Supplementary information for Research Article:

Three Dimensional Porous SERS Powder for Sensitive Liquid and Gas Detections Fabricated by Engineering Dense "Hot Spots" on Silica Aerogel

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Fig. S1 The dependence of Ag nanoparticles size and coverage on the AgNO₃ concentration. (a), (b) and (c) demonstate the SEM images of AgNPs-SA and the corresphonding magnified view under the AgNO₃ concentrations of 10 mM, 20 mM and 30 mM, respectively. The concentrations of sodium citrate were all 4 mM.



Fig. S2 The cross-sectional SEM images of AgNPs-SA particle. (a) and (b) The optical micrographic images of AgNPs-SA particle before and after being cut open by micromanipulator. (c) The SEM image of the crushed AgNPs-SA particle. (d) The magnified SEM image of the cross section.



Fig. S3 The EDS mapping analysis of AgNPs-SA particle. (a) The surface morphology of a representative AgNPs-SA particle. (b) The cross-sectional SEM image of the AgNPs-SA particle shown in (a). (c) The elemental mapping of Ag corresponding to the particle in (a). (d) The elemental mapping of Ag corresponding to the region indicated by the rectangle in (b).

Preparation of AgNPs aggregates

Firstly, silver colloid was synthesized by the citrate reduction method. 90 mg of AgNO₃ was dissolved in 500 mL boiling deionized distilled water, then 10 mL of 1% sodium citrate solution was added dropwise under vigorous stirring over a period of ~45 minutes. The mixture was then kept boiling for ~30 minutes with continued stirring and cooled down to room temperature. Then, 0.5 M NaCl (20 mL) was added into the silver colloid (300 mL). After stirring for 5 min, the silver colliod turned to black, which indictaed the formation of silver nanoparticles (AgNPs) aggregates. Finally, the sediments (AgNPs aggregates) were collected and dried for use.



Fig. S4 Nitrogen adsorption-desorption isotherms of silica aerogel (a) collapsed-aerogel (c) and AgNPs-SA powder (e). (b), (d) and (f) present the corresponding pore size distributions and cumulative pore volume calculated from Barrett-Joyner-Halenda (BJH) theory on the basis of nitrogen desorption data. The isotherms were measured with a Micromeritics ASAP 2460 system at 77.3 K.



Fig. S5 The normalized UV-Vis extinction spectrum of AgNPs-SA powder. A broad band with peak at around 510 nm is observed. Hence, 532 nm laser was chosen for optimal SERS excitation.

SERS enhancement factor (EF) estimation

Generally, the SERS EF can be evaluated by the equation as follow:

$$EF = \frac{I_{SERS}}{I_{Bulk}} \times \frac{N_{Bulk}}{N_{SERS}}$$
(1)

where I_{SERS} and I_{Bulk} are the intensity of a Raman mode with and without surface enhancement, respectively, N_{SERS} and N_{Bulk} refer to the corresponding number of analyte molecules. In SERS measurements, 3 mg of AgNPs-SA powder was added into 10 ml R6G alcohol solution (1.0×10⁻¹⁰ M). Then, the 20 µL of precipitate was dropped on Si slice (5 mm×5 mm) and dried under ambient condition for SERS measurements. For Raman sample preparation, 20 µL of R6G alcohol solution (10⁻³ M) was directly dropped on a Si slice (5 mm×5 mm), and dried for use. Here, we assumed that R6G molecules are distributed homogeneously on the Si slices. Hence, the number of R6G molecules contribute to the SERS or Raman signal can be calculated by the equation:

$$N = N_A C_{R6G} V_{solution} S_{laser} / S_{Si}$$
(2)

where N_A is the Avogadro number, C_{R6G} is the concentration of R6G solution, $V_{solution}$ is the volume of the droplet, S_{laser} and S_{Sl} represent the area of laser spot and Si slice, respectively. Both the SERS and Raman measurements are performed under identical experimental conditions with the excitation 532 nm, power 70 μ W, integration time 10 s and 50×objective. According to the SERS and Raman data in Fig. S6, the EF can be estimated to be as large as 1.0×10^8 by choosing the R6G band at 1362 cm⁻¹ as a reference. Here, we should note that, under the excitation of 532 nm, resonant Raman can be achieved for R6G molecule. Hence, the enhancement should come from the combined contributions of plasmonic effect and molecular resonance effect. While, the molecular resonance effect can be offset to some extent in EF evaluation by the equation 1. Hence, the calculated EF is mainly from the electromagnetic enhancement of AgNPs-SA.



Fig. S6 The SERS and normal Raman signal of R6G detected on AgNPs-SA substrate (10^{-10} M) and Si slice (10^{-3} M), respectively.



Fig. S7 (a) The SERS spectra of R6G measured at one AgNPs-SA particles with the R6G concentration 10⁻¹¹ M. (b) The statistics of SERS intensity at 1362 cm⁻¹.



Fig. S8 (a) The SERS spectra of R6G measured at the concentrations from 10^{-8} M to 10^{-12} M. At each concentration, SERS spectra were acquired by randomly selecting 30 spots on different AgNPs-SA particles. (b) The statistics of SERS intensity at 1362 cm⁻¹.

The ultra-trace detections of Melamine and Thiram

The potential of AgNPs-SA for food safety evaluations was investigated by detecting trace amount of Melamine in aqueous solution. The Melamine is an organic compound, which has been illegally added in dairy foods to improve the apparent protein content. The large-dose ingestion can lead to kidney disease and even infant death. Fig. S9a shows the SERS spectra of Melamine at various concentrations, inset demonstrates the schematic of Melamine molecule. The dominant triazine ring-breathing modes at 988 cm⁻¹ (I) and 680 cm⁻¹ (II) can be clearly identified even at the concentration 10⁻¹¹ M. This is far below the safety limits of Melamine for liquid infant milk (0.15 mg/kg, set by Codex Alimentarius Commission in 2012). The ultrasensitive detection of another pesticide (Thiram) down to 10⁻⁸ M is shown in Fig. S9c. These proof-of-concept experiments clearly demonstrates that the 3D porous AgNPs-SA substrates are promising for food safety inspections.



Fig. S9 (a) SERS spectra Melamine of different concentrations $(10^{-7} \text{ M}, 10^{-9} \text{ M} \text{ and } 10^{-11} \text{ M})$. The inset shows the molecule structure of Melamine. (b) The SERS intensity at 680 cm⁻¹ as a function of Melamine logarithmic concentrations. (c) SERS spectra Thiram of different concentrations $(10^{-6} \text{ M}, 10^{-7} \text{ M} \text{ and } 10^{-8} \text{ M})$. The inset shows the molecule structure of Thiram. (d) The SERS intensity at 1387 cm⁻¹ as a function of Thiram logarithmic concentrations.





Fig. S10 (a) The SERS spectra of gaseous 4-ATP measured at the concentrations from 0.05 ppm to 1 ppm. At each concentration, SERS spectra were acquired by randomly selecting 30 spots on different AgNPs-SA particles. (b) The statistics of SERS intensity at 1436 cm⁻¹.

The calculation of 4-ATP coverage

The 4-ATP coverage (Θ) can be calculated by Hill equation:

$$\Theta = \frac{1}{1 + \left(\frac{K_A}{C}\right)^n}$$
(3).

According to the fitting curve in Fig. 3B, we can extract the key parameters: n = 3.16 and $K_A = 0.13$ ppm. As our experiments demonstrated, effective SERS can be obtained, when C = 0.05 ppm. According to the equation (3), we can get $\Theta = 5\%$.



Fig. S11 The SERS of gaseous Pyridine. (a) SERS spectra showing the increasing concentration of gaseous Pyridine from 0.1 ppm to 1.5 ppm. (b) Calibration measurements as the function of gaseous Pyridine concentrations. Black squares: experimental SERS intensity at 1035 cm⁻¹. Red curve: fitting by Hill equation.