Electronic Supplementary Information (ESI)

A label-free fluorescent assay for hydrogen peroxide and glucose based on bifunctional MIL-53(Fe) nanozyme

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1 Experimental

1.1 Materials

Iron chloride hexahydrate ($FeCl_3 \bullet 6H_2O$) was purchased from Aladdin Reagent Co., Ltd. (Shanghai, China) and terephthalic acid (TA) was purchased from Tokyo Chemical Industry (Japan, Tokyo). Hydrogen peroxide (H_2O_2), sodium dihydrogen phosphate ($NaH_2PO_4 \bullet 12H_2O$), sodium dianhydride ($Na_2HPO_4 \bullet 7H_2O$), ethanol and dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Glucose and Glucose Oxidase (GOx, 100U mg^{-1}) were purchased from Shanghai Sangon Biological Engineering Technology & Services Co., Ltd. (Shanghai, China). Phosphoric acid (H_3PO_4) was obtained from Chengdu Chemical Industry Co., Ltd.(Chengdu, China). All these chemical reagents were analytical grade and used as received unless otherwise specified. Ultrapure water (18.2 MΩ.cm) was generated by a Millipore purification system (Bedford, MA, USA) and used for preparation of all aqueous solutions.

1.2 Apparatus

Powder X-ray diffraction (XRD) pattern of MIL-53(Fe) was obtained using a D/max 2550 VB/PC diffractometer (Rigaku, Japan) using Cu Kα radiation (λ = 0.15418 nm). Fourier transform infrared (FTIR) spectroscopy was achieved by spectrum-2000 (Perkin-Elmer, USA). Thermogravimetric analysis (TGA) was performed with a LABSYS evo TG-DSC/DTA instrument (Setaram Instrumentation, France). Scanning electron microscopy (SEM) images were recorded on a NovaTM NanoSEM 430 (FEI, USA). Fluorescence spectra and emission intensity were recorded on an RF-5031PC luminescence spectrometer (Shimadzu, Japan). The emission spectra at 314 nm excitation wavelength were used for analysis. Excitation spectra were recorded by observing the emission intensity of MIL-53(Fe) at 440 nm.

1.3 Synthesis of MIL-53(Fe)

MIL-53(Fe) was synthesized by a solvothermal method according to the literature with a minor modification (Chem. Mater., 2010, 22, 4237-4245).

Typically, 1.09g $FeCl_3 \cdot 6H_2O$ was dissolved in 20 mL DMF solution, and 0.67g TA was added. The solution was stirred vigorously for 10 min, and then transfer to a 50 mL Teflon-lined stainless-steel autoclave. The autoclave was heated at 150°C for 48 h. After natural cooling, the yellow precipitate was collected by centrifugation and washed with distilled water and ethanol several times. Finally, the yellow precipitate was dried at 60 °C for 24 h under vacuum. A yellow powder was obtained with a mass of 0.43 g.

1.4 Detection of H_2O_2 and glucose using MIL-53(Fe) as sensing platform

H_2O_2 detection was carried out as follows: 120 μL MIL-53(Fe) (500 mg L^{-1}) and 780 μL phosphate buffer (PB) buffer (200 mmol L^{-1}, pH 4.0) were mixed. Then 100 μL H_2O_2 with different concentration was added and the mixture was further incubated at 65 ºC for 70 min. A RF-5031PC luminescence spectrometer was used for analysis of the solutions, and the corresponding emitting spectra were obtained.

Glucose detection was realized as follows: 200 μL GOx (1 mg mL^{-1}) was mixed with 200 μL glucose solution with different concentrations and the mixture was incubated at 37 ºC for 30 min to produce H_2O_2. Then, 100 μL of the mixture, 120 μL MIL-53(Fe) (500 mg L^{-1}) and 780 μL PB buffer (200 mmol L^{-1}, pH 4.0) were mixed and further incubated at 65 ºC for 70 min. The corresponding emitting spectra of the solutions were recorded and used for analysis.

Before the detection of glucose in serum samples, the proteins in serum samples were removed by precipitation. 30 μL of serum sample was diluted with 20 μL water, and then 500 μL $Ba(OH)_2$ (0.08 mmol L^{-1}) and 500 μL $ZnSO_4$ (0.10 mmol L^{-1}) were added and blended. The mixture was centrifugated at 8000 rpm for 10 min. The other detection procedure was the same as that of glucose detection.

To further verify the accuracy and precision of glucose concentration obtained by this method, a standard addition method was used, and the serum samples were prepared as follows: 30 μL of serum sample was mixed

with 20 μL different concentrations of glucose solution. Then, 500 μL $Ba(OH)_2$ (0.08 mmol L^{-1}) and 500 μL $ZnSO_4$ (0.10 mmol L^{-1}) were added and blended. The mixture was centrifugated at 8000 rpm for 10 min. The other detection procedure was the same as that of serum glucose detection.

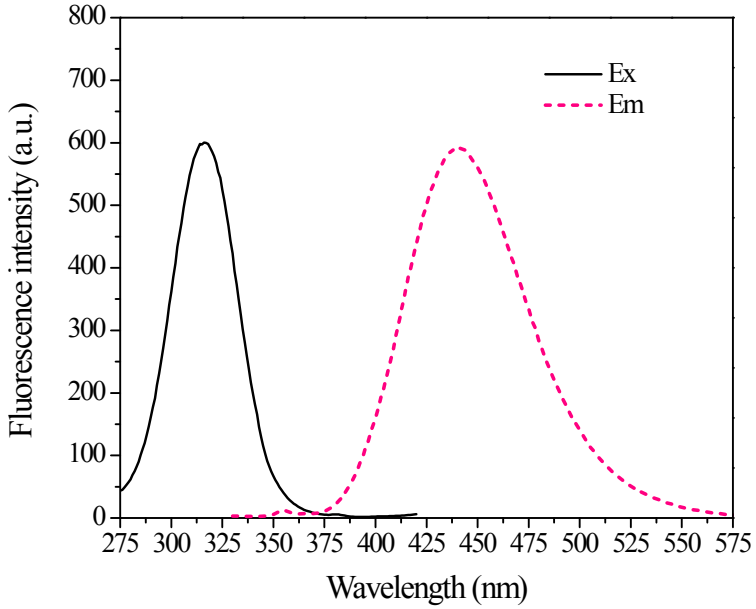

Fig. S1. Excitation (Ex) and emission (Em) spectra of MIL-53 (Fe)/H_2O_2 system. The concentrations of MIL-53(Fe) and H_2O_2 were 60 mg L^{-1} and 15 μmol L^{-1}, respectively.

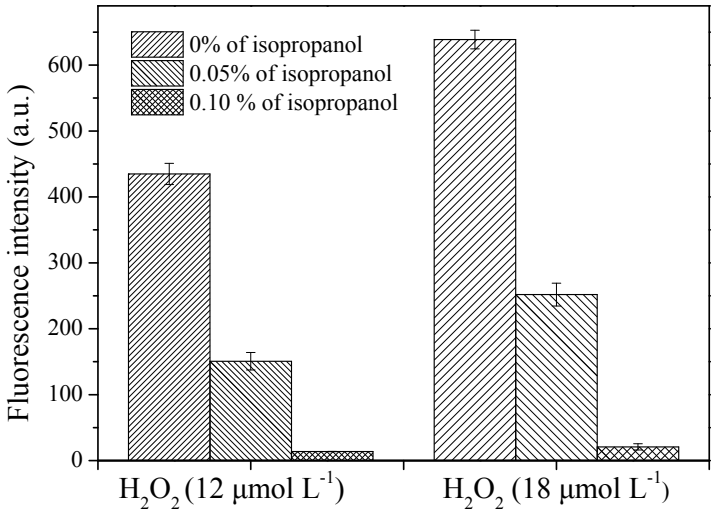

Fig. S2. The catalytic oxidation of MIL-53(Fe) by H_2O_2 at the presence of different concentration of isopropanol. Procedures: 780 μL PB buffers (0.2 mol L^{-1}, pH 4.0) with different concentration of isopropanol was mixed with 120 μL MIL-53 (Fe) (500 mg L^{-1}) and 100 μL H_2O_2 (120 μmol L^{-1} and 180 μmol L^{-1}). The mixture was incubated under 65℃ for 70 min and then the fluorescence intensities at 440nm were recorded. The error bars represent the standard deviation of three measurements.

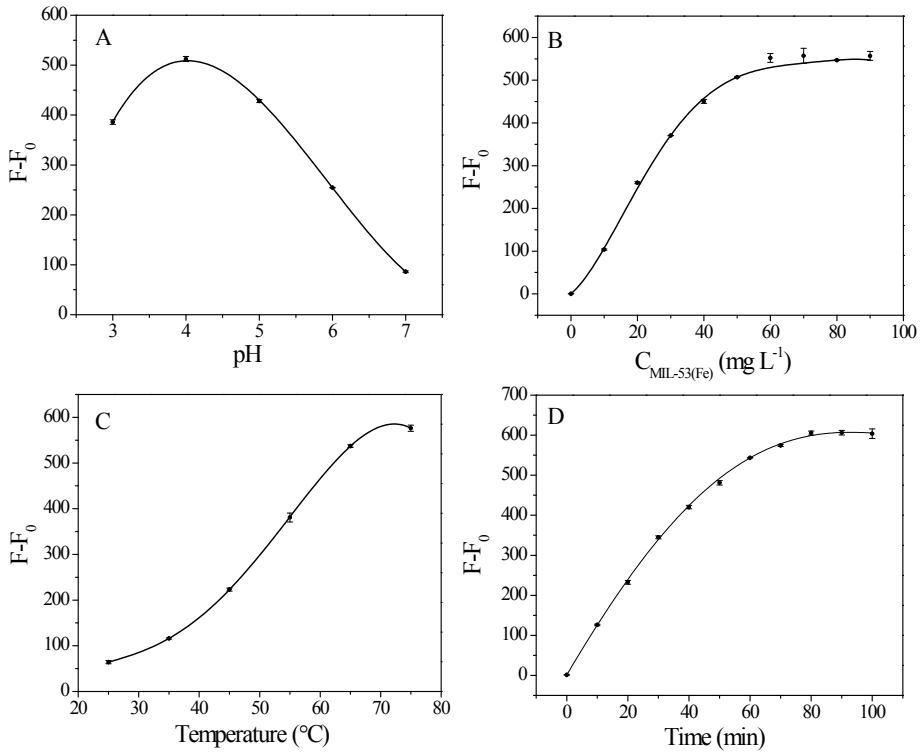

Fig. S3. Effect of (A) pH, (B) MIL-53(Fe) concentrations, (C) reaction temperature and (D) reaction time on the MIL-53(Fe) system for the H_2O_2 detection. The error bars represent the standard deviation of three measurements.

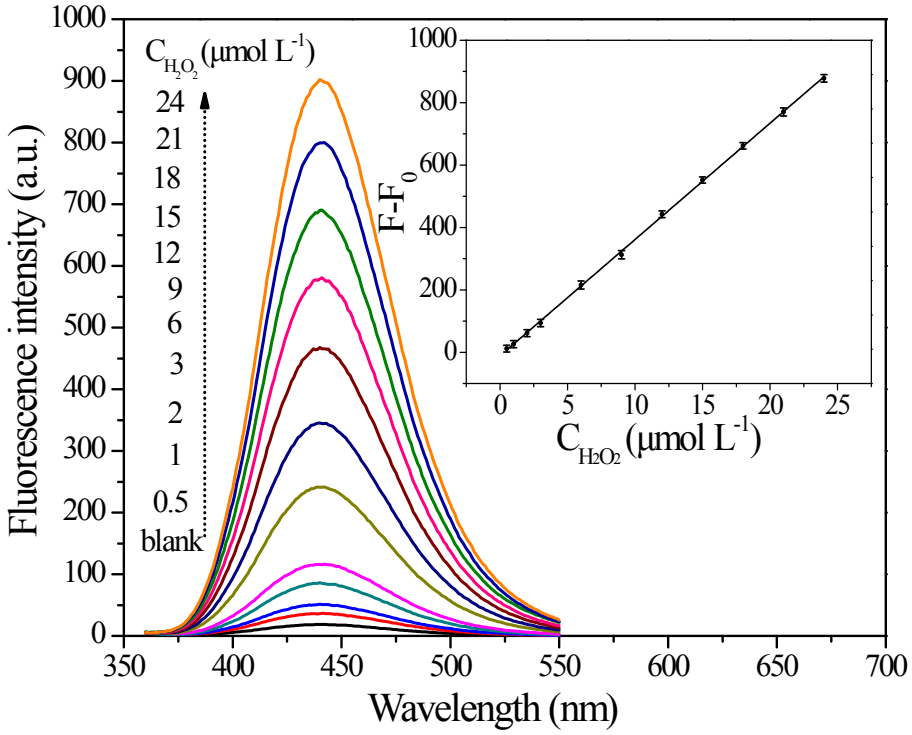

Fig. S4 (A) Fluorescent determination of H_2O_2 based on bifunctional MIL-53(Fe). Inset is the linear calibration plot for H_2O_2. The error bars represent the standard deviation of three measurements.

Table S1. Sensitivity comparison for glucose detection using nanomaterials

Nanomaterials	Method	Limit of detection ($\mu mol\ L^{-1}$)	Reference
Fe_3O_4 magnetic nanoparticles	colorimetric	30	S1
Graphene Oxide	colorimetric	1.0	S2
Carbon nanodots	colorimetric	0.4	S3
Co_3O_4 nanoparticles	colorimetric	5.0	S4
Pt Nanoclusters	colorimetric	0.28	S5
mZIF-8@GOx	colorimetric	1.9	S6
MoS_2 nanosheets	colorimetric	1.2	S7
Fe-MIL-88NH_2	colorimetric	0.48	S8
MIL-53(Fe)	colorimetric	0.25	S9
Fe-MIL-101 MOF	colorimetric	2.5	S10
Au NPs/Cu-TCPP(Fe)	colorimetric	8.5	S11
copper metal–organic polyhedra	colorimetric	1.5	S12
Fe-Co bimetallic alloy nanoparticles	colorimetric	0.01	S13
$ZnFe_2O_4$ magnetic nanoparticles	colorimetric	0.3	S14
$ZnFe_2O_4$ decorated ZnO heterostructures	colorimetric	0.4	S15
carbon nitride dots	colorimetric	0.5	S16
g-C_3N_4 nanosheets	colorimetric	1.0	S17
TiO_2 nanotubes	electrochemical	5	S18
g-C_3N_4 nanosheets	electrochemical	11	S19
GOx/PDA/ZIF-8@rGO/GCE	electrochemical	0.333	S20
Graphitic Carbon Nitride Nanosheets	fluorescent	0.4	S21
Lanthanide coordination polymer nanoparticles	fluorescent	0.065	S22
MIL-53(Fe)	fluorescent	0.00844	This work

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Table S2 Results of determination of glucose in serum samples

Samples [a]	Conventional enzymatic method [b] (mmol L^{-1})	Proposed method (mmol L^{-1}) Mean[c] ± SD[d]	Recovery (%)	RSD（%）
Sample 1	4.48	4.13±0.10	92.2	2.4
Sample 2	5.05	4.92±0.05	97.4	1.0
Sample 3	5.67	5.90±0.20	104	3.4
Sample 4	6.96	6.65±0.17	95.5	2.6
Sample 5	7.66	7.73±0.01	101	0.13
Sample 6	8.02	8.57±0.09	107	1.1
Sample 7	16.96	17.44±0.14	103	0.80

[a] The serum samples were obtained from the Guilin Hospital of Chinese Traditional and Western Medicine.

[b] The glucose determination was performed by the conventional enzymatic method at the Guilin Hospital of Chinese Traditional and Western Medicine.

[c] n=3

[d] SD: Standard Deviation

Table S3 Results of determination of glucose in serum samples by using a standard addition method.

Sample [a]	Conventional enzymatic method [b] (mmol L^{-1})	Added (mmol L^{-1})	Proposed method (mmol L^{-1}) Mean[c] ± SD[d]	Recovery (%)	RSD (%)
Sample 1	4.48	0.35	4.48±0.09	92.8	2.0
		0.70	4.87±0.07	94.0	1.4
		1.4	5.60±0.09	95.2	1.6
		2.1	6.10±0.06	92.7	0.98
		2.8	6.85±0.10	94.1	1.5
		3.5	7.59±0.16	95.1	2.1
		4.2	8.39±0.04	96.7	0.48
		4.9	9.35±0.03	99.7	0.32
		5.6	9.83±0.05	97.5	0.51
		7.0	11.30±0.07	98.4	0.62
		8.4	12.06±0.28	93.6	2.3
		9.8	13.43±0.19	94.0	1.4
		11.2	15.75±0.30	100	1.9

[a] The serum samples were obtained from the Guilin Hospital of Chinese Traditional and Western Medicine.

[b] The glucose determination was performed by the conventional enzymatic method at the Guilin Hospital of Chinese Traditional and Western Medicine.

[c] n=3

[d] SD: Standard Deviation