Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

Encapsulation of enzyme into mesoporous cages of metal-organic frameworks for the development of highly stable electrochemical biosensors

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Table S1. Comparison of the performances of different H_2O_2 electrochemical biosensors based on HRP.

Elements / Electrodes	Sensitivity ($\mu A\ mM^{-1}$)	Linear range (μM)	Detection limit (μM)	References
Nafion/HRP-gold nanoseed-TiO_2/GCE	0.23	41–630	6.5	1
HRP/RTIL/GNPs-TNTs	-	5–1000	2.1	2
HRP/AuNP-PTA-TNT/[Demim]Br/GCE	10.7	90–1400	6.5	3
CHIT/HRP/KN/Au electrode	-	40–6000	12	4
HRP/sol-gel/ MWNTs/GCE	-	70–3000	14	5
ZIFs@HRP/GO	-	20–6000	3.4	6
HRP@PCN-333(Fe)/GCE	9.74	0.5–1472	0.09	This work

RTIL, room-temperature ionic liquid; GNPs, gold nanoparticles; TNTs, TiO_2 nanotubes; PTA, 12-phosphotungstic acid; CHIT, chitosan; KN, $KNbO_3$ nanoneedles; MWNTs, multi-walled carbon nanotubes; GO, graphene oxide.

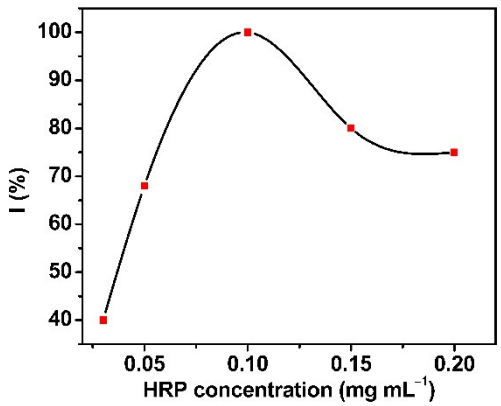

Fig. S1. Effect of the loading amounts of HRP into PCN-333(Fe) on the current responses of the HRP@PCN-333(Fe)/GCE for 0.1 mM H_2O_2.

The loading amout of HRP into PCN-333(Fe) was optimized according to the current responses of the HRP@PCN-333(Fe)/GCE for 0.1 mM H_2O_2. The current response of the modified electrode increased sharply with increasing the amount of HRP to the maximal value of 0.1 mg mL^{-1}. Then the current response began decreasing with further increasing the amount of HRP (see Fig. S1). Hence a loading amount of 0.1 mg mL^{-1} was selected for further studies. Furthermore, the agitating time for loading HRP was also optimized from 10 to 60 minutes, the sensor could obtain the highest current response at 40 minutes. Therefore, 40 minutes was chosen for the following experiments.

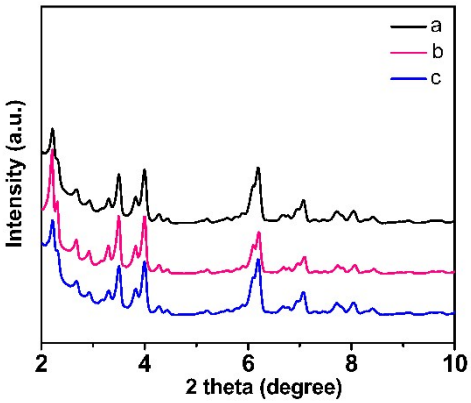

Fig S2. The powder XRD patterns of PCN-333(Fe) (a) original, (b) after being immersed in H_2O overnight and (c) after electrochemical measurements (100 consecutive cyclic voltammetric scans).

The powder of PCN-333(Fe) was dispersed in the deionized water overnight. Then the precipitate was separated by centrifugation and dry at 85 ^oC for the XRD characterization. On the other hand, in order to test the structure stability of the PCN-333(Fe) in electrochemical measurements, the suspension of PCN-333(Fe) (1mg mL^{-1}) was dropped on surface of the ITO electrode (considering the amount of sample required for XRD testing, an ITO electrode with the larger area was used). The modified electrode was dry at room temperature and then consecutively scanned for 100 cycles in 0.1 M PBS (pH 7.0) at a scanned rate of 100 mV s^{-1} (in the potential widows of –0.4 – 0.6 V). Finally, the PCN-333(Fe) was scraped off the working electrode and dry at 85 ^oC for the XRD characterization.

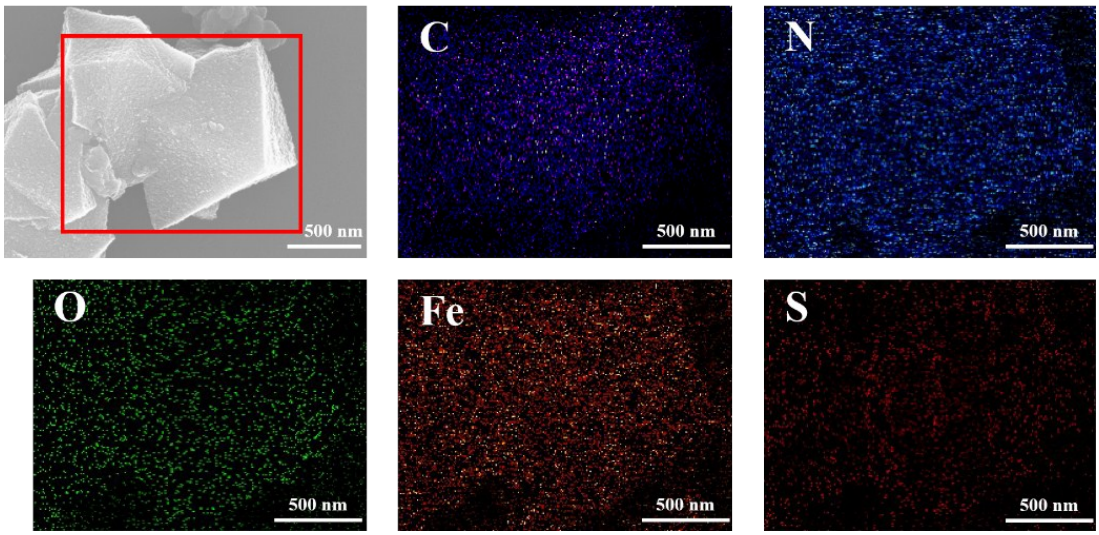

Fig. S3. A typical SEM image and EDS element mapping of HRP@PCN-333(Fe).

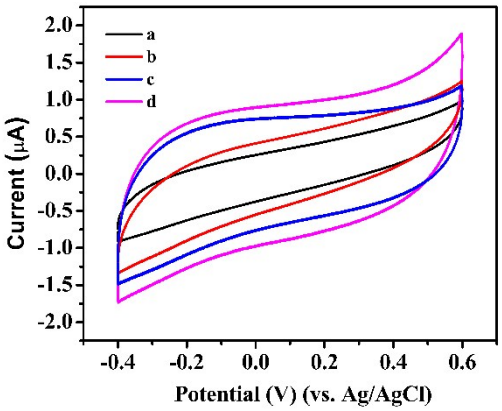

Fig. S4. CVs of the bare GCE (a), HRP/GCE (b), PCN-333(Fe)/GCE (c) and HRP@PCN-333(Fe)/GCE (d) in 0.1 M PBS (pH 7.0) at a scan rate of 100 mV s^{-1}.

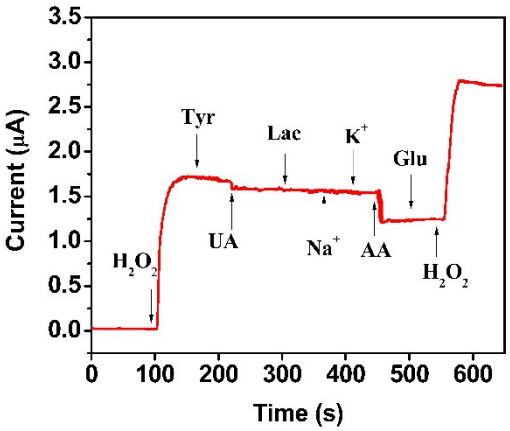

Fig. S5. **A**mperometric responses of the HRP@PCN-333(Fe)/GCE to respectively added 0.1 mM H_2O_2, 0.5 mM Tyr, UA, Lac, Na^+, K^+, AA, and Glu in 0.1 M PBS (pH 7.0). The applied potential: −0.10 V.

References:

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