Supporting Information

of

A novel SERS substrate of MIL-100(Fe)/AgNFs for sensitive detection of ascorbic acid in cellular media

Wang Qiao [a,b], Yiran Wang [a,b], Zhenxia Zhao [a], Yujiao Wang [b], Kui Chen[b], Zhongxing Zhao[a,*], Min Li[b,*]

[a] *School of Chemistry and Chemical Engineering, Guangxi Key Laboratory of Agro-Environment and Agro-Product Safety, Guangxi University, Nanning 530004, China.*
[b] *CAS Key Laboratory for Biomedical Effects of Nanomaterials and Nanosafety, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China.*

Experimental section

Materials

All chemicals are analytical grade and used without further purification. Silver nitrate, 3-mercaptopropyltrimethoxyalkane were purchased from Alfa Aesar Chemicals Co., Ltd. Mercaptopropionic acid, ferrous chloride, 1,3,5-benzenetricarboxylic acid, glutathione, glutamic acid, glycine and cysteine were obtained from Sigma-Aldrich Co. All other chemicals were bought from Chemical Reagent Beijing Co., Beijing, China. Deionized water from a triple distillation system was used throughout this work.

Synthesis of AgNFs substrate

The synthesis method of silver nanofilms is based on our previous research work with slight modifications.[1] The glass slides were ultrasonically washed in ethanol and blown dried with nitrogen before treated with piranha solution (H_2SO_4:H_2O_2 = 3:1, solution should be handled with great care) at 95 °C for 40-60 min. After cleaning with deionized water, the glass slides were functionalized in a toluene solution containing 2% 3-mercaptopropyltrimethoxyalkane for 12 h. The modified glass sheets were immersed in a silver ammonia solution containing glutaraldehyde, and reacting at 90 °C for 4-6 min to obtain a silver nano-film (AgNFs). The surface of AgNFs substrate covered with a thin film of gold by using Ion Sputtering Instrument. Then the AgNFs substrate incubated with 10 mM mercaptopropionic acid (MPA) in ethanol solution for 3 h at room temperature. After cleaning with ethanol thoroughly, the modified substrate was soaked in ethanol for later use.

Preparation of AgNFs/MIL-100(Fe)

The MIL-100(Fe) crystals anchored on the surface of silver nanofilms (AgNFs) were prepared by an in-situ synthesis method reported in the literature.[2] Briefly, 5.7 mmol ferrous chloride tetrahydrate ($FeCl_2 \cdot H_2O$) was dissolved in 48.6 mL deionized water (solution A). Secondly, prepare solution B: 11.4 mmol sodium hydroxide (NaOH) and 3.8 mmol 1,3,5-benzenetricarboxylic acid (H_3BTC) was dissolved in 11.4 mL deionized water (solution B). Then solution B was added dropwise to solution A. The mixture was stirred at room temperature. After 4 h, AgNFs was suspended into the mixed solution. At this stage, Fe^{2+} was oxidized to Fe^{3+} which gradually combined with H_3BTC to form the crystal structure of MIL-100(Fe) on AgNFs in situ. After 24 h, the formation of the composite MIL-100(Fe)/AgNFs was completed and the AgNFs substrate was taken out and washed with deionized water.

Gold spraying

Two groups of MIL-100(Fe)/AgNFs substrates were selected to spray gold for comparison. The current of the first group was set at 2 mA with the spraying time of 60-140 s. The current of the second group was set at 5 mA with the spraying time of 10-80 s. After gold spraying, the substrate was used for in situ growth of MIL-100 (Fe) on AgNFs to form MIL-100(Fe)/AgNFs for SERS measurements.

Effect of pH on L-AA sensing

MIL-100(Fe)/AgNFs was exposure to 5 mL of 10^{-8} M L-AA aqueous solution with pH of 4, 4.5, 5, 5.2, 5.5, 6, 6.5, and 7, respectively, for 30 min reaction before SERS spectra were collected. In addition, MIL-100(Fe)/AgNFs was exposure to the aqueous solutions with the above pH value in the absence of L-AA was also tested as the control group. The pH was adjusted by using NaOH and HCl.

Preparation of Orange and Effervescent tablet

Weigh 16.27g of oranges, squeeze out the juice and remove 4.81g of the residue. Dissolve the obtained orange juice in 100 mL of water and dilute to 10^{-8} M~10^{-10} M. Weigh 4g of effervescent tablets, dissolve in 500 mL of water, and dilute to 10^{-9} M~10^{-11} M. The L-AA content given in the content table of effervescent tablets is 203 mg/g.

Preparation of 4T1 cells and B16 cells

4T1/B16 cells were seeded into 10 cm dishes and cultured in DMEM high-glucose medium containing 10 % fetal bovine serum and 1 % double antibody at 37 °C, 5 % CO_2. When the cell confluence was about 80%, the cells were trypsinized and collected before being washed for three times with PBS. 4T1 or B16 cells were disrupted, centrifuged centrifugation at 12,000 rpm at 4°C for 10 min. Collections were diluted with different concentrations of L-AA in TBS buffer (pH=5.2). The cell concentration in each solution is approximately 2.5×10^4 cells/mL.

Measurements

Scanning electron microscopy (SEM) characterization was underwent using a Hitachi S-4800 at 3.0 and 10 kV. The samples was analyzed by X-ray diffraction (XRD, D8 Advance, Germany) at a scan rate of 5 °/min and a monochromatic X-ray beam at 40 kV. Raman spectra were obtained on a DXR Smart Raman spectrometer (Thermo Fisher, 780 nm, 60 mW, 10 μm diameter focal spot laser excitation, 15s integration time, and room temperature).

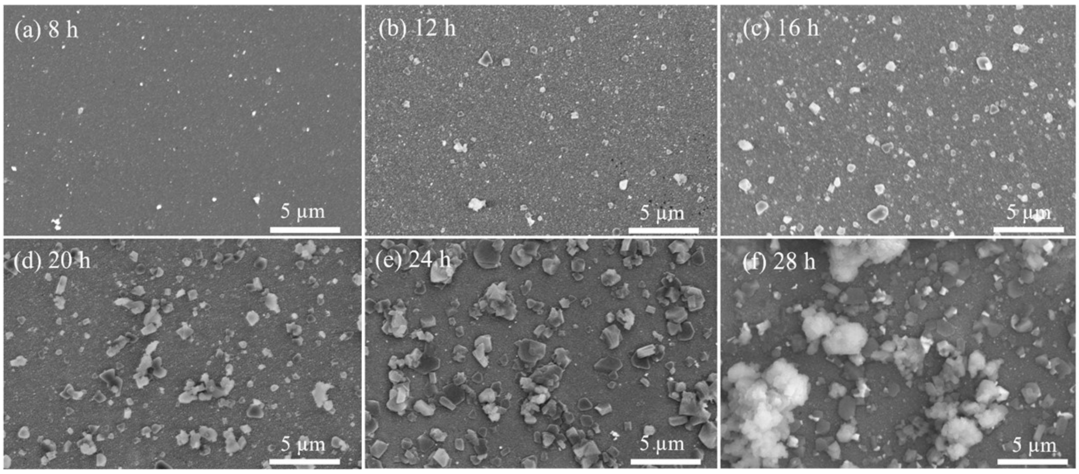

Fig. S1 SEM characterization of MIL-100(Fe)/AgNFs growing for different time.

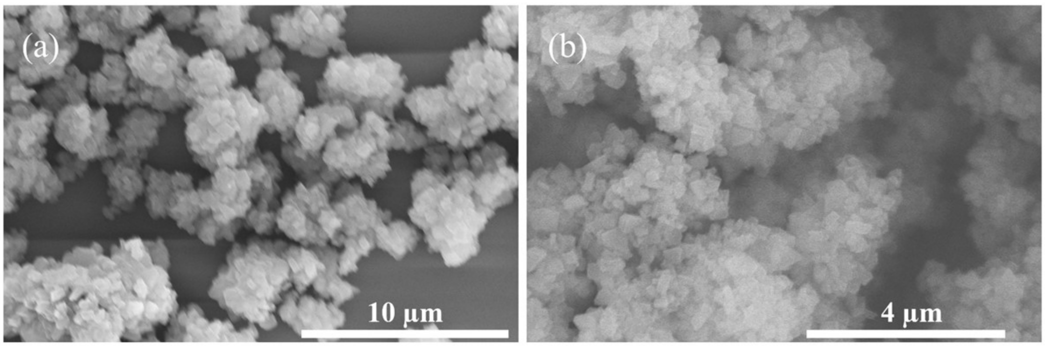

Fig. S2 SEM characterization of MIL-100(Fe) in solution instead on AgNFs surface after growing for 24 h.

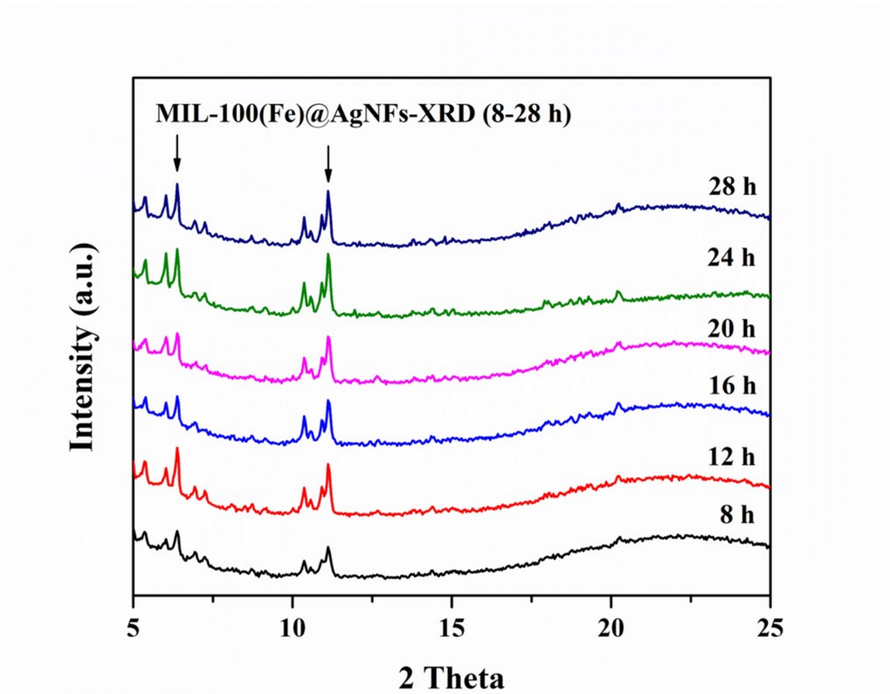

Fig. S3 (a) XRD of MIL-100(Fe) growing for 8~28 h on AgNFs.

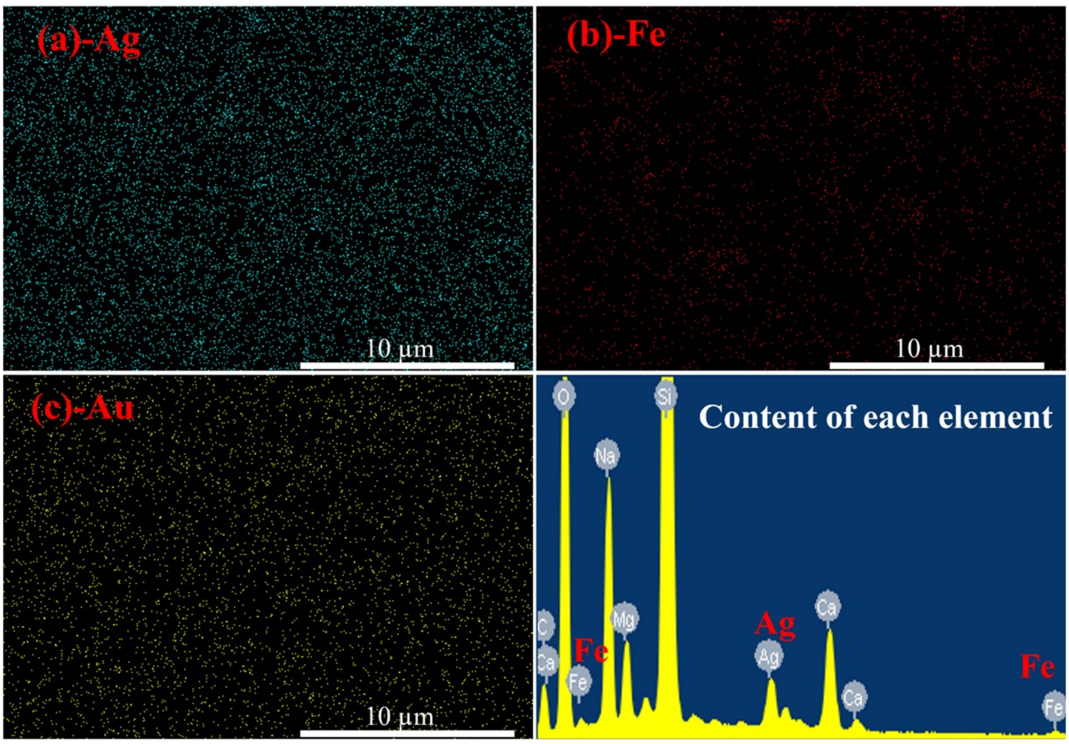

Fig. S4 EDS Characterization of Ag, Fe, Au elements in the as-prepared MIL-100(Fe)

/AgNFs substrate.

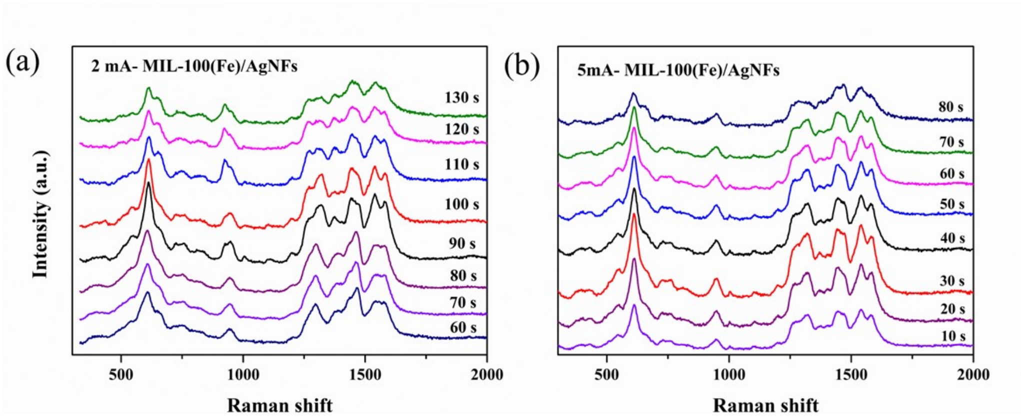

Fig. S5 Raman spectra of MIL-100(Fe)/AgNFs for different spraying time at the current of (a) 2 mA, (b) 5 mA.

References:

1. W. F. Zhu, L. X. Cheng, M. Li, D. Zuo, N. Zhang, H. J. Zhuang, D. Xie, Q. D. Zeng, J. A. Hutchison and Y. L. Zhao, Anal Chem, 2018, **90**, 10144-10151.
2. K. Guesh, C. A. D. Caiuby, Á. Mayoral, M. Díaz-García, I. Díaz and M. Sanchez-Sanchez, Crystal Growth & Design, 2017, **17**, 1806-1813.