

**Synergistic effect of “stellate” mesoporous SiO<sub>2</sub>@Au nanoprobe and coffee-ring-free hydrophilic-hydrophobic assembly substrate in ultrasensitive SERS-based immunoassay of tumor marker**

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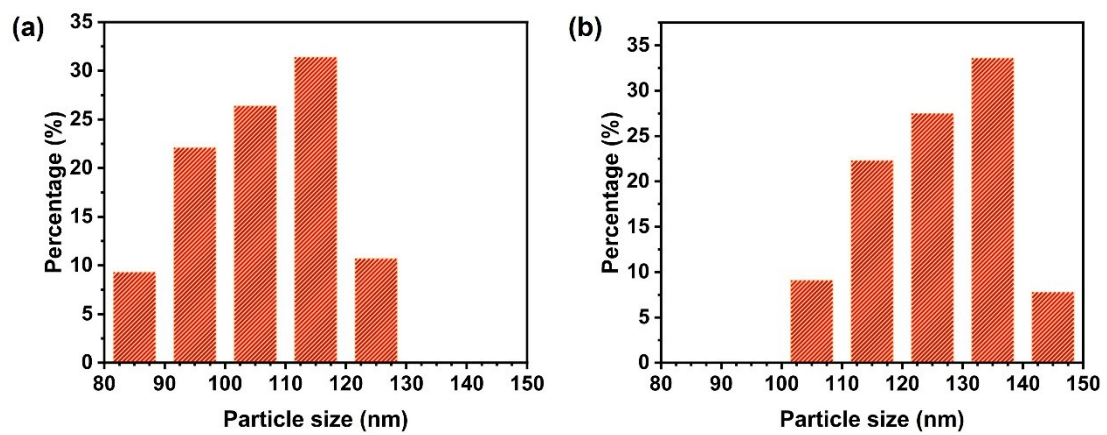


Fig. S1 Size-distribution histograms of (a) SMSiO<sub>2</sub> and (b) SMSiO<sub>2</sub>@Au NPs.

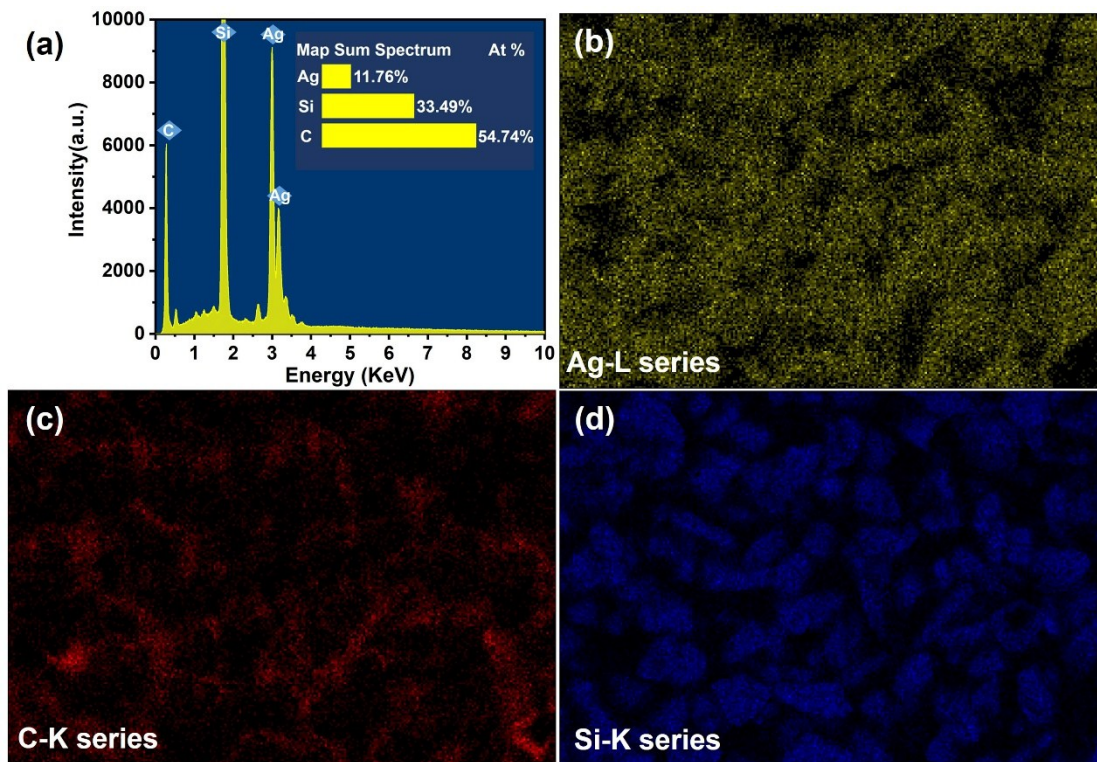


Fig. S2 (a) EDS of Ag-coated sandpaper and the corresponding local elemental mapping of (b) Ag, (c) C, and (d) Si.

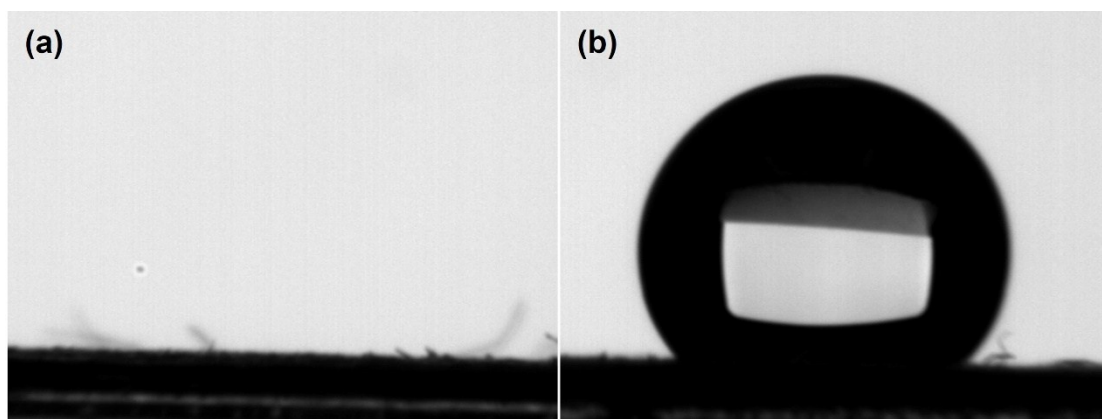


Fig. S3 Water CAs of filter paper (a) before and (b) after hydrophobic treatment.

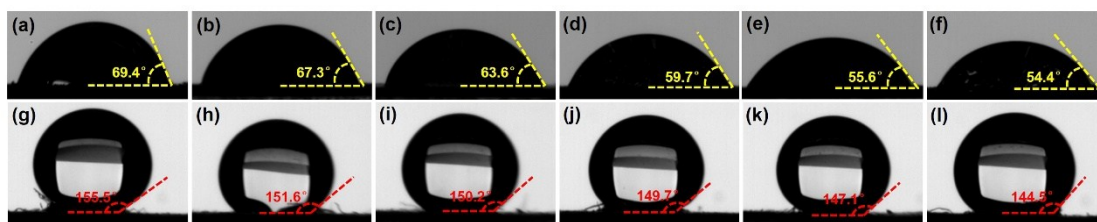


Fig. S4 Water CAs of the hydrophilic-hydrophobic SERS-active structure using Ag-coated sandpapers with different grit sizes of (a, g) 120, (b, h) 220, (c, i) 800, (d, j) 1500, (e, k) 3000, and (f, l) 7000 mesh before (up) and after (down) assembly.

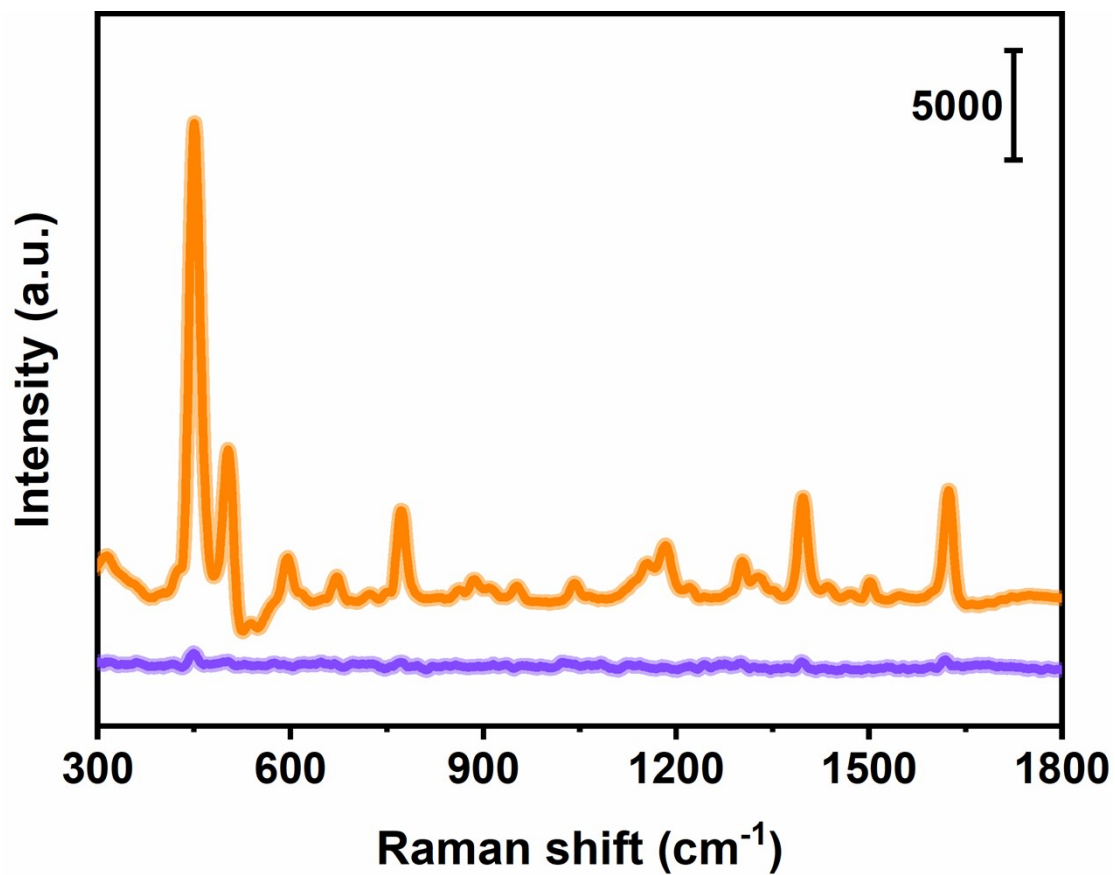


Fig. S5 SERS spectrum of MB on the SERS-active substrate and Raman spectrum of MB powder.

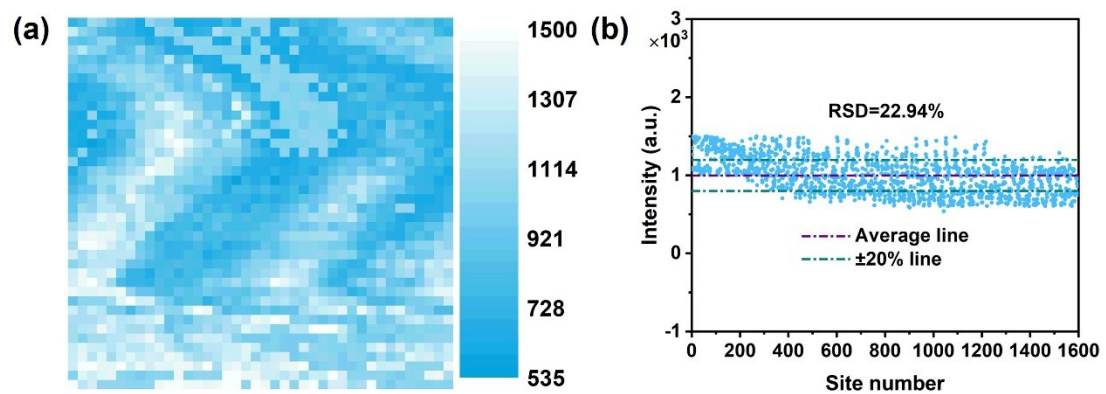


Fig. S6 (a) SERS mappings and (b) the corresponding intensity distribution of the peak at  $451\text{ cm}^{-1}$  recorded from the substrates before assembly modified by MB.

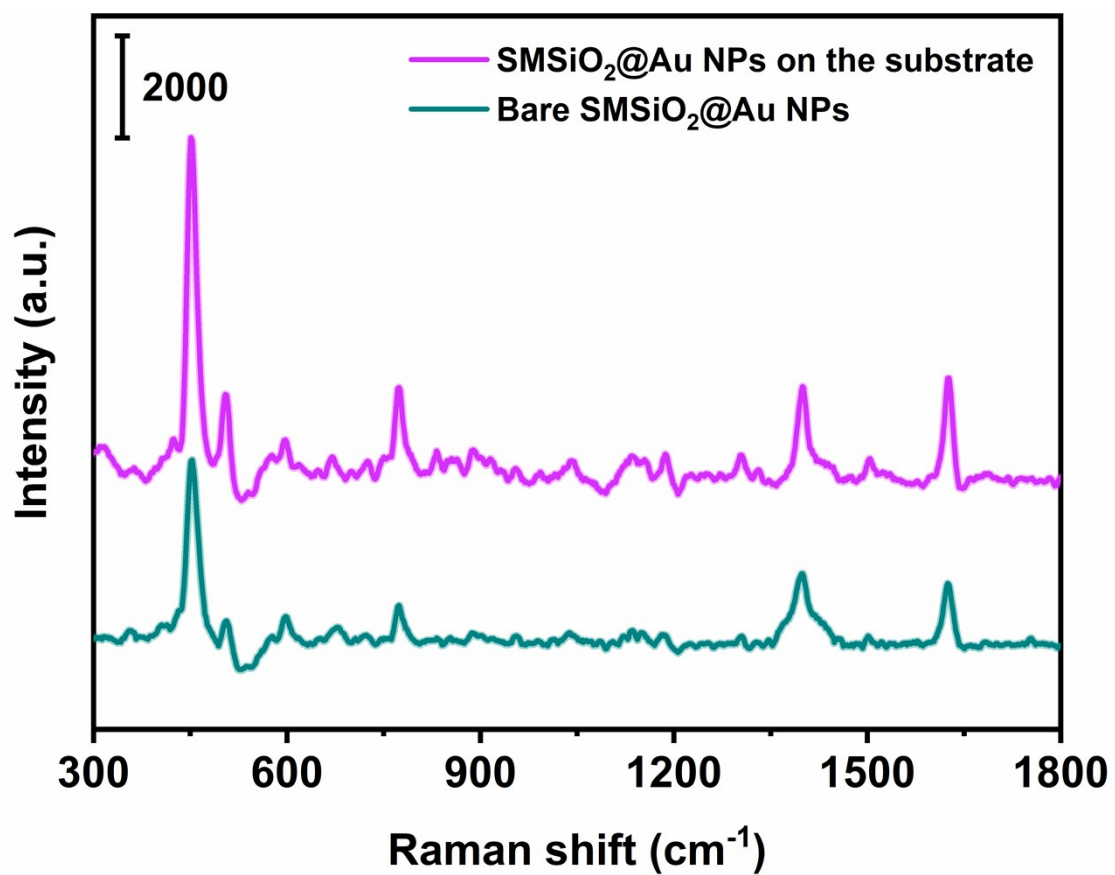


Fig. S7 SERS spectra of SMSiO<sub>2</sub>@Au NPs modified with MB molecules (0.5 mM) dropped onto the hydrophilic-hydrophobic substrate without immunoreaction and bare SMSiO<sub>2</sub>@Au NPs.