Supporting Information

Enhanced peroxidase-like activity of MOF nanozyme by co-catalysis for colorimetric detection of cholesterol

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Experimental Section

Reagents and materials

Cupric nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), Sodium chloride (NaCl) and potassium chloride (KCl) were provided from Sinopharm Chemical Reagent Co., Ltd. (China). Na_2MoO_4 was acquired from Shanghai Titan Scientific Co., Ltd. (Shanghai, China). 2-Methylimidazole (2-MI) was obtained from Hebei Bailingwei Ultrafine Materials Co., Ltd. (Hebei, China). Sodium aside (NaN_3), benzoquinone (BQ), 3,3',5,5' -tetramethylbenzidine (TMB) were acquired from Shanghai TCI chemical reagent company. Cholesterol and cholesterol oxidase were purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Acetic acid, sodium acetate, magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), glucose (Glu), urea and 30% H_2O_2 were obtained from Xilong Scientific Co., Ltd. (Guangdong, China). Arginine (Arg) and lysine (Lys) was obtained from Nine-Dinn Chemistry Co., Ltd. (Shanghai, China). Uric acid (UA), ascorbic acid (AA), L-cysteine (L-Cys) and cholesterol esterase were provided from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Ultrapure water (≧18.2 MΩ•cm) was taken from Milipore Purifier (Bedford, MA). Besides, serum samples were taken from Chinese Traditional and Western Medicine Hospital in Guilin.

Characterizations and instruments

Powder X-ray diffraction (XRD) pattern was conducted on a D/max 2550 VB/PC diffractometer (Rigaku, Japan) with Cu Kα radiation (λ = 0.15418 nm). The scanning electron microscopy (SEM) was performed on a FEI Quanta 200 FEG (FEI, Netherlands). And the transmission electron microscopy (TEM) was taken on a Tecnai F-20 (Thermo Fisher Scientific, USA). The Fourier Transformed infrared spectroscopy (FTIR) was recorded on a Spectrum Two FT-IR spectrometer (Perkin-Elmer, USA). X-ray photoelectron spectroscopy (XPS) data were obtained with a Thermo ESCALAB 250XI electron spectrometer (Thermo Fisher Scientific, USA) using 150 W Al Kα radiation. Electrochemical impedance measurement was estimated on a CHI 660E electrochemical workstation (Chenhua Instrument, China) with an ordinary three-electrode system. Additionally, UV-vis spectra were determined by Agilent Cary 60 spectrophotometer (Agilent, USA).

Synthesis of Cu-2MI

The synthesis of Cu-2MI was carried out according to the preparation method reported by Yang et al,[1] and the detailed steps were as follows: Firstly, 0.4832 g $Cu(NO_3)_2 \cdot 3H_2O$ was completely dissolved in

the mixture of 25 mL methanol and water (V:V=1:1) under stirring. Meanwhile, 0.1642 g 2-MI was added to the mixture of 25 mL methanol and water (V:V=1:1). Then, the above two solutions were mixed and continuously stirred at room temperature for 1 h until blue precipitation appeared. At the end of the reaction, it was centrifuged (9000 rpm, 3min) and washed three times with a mixture of methanol and water (V:V=1:1). Then, the obtained Cu-2MI solids were dried in a vacuum drying oven at 60 ℃ for 12 h. Finally, the dried product was ground for subsequent experimental use.

Synthesis of MoCu-2MI

Firstly, 40 mg of weighed Na_2MoO_4 was dissolved in 20 mL of deionized water to form a solution. Subsequently, 80 mg Cu-2MI was weighed and dispersed in 40 mL anhydrous ethanol. Then, the obtained Na_2MoO_4 solution was added to the Cu-2MI solution by drops under agitation, and the reaction was stopped by continuously stirring at 80 ℃ for 2 h. After cooling to room temperature, the solids were collected by centrifugation (9000 rpm, 3min) and washed four times with ethanol, and dried in vacuum at 50 ℃ for 12 h to obtain MoCu-2MI.

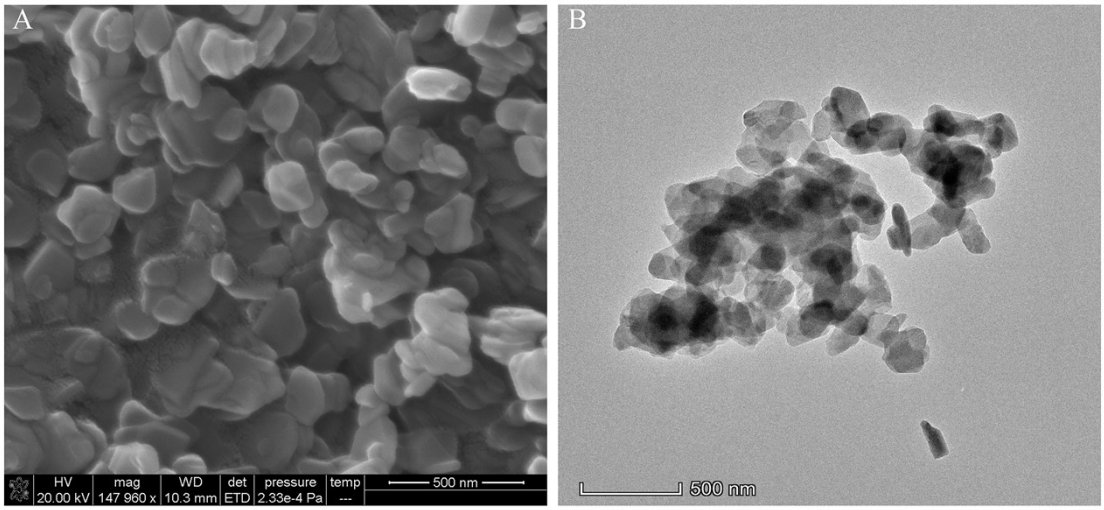

Fig. S1. SEM (A) and TEM images (B) of Cu-2MI.

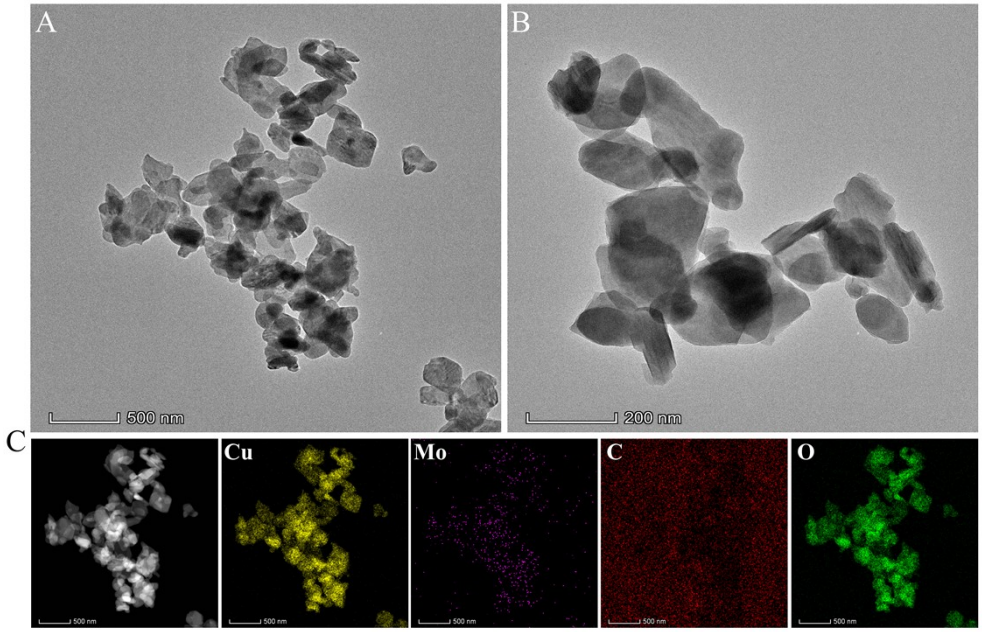

Fig. S2. TEM (A and B) and EDS-mapping images (C) of MoCu-2MI.

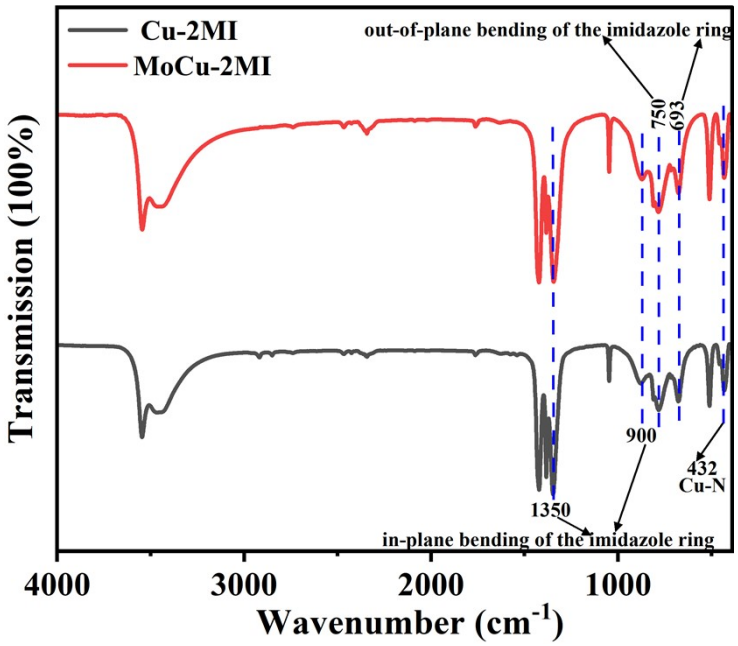

Fig. S3. FT-IR spectra of Cu-2MI (black) and MoCu-2MI (red).

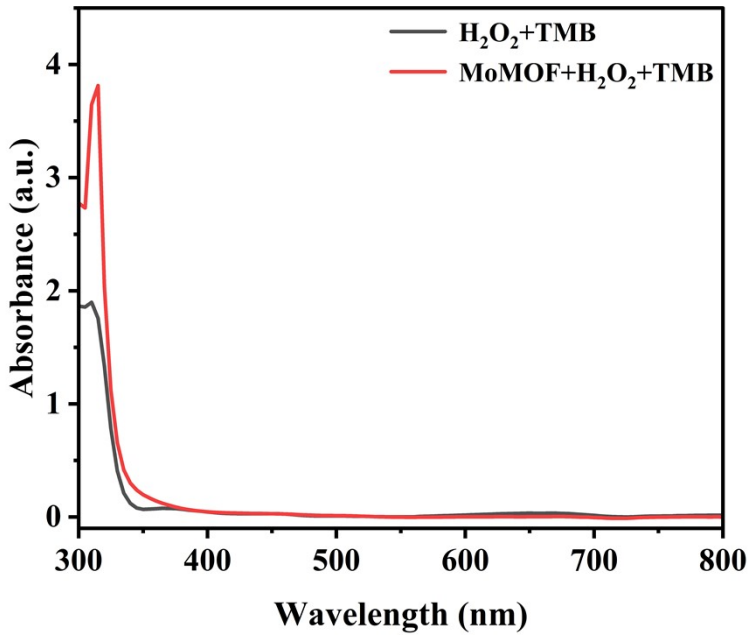

Fig. S4. UV-vis spectra of MoMOF in the H_2O_2/TMB solution.

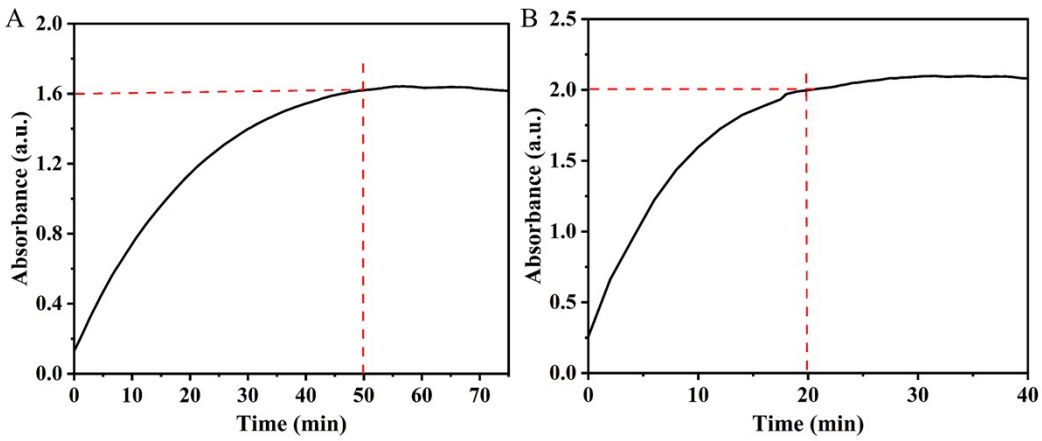

Fig. S5. The equilibrium time of Cu-2MI (A) and MoCu-2MI (B) catalytic systems.

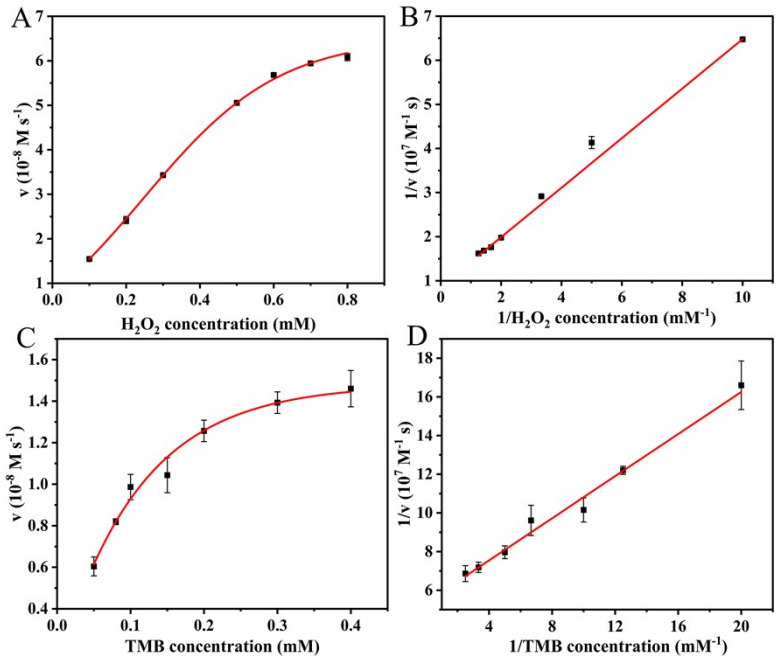

Fig. S6. Steady-state kinetic assay of Cu-2MI. (A) various H_2O_2 concentrations and (C) TMB concentrations, with (B) and (D) the corresponding Lineweaver−Burk reciprocal plots.

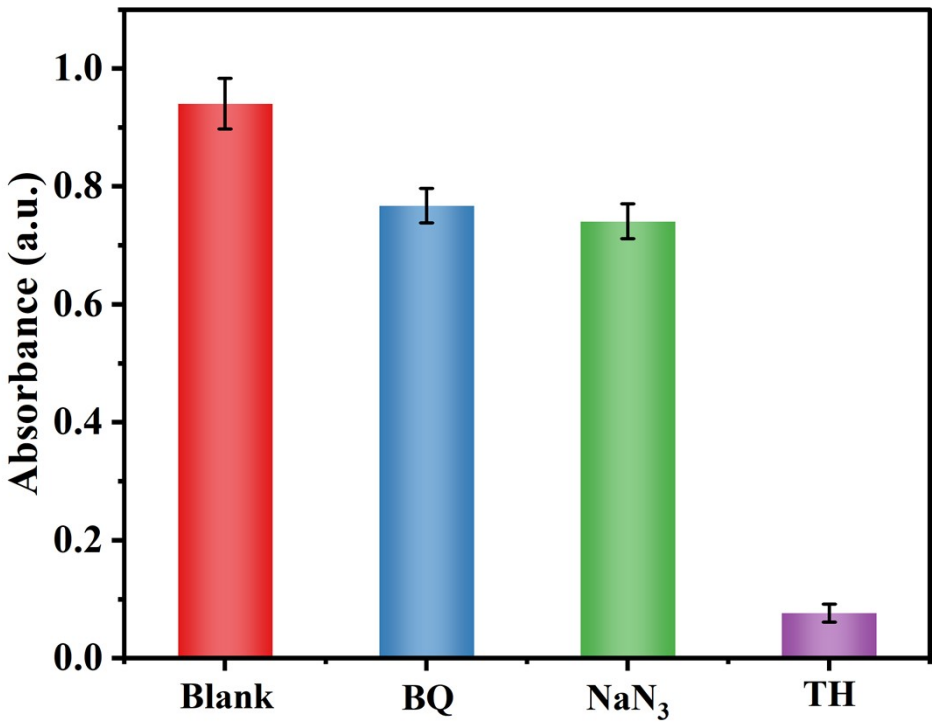

Fig. S7. UV-vis spectra of reactions of different ROS scavengers with MoCu-2MI (H_2O_2: 1 mM, TMB: 0.5 mM, BQ: 1 mM, NaN_3: 1 mM, TH: 0.1 mM).

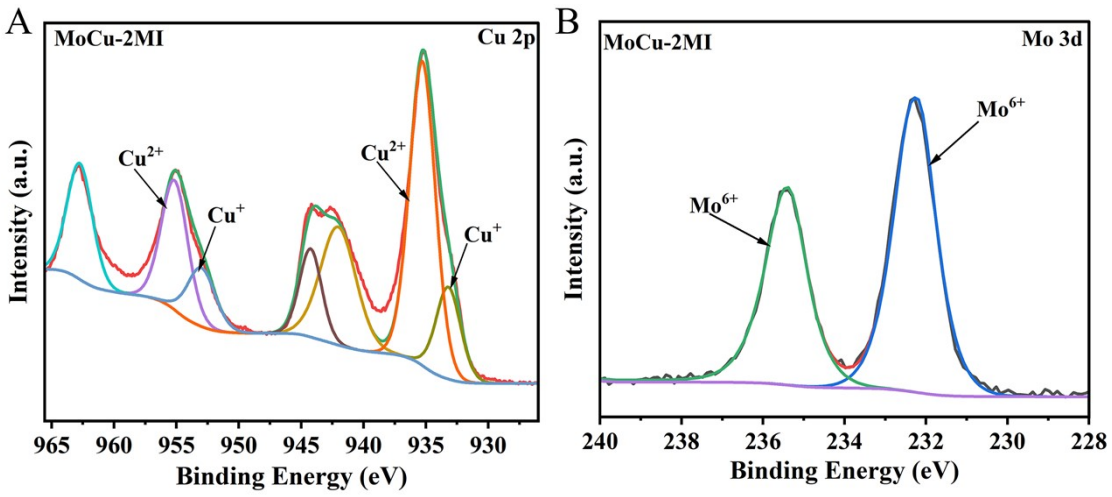

Fig. S8. (A) Cu 2p and (B) Mo 3d XPS spectra in MoCu-2MI.

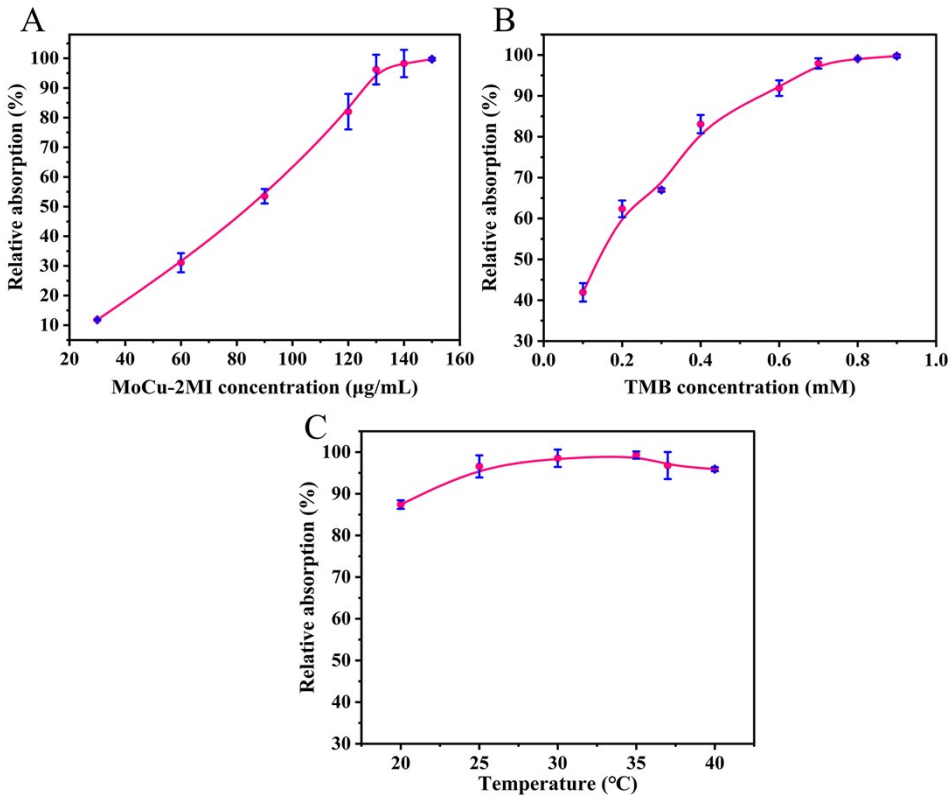

Fig. S9. The influence of MoCu-2MI concentration (A), TMB concentration (B) and temperature (D) on the catalytic activity of MoCu-2MI.

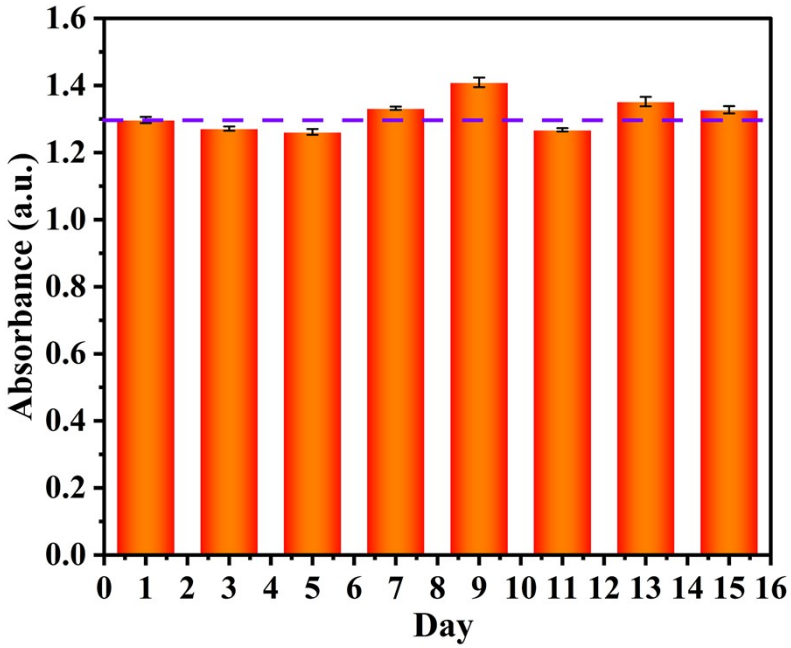

Fig. S10. The system stability based on MoCu-2MI colorimetric detection.

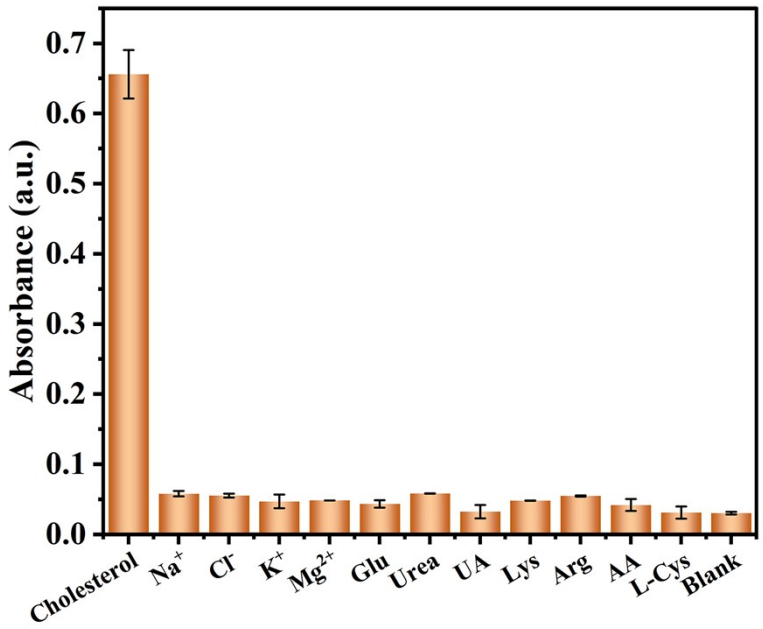

Fig. S11. Selective analysis for cholesterol colorimetric detection (cholesterol concentration was 0.06 mM, while potential interfering species were 0.6 mM).

Table S1 Comparison of the kinetic parameters of H_2O_2 and TMB with the use of different catalysts.

Catalyst	Substance	K_m [mM]	V_{max} [10^{-8} M s^{-1}]	References
HRP	TMB	0.434	10.0	[2]
	H_2O_2	3.70	8.71	
Fe_3O_4	TMB	0.098	3.44	[2]
	H_2O_2	154	9.78	
MIL-53(Fe)	TMB	1.08	8.78	[3]
	H_2O_2	0.04	1.86	
Fe-MIL-88NH_2	TMB	0.284	10.47	[4]
	H_2O_2	2.06	7.04	
Pt-MoO_3	TMB	0.106	4.3	[5]
	H_2O_2	3.2	3.8	
Zn-CuO	TMB	10	2.877	[6]
	H_2O_2	71	0.3	
Cu-2MI	TMB	0.10	1.86	
	H_2O_2	0.65	11.50	
MoCu-2MI	TMB	0.18	6.42	This work
	H_2O_2	0.18	11.90	

Table S2 Comparison of cholesterol detection performance based on different nanomaterials.

Materials	Detection methods	Linear range (μM)	LOD (μM)	References
ChOx/hemoglobin	Electrochemistry	10–600	9.5	[7]
AuNPs/ChOx	Electrochemistry	40–220	34.6	[8]
ChOx/CoOx NPs	Electrochemistry	4.2–50	4.2	[9]
Mo-CQDs	Colorimetry	10–600	7	[10]
Au/MoS_2	Colorimetry	40–1000	15	[11]
BNNSs@CuS	Colorimetry	10–100	2.9	[12]
CuO/graphene nanosphere	Colorimetry	100–800	78	[13]
MXene/CuS	Colorimetry	10−100	1.9	[14]
MoCu-2MI	Colorimetry	2−140	1.2	This work

Table S3 Comparing the cholesterol values measured by this colorimetric method and from the hospital.

Samples	Determined in the hospital (mM)	Determined by the proposed method (mM) (mean ± SD) (n = 3)	Relative deviation (%)
1	4.14	4.28±0.41	3.38
2	5.09	5.21±0.30	2.36
3	7.05	7.06±0.19	0.14
4	12.55	11.80±0.72	-5.98

Table S4 Recovery experiments for cholesterol detection in human serums.

Sample	Original (mM)	Added (mM)	Found (mM)	Recovery (%)	RSD (%, n=3)
1	4.14	2.30	6.29±0.23	97.67	3.62
		5.70	10.43±0.35	106.00	3.64
2	5.09	2.30	7.73±0.53	104.60	6.84
		5.70	10.51±0.57	97.41	5.67

References

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