Electronic Supplementary Information

Evaluation of cigarette flavoring quality by surface-enhanced Raman spectroscopy

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Experimental Section

Preparation of Au nanoparticles

50 nm Au nanoparticles were prepared according to Frens method.[1] First, 1.4 mL of 1 wt% sodium citrate solution was added into 200 mL of 0.01 wt% boiling $HAuCl_4$ solution. Then, the mixture was refluxed for 30 min and finally cooled down to room temperature for the following experiment.

Preparation of two-dimensional SERS substrate

25 mL H_2O was added into 50 mL Au nanoparticles. Then, 2-3 mL cyclohexane was added in the mixture, leading to the formation of a two-phase interface. After that, ethanol was added into the mixture. A two-dimensional film consisting of Au

nanoparticles monolayer would appear at the two-phase interface. The monolayer film was then transferred on a gold wafer. Thus, the two-dimensional SERS substrate was obtained.

The SERS for Cigarette Flavoring Evaluation

The as-prepared SERS substrate was put into the cigarette flavoring solution for 1-2 h, allowing the essence molecules to adsorb on the substrate. Took the substrate out from the cigarette flavoring solution and then put it into Milli-Q water for 5 minutes. Washed the substrate 3-4 times to remove the essence molecules that physically adsorbed on the surface. After natural drying, the SERS spectra of the essences were then acquired with a confocal Raman system Xplora (Jobin-Yvon Horiba). According to our previous studies,[2,3] the Au substrate has much higher Raman enhancement under the excitation of a 638 or 785 nm laser compared to a 532 nm laser. At the same time, the essence displays strong fluorescence signals under the excitation of the 638 nm laser during the SERS measurement, which significantly interferes the Raman signals of the essence. Therefore, we chose a laser with a wavelength of 785 nm as the excitation light.

The method of data processing

The data processing can be described by the following steps, including S-G filtering and PCA: (1) Pretreatment to the raw data (X_{raw}, m×n matrix, where m is the number of Raman spectra, n is the number of wavenumber points): S-G filtering (or other proper de-noising algorithms) and centering the data to zero mean; (2) Calculate the covariance matrix (C, n×n matrix) of the centered data (X, m×n matrix), and calculate its eigenvalues and eigenvectors; (3) Sort the n eigenvalues in descending order and choose the largest k ones, as well as the corresponding eigenvectors (k=2 in this paper, PC1 and PC2 in Fig. 5, the maximum possible value of k is n); (4) Transform each spectrum in X to the k-dimension space using the eigenvectors in Step 3, and give the new data matrix (XPCA, m×k matrix). PC1 and PC2 used in this work are the first and second column of XPCA, respectively.

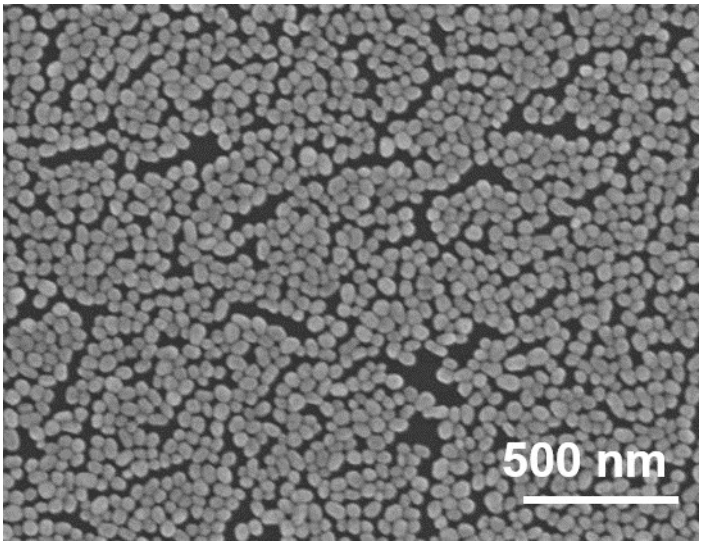

Fig. S1 High-magnification SEM image of the Au nanoparticles assembled on the smooth Au surface.

Reference

1 G. Frens, *Nature*, 1973, **241**, 20-22.

2 S. Chen, Z. L. Yang, L. Y. Meng, J. F. Li, C. T. Williams and Z. Q. Tian, *J. Phys. Chem. C*, 2015, **119**, 5246-5251.

3 S. Chen, L. Y. Meng, H. Y. Shan, J. F. Li, L. H. Qian, C. T. Williams, Z. L. Yang and Z. Q. Tian, *ACS Nano*, 2016, **10**, 581-587.