Electronic Supplementary Information Coordination-driven SERS platform for trace detection of nerve agent

hydrolysis product using plasmonic metal-organic framework

Renyong Liu,*ab Peng Sun,ab Ziyan Zheng,a Wang Song,a Xinle Zhang,a Yehan Yan,a

Tao Xie,^a Kui Zhang*c and Lijuan Chen*a

^aAnhui Province Key Laboratory of Conservation and Utilization for Dabie Mountain Special

Bio-Resources, School of Materials and Chemical Engineering, West Anhui University,

Lu'an, Anhui 237012, China. E-mail: ahlry@mail.ustc.edu.cn, lijuanch@mail.ustc.edu.cn

^bCollege of Materials Science and Engineering, Guilin University of Technology, Guilin 341004, China.

^cSchool of Chemistry and Chemical Engineering, Anhui University of Technology,

Ma'anshan, Anhui 243032, China. E-mail: zhangkui@mail.ustc.edu.cn

EXPERIMENTAL SECTION

Chemicals and Materials. Chromium(III) nitrate nonahydrate (Cr(NO₃)₃·9H₂O, \geq 99%) and terephthalic acid (H₂BDC, \geq 99%) were purchased from Sigma-Aldrich (USA). Methylphosphonic acid (MPA, 98%), diisopropyl methylphosphonate (DIMP, \geq 97%), hydrogen tetrachloroaurate(III) tetrahydrate (HAuCl₄·4H₂O, Au \geq 47.8%), trisodium citrate (C₆H₅O₇Na₃·2H₂O, \geq 99%), Sodium bicarbonate (NaHCO₃, 99%), nitric acid (HNO₃, 69 wt%), hydrochloric acid (HCl, \geq 37%), ethanol and N, N-dimethylformamide (DMF) were obtained from Beijing InnoChem Science & Technology Co., Ltd. (Beijing, China). Ultrapure water with a resistivity of 18.2 MΩ·cm was used. The human serum samples were collected from a healthy volunteer and provided by the First People's Hospital of Ma'anshan (Ma'anshan, China) for practical application. Synthesis of AuNPs/MIL-101 Substrates. MIL-101 was first synthesized and purified according to the previously reported solvothermal method.¹ Then, 50 mg of the as-synthesized MIL-101 was suspended into 30 mL of aqueous solution of HAuCl₄·4H₂O with the concentration of 1% (w/v). After stirring at 45 °C for 2.5 h, the solution was heated to vigorous boiling, followed by the addition of 220 μ L of 10% (w/v) C₆H₅O₇Na₃·2H₂O and further stirring for another 40 min at boiling temperature. After being cooled down, the resulting products were centrifuged and washed three times with water. Finally, the obtained AuNPs/MIL-101 was redispersed in water (0.2 mg·mL⁻¹) and stored at 4 °C for further use.

SERS Detection of MPA in Aqueous Solution. For each assay, 200 μL of MPA solution with different concentrations was mixed with 1.8 mL of AuNPs/MIL-101 aqueous solution, and allowed to react for 180 min at room temperature, and then 20 μL of the resulting solution was dripped onto a cleaned silicon wafer for SERS detection. The laser power and accumulation time were 100 mW and 2 s, respectively. All measurements were carried out three times and the average maximum intensity was recorded. To validate the synergistic effect of MOFs and PNPs, the single MIL-101 and AuNPs were used as controls. In addition, the regeneration of the as-synthesized AuNPs/MIL-101 substrates were performed as follows: after the first incubation with MPA, the AuNPs/MIL-101 substrates were centrifuged and suspended into 5 mL of 4 mM NaHCO₃ solution for the exchange of the adsorbed phosphates. After treatment for 5 h, the solution was centrifuged and dispersed into 5 mL of 4 mM HCl solution for the decomposition of the entrapped hydrogencarbonate anions. Finally, the regenerated substrates were obtained after the solution was centrifuged and washed with water, and used for further binding of MPA.

SERS detection of MPA in real samples. The human serum samples were collected from a healthy volunteer and provided by the First People's Hospital of Ma'anshan. The serum experiments were performed with the approval of the local ethical committee of Anhui University of Technology. Informed consent was obtained from the volunteer and experiments were performed in compliance with the Measures of the Ethical Reviews of Life Science and Medical Research Involving Humans in China. The obtained samples were stored at -80 °C before analysis. The human serum samples were spiked with known amounts of MPA and then mixed with the AuNPs/MIL-101 substrates for SERS measurement. Each concentration was done in triplicate and the average was present with the relative standard deviation.

SERS detection of MPA vapor with the AuNPs/MIL-101 paper sensor. The paperbased SERS sensor for the detection of MPA vapor was fabricated by the assembly of AuNPs/MIL-101 on a piece of filter paper. The AuNPs/MIL-101 suspension was first filtrated with a commercial filter paper (pore size 3~6 μm), followed by drying at room temperature, forming a dense and stable monolayer of the AuNPs/MIL-101 onto the surface of the filter paper. Then, a methanol sample containing certain amounts of MPA in a capped centrifuge tube was used to promote the vapor-phase concentration of MPA. The sampling temperature for MPA vapor detection was selected as 25 °C or 50 °C. Finally, the AuNPs/MIL-101 paper was placed at upside of the tube to collect the vapor molecules emanating from MPA methanol samples. The Raman spectra were recorded from the AuNPs/MIL-101 paper after a set time of collection.

Characterization and Instruments. The morphology and size of the as-synthesized

materials were examined by Hitachi SU8010 field emission scanning electron microscopy (SEM) and FEI Tecnai F20 transmission electron microscopy (TEM). UV-Vis absorption spectra were recorded with a Purkinje TU-1950 spectrometer. The infrared spectra were recorded with Nicolet iS5 FT-IR spectrometer using KBr method. Powder X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance X-ray diffractometer with Cu-K α radiation. X-ray photoelectron spectroscopy (XPS) data was collected on UIVAC-PHI 5000 Versaprobe using monochromatic Al-K α X-rays as the excitation source. Nitrogen adsorption-desorption analysis was conducted using a Micromeritics ASAP 2460 at 77 K. Raman spectra were recorded by a BWS465-785S system (B&WTEK) equipped with a 785 nm excitation laser and a charge-coupled device detector. Inductively coupled plasma mass spectrometry analysis (ICP-MS) was carried out with Thermo Scientific iCAP RQ.

References for Electronic Supplementary Information

1 Y. L. Hu, J. Liao, D. M. Wang and G. K. Li, Anal. Chem., 2014, 86, 3955.



Fig. S1 SEM images of (A) MIL-101 and (B) AuNPs/MIL-101.



Fig. S2 (A) XRD patterns and (B) XPS survey spectra of MIL-101 and AuNPs/MIL-101, respectively.



Fig S3 The absorption curves of MIL-101 and AuNPs/MIL-101.



Fig. S4 SERS spectra of MPA $(1.0 \times 10^{-3} \text{ M})$ from MIL-101, AuNPs and AuNPs/MIL-101, respectively.



Fig. S5 The electric field distributions for the AuNPs/MIL-101 at 785 nm.



Fig. S6 High-resolution (A) P 2p, and (B) C 1s XPS spectra of AuNPs/MIL-101 after binding with MPA, respectively.



Fig. S7 FT-IR spectra of MPA, AuNPs/MIL-101 before and after binding with MPA, respectively.



Fig. S8 The linear correlation of SERS intensity ratio (I_{759}/I_{1603}) with the logarithm of MPA concentrations from 1.0×10^{-7} M to 1.0×10^{-3} M.



Fig. S9 The selectivity of the SERS assay of MPA $(1.0 \times 10^{-3} \text{ M})$ to DIMP $(1.0 \times 10^{-3} \text{ M})$. It could be seen that the Raman readouts were similar to that of the blank sample, revealing the selectivity of this SERS assay.



Fig. S10 (A) The adsorption and regeneration study of AuNPs/MIL-101. (B) FT-IR spectra of regenerated AuNPs/MIL-101 before and after binding with MPA.



Fig. S11 XRD patterns of the regenerated AuNPs/MIL-101 substrates (1-st and 3-rd cycles).

Spiked (ppm)	Measured (ppm)	Recovery (%)
0	0.2	/
5	4.8	96.0 ± 1.6
10	10.3	103.0 ± 2.1
50	48.9	97.8 ± 1.5

Table S1 Recovery test of MPA spiked in human serum samples.



Fig. S12 (A) The evolution of SERS spectra of MPA after exposing the AuNPs/MIL-101 paper to MPA vapor at a sampling temperature of 25 °C. (B) Linear relationship between SERS intensity ratio (I_{759}/I_{1603}) and the exposure time to MPA vapor.