Supporting Information

A Nano-sized Cu-MOF with High Peroxidase-Like Activity and Its Potential Application in Colorimetric Detection of H_2O_2 and Glucose

Hao Yu[1], Hanliu Wu[1], Xuemei Tian[1], Yafen Zhou[1], Chunguang Ren[2*], Zhonghua Wang[1*]

1. Chemical Synthesis and Pollution Control Key Laboratory of Sichuan Province, College of Chemistry and Chemical Engineering, China West Normal University, Nanchong, Sichuan 637002, P. R. China.

2. Yantai Institute of Materia Medica, Yantai 264000, Shandong, P. R. China.

*Corresponding authors.

Email: zhwangs@163.com (Z. Wang)

Tel: (+86) 817-2568081, Fax: (+86) 817-2445233.

E-mail: cgren@yimm.ac.cn (C. Ren)

Experimental Section

1. Effects of pH, catalyst concentration and reaction temperature on the peroxidase activity of Cu-MOF

The pH effect was performed with the catalytic oxidation of OPDA in 0.1 M phosphate buffer (pH 7.4). HCl or NaOH solution was used to adjust the pH. The concentration of Cu-MOF was fixed at 0.06 mg·mL^{-1} and temperature at 30 °C with a series of pH (3.0, 4.0, 5.0, 6.0, 7.0, 8.0, and 9.0) for 20 min. The pH effect was performed by catalytic oxidation of TMB in acetate buffer (0.1 M) with a series of pH (3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0), and the other conditions are consistent with the above. The catalyst concentration effect was performed by catalytic oxidation of OPDA and TMB with fixed H_2O_2 (1.8 mM), OPDA (3 mM), and the temperature remained at 30 °C. The concentrations range of Cu-MOF solution (0.03, 0.04, 0.05, 0.06, 0.07, 0.08 and 0.09 mg·mL^{-1}). The temperature effect was performed by catalytic oxidation of OPDA in fixed H_2O_2 (1.8 mM), OPDA (3 mM) 30 ℃. Mixed solution was incubated for 20 min at a series of temperatures (25, 30, 35, 40, 45, 50, 55, 60, 65 and 70 °C). The temperature effect on catalytic oxidation of TMB was performed with temperature range from 25 to 50 °C (25, 30, 35, 40, 45, and 50 °C) and the other conditions are consistent with above.

2. Detection of H_2O_2

300 μL TMB solution (10 mM, dissolve in DMF), 100 μL different concentrations of H_2O_2 with varying concentrations increase successively were added to 2.6 mL 0.06 mg·mL^{-1} Cu-MOF solution (Cu-MOF solid was dispersion in acetic acid). The resultant solution was used for conducting the absorption spectroscopy measurements by ultraviolet-visible spectrophotometer at 652 nm after incubation for 20 min at 30 °C.

3. Detection of glucose

First, 100 μL glucose solution with different concentrations, 100 μL 1.0 mg· mL^{-1} GOX (prepared in 0.5 mL NaH_2PO_4, pH 7.0) was incubated at 37 °C for 20 min to yield H_2O_2. Followed by addition of 300 μL 5mM TMB (dissolved DMF) and 4 mL

0.08 mg·ml^{-1} Cu-MOF (dispersed in 0.1 M HAc-NaAc buffer, pH 4.0). The resultant solution was used to conduct the absorption spectroscopy performances by ultraviolet-visible spectrophotometer at 652 nm after incubation for 20 min at 30 °C. In order to determine the selectivity of glucose, the interference of other sugars on the determination of glucose was explored. Under the same conditions, 2 mM sucrose, 2 mM lactose, 2 mM maltose were used to replace glucose (300 μM) in the experiment.

4. Detection of ascorbic acid

200 μL TMB solution (0.67 mM, dissolving DMF), 100 μL H$_2$O$_2$ solution 100 μL (0.67 mM), and successively increasing ascorbic acid solutions with different concentrations, and add them to 2.6 mL 0.06 mg·mL^{-1} Cu-MOF solution. After reacting for 20 min at 30 °C, the resulting solution was used to measure the absorption spectrum at 652 nm by an ultraviolet-visible spectrophotometer. In order to explore the influence of potential interfering substances on the experimental results, we did an anti-interference experiment, using 400 μM K$^+$, Zn^{2+}, K$^+$, L-glutamic acid, glycine, and L-histidine to replace 400 μM in the system, respectively. Ascorbic acid did a selective control experiment.

5. Detection of sodium thiosulfate

200 μL TMB solution (0.67 mM, dissolved in DMF), 100 μL H$_2$O$_2$ (0.67 mM), and sodium thiosulfate solution with desired concentration were added to 2.6 mL 0.06 mg·mL^{-1} Cu-MOF solution (dissolved in 0.1 M HAc-NaAc buffer, pH 4.0). The resultant solution was used for conducting the absorption spectroscopy measurements by ultraviolet-visible spectrophotometer at 652 nm after incubation for 20 min at 30 °C.
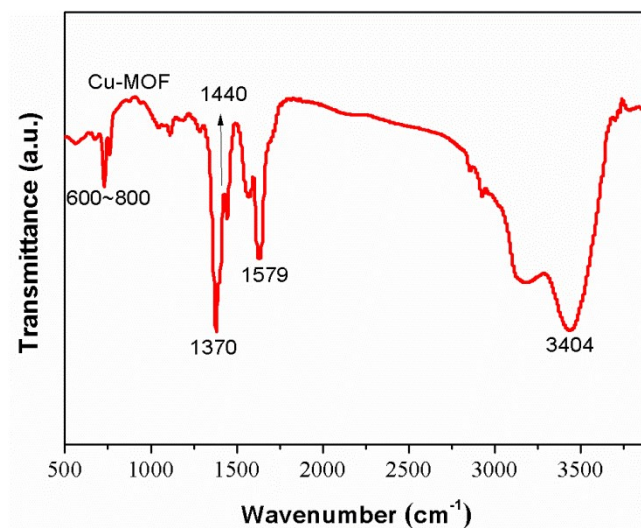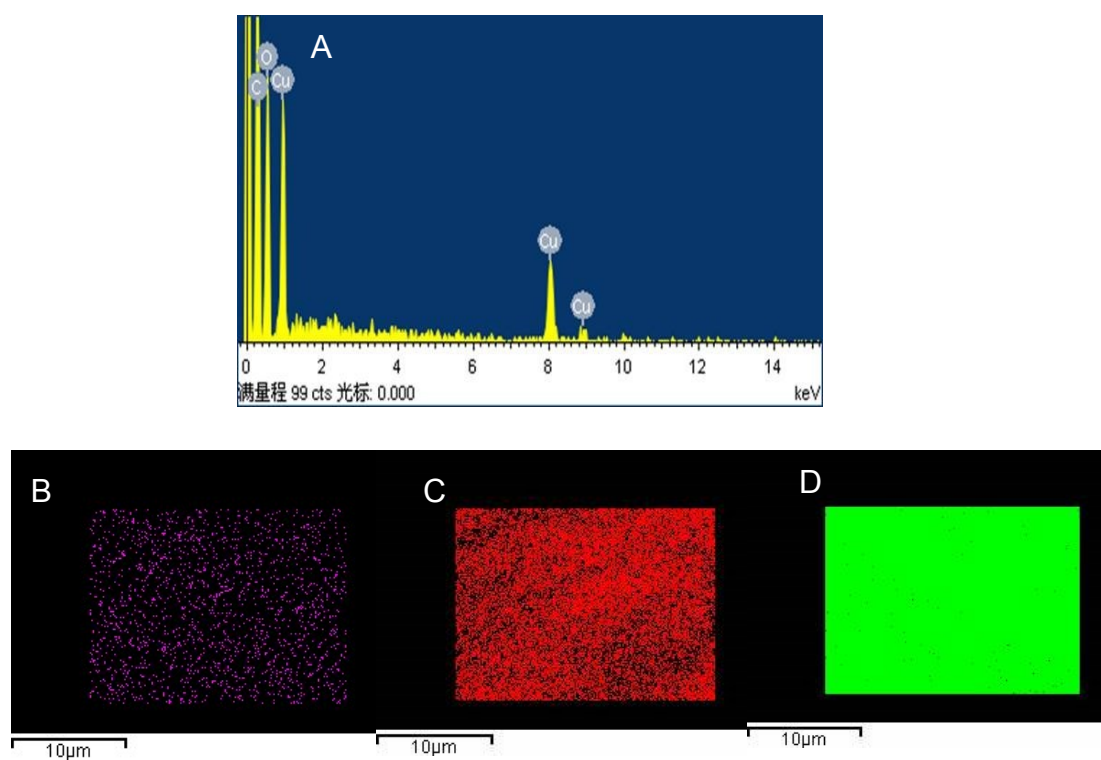
Fig. S1. The FTIR spectra of Cu –MOF

Fig.S2. The EDS spectrum (A) and elemental mapping of Cu, C and O elements (B, C, D)

Table S1 Study on oxidation kinetic parameters of OPDA in Cu-MOF and some other reported nanomaterials

Catalyst	K_m		V_{max}（Ms^{-1}）		Reference
	OPDA	H_2O_2	OPDA	H_2O_2	
HRP	0.59	0.34	4.65×10^{-8}	9.48×10^{-8}	[1]
MnO_2	0.31	0.12	8.21×10^{-8}	5.71×10^{-8}	[1]
Cu_2O-NWCs	0.47	242	5.54×10^{-8}	4.30×10^{-8}	[2]
$Fe_3O_4@Cu@Cu_2O$	0.85	2.3	13.1×10^{-8}	11.9×10^{-8}	[3]
Cu-MOF	0.54	0.178	7.87×10^{-8}	2.56×10^{-8}	This work

Table S2 Study on oxidation kinetic parameters of TMB in Cu-MOF and some other reported nanomaterials

Catalyst	K_m		V_{max}（Ms^{-1}）		Reference
	TMB	H_2O_2	TMB	H_2O_2	
HRP	0.434	3.70	10.0×10^{-8}	8.71×10^{-8}	[4]
Cu NCs	0.648	29.16	5.96×10^{-8}	4.22×10^{-8}	[5]
Fe_3O_4 MNPs	0.098	154	3.44×10^{-8}	9.78×10^{-8}	[4]
MoO_2	8.85	0.014	5.20×10^{-8}	0.41×10^{-8}	[6]
MoS_2	0.525	0.0116	5.16×10^{-8}	0.99×10^{-8}	[6]
Fe-MIL-88NH_2-MOF	0.284	2.06	10.47×10^{-8}	7.04×10^{-8}	[7]
Cu-MOF	0.456	28.58	2.478×10^{-8}	5.45×10^{-8}	This work

Table S3 Cu-MOF materials and some other reported peroxidase-like materials related to colorimetric determination of H_2O_2

Catalyst	Substance	Liner range(μM)	Detection limit(μM)	Reference
CuS-GNS	TMB	2-20	1.2	[8]
MnO_2	TMB	$16-3.33 \times 10^5$	10	[1]
Fe_3O_4 MNPs	ABTS	5-100	3	[9]
MoO_2	TMB	1-100	0.7	[6]
MOF-808	TMB	10-15000	4.5	[10]
Cu–hemin MOFs	TMB	1-1000	0.42	[11]
Cu-MOF	TMB	5-300	4.6	This work

Table S4 Cu-MOF materials and some other reported peroxidase-like materials related to colorimetric determination of glucose

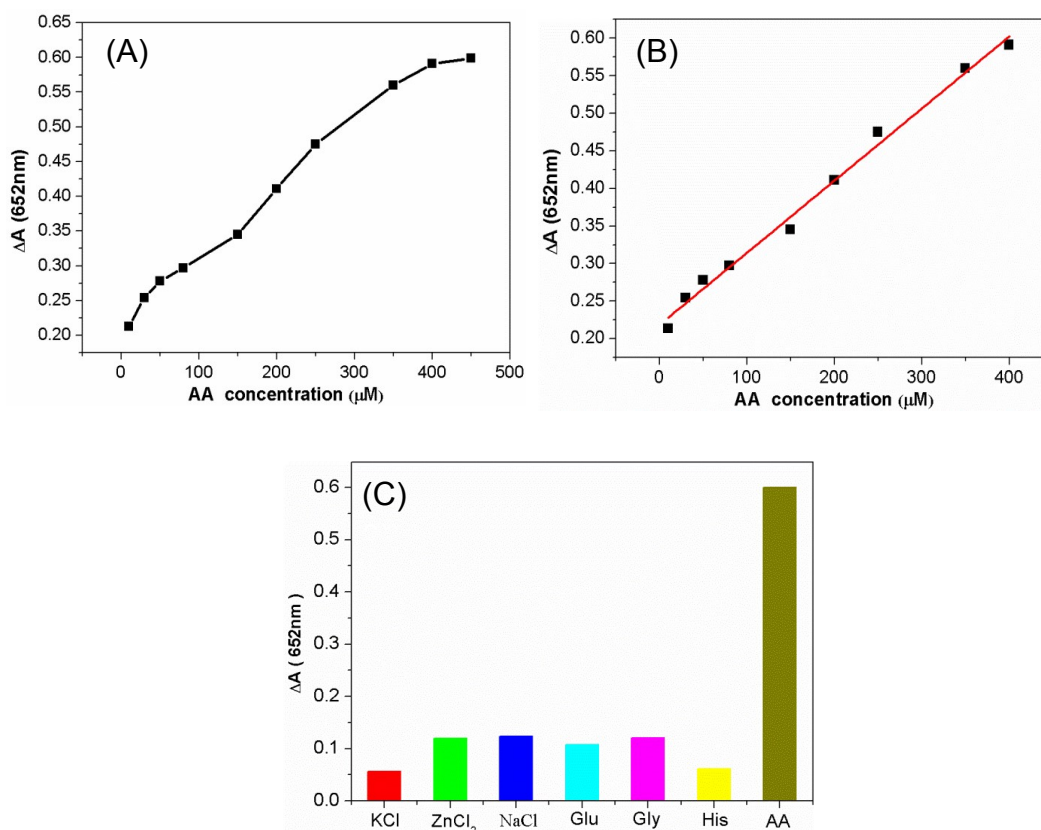| Catalyst	Substance	Liner range(μM)	Detection limit(μM)	Reference
CuS NPs	TMB	2-1800	0.12	[12]
$NiFe_2O_4$ MNPs	ABTS	0.94-25	0.45	[13]
Ch-Ag NPs	TMB	5-200	0.1	[14]
MOF-808	TMB	5.7-1700	5.7	[10]
Cu–hemin MOFs	TMB	10-3000	6.9	[11]
Cu-MOF	TMB	50-500	4.7	This work

Fig. S3 Colorimetric detection of ascorbic acid. (A) Dose-responsive curve; (B) Linear calibration plot; (C) The inhibition ability of interfering substances. The concentration of K^+, Zn^{2+}, Na^+, L-glutamic acid (Glu), glycine (Gly), L-histidine (His) was 400 μM. (ΔA was the absorbance difference of TMB oxidation at 652 nm between the absorbance of the blank group and that of addition of AA or interfering substances)

Ascorbic acid (AA), also known as vitamin C, is a water-soluble vitamin necessary to maintain normal body functions. It is abundant in fruits and vegetables[15]. Ascorbic acid is also an antioxidant[16]. A colorimetric detection of AA was established based on the fact that the Cu-MOF catalyzed color reaction of TMB with H_2O_2 can be inhibited by the addition of AA.

As shown in Fig. S3, the absorbance difference (△A) of TMB oxidation at 652 nm gradually increases with the concentration of AA from 1 μM to 450 μM. The change of △A becomes slow when the concentration of AA reaches 400 μM. A good linear

relationship between the concentration of AA and $\triangle A$ can be achieved when concentration of AA is in the range of 1 μM to 400 μM with a correlation coefficient of 0.991. The limit of detection was measured to be 0.69 μM. When 400 μM K^+, Zn^{2+}, Na^+, L-glutamic acid, glycine, or L-histidine was used to replace ascorbic acid in the reaction system, the absorbance differenced was much smaller than that of the AA, indicating the high selectivity of AA detection.
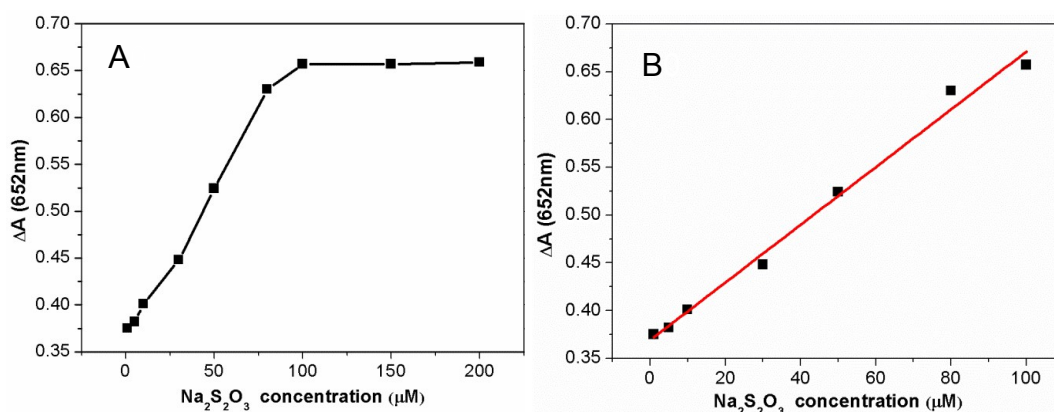
Fig. S4 Colorimetric detection of sodium thiosulfate ($Na_2S_2O_3$). Dose-response curve (A) and linear calibration plot (B). (ΔA was the absorbance difference of TMB oxidation at 652 nm between the absorbance of the blank group and that of addition of $Na_2S_2O_3$, namely, ΔA (652 nm) = Abs (blank, 652 nm) – Abs (thiosulfate, 652 nm))

Sodium thiosulfate ($Na_2S_2O_3$) is a compound with strong antioxidant properties and has no toxic effect on human body. It was used in the treatment of cyanide poisoning a century ago. Studies have shown that sodium thiosulfate can inhibit the activity of peroxidase, and there is a significant dose effect. Therefore, we try to establish a simple colorimetric method for the determination of sodium thiosulfate. As shown in Fig. S4, The ΔA at 652 nm was almost linearly increased with the increasing of $Na_2S_2O_3$ concentration up to 100 μM. When the concentration of $Na_2S_2O_3$ was beyond to 100 μM, the oxidation of TMB by H_2O_2 was completely inhibited. The linear detection range of $Na_2S_2O_3$ was from 1 to 100 μM (the correlation coefficient was 0.989), and the limitation of detection was 0.52 μM.

Reference

[1] X. Liu, Q. Wang, H. Zhao, L. Zhang, Y. Su, Y. Lv, BSA-templated MnO_2 nanoparticles as both peroxidase and oxidase mimics, Analyst, 137 (2012) 4552-4558.

[2] G.L. Li, P. Ma, Y.F. Zhang, X.L. Liu, H. Zhang, W.M. Xue, Y. Mi, Y.E. Luo, H.M. Fan, Synthesis of Cu_2O nanowire mesocrystals using PTCDA as a modifier and their superior peroxidase-like activity, J. Mater. Sci., 51 (2016) 3979-3988.

[3] Z. Wang, M. Chen, J. Shu, Y. Li, One-step solvothermal synthesis of $Fe_3O_4@Cu@Cu_2O$ nanocomposite as magnetically recyclable mimetic peroxidase, J. Alloys Compd., 682 (2016) 432-440.

[4] L. Gao, J. Zhuang, L. Nie, J. Zhang, Y. Zhang, N. Gu, T. Wang, J. Feng, D. Yang, S. Perrett, X. Yan, Intrinsic peroxidase-like activity of ferromagnetic nanoparticles, Nat. Nanotechnol., 2 (2007) 577-583.

[5] L. Hu, Y. Yuan, L. Zhang, J. Zhao, S. Majeed, G. Xu, Copper nanoclusters as peroxidase mimetics and their applications to H_2O_2 and glucose detection, Anal Chim Acta, 762 (2013) 83-86.

[6] L. Huang, Z. Li, L. Guo, Colorimetric assay of acetylcholinesterase inhibitor tacrine based on MoO_2 nanoparticles as peroxidase mimetics, Spectrochim Acta A Mol Biomol Spectrosc, 224 (2020) 117412.

[7] Y.L. Liu, X.J. Zhao, X.X. Yang, Y.F. Li, A nanosized metal-organic framework of Fe-MIL-88NH($_2$) as a novel peroxidase mimic used for colorimetric detection of glucose, Analyst, 138 (2013) 4526-4531.

[8] G. Nie, L. Zhang, X. Lu, X. Bian, W. Sun, C. Wang, A one-pot and in situ synthesis of CuS-graphene nanosheet composites with enhanced peroxidase-like catalytic activity, Dalton Trans, 42 (2013) 14006-14013.

[9] H. Wei, E. Wang, Fe_3O_4 magnetic nanoparticles as peroxidase mimetics and their applications in H_2O_2 and glucose detection, Anal. Chem., 80 (2008) 2250-2254.

[10] H.Q. Zheng, C.Y. Liu, X.Y. Zeng, J. Chen, J. Lu, R.G. Lin, R. Cao, Z.J. Lin, J.W. Su, MOF-808: A Metal-Organic Framework with Intrinsic Peroxidase-Like Catalytic Activity at Neutral pH for Colorimetric Biosensing, Inorg Chem, 57 (2018) 9096-9104.

[11] F. Liu, J. He, M. Zeng, J. Hao, Q. Guo, Y. Song, L. Wang, Cu–hemin metal-organic frameworks with peroxidase-like activity as peroxidase mimics for colorimetric sensing of glucose, J. Nanopart. Res., 18 (2016).

[12] A.K. Dutta, S. Das, S. Samanta, P.K. Samanta, B. Adhikary, P. Biswas, CuS nanoparticles as a mimic peroxidase for colorimetric estimation of human blood glucose level, Talanta, 107 (2013) 361-367.

[13] L. Su, W. Qin, H. Zhang, Z.U. Rahman, C. Ren, S. Ma, X. Chen, The peroxidase/catalase-like activities of MFe_2O_4 (M=Mg, Ni, Cu) MNPs and their application in colorimetric biosensing of glucose, Biosens Bioelectron, 63 (2015) 384-391.

[14] H. Jiang, Z. Chen, H. Cao, Y. Huang, Peroxidase-like activity of chitosan stabilized silver nanoparticles for visual and colorimetric detection of glucose, Analyst, 137 (2012) 5560-5564.

[15] S.-D. Wang, L.-X. Xie, Y.-F. Zhao, Y.-N. Wang, A dual luminescent sensor coordination polymer for simultaneous determination of ascorbic acid and tryptophan, Spectrochim. Acta, Part A, 242 (2020) 118750.

[16] W. He, X. Wu, J. Liu, X. Hu, K. Zhang, S. Hou, W. Zhou, S. Xie, Design of AgM bimetallic alloy nanostructures (M= Au, Pd, Pt) with tunable morphology and peroxidase-like activity, Chem.

Mater., 22 (2010) 2988-2994.