Supporting Information

Hybrid ZIF-8-90 for Selective Solid-Phase Microextraction of Exhaled Breath from Gastric Cancer Patients

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Appendix: Experimental Section

Chemicals. All chemicals and reagents used in this work were at least of analytical grade. $Zn(NO_3)_2 \cdot 6H_2O$, hexanal (97%), 2-methylimidazole (2-MeIm) and imidazole-2-carboxaldehyde (OHC-IM) were purchased from Shanghai Aladdin Biochemical Technology (Shanghai, China). The isoprene (99%), heptane (99%), nonane (99%), decane (99%) was obtained from Shanghai Macklin Biochemical Technology (Shanghai, China). Hexanol (99.5%) was supplied from Tianjin Standard Science and Technology Company (Tianjin, China). Methyltrimethoxysilane (MTMOS), trifluoroacetic acid (TFA) and methanol (99.5%) were provided from Alfa Aesar Company (Tianjin, China). Dimethicone and dichloromethane were bought from Tianjin Kermel Chemical Reagent Company (Tianjin, China). Carbon tetrachloride (99.8%), acetone (99.5%) and ethanol (95%) were supplied from Nanjing Reagent Company (Nanjing, China). Working standard solutions were prepared by stepwise diluting the stock solution with carbon tetrachloride just before use. The 5 μL GC microsyringe and stainless steel wire were purchased from Shanghai Gaoge Industrial and Trade Company (Shanghai, China). Before use, the needle of the 5 μL GC microsyringe was cut off 2 cm to expose the coating to the extracted sample.

Instrumentations. A Thermo Fisher Scientific (Massachusetts, U.S.A.) GC-Trace 1300 equipped with a flame ionic detector was used for the SPME analysis. The GC capillary column (TG-624, 60 m × 0.25 mm × 1.4 μm) was purchased from Thermo Fisher Scientific for all separations. The column temperature was initially maintained at 40 ^{o}C for 1 min and then raised to 200 ^{o}C for 2 min at a temperature increase rate of 10 ^{o}C min^{-1}. The injector and detector temperatures were both set at 250 ^{o}C. High purity nitrogen (99.99%, Jinglian gas plant, Baoding, China) was used as the carrier gas at a flow rate of 20 mL min^{-1}. Hydrogen was used as the fuel gas at a flow rate of 30 mL min^{-1}.

The X-ray diffraction (XRD) patterns were recorded on a D/max-2500 diffractometer (Rigaku, Japan) using $Cu_{K\alpha}$ radiation (λ= 1.5418 Å). Fourier transform-infrared (FT-IR) was performed with a Nicolet iS10 (U.S.A) FT-IR spectrometer. The thermal gravimetric (TGA) analysis was performed on a PTC-10A thermal gravimetric analyzer (Rigaku, Japan) to evaluate the thermal stability from room temperature to 700 ^{o}C at a ramp rate of 10 ^{o}C·min^{-1} under N_2. The

scanning electron microscope (SEM) images were recorded on a Shimadzu SS-550 (Japan) scanning electron microscope at 15.0 kV. BET surface area was measured on an ASAP 2020 microspore physisorption analyzer (Micromeritics, Norcross, GA, USA) using nitrogen adsorption at 77 K in the range $0.02 \leq P/P0 \leq 0.20$, respectively.

Fabrication of the ZIF-8-90 Coated Fiber. The ZIF-8-90 coated fiber is prepared as follows: (a) Stainless steel wires with a length of 20 cm were used to fabricate the ZIF-8-90 coated SPME fiber. One end of the stainless steel wire (about 2.0 cm in length) was etched by aqua regia (HCl/HNO_3 = 3:1, v/v) about 5 minutes to produce a rough surface with a diameter of about 0.15 mm. The etched part of the stainless steel wire was washed with ethanol and ultrapure water gently and then air-dried. (b) The sol−gel solution was obtained by mixing 200 μL MTMOS, 200 μL dimethicone, 200 μL dichloromethane and 100 μL TFA thoroughly, and then the prepared ZIF-8-90 powder was dispersed into it under ultrasonication to acquire a uniform sol−gel/ZIF-8-90 solution. (c) The pretreated stainless steel wire was vertically dipped into the sol−gel/ZIF-8-90 solution to a depth of 2.0 cm for 1 min with the solution being whirled, then pulled out slowly and dried at room temperature. The above operations were repeated three times and the desirable coating thickness was obtained. (d) The ZIF-8-90 coated fiber was assembled into an adapted 5 μL GC microsyringe and ought to be aged in the GC injector at 250 ^{o}C under nitrogen until a stable GC baseline was obtained before use.

Exhaled Breath Collection. A Tedlar bag made of poly (vinyl fluoride) was used as a sample container, and flushed with nitrogen to eliminate any contaminants before use. The subjects cleaned their mouth with water and freely breathed at least 30 minutes, and then sampling. The collected exhalation samples were saved in dark to avoid possible photo-oxidation of volatile prior to analysis. Next up, 20 mL exhalation sample was taken to an evacuated 120 mL hermetically sealed glass vial for SPME. Each sample was analyzed for three times in parallel.

Appendix: Results and Discussion

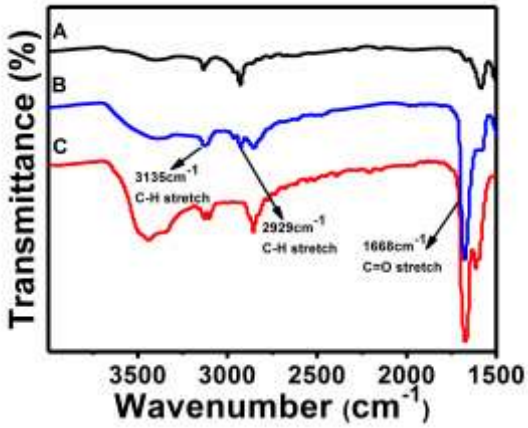

Figure S1. FT-IR spectra of the as-synthesized ZIF-8 (A)，ZIF-8-90(B)，ZIF-90(C).

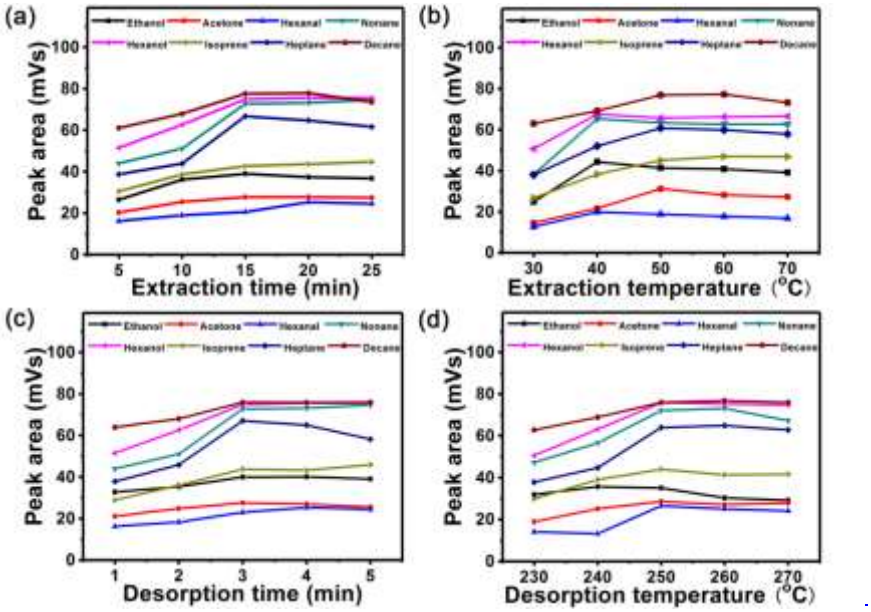

Figure S2. Effect of the experimental conditions on the extraction efficiency using the ZIF-8-90 coated fiber for SPME: (a) Extraction time; (b) Extraction temperature; (c) Desorption time; (d) Desorption temperature.

In order to obtain good analytical performance, four parameters including extraction time, extraction temperature, desorption time and desorption temperature on the SPME of eight biomarkers using the ZIF-8-90 coated fiber were optimized.

SPME is based on partition equilibrium of analytes, thus the extracted amount of the analytes increases with extraction time before equilibrium. As shown in Figure S2a, the peak areas of the analytes significantly increased as extraction time increased from 5 to 15 min, but almost kept constant with further increase of extraction time. Therefore, 20 min was chosen as the optimal extraction time for the following experiments to ensure extraction equilibrium.

Generally, increasing the extraction temperature is favorable for the dispersion of the analytes

in the gaseous sample to achieve higher extraction efficiencies. The effect of extraction temperature on the peak areas of the analytes is shown in Figure S2b. The peak areas of the analytes increased as extraction temperature increased from 30 ^{o}C to 70 ^{o}C. Nevertheless, adsorption is an exothermic process, further heating can reduce the extraction efficiency. Accordingly, 40 ^{o}C was used as the optimal extraction temperature in the subsequent experiments.

In addition, desorption time and temperature should be sufficient to release all the extracted analytes from the SPME fiber. It can be seen from Figure S2c that the peak area of the analytes reached the maximum at 3 min for all the studied analytes. The effect of desorption temperature on the peak areas of the analytes was measured from 230 ^{o}C to 270 ^{o}C (Figure S2d). The result shows that the peak areas of the analytes increased as desorption temperature increased from 230 ^{o}C to 250 ^{o}C, then kept constant with further increase of desorption temperature. To extend the lifetime of the SPME fiber and to minimize the carryover effect, the desorption time of 3 min and desorption temperature of 250 ^{o}C were used for the rest of experiments.

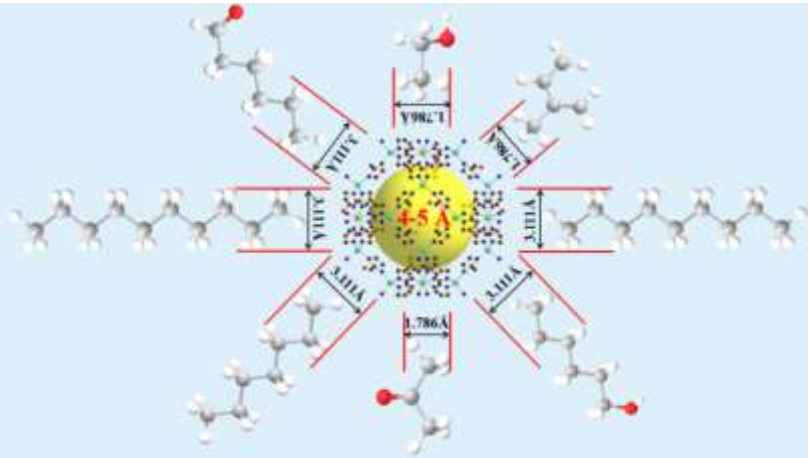

Figure S3. The molecular 3D structures obtained from Chem 3D on the basis of the energy minimum state using MM2 method.

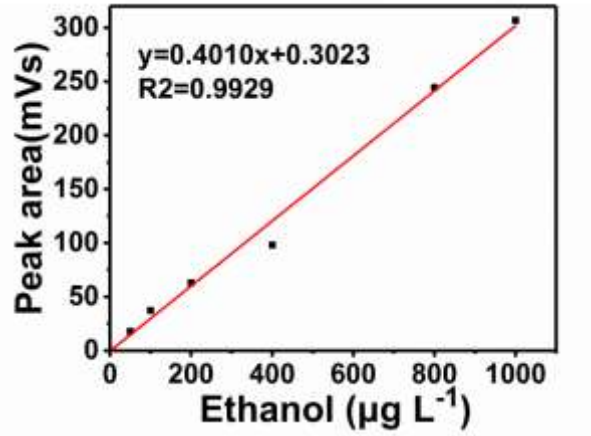

Figure S4. The calibration plot for ethanol.