EF = $(I_{SERS}/N_{SERS})/ (I_{NRS}/_{NNRS}) = [1.3\times10^4\times1.66\times10^6/(1\times10^{-9})]/[(3.1\times10^3\times4\times10^4/(1\times10^{-2})] =$

6.96×10^9.

References

1 Q. Zhao, G. Liu, H. Zhang, F. Zhou, Y. Li, W. Cai, *J Hazard Mater*, 2017, **324** 194-202.