Supporting Information

Portable SERS Sensing of Volatile Aldehydes in Alcohols by Aldol Condensation Reaction on Liquid Interfacial Plasmonic Arrays

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Experimental Section

Chloroauric acid (HAuCl$_4$·4H$_2$O, 99.9%)，Hydroxylamine hydrochloride (NH$_2$OH·HCl, 98.5%)，Sodium citrate dihydrate (C$_6$H$_5$Na$_3$O$_7$·2H$_2$O, 99%) and Ethanol (CH$_3$CH$_2$OH，95%) are all purchased from Sinopharm Chemical Reagent Co. 4-(Methylthio)benzaldehyde（C$_8$H$_8$S, MTBH, 98%）， Acetaldehyde (CH$_3$CHO, 35%) and Benzaldehyde (C$_7$H$_6$O, 98%) are purchased from Shanghai Aladdin Biochemical Technology Co. 1-Pyrenecarboxaldehyde (C$_{17}$H$_{10}$O, 98%) and 9-Anthracenecarboxaldehyde (C$_{15}$H$_{10}$O, 98%) are purchased from Shanghai Macklin Biochemical Technology Co. 18.2 MΩ.cm ultrapure water is produced by Millipore water purification systems. All glassware was soaked in freshly prepared aqua regia (HCl: HNO$_3$=3:1), followed by ultra-pure water washing and hydrophilic treatment of all vials used in the assembly of liquid-liquid interfaces with saturated NaOH solution.

AuNPs were prepared by a previous method in our laboratory (Liu et al., Chem. Comm., 2022, 58, 1720.). The AuNPs were characterized by UV-Vis absorption spectroscopy using a UV-2600 spectrophotometer (Shimadzu, Kyoto, Japan), and the gold films were photographed before and after assembly using a BCA151B video microscope and a JEOL 2010 transmission electron microscope (TEM). Normal Raman and SERS experiments were performed on a portable BWTek i-Raman Plus Raman spectrometer (model BWS465-785S) equipped with the standard BCR100A accessory. The excitation wavelength was 785 nm, the laser power used in the experiment was 10% without special labeling, and the accumulation time was 10,000 ms each time. The laser scattering volume is focused on the side wall of a 3D marble in a 1 cm × 1 cm × 4 cm quartz cuvette.

The aldol condensation reaction was carried out in a vial that served as a reactor containing 1 mL of chloroform solution dissolved with 10^{-2} M MTBH molecules and 1 mL of 95% anhydrous ethanol, 10 μL of 35% acetaldehyde solution and 100 μL of 2M NaOH as catalyst. The reactor was placed in a shaker at 200 rpm and shaken to increase mass transfer. During the reaction, 200 μL of the mixing solution was withdrawn from the reactor at a time, then 800 μL of chloroform and 3 mL of gold sol were added and mixed with vigorous shaking to make them self-assemble to form a three-dimensional liquid-liquid interface.

For the portion of the volatile acetaldehyde assay, a 40 mL mixture containing various final

concentrations of acetaldehyde and interfering substances (ethanol solution) in a three-neck flask was heated at a constant temperature of 70 °C with an electric heating jacket. The gas mixture blown from the three-mouth flask is passed through a rubber hose into the subsequent glass bottle. The glass bottle contains 5 mL chloroform with 10^{-2} M MTBH, 5 mL 95% ethanol, and 500 μL 2 M NaOH. The speed of magnetic stirrer is 500 rpm. The measurement method after subsequent extraction is the same as above.
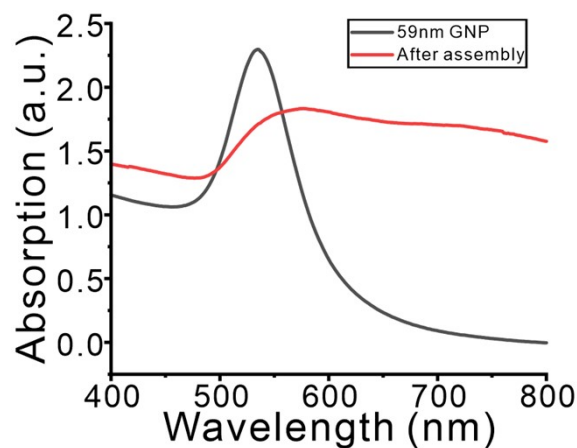
Supplementary Figures

Fig.S1 UV-Vis absorbance spectra of gold particles before assembly (black line) and of gold films after assembly (red line).
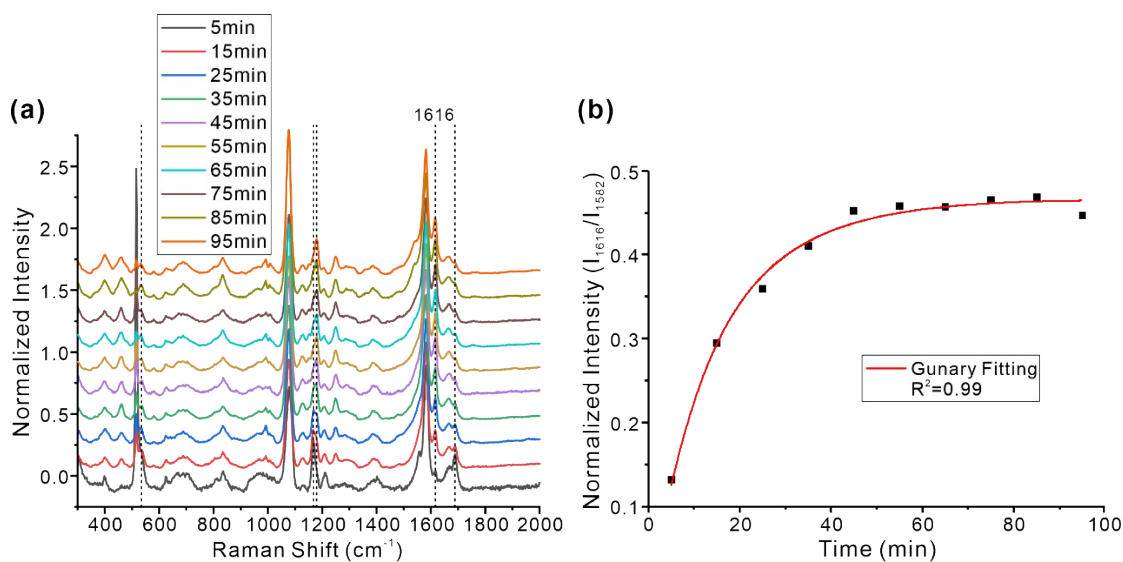

Fig.S2 (a) The time variation spectrum of aldol condensation measured by taking 5 μL of the mixture droplet dissolved with 5×10^{-3} M MTBH at a time from the chloroform phase on a solid substrate, which has a sharp silicon signal at 515 cm^{-1}. All spectra were normalized against the ring vibration mode at 1582 cm^{-1}. (b) A nonlinear fit of the reaction degree (relative peak intensity of C=C) with time.
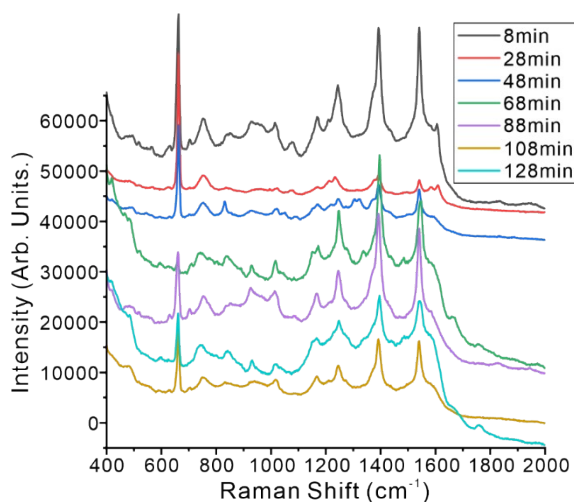
Fig.S3 SERS variation spectra of 10^{-3} M 9-Anthracenecarboxaldehyde after the addition of excess acetaldehyde, with different acquisition time indicated in the figure notes.
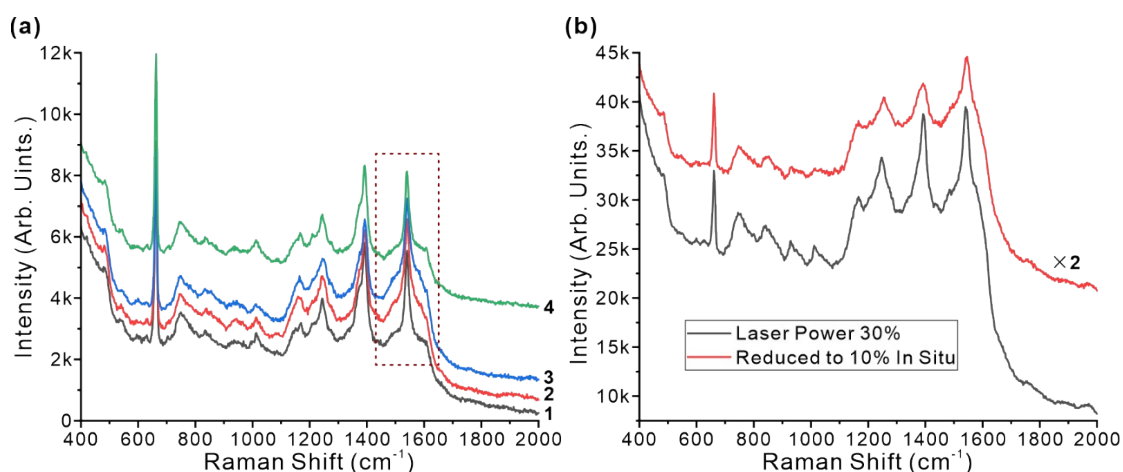

Fig.S4 (a)Line 1: SERS spectra of the product of 10^{-3} M 9-Anthracenecarboxaldehyde after 12h reaction. Line 2: The laser in situ irradiation lasts for 1 min. Line 3: Continue irradiation in situ for 1 min. Line 4: Shifting the position of laser focus. The laser intensity used is all 10% and the integration time is 10s. (b) Black line: SERS spectrum at 30% laser power. Red line: Acquired after reducing the power to 10% in situ, where the spectrum was amplified by a factor of two.
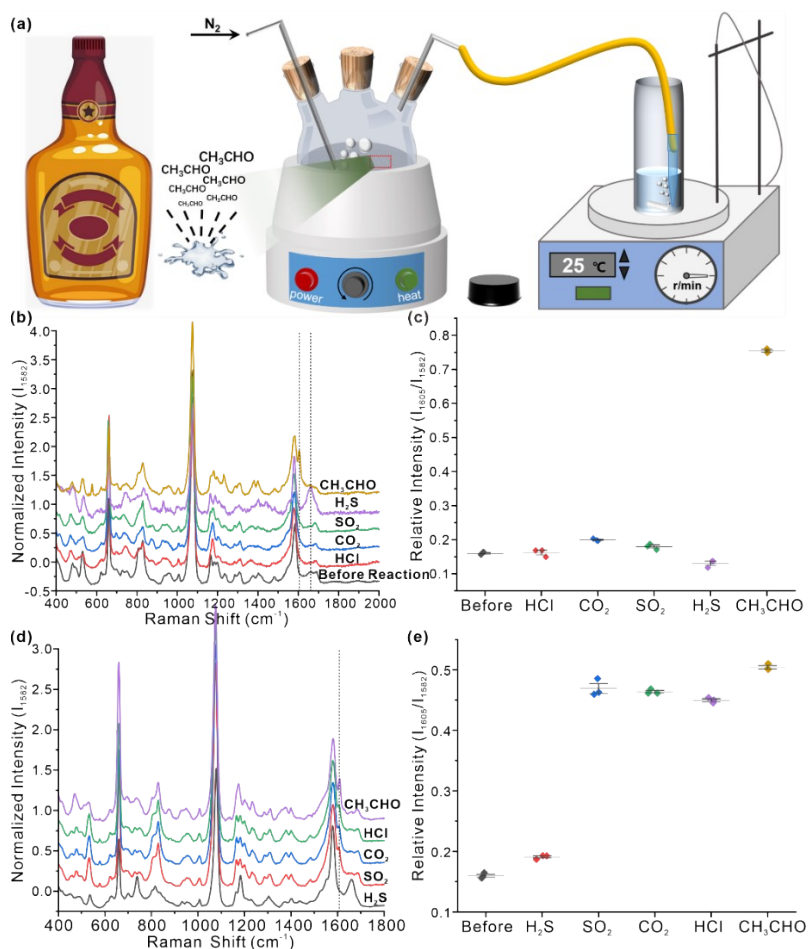
Fig. S5. (a) Schematic diagram of a simple device for the standard sample and actual system detection of volatile AA. (b), (d) The concentrations of AA and other molecules in both selective and anti-interference experiments were 10^{-4} M, the concentration of MTBH was 5×10^{-3} M, the reaction time was 40 min, and the spectra were treated with reduced baselines. (c), (e) The scatter spacing plots were obtained by correcting the product signal intensity based on the benzene ring vibration mode and each set of experiments were averaged for three times.
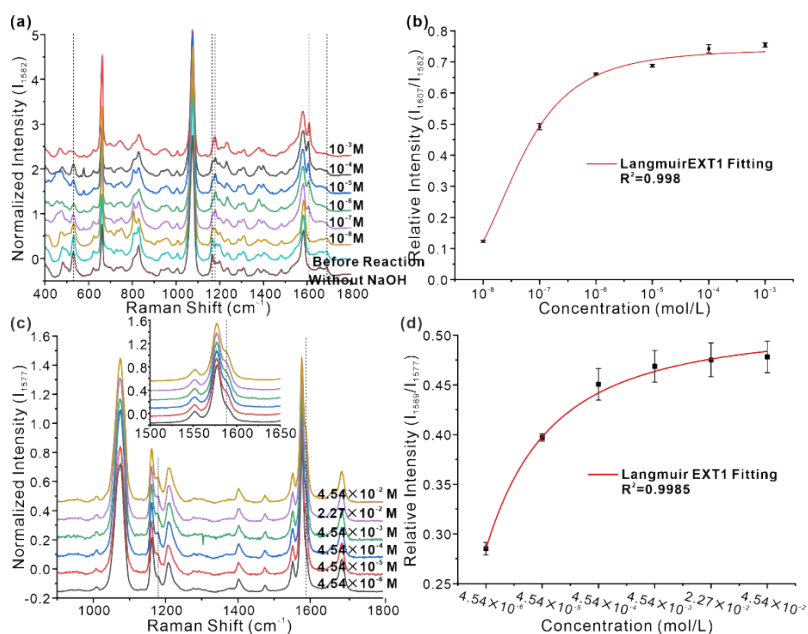
Fig. S6. (a) Spectral lines were collected in the standard sample system for AA concentrations from 10^{-8} M to 10^{-3} M from the post-reaction mixture, with the light blue line being the spectrum before the reaction and the brown line being collected after the reaction without the addition of the alkali catalyst, with an MTBH concentration of 5 mM. (c) Condensation reactions were carried out for different whisky samples with AA additions from 4.54×10^{-6} M to 4.54×10^{-2} M. The concentration of MTBH was 50 mM, and the spike at 1300 cm^{-1} of the green line was attributed to the cosmic rays that were not deducted. The inset is a local enlargement of the 1500-1650 cm^{-1} band. (b), (d) The double bond signal was fitted nonlinearly based on the correction of the vibrational modes of adjacent benzene rings. The reaction time was all 40 min, the spectra were treated with reduced baselines, and the error bars represent the variance of the data from three parallel sets of experiments.