Facile synthesis of Cu-based MOF confined in macroporous carbon hybrid material with enhanced electrocatalytic ability

Experimental

Chemical reagents

 β -NADH and H₂O₂ were obtained from Sigma. N,N'-dimethylformamide (DMF) (HPLC grade), 1,3,5-benzene-tricarboxylic acid (H₃BTC) and Cu(NO₃)₂·3H₂O were used as purchased from Beijing Chemical Co. Ltd. The 0.1 M phosphate buffer solution (PBS pH 7.0), which was made up from NaH₂PO₄, Na₂HPO₄, and H₃PO₄, was employed as a supporting electrolyte. All other reagents were of analytical grade, and all solutions were prepared with double distilled water.

Instrumentation

All the electrochemical experiments were performed with a CHI 830B electrochemical Analyzer (CH Instruments, Shanghai Chenhua Instrument Corporation, China) and a PARSTAT 2273 (AMETEK Instruments, USA) electrochemical workstation. A conventional three electrode cell was used, the working electrode used was glassy carbon electrode (GCE) or the modified electrode, a platinum electrode was applied as the counter electrode and an Ag/AgCl (in saturated KCl solution) electrode served as a reference electrode. All potentials in this paper were measured and reported versus Ag/AgCl. In this study, all the sample solutions were purged with purified nitrogen for 20 min to remove oxygen prior to the beginning of a series of experiments and all experiments were carried out at laboratory temperature. X-Ray diffraction (XRD) patterns were obtained on an X-ray

D/max-2200vpc (Rigaku Corporation, Japan) instrument operated at 40 kV and 20 mA using Cu K α radiation (k = 0.15406 nm). Fourier transform infrared (FT-IR) spectroscopy of the sample was recorded with Nicolet Magna 560 FT-IR spectrometer with a KBr plate. Nitrogen adsorption–desorption isotherms were measured on ASAP 2020 Micromeritics (USA) at 77 K. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area. Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectra (EDX) were determined with a Philips XL-30 ESEM operating at 3.0 kV.

Preparation of the modified electrodes

Prior to the modification, GCE (model CHI104, 3 mm diameter) was polished before each experiment with 1, 0.3 and 0.05 μ m alumina power, respectively, rinsed thoroughly with doubly distilled water between each polishing step, and then sonicated successively in 1 : 1 nitric acid, absolute alcohol, double distilled water. The cleaned electrode was dried with a high-purify nitrogen steam for the next modification. To prepare the modified electrodes, 5 mg of the as-prepared samples were dispersed into 1 mL DMF to give homogeneous suspension upon bath sonication. A 5 μ L of the suspension was dip-coated onto GCE and the electrode was then dried at room temperature.

Preparation of MPC

The SiO₂ template was prepared by the typical Stöber's method¹. The carbon was introduced into the interstices of the template using the modified method of Jun et al². In a typical synthesis, 2.0 g of sucrose was dissolved in 10 mL aqueous solution

containing 0.15 mL of 98% H₂SO₄. 2.0 g of SiO₂ template was immersed into sucrose solution and kept in vacuum for 3 h at room temperature for thorough impregnation. Then the mixture was heated at 100 °C for 6 h, followed by heating at 160 °C for a further 6 h for polymerization of sucrose. The solid was subsequently carbonized at 900 °C in N₂ for 3 h in a tube oven. The SiO₂ template was then etched away by overnight dissolution in 10% aqueous HF to leave behind a MPC.

Synthesis of Cu-MOF and Cu-MOF/MPC

The Cu-MOF was prepared as reported previously^{3, 4}. In a typical synthesis, 0.875 g (3.6 mmol) Cu(NO₃)₂.3H₂O were dissolved in 12 mL de-ionized water and mixed with 0.42 g (2.0 mmol) of H₃BTC dissolved in 12 mL ethanol. The solution was filled in a 40 mL Teflon liner, placed in an autoclave, and heated to 120 °C for 12 h. The obtained blue powder was recovered by filtration, and then washed with water and DMF. Thereafter, the Cu-MOF obtained by vacuum drying at 80 °C.

The Cu-MOF/MPC composite materials were prepared by dispersing MPC powder in the well-dissolved Cu(NO₃)₂/BTC mixture. The resulting suspensions were subsequently stirred and subjected to the same synthesis procedure as for Cu-MOF. The added MPC consisted of 60, 70, 80, or 90 wt% of the final material. The composites are referred to as Cu-MOF/MPC-1, Cu-MOF/MPC-2, Cu-MOF/MPC-3, and Cu-MOF/MPC-4, where 1, 2, 3, and 4 represent the 60, 70, 80, and 90 wt% of MPC in the samples, respectively.



Fig. S1 XRD patterns of Cu-MOF/MPC-1 (a), Cu-MOF/MPC-2 (b), Cu-MOF/MPC-3 (c), and Cu-MOF/MPC-4 (d).



Fig. S2 Nitrogen adsorption–desorption isotherms of Cu-MOF/MPC-1 (a), Cu-MOF/MPC-2 (b), Cu-MOF/MPC-3 (c), and Cu-MOF/MPC-4 (d).

Samples	$S_{\text{BET}} (\text{m}^2 \text{g}^{-1})$	$V_{\rm BJH}~({\rm cm}^3~{\rm g}^{-1})$
MPC	366.3	0.273
Cu-MOF	1146.8	0.551
Cu-MOF/MPC-1	491.2	0.365
Cu-MOF/MPC-2	440.7	0.332
Cu-MOF/MPC-3	407.9	0.303
Cu-MOF/MPC-4	382.8	0.301

Table S1 Parameters of the porous structures calculated from the adsorption of

 nitrogen values derived assuming the physical mixture of the composite components.

The detailed wavenumber range of 1300-1800 cm⁻¹ for MPC is presented in Fig. S3. The band around 1630 cm⁻¹ is attributed to C=O stretch vibration and the bands around 1560 and 1518 cm⁻¹ are ascribed to COO⁻ stretch asymmetric vibration. It is confirm that the presence of the oxygen-containing functional groups on the surface of MPC.



Fig. S3 FT-IR spectroscopy of MPC over the wavenumber range of 1300-1800 cm^{-1} .



Fig. S4 FT-IR spectroscopy of Cu-MOF/MPC-1 (a), Cu-MOF/MPC-2 (b), Cu-MOF/MPC-3 (c), and Cu-MOF/MPC-4 (d) over the wavenumber range of $400-2000 \text{ cm}^{-1}$.



Fig. S5 SEM images of MPC (A) and Cu-MOF (B).



Fig. S6 EIS of Cu-MOF/MPC-x composites in a 0.1 M KCl solution containing 5.0 mM $K_3Fe(CN)_6/K_2Fe(CN)_6$ and from 0.1 Hz to 10.0 KHz. Inset: the enlarged curves of these composites.

Table S2 Comparison of the R_{ct} and response to K ₃ Fe(CN) ₆ /K ₂ Fe(CN) ₆ with different	
electrodes (for five determinations)	

Electrode	GCE	MPC/	Cu-MOF/	Cu-MOF/M	Cu-MOF/M	Cu-MOF/M	Cu-MOF/M
		GCE	GCE	PC-1/GCE	PC-2/GCE	PC-3/GCE	PC-4/GCE
$R_{ct}(\Omega)$	462.1	5.9	991.2	48.6	21.7	8.2	7.6

Fig. S7 shows typical cyclic voltammograms (CVs) of Cu-MOF/MPC-3 in the absence (dash line) and presence (solid line) of 5 mM H_2O_2 . The Cu-MOF/MPC-x materials toward the reduction of H_2O_2 are shown in Fig. S8. Compared with other electrodes, Cu-MOF/MPC-3 exhibits highest response current and lowest overvoltage (Table S3).



Fig. S7 CVs of Cu-MOF/MPC-3/GCE in the absence (dash line) and presence (solid line) of 5 mM H_2O_2 (pH=7.0).



Fig. S8 CVs of Cu-MOF/MPC-x/GCE in the presence of 5 mM H_2O_2 (pH=7.0).

Electrodes	peak potential (V)	peak currents (µA)
Cu-MOF/MPC-1	-0.31	112.6
Cu-MOF/MPC-2	-0.32	119.3
Cu-MOF/MPC-3	-0.22	187.4
Cu-MOF/MPC-4	-0.26	169.9

Table S3 The peak potential and peak currents of H₂O₂ at the Cu-MOF/MPC-x/GCE.

The electrochemical results indicate that the Cu-MOF/MPC-3 composite perform the best among the synthesized materials so far in this study. Thus, we focused on the investigation of the electrochemical properties of Cu-MOF/MPC-3. Fig. S9 displays the current-time responses of Cu-MOF/MPC-3/GCE for H₂O₂ detection at pH 7.0 with the applied potential of -0.22 V. Left Inset of Fig. S9 shows the amperometric response of low concentration of H₂O₂ at Cu-MOF/MPC-3/GCE. The corresponding calibration plot for the reduction of H₂O₂ at Cu-MOF/MPC-3/GCE (RSD=4.7%, n=5) was shown in Fig. S10. Error bars are the standard deviation of five repetitive experiments. The current increased linearly with the good linear ranges are from 10 to 11600 μ M (R² = 0.998) for H₂O₂ detection with a sensitivity of 2.97 μ A mM⁻¹ and a detection limit of 3.2 μ M (S/N = 3). The current response of Cu-MOF/MPC-3/GCE generally reached a steady-state level within 2 s after the H₂O₂ addition.

The reproducibility of the sensor was also investigated by current-time method for five repetitive measurements with additions of H_2O_2 concentration of 0.5 mM at -0.22 V (pH 7.0). The RSD of the sensitivity was less than 4.1%. When the Cu-MOF/MPC-3/GCE was stored at 4 °C for two weeks, the current response to 0.5 mM H_2O_2 remained 92.6% of its original value, suggesting the long-term stability of the electrode. The performance of the Cu-MOF/MPC-3/GCE is also compared with other H_2O_2 sensors (Table S4).



Fig. S9 Typical amperometric current-time curve of Cu-MOF/MPC-3/GCE with successive additions of H_2O_2 (pH=7.0).



Fig. S10 Relationship between H_2O_2 concentration and current signal for Cu-MOF/MPC-3/GCE.

Table S4 Comparison of the performance of the Cu-MOF/MPC-3/GCE for the

Working electrode	potential	Linear range	sensitivity	Limit of	Response	Reference
	(V)	(µM)	$(\mu A m M^{-1})$	detection	time	
				(µM)	(s)	
Hb/Nafion/GMC/GCE ^a	-0.388	1-267	7.21	1.2	3	5
PDDA/Fe ₃ O ₄ /ITO ^b	-0.3	4.18-800	-	1.4	3.5	6
HRP/Nafion/SPE ^c	-0.35	5.98-35.36	10.17	0.15	-	7
Hb/SA-MWCNTs/GCE ^d	-0.4	40-200	15.87	16.41	10	8
Ti(III)–TNTs/Hb ^e	-0.4	4.9-1100	2.26	1.5	5	9
PLL-GA/GCE ^f	-0.3	2.5-6850	1.69	-	-	10
ZnO/Au/Nafion/HRP/GCE ^g	-0.3	15-1100	-	9	5	11
Mb/Fe ₂ O ₃ @Au/MGCE ^h	-0.35	1.3-280	-	0.4	5	12
PP/GCE ⁱ	-0.35	1-80	0.967	1	2	13
Ag/CNT/GCE ^j	-0.45	50-500	-	1.6	3	14
Cu-MOF/MPC-3/GCE	-0.23	10-11600	2.97	3.2	2	This work

electrochemical detection of H_2O_2 with that of other modified electrodes.

a hemoglobin/Nafion/graphitized ordered macroporous carbon modified glassy carbon electrode

b poly(diallyldimethylammonium chloride)/Fe₃O₄ at ITO electrode

c horseradish peroxidase/Nafion modified porous screen-printed carbon electrodes.

d hemoglobin immobilized sodium alginate- multiwall carbon nanotubes modified glassy carbon electrode

e TiO₂ nanotubes in situ self-doped with Ti(III)- hemoglobin modified glassy carbon electrode

f phosphotungstate-doped glutaraldehydecross-linked poly-l-lysine film modified glassy carbon electrode

g ZnO-gold nanoparticles-nafion nanocomposite modified glassy carbon electrode

h immobilized myoglobin on Fe $_3O_4$ @Au nanoparticle attached to the surface of a magnetic glassy carbon electrode

i glassy carbon electrode surface was modified by electrochemical reduction of a diazonium salt

j silver decorated carbon nanotube modified glassy carbon electrode

Fig. S11 presents typical CVs of Cu-MOF/MPC-3 in the absence (dash line) and presence (solid line) of 1 mM NADH. The composite based on Cu-MOF and MPC were prepared with different percentages of MPC toward the oxidation of NADH are shown in Fig. S12. Compared with other electrodes, Cu-MOF/MPC-3 exhibits highest response current and it is selected as an amperometric sensor for NADH (Table S5).



Fig. S11 CVs of Cu-MOF/MPC-3/GCE in the absence (dash line) and presence (solid line) of 1 mM NADH (pH=7.0).



Fig. S12 CVs of Cu-MOF/MPC-x/GCE in the presence of 1 mM NADH (pH=7.0).

Table S5 The peak potential and peak currents of NADH at theCu-MOF/MPC-x/GCE.

Electrodes	peak potential (V)	peak currents (µA)
Cu-MOF/MPC-1	0.33	2.5
Cu-MOF/MPC-2	0.33	5.2
Cu-MOF/MPC-3	0.3	34.8
Cu-MOF/MPC-4	0.3	14.3

Fig. S13 typical amperometric current-time shows a curve of Cu-MOF/MPC-3/GCE with successive additions of NADH. The best potential to be applied was chosen at +0.3 V based on the CVs measurements (pH 7.0). The NADH relationship between concentration and current signal for Cu-MOF/MPC-3/GCE is illustrated in Fig. S14. The NADH sensor displays a linear range of 20 and 100 μ M (R² = 0.999, n = 5) with a sensitivity of 9.79 μ A mM⁻¹ and 100 to 1900 μ M (R² = 0.998, n = 15) with a sensitivity of 25.28 μ A mM⁻¹. The detection limit is calculated as 6.52 μ M with the signal to noise ratio of three (S/N = 3). The Cu-MOF/MPC-3/GCE responds very rapidly to the changes in the level of H₂O₂, producing steady-state signals less than 3 s (Right inset of Fig. S13).

The reproducibility of the sensor was also investigated by current-time methods. The relative standard deviation (RSD) of current signal for 0.2 mM NADH was less than 7.2% for five measurements for the same electrode. After being stored at 4 °C for two weeks, 9.3% current loss at Cu-MOF/MPC-3/GCE was obtained by the amperometric response of 0.2 mM NADH. This means Cu-MOF/MPC biosensors could be used as stable sensor for NADH detection. The performance of the Cu-MOF/MPC-3/GCE is also compared with other NADH sensors (Table S6).



Fig. S13 Typical amperometric current–time curve of Cu-MOF/MPC-3/GCE with successive additions of NADH (pH=7.0).



Fig. S14 Relationship between NADH concentration and current signal for Cu-MOF/MPC-3/GCE.

Table S6 Comparison of the performance of the Cu-MOF/MPC-3/GCE for the

Working electrode	potential	Linear	sensitivity	Limit of	Response	Reference
	(V)	range	$(\mu A m M^{-1})$	detection	time	
		(µM)		(µM)	(s)	
graphene/GCE ^a	0.5	50-1400	12.6	20	10	15
GNS/GCE ^b	0.32	2-197	37.8	0.23	6	16
		10-4690				
PGE ^c	0.3	0.5-100	34	0.15	10	17
CR-GO/GCE ^d	0.45	40-800	0.19	10	8	18
Au-TiO ₂ /GR/GCE ^e	0.61	10-240	16.24	0.2	2	19
APTS-Fe ₃ O ₄ /PDC/GCE ^f	0.55	0.05-25	-	0.01	-	20
nano-ZrO2/PFA/GCEg	0.4	1-100	-	1	-	21
Au/GCE ^h	0.39	1.25-308	16.9	0.25	-	22
CNF/GCE ⁱ	0.35	30-2100	0.26	11	3	23
GNS/GCE ^j	0.4	45-360	19.7	15	-	24
Cu-MOF/MPC/GCE	0.3	20-100	9.79	6.52	3	This work
		20-3000	25.28			

electrochemical detection of NADH with that of other modified electrodes.

a graphene sheets modified glassy carbon electrode

b graphite nanosheet modified glassy carbon electrode

c pencil graphite electrode

d chemically reduced graphene oxide modified glassy carbon electrode

e Au-TiO₂/graphene nanocomposites modified glassy carbon electrode

f Fe₃O₄ nanoparticles and poly-2,6-pyridinedicarboxylic acid modified glassy carbon electrode

g a glassy carbon electrode modified with a film of chitosin containing acid fuchsin adsorbed onto zirconia nanotubes

h Au nanoparticles modified glassy carbon electrode

i carbon nanofibers modified glassy carbon electrode

j graphite nanosheet modified glassy carbon electrode

References

- S. Jun, J. Sang Hoon, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna and O. Terasaki, J. Am. Chem. Soc., 2000, 122, 10712-10713.
- 2. W. Stöber, A. Fink and E. Bohn, J. Colloid Interface Sci., 1968, 26, 62-69.
- 3. S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148-1150.
- 4. K. Schlichte, T. Kratzke and S. Kaskel, *Microporous Mesoporous Mater.*, 2004, **73**, 81-88.
- 5. X. Lu, Y. Xiao, Z. Lei and J. Chen, *Biosens. Bioelectron*, 2009, 25, 244-247.
- L. Zhang, Y. Zhai, N. Gao, D. Wen and S. Dong, *Electrochem. Commun.*, 2008, 10, 1524-1526.
- 7. Y. J. Teng, S. H. Zuo and M. B. Lan, *Biosens. Bioelectron*, 2009, 24, 1353-1357.
- H. Y. Zhao, W. Zheng, Z. X. Meng, H. M. Zhou, X. X. Xu, Z. Li and Y. F. Zheng, *Biosens. Bioelectron*, 2009, 24, 2352-2357.
- M. Liu, G. Zhao, K. Zhao, X. Tong and Y. Tang, *Electrochem. Commun.*, 2009, 11, 1397-1400.
- 10. R. Thangamuthu, Y.-C. Pan and S.-M. Chen, Sens. Actuators, B, 2011, 151, 377-383.
- 11. C. Xiang, Y. Zou, L.-X. Sun and F. Xu, Sens. Actuators, B, 2009, 136, 158-162.
- J. D. Qiu, H. P. Peng, R. P. Liang and X. H. Xia, *Biosens. Bioelectron*, 2010, 25, 1447-1453.
- 13. S. Han, Y. Yuan, L. Hu and G. Xu, *Electrochem. Commun.*, 2010, **12**, 1746-1748.
- 14. Y. Shi, Z. Liu, B. Zhao, Y. Sun, F. Xu, Y. Zhang, Z. Wen, H. Yang and Z. Li, *J. Electroanal. Chem.*, 2011, **656**, 29-33.
- 15. K. Guo, K. Qian, S. Zhang, J. Kong, C. Yu and B. Liu, *Talanta*, 2011, **85**, 1174-1179.
- 16. J. Zhu, X. Chen and W. Yang, Sens. Actuators, B, 2010, 150, 564-568.
- 17. Y. Dilgin, B. Kizilkaya, D. G. Dilgin, H. I. Gokcel and L. Gorton, *Colloids Surf B Biointerfaces*, 2013, **102**, 816-821.
- 18. M. Zhou, Y. Zhai and S. Dong, Anal. Chem., 2009, 81, 5603-5613.
- 19. Y. Fan, X. Yang, C. Yang and J. Liu, *Electroanalysis*, 2012, **24**, 1334-1339.
- 20. L. Cui, S. Ai, K. Shang, X. Meng and C. Wang, *Microchim. Acta*, 2011, **174**, 31-39.
- 21. X. Liu, B. Li, M. Ma, G. Zhan, C. Liu and C. Li, *Microchim. Acta*, 2011, **176**, 123-129.
- 22. L. Tang, G. Zeng, G. Shen, Y. Zhang, Y. Li, C. Fan, C. Liu and C. Niu, *Anal. Bioanal. Chem.*, 2009, **393**, 1677-1684.
- 23. A. Arvinte, F. Valentini, A. Radoi, F. Arduini, E. Tamburri, L. Rotariu, G. Palleschi and C. Bala, *Electroanalysis*, 2007, **19**, 1455-1459.
- 24. G. P. Keeley, A. O'Neill, M. Holzinger, S. Cosnier, J. N. Coleman and G. S.

Duesberg, Phys Chem Chem Phys, 2011, 13, 7747-7750.