Electronic Supporting Information

A low-cost commercial Cu(II)-EDTA complex for electrocatalytic water oxidation in neutral aqueous solution

Kaishan Yu, Yue Sun, Dingwei Zhu, Ziyi Xu, Jiayi Wang, Junyu Shen*, Qijian Zhang* and Wei Zhao*

Jiangsu Laboratory of Advanced Functional Materials, School of Materials Engineering, Changshu Institute of Technology, Changshu 215500, China.

Materials

Commercially available chemicals, [Cu(EDTA)(H$_2$O)], CuSO$_4$·5H$_2$O, [Zn(EDTA)], [Mg(EDTA)], EDTA-2Na, sodium phosphate monobasic dihydrate, sodium phosphate dibasic dodecahydrate, sodium acetate, acetic acid glacial, sodium tetraborate, boracic acid, sodium hydroxide, were purchased from Adamas Reagent and used as received. Glassy carbon electrode, fluorine-doped tin oxide (FTO) glass plate, and platinum wire were purchased from Tianjin Gaoss Union for the electrochemical studies. All buffers were prepared with deionized water (18 MΩ-cm resistivity).

Instruments

Mass spectra were recorded with HP 1100 HPL/ESI-DAD-MS and Waters/Micromass LC/Q-TOF-MS instruments. Elemental analyses were performed with a Thermoquest-Flash EA 1112 elemental analyzer. UV-Vis absorption measurements were carried out on an Agilent 8453 spectrophotometer. SEM images and EDX spectra were obtained with a HITACHI UHR FE-SEM SU8220 instrument equipped with an EDX detector. XPS surveys were acquired with a Thermo Fisher ESCALAB 250Xi surface analysis system. The measurements of dynamic light scattering (DLS) spectra were measured with a Zetasizer Nano ZS90 instrument. EPR spectra were collected on a Bruker electron paramagnetic resonance spectrometer (A200) with microwave frequency of 9.538 GHz at RT.

Synthesis

Preparation of [Cu(EDTA)(H$_2$O)]: copper salt CuSO$_4$·5H$_2$O (0.250 g, 1.0 mmol)

was added into a water solution (40 mL) of EDTA-2Na (0.346 g, 1.0 mmol) with magnetic stirring for 8 h at room temperature. Then, the solution was concentrated to about 20 mL by vacuum pump. Light blue crystals were generated with solvent evaporation under air and collected in a yield of 82% (0.305 g). Anal. Calcd for $C_{10}H_{16}N_2O_9Cu$ (%): C 32.31, H 4.34, N 7.53; found: C 31.89, H 4.48, N 7.41. TOF-MS: Calcd for $[M-H]^-$: m/z 370.0074; found: 370.0073.

CuSO₄·5H₂O / Water
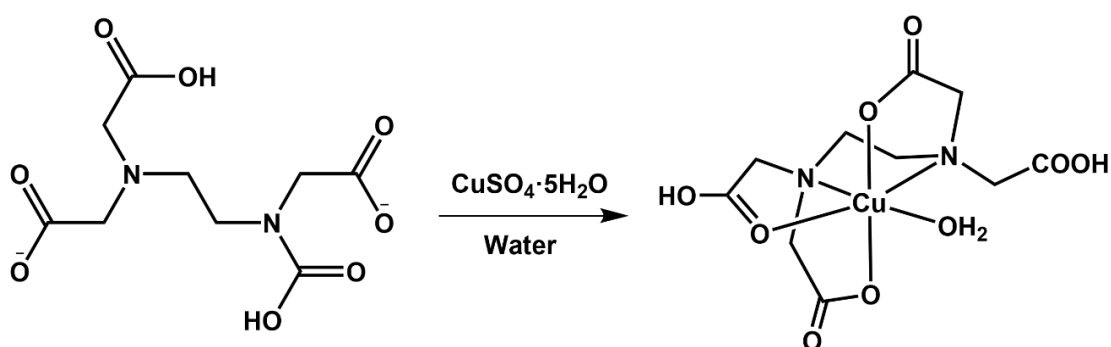
Crystallographic structure determinations

The single-crystal X-ray diffraction data were collected on a Bruker Smart Apex II CCD diffractometer with a graphite-monochromated Mo-K_α radiation (λ = 0.071073 Å) at 296 K using the ω-2θ scan mode. Data processing was accomplished with the SAINT processing program.[S1] Intensity data were corrected for absorption by the SADABS program.[S2] All structures were solved by direct methods and refined on F^2 against full-matrix least-squares methods by using the SHELXTL 97 program package.[S3] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by geometrical calculation. Crystallographic data and selected bond lengths and angles for [Cu(EDTA)(H₂O)] are given in Tables S2 and S3 (CCDC-2194005 for [Cu(EDTA)(H₂O)]).

Electrochemical testing

CV experiments: cyclic voltammetry experiments were carried out in a three-electrode cell under argon. The working electrode was a glassy carbon electrode disc (0.071 cm^2), the reference electrode was an aqueous Ag/AgCl electrode, and the counter electrode was a platinum wire. The solution of 0.1 M phosphate buffer at pH 7.0 was used as supporting electrolyte, which was degassed by bubbling with argon for 15 min before measurement. All potentials are reported versus the normal hydrogen electrode (NHE) by addition of 0.197 V to the experimentally measured values.

Kinetic equations

$$i_d = 0.4463 n_d FA[Cu](n_d F v D_{Cu}/RT)^{1/2} \qquad \text{(eq. 1)}$$

$$i_c = n_c FA[Cu](k_{cat} D_{Cu})^{1/2} \qquad \text{(eq. 2)}$$

$$i_c/i_d = 2.24 n_c n_d^{3/2}(k_{cat} RT)^{1/2}(Fv)^{-1/2} \qquad \text{(eq. 3)}$$

where i_d is the plateau current density of noncatalytic wave (here taken from the peak current of Cu^I to Cu^{II}), n_d is the number of electron transferred for the Cu^I/Cu^{II} couple (n_d = 1), v is the scan rate, R is the universal gas constant, and T is the temperature in Kelvin (T = 298.15 K), i_c is the limiting catalytic peak current, n_c is the number of electrons transferred for producing a molecule of O$_2$ in water oxidation (n_c = 4), F is Faraday constant, A is the surface area of the electrode (in cm^2), [Cu] is the initial concentration of catalyst (in mol L^{-1}), k_{cat} is the apparent first-order rate constant, and D_{Cu} is the diffusion coefficient of the copper catalyst in 0.1 M phosphate

buffer solution at pH 7.0.

Substituting data into eq. 3, it could be simplified to eq. 4.

$$i_c/i_d = 1.436(k_{cat}/v)^{1/2} \quad \text{(eq. 4)}$$

CPE experiments: the controlled potential electrolysis (CPE) experiment was carried out in a home-made H-type electrochemical cell with an FTO (1.0 cm^2) glass slide as working electrode. The FTO was pre-electrolyzed at 1.6 V for 10 min in 0.1 M PBS without copper complex before using. The auxiliary electrode was a platinum wire which was protected by a casing pipe and the reference electrode was a commercially available aqueous Ag/AgCl electrode. The sample was bubbled with argon for 20 min before measurement with constantly stirring.

The determination of FE: the Faradaic efficiency (FE) was determined from CPE experiment of [Cu(EDTA)(H$_2$O)] in 0.1 M phosphate buffer at pH 7.0 in a custom-built gas-tight electrochemical cell at an applied potential of 1.6 V vs. NHE for 6 h. The gas in the headspace of the cell was analyzed by CEAULIGHT GC-7920 gas chromatograph equipped with a 5 Å molecular sieve column (2 mm × 2 m) during the electrolysis and the oxygen dissolved in the solution was neglected. Faradaic efficiencies of electrochemical O$_2$ evolution were determined according to the amount of O$_2$ evolved and the amount of O$_2$ calculated from the total consumed charge during the CPE experiment by assuming a 4e$^-$ catalytic process (eq. 5).

$$\text{FE} = \frac{\text{Produced O}_2 \text{ (n}_{\text{measured}})}{\text{Calculated O}_2 \text{ (n}_{\text{caculated}})} \times 100\% \quad \text{(eq.5)}$$

Produced oxygen was obtained from peak area of gas chromatograph and

standard curve of O_2. Calculated oxygen can be got through the eq. 6:

$$n_{caculated} = \frac{Q}{n \times e \times NA}$$

(eq.6)

Where Q is the total amount of charge consumed during electrolysis, n is number of electron transferred for water oxidation ($n = 4$), e is the elementary charge ($e = 1.6 \times 10^{-19}$ C), NA is Avogadro constant ($NA = 6.02 \times 10^{23}$).

Calculation of TON:

$$TON = n_{O_2} / n_{catalyst} = 3 \times 10^{-5} \text{ mol}/(3.5 \times 10^{-2} \text{ L} \times 10^{-3} \text{ mol L}^{-1}) = 0.86$$

Testing peroxide intermediates formed during CPE experiments in electrolytes.

Ampliflu red (AR) was dissolved in DMSO and horseradish peroxidase (HRP) in 0.5 M PBS, both in a concentration of 0.4 mg mL^{-1}. The controlled potential electrolysis (CPE) experiment of [Cu(EDTA)(H$_2$O)] (1 mM) in 0.1 M PBS at pH 7 was carried out at 1.6 V vs. NHE in an electrochemical cell with cathode and anode isolated by a porous ceramic frit. A fluorine-doped tin oxide (FTO) with a surface area of 1.5 cm^2 was used as working electrode. After 3 h of electrolysis, the HRP solution (1.0 mL) and AR solution (1.0 mL) were successively added into the resulting electrolyte (3.0 mL). The blue color of the solution turned pink after the sample was stirred for about 15 s (Fig. S19).

Ampliflu red (colorless)　　　　　　　Resorufin (red)
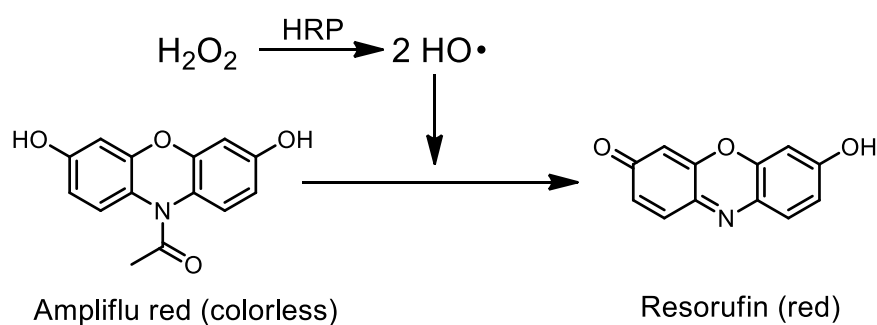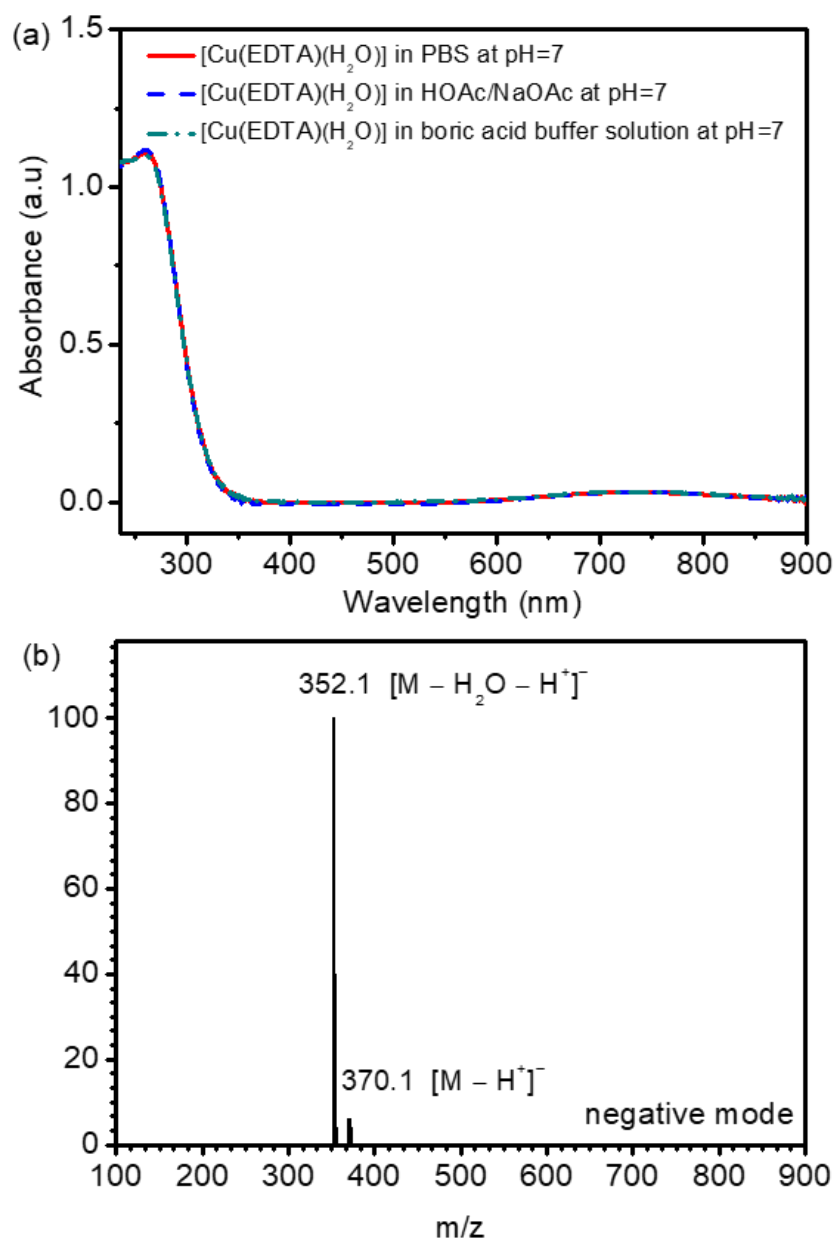
Fig. S1 (a) UV-vis spectra of [Cu(EDTA)(H₂O)] (0.5 mM) in 0.1 M phosphate buffer, HOAc/NaOAc buffer and borate buffer solutions at pH 7. (b) ESI-MS of [Cu(EDTA)(H₂O)] (0.5 mM) in 0.1 M phosphate buffer at pH 7.
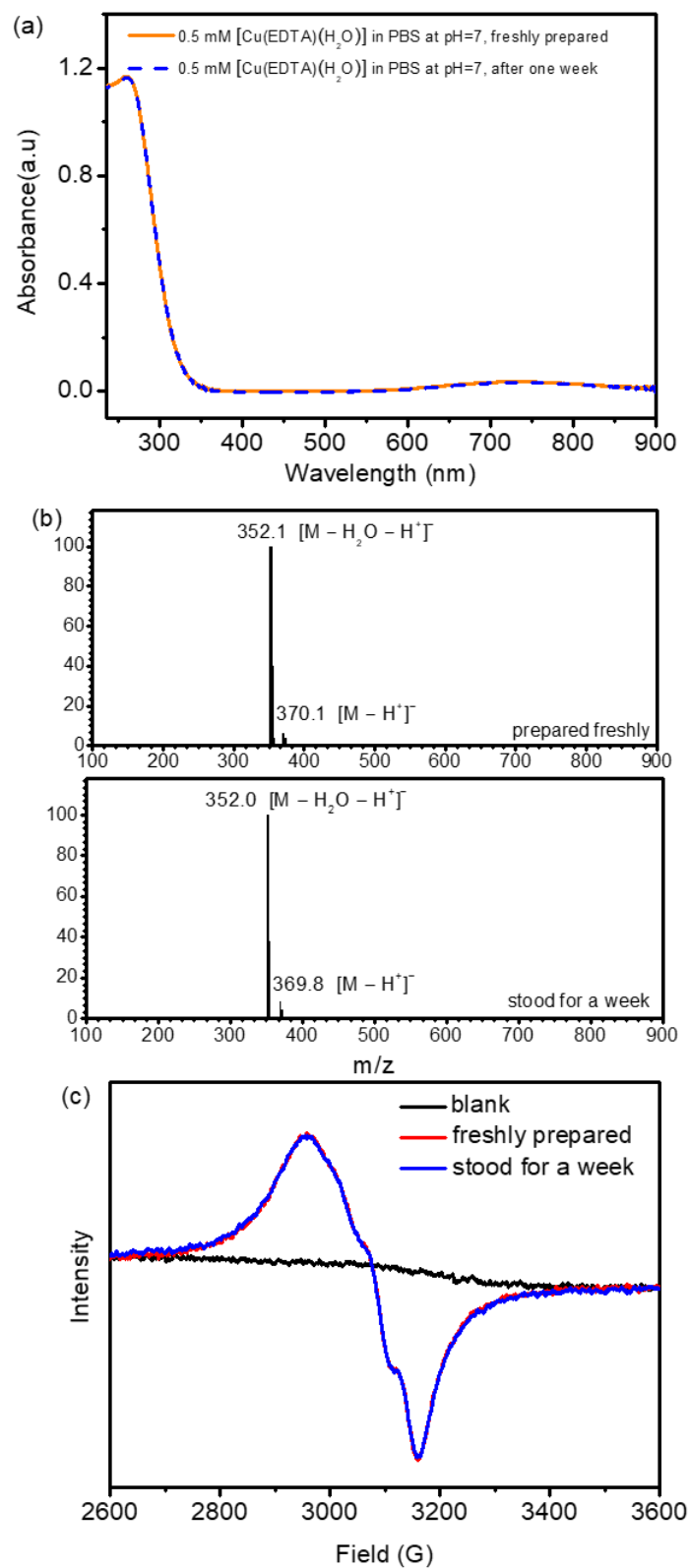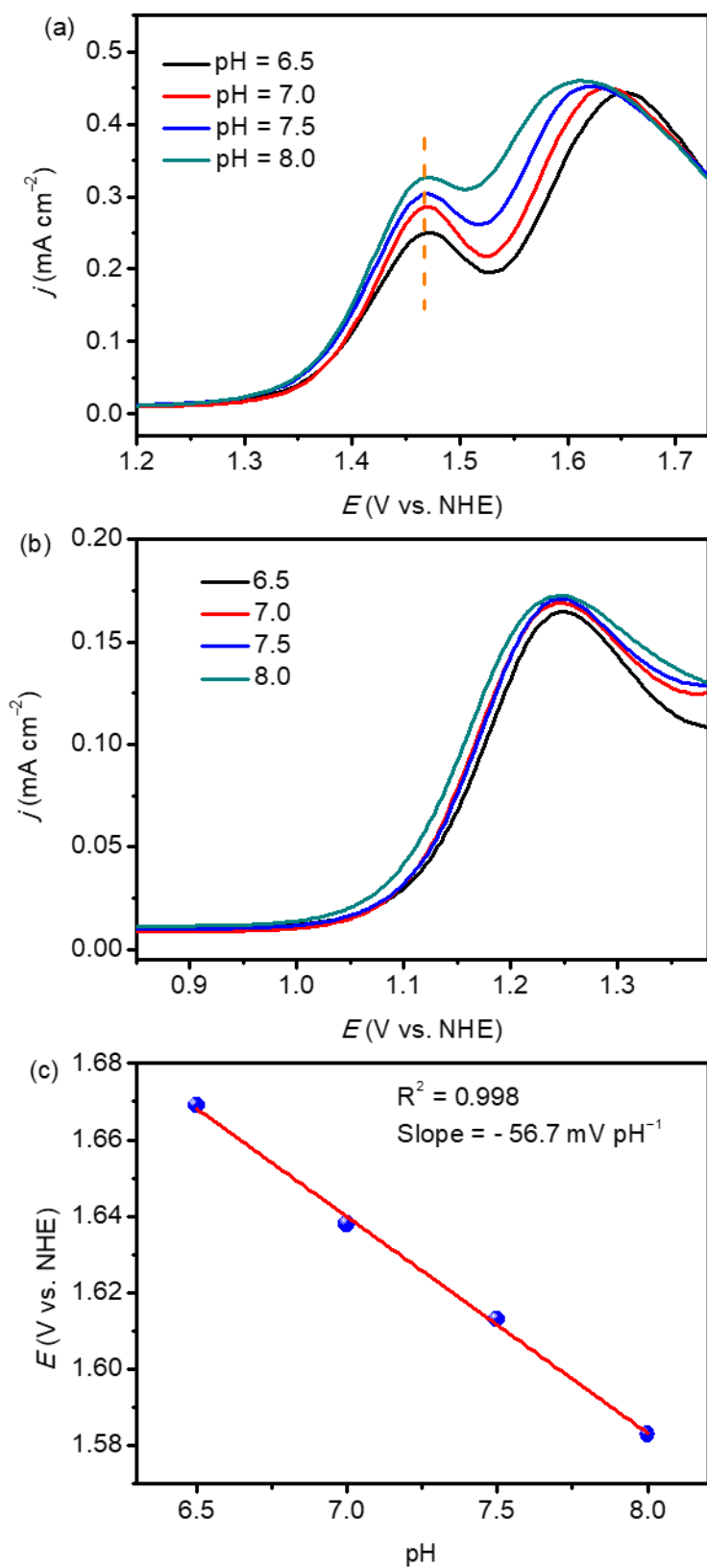
Fig. S2 (a) UV-Vis spectra, (b) ESI-MS and (c) continuous wave X-band EPR spectra of [Cu(EDTA)(H$_2$O)] (0.5 mM) in 0.1 M PBSs at pH 7, which are freshly prepared and after stood for a week under air.
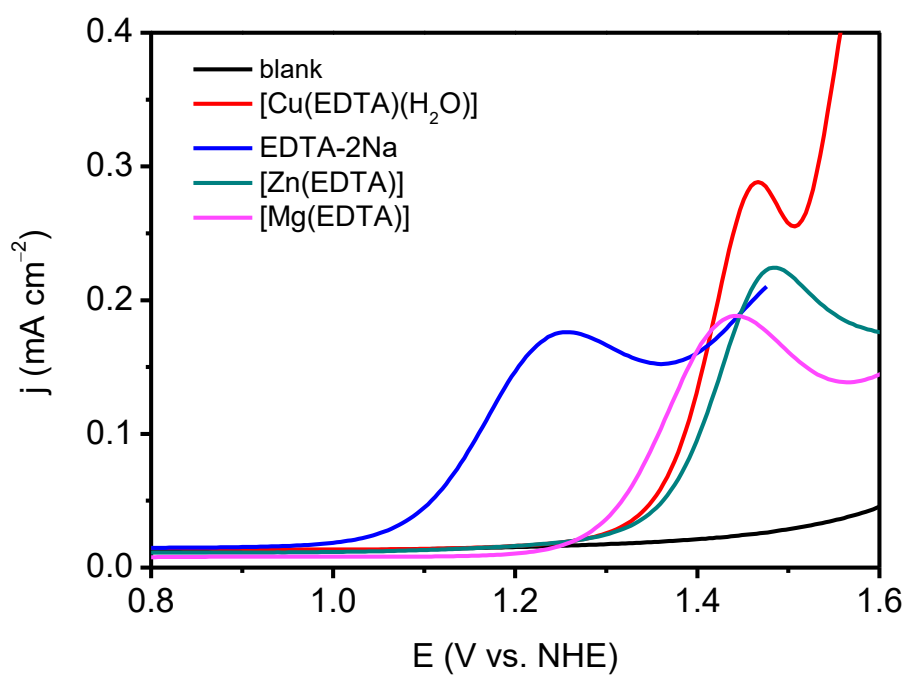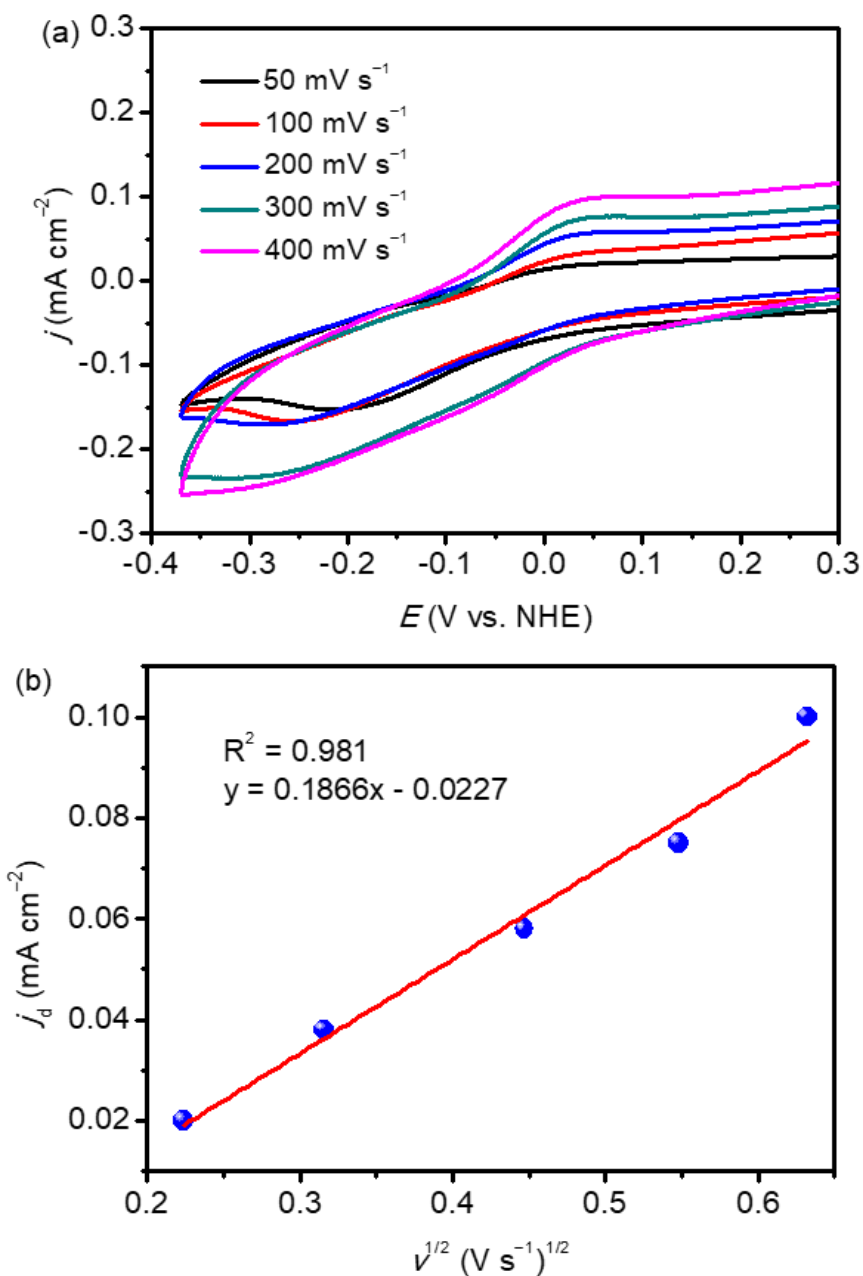
Fig. S3 DPV of [Cu(EDTA)(H$_2$O)], EDTA-2Na, [Zn(EDTA)], and [Mg(EDTA)] (all in 1 mM) in 0.1 M neutral PBSs at a scan rate of 8 mV s^{-1}

Fig. S4 DPV of (a) [Cu(EDTA)(H₂O)] and (b) EDTA-2Na (both in 1.0 mM) in 0.1 M PBSs with pH varied from 6.5 to 8.0. (c) Pourbaix plots for the second oxidation peak of [Cu(EDTA)(H₂O)].

Fig. S5 (a) Cyclic voltammograms of [Cu(EDTA)(H$_2$O)] (1.0 mM) in 0.1 M PBSs at pH 7 with scan rate varying from 50 to 400 mV s^{-1}. (b) Plot of the anodic current density maximum of the Cu^{I}/Cu^{II} couple as a function of the square root of scan rate.
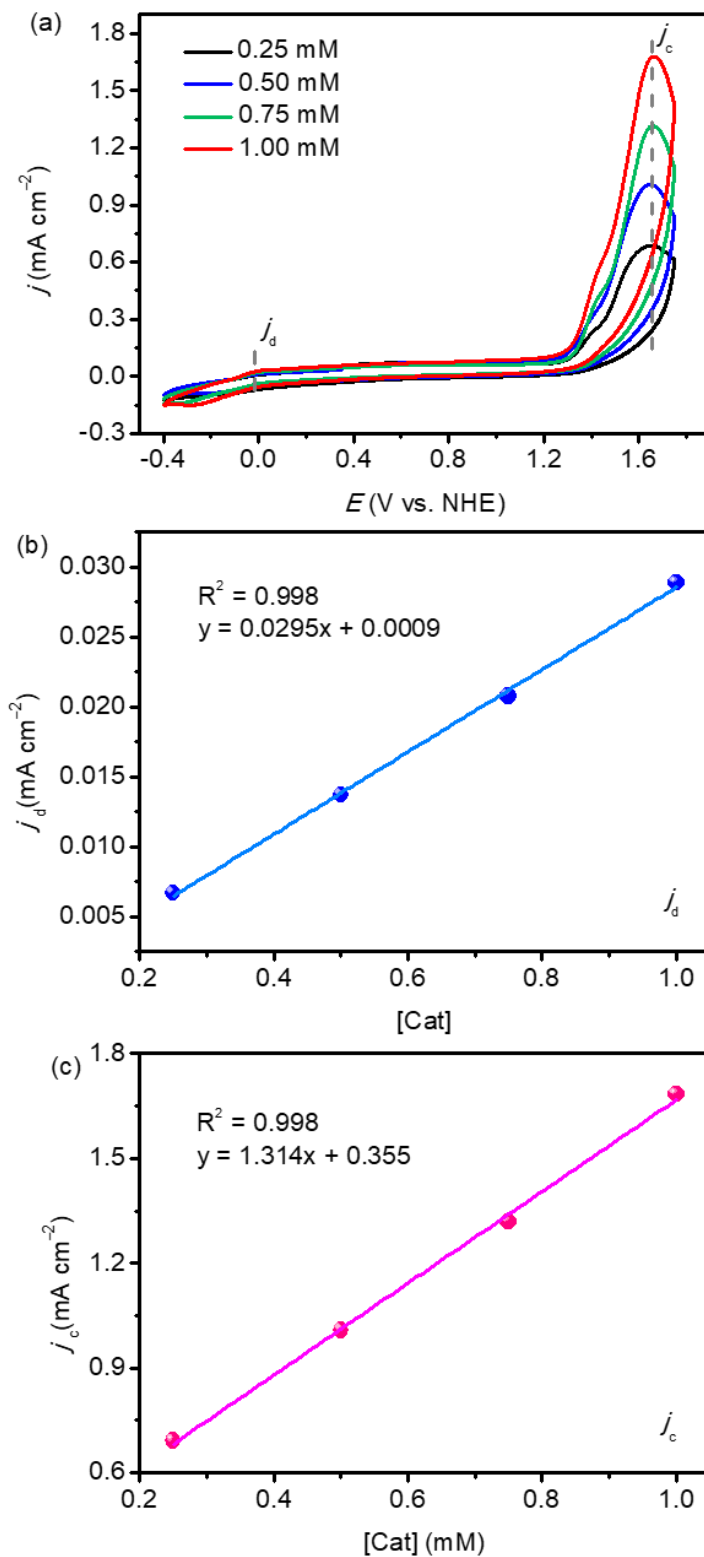
Fig. S6 (a) Cyclic voltammograms of [Cu(EDTA)(H$_2$O)] in 0.1 M PBSs at pH 7 at a scan rate of 100 mV s^{-1} with the concentration varying from 0.25 to 1.00 mM. (b) Plots of the current density maxima (j_d), as a function of catalyst concentration. (c) Plots of the current density maxima (j_c), as a function of catalyst concentration.
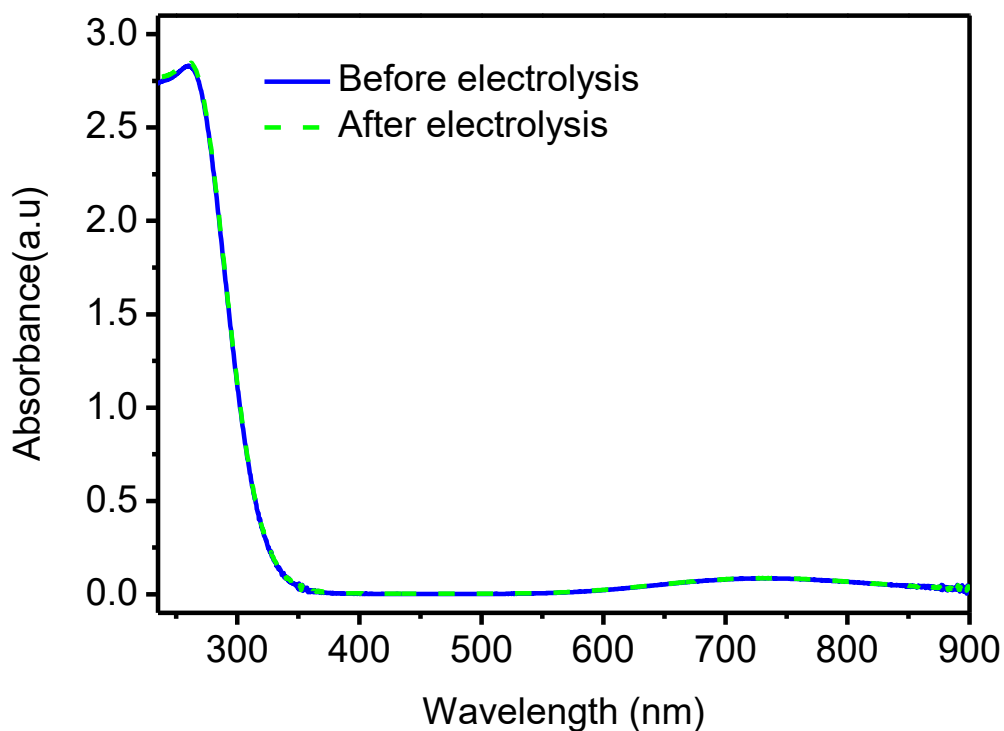
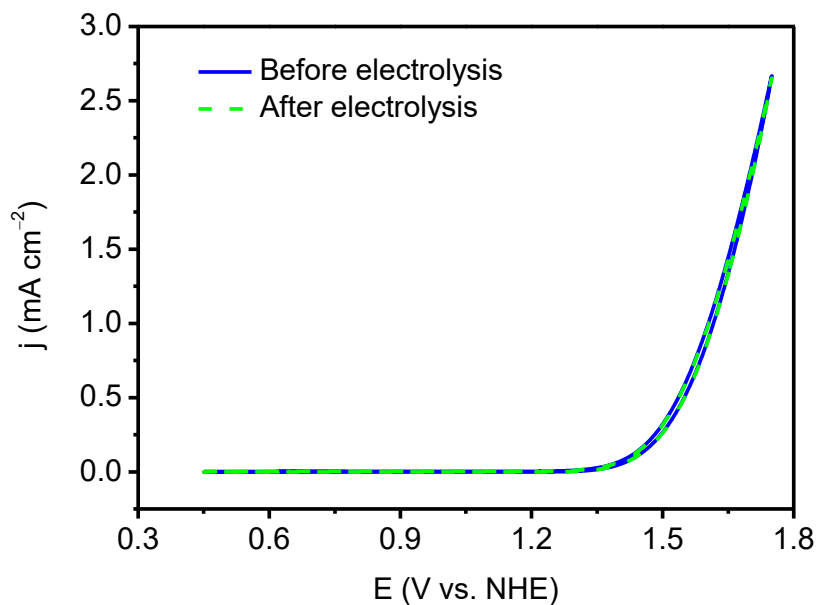**Fig. S7** UV-vis spectra of [Cu(EDTA)(H$_2$O)] (1.0 mM) in 0.1 M PBSs at pH 7 before and after electrolysis (optical length: 10 mm).
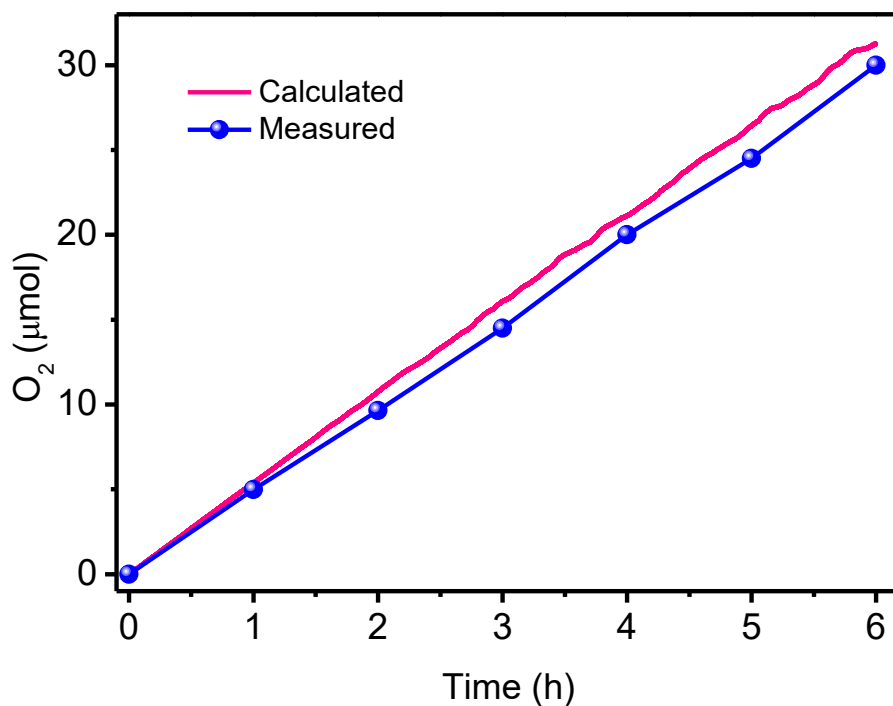
Fig. S8 Faradaic efficiency of O$_2$ evolution for [Cu(EDTA)(H$_2$O)] (1 mM) under 6 h of electrolysis at 1.6 V vs. NHE in 0.1 M PBS at pH 7.0.
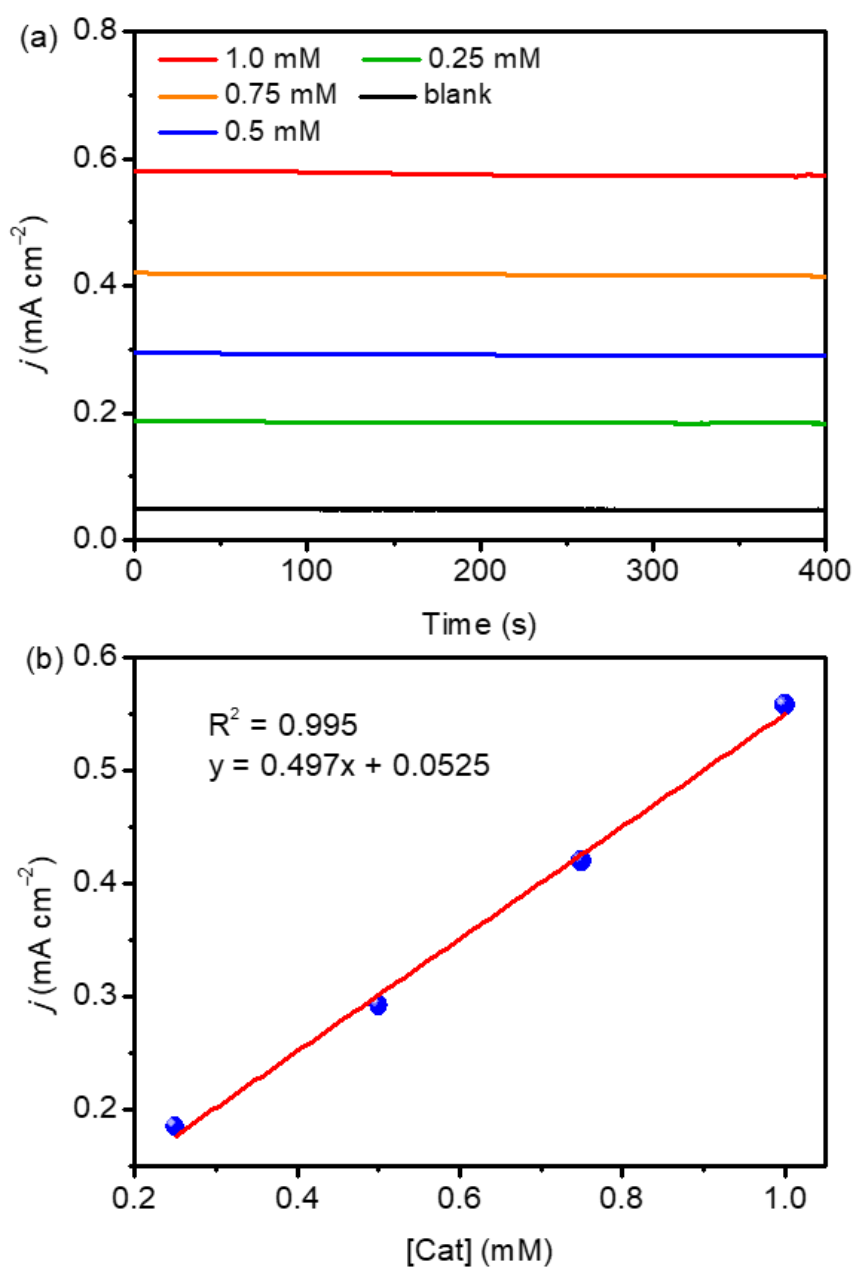
Fig. S9 (a) CPE experiments of [Cu(EDTA)(H$_2$O)] at 1.6 V vs. NHE in 0.1 M PBSs at pH 7.0 with the concentration varying from 0.25 to 1.00 mM. (b) Plots of the electrolytic current density, as a function of catalyst concentration.
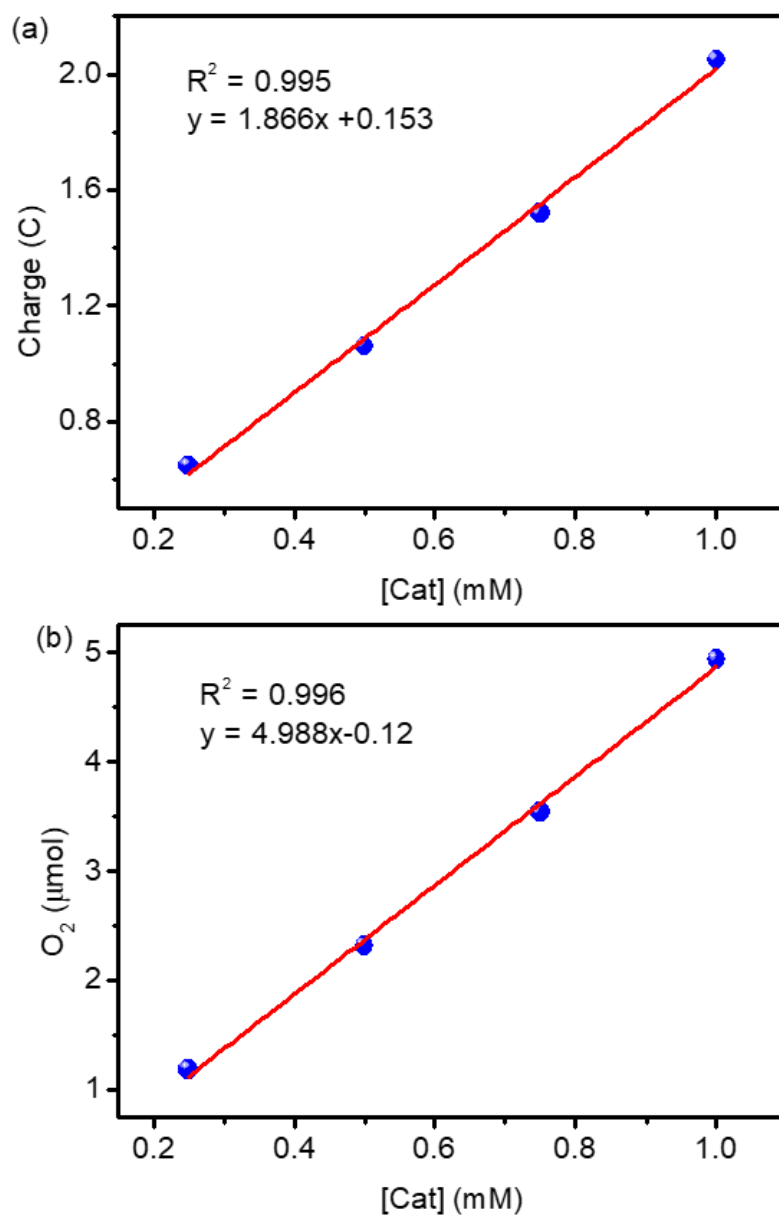
Fig. S10 Plots of (a) total charge and (b) O_2 production vs. concentration of [Cu(EDTA)(H_2O)] after 1 h of electrolysis.
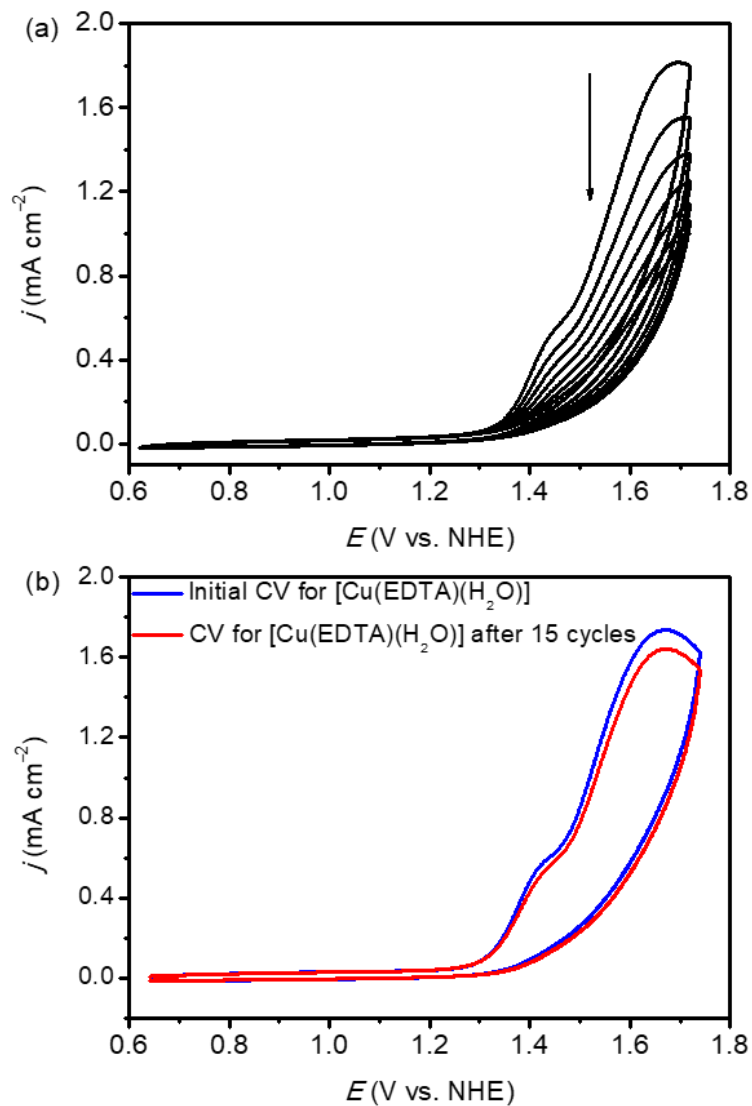
**Fig. S11** (a) Multiple CV of [Cu(EDTA)(H$_2$O)] (1.0 mM) in 0.1 M neutral PBS at a scan rate of 100 mV s^{-1}; (b) CVs of [Cu(EDTA)(H$_2$O)] (1.0 mM) before and after multiple scanning in 0.1 M neutral PBS at a scan rate of 100 mV s^{-1}. (Red line: the solution was stirred for a few minutes without electrode grinding)
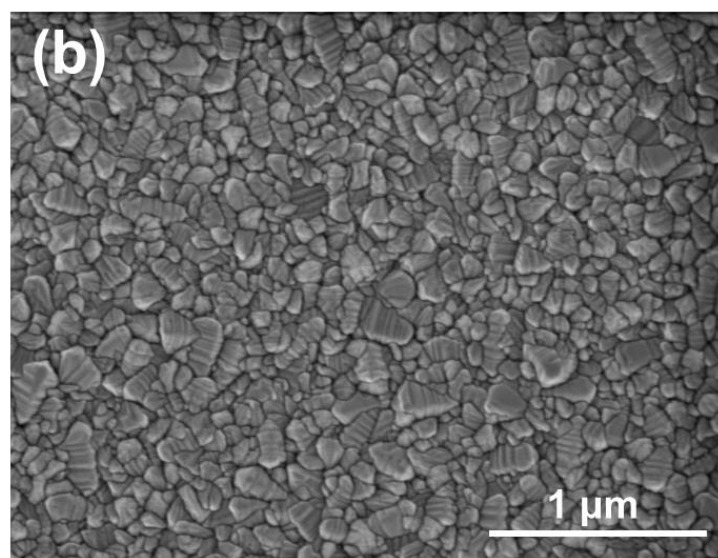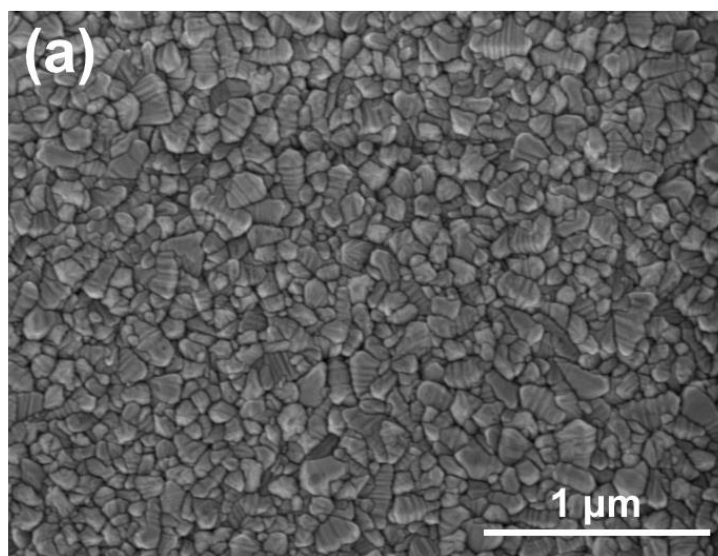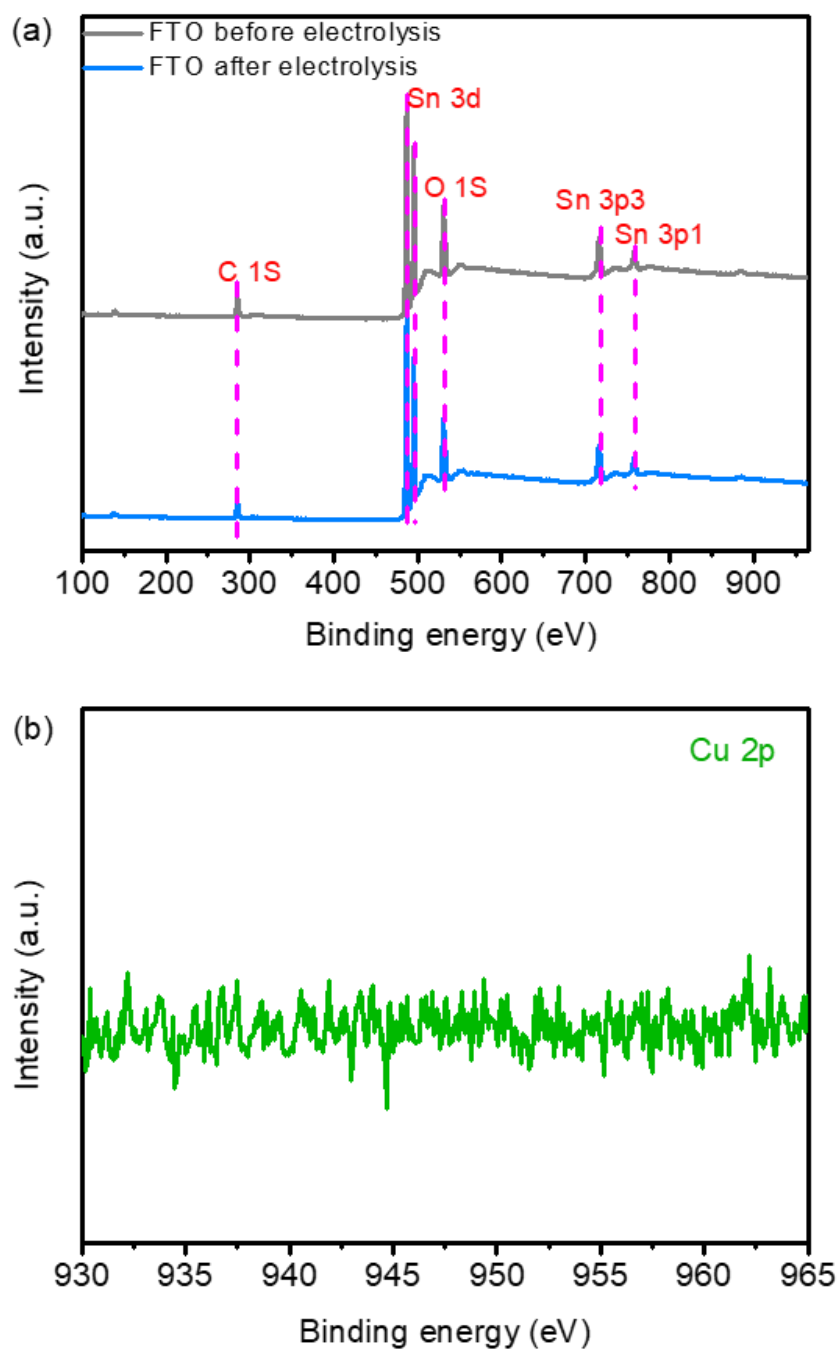
Fig. S12 CVs of [Cu(EDTA)(H$_2$O)] (1.0 mM) in 0.1 M PBSs at pH 7 at a scan rate of 100 mV s^{-1} with an FTO electrode (1 cm^2) before and after electrolysis.
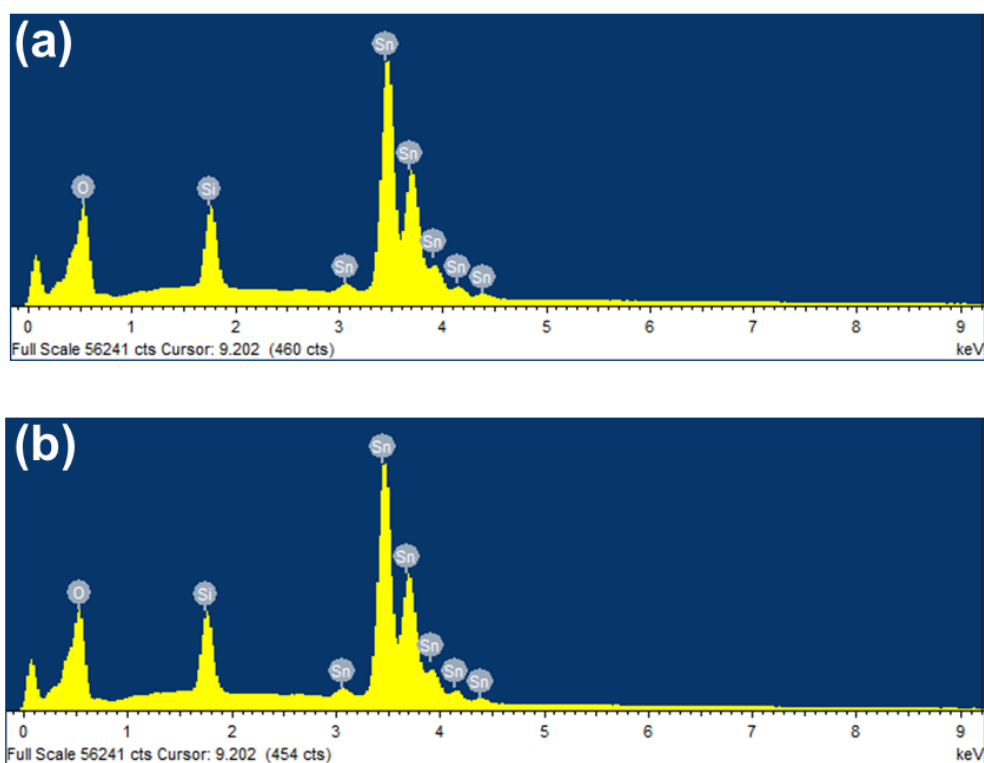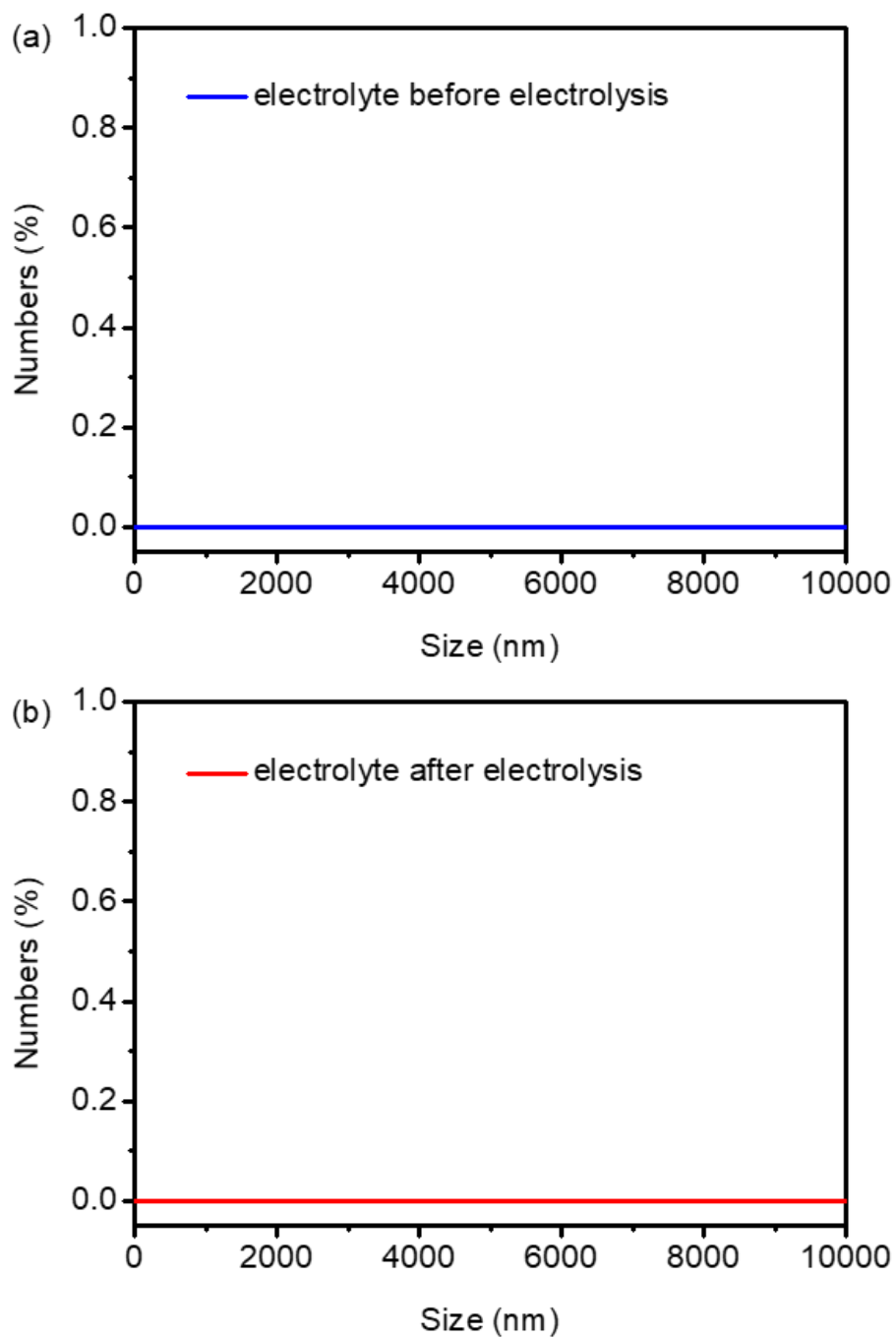

Fig. S13 EDX spectra of FTO (a) before and (b) after 6 h of CPE experiment with [Cu(EDTA)(H$_2$O)] as a catalyst.

**Fig. S14** SEM images of FTO (a) before and (b) after 6 h of CPE experiment (b) with [Cu(EDTA)(H$_2$O)] as a catalyst.

Fig. S15 (a) XPS surveys of FTO before and after 6 h of CPE experiment with [Cu(EDTA)(H$_2$O)] as catalyst. (b) XPS spectra of Cu 2p for FTO after 6 h electrolysis with [Cu(EDTA)(H$_2$O)] as a catalyst.

Fig. S16 DLS spectra of electrolytes (a) before and (b) after 6 h of electrolysis with [Cu(EDTA)(H$_2$O)] as a catalyst. The whole electrolysis process is carried out in a clean room.
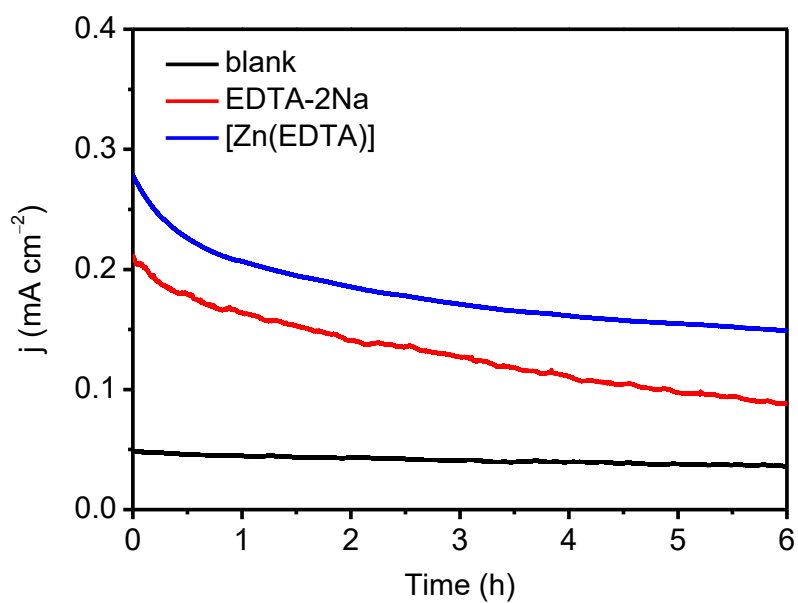
Fig. S17 Long time electrolysis of EDTA-2Na and [Zn(EDTA)] (both in 1.0 mM) at 1.6 V vs. NHE in 0.1 M PBSs at pH 7.0.
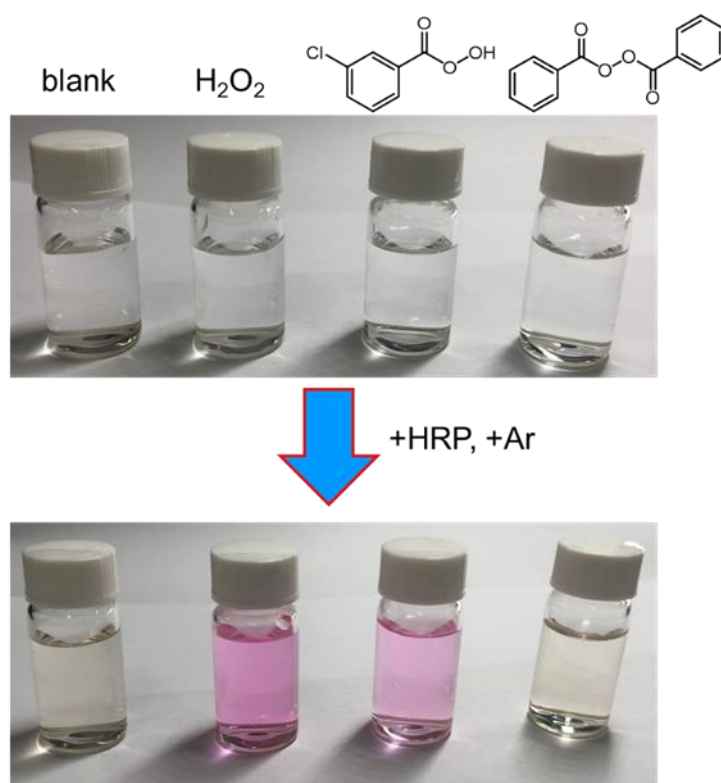

Fig. S18 Chromogenic reactions of blank, H_2O_2, 3-chloroperbenzoic acid, and benzoyl peroxide with the addition of HRP and AR in acetonitrile.
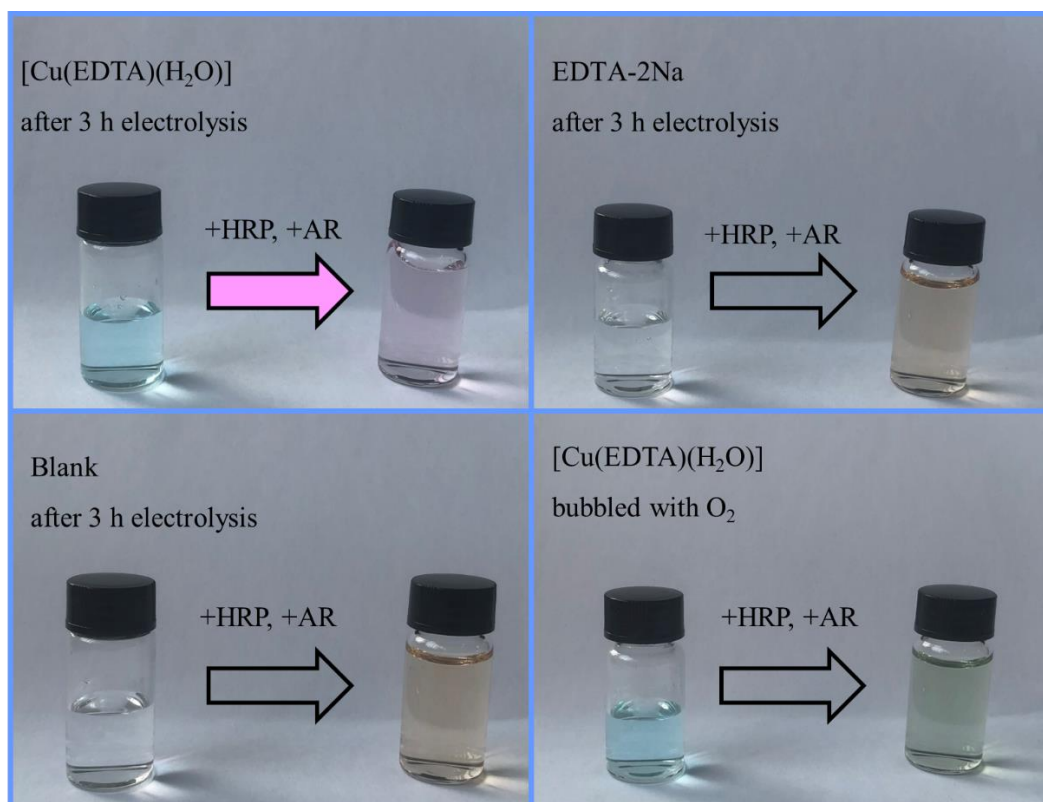
Fig. S19 Chromogenic reactions of the electrolytes containing [Cu(EDTA)(H₂O)], EDTA-2Na, blank after 3 h electrolysis, as well as the [Cu(EDTA)(H₂O)] solution bubbled with O₂.
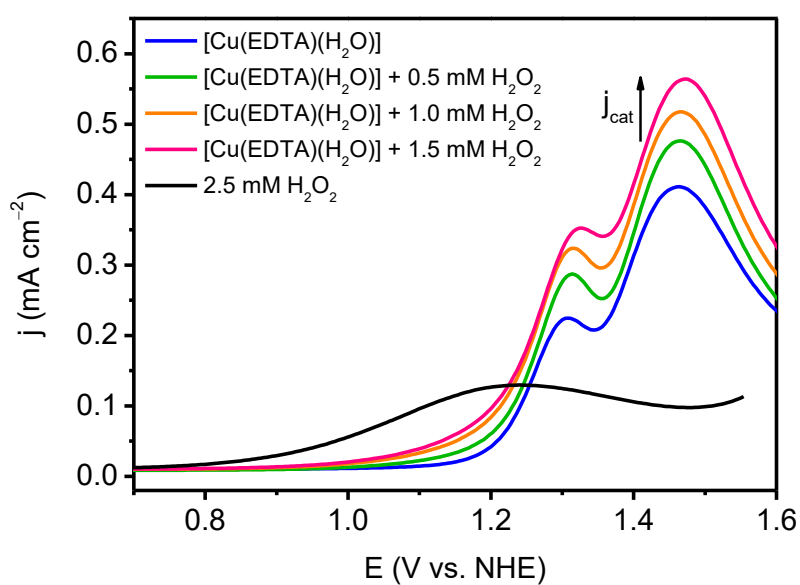
Fig. S20 DPV of [Cu(EDTA)(H₂O)], [Cu(EDTA)(H₂O)] + H₂O₂, and H₂O₂ in 0.1 M PBSs at pH 7 with a scan rate of 100 mV s^{-1}.
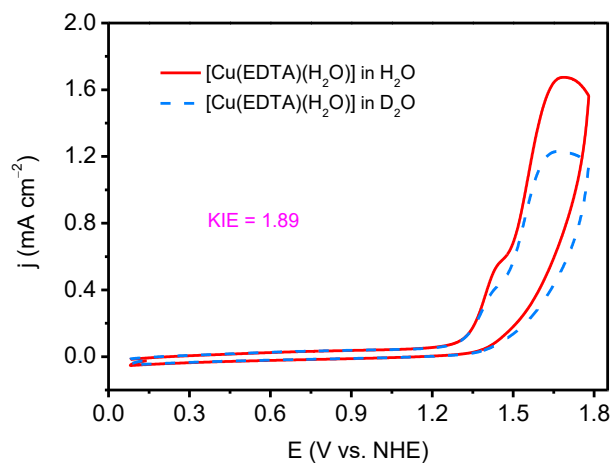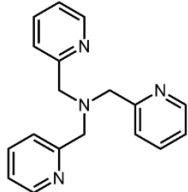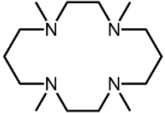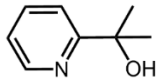
Fig. S21 Cyclic voltammogram of [Cu(EDTA)(H₂O)] (1.0 mM) in 0.1 M phosphate buffer H₂O and D₂O solution at pH 7. KIE = $k_{cat,H_2O}/k_{cat,D_2O}$, the value of KIE for [Cu(EDTA)(H₂O)] is 1.89.
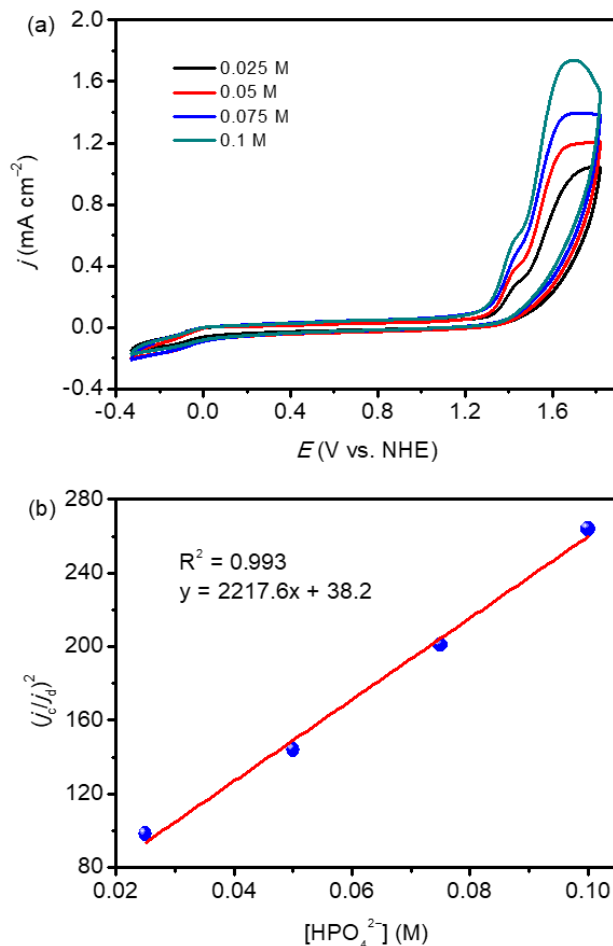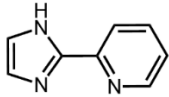

Fig. S22 (a) Cyclic voltammograms of [Cu(EDTA)(H₂O)] at a scan rate of 100 mV s^{-1} with the concentration of phosphate buffer solution varied from 0.025 to 0.1 M at pH 7. (b) Plots of $(j_c/j_d)^2$ as a function of [HPO$_4^{2-}$] at constant concentration of [Cu(EDTA)(H₂O)].

Table S1 The market prices of some commercial ligands for Cu complexes applied in electrocatalytic water oxidation

Ligand	Price ($/kg)
EDTA-2Na	12
2,2'-Bipyridine	99
	10979
	14730
	132493
	255638

Table S2 Crystallographic data and processing parameters for [Cu(EDTA)(H₂O)]

Complex	[Cu(EDTA)(H₂O)]
Formula	$C_{10}H_{16}N_2O_9Cu$
Formula weight	371.79
Crystal system	Monoclinic
Space group	*P2(1)/c*
Z	4
a / Å	11.5818(2)
b / Å	7.0011(0)
c / Å	16.4763(2)
α / deg	90.00
β / deg	91.7420(10)
γ / deg	90.00
V / Å³	1335.37(3)
D_{calcd} / g m⁻³	1.849
μ / mm⁻¹	1.688
Crystal size / mm	0.21 × 0.20 × 0.17
θ Range / deg	2.47 / 32.89
Reflns collected / Indep.	2237 / 2353
Parameters refined	203
$F(000)$	764
GOF on F^2	0.993
Final R_1 ($I > 2(I)$)	0.0252
Final wR_2 ($I > 2(I)$)	0.0664
max. peak/hole / e Å⁻³	0.308, -0.336

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(|F_o|^2 - |F_c|^2)^2/\Sigma(F_{o2})]^{1/2}$

Table S3 Selected bond lengths (Å) and angles (deg) for [Cu(EDTA)(H₂O)]

| [Cu(EDTA)(H$_2$O)]	
Bond lengths (Å)	
Cu–N1	2.060(7)
Cu–N2	2.303(6)
Cu–O1	1.970(3)
Cu–O2	1.925(8)
Cu–O3	2.462(4)
Cu–O4	1.976(0)
Bond angles (deg)	
N1–Cu–N2	84.47(7)
N1–Cu–O1	93.04(7)
N1–Cu–O2	85.98(7)
N1–Cu–O3	75.45(4)
N1–Cu–O4	172.79(8)
N2–Cu–O1	80.11(7)
N2–Cu–O2	102.55(7)
N2–Cu–O3	154.65(7)
N2–Cu–O4	102.37(8)
O1–Cu–O2	177.05(7)
O1–Cu–O3	85.63(4)
O1–Cu–O4	90.44(8)
O2–Cu–O3	91.42(2)
O2–Cu–O4	90.24(8)
O3–Cu–O4	98.54(9)

Table S4 OER properties for copper complexes reported as WOCs in pH 7 buffer solutions

Entry	Catalyst[a]	$\eta_{\text{half peak potential}}$ (mV) [b]	j_{cat} (mA cm^{-2}) [c]	k_{cat} (s^{-1})
1	**2**$^{2-}$ [S4]	184	1.2	140
2	[(IndPY2)Cu$^{\text{II}}$(OTf)$_2$] [S5]	284	0.55	0.02
3	Cu porphyrin 1 [S6]	474	1.25	30
4	[(DAM)Cu$_3$(μ^3-O)][Cl]$_4$ [S7]	550	0.8	19.1
5	[Cu$^{\text{II}}$(H$_2$L)]$^{2+}$ [S8]	580	0.6	11.09
6	[Cu(L$_1$H)(L$_1$)(OH$_2$)]$^+$ [S9]	724	0.7	100
7	CuSO$_4$ in borate buffer [S10]	734	1.8	-
8	[Cu(TMC)(H$_2$O)]$^{2+}$ [S11]	784	1.5	30
9	[Cu(Me$_4$cyclam)]$^{2+}$ [S12]	784	-	7
10	[Cu$_4$(bpy)$_4$(μ_2-OH)$_2$(μ_3-OH)$_2$(H$_2$O)$_2$]$^{2+}$ [S13]	904	3.5	-
11	[(TPA)Cu$^{\text{II}}$(OH$_2$)]$^{2+}$ [S14]	934	1.1	0.1
12	[Cu$_2$(BPMAN)(μ-OH)]$^{3+}$ [S15]	984	2.8	0.6
13	[Cu(EDTA)(H$_2$O)] (this work)	684	1.9	8.03

[a] The structures of the catalysts listed in Table S4 are given below.

[b] The $\eta_{\text{half peak potential}}$ of some catalysts is estimated in the literatures.

[c] The j_{cat} is the current density of catalytic peak.

[Cu₂(BPMAN)(μ-OH)]³⁺   [Cu₄(bpy)₄(μ₂-OH)₂(μ₃-OH)₂(H₂O)₂]²⁺   [Cu(R₄cyclam)]²⁺
R = H, CH₃

Cu porphyrin 1
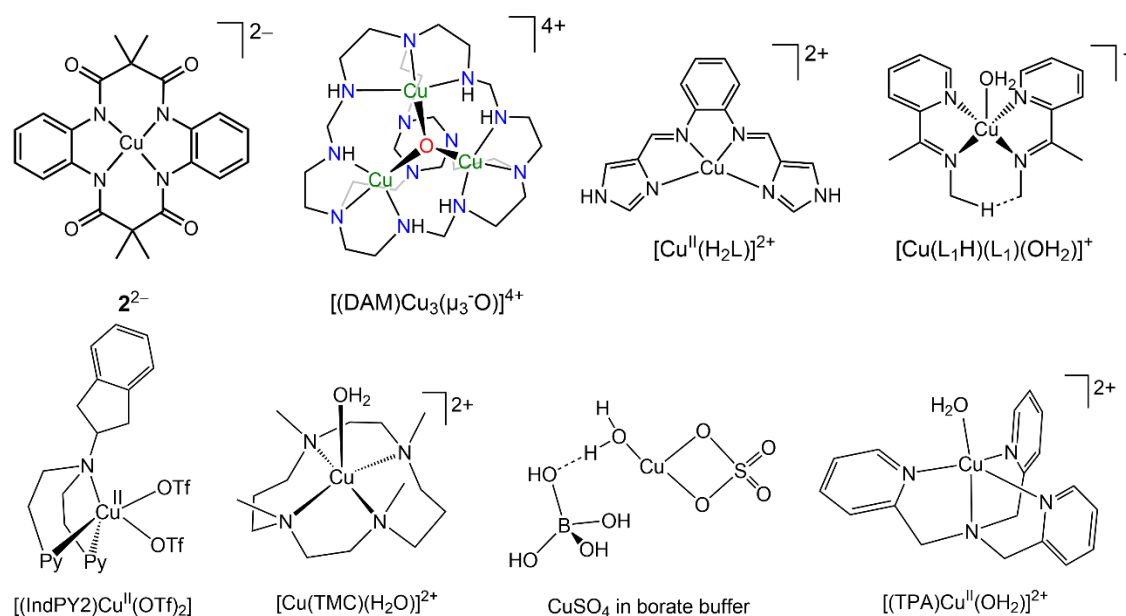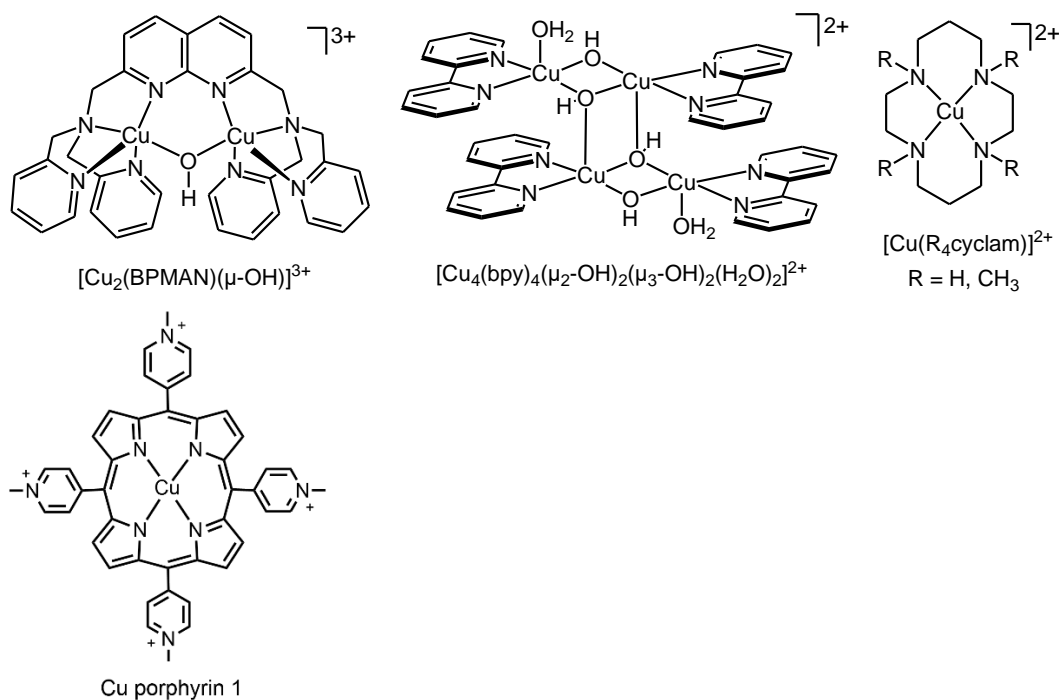
S1 Sheldrick, G. M. *SHELXTL97 Program for the Refinement of Crystal Structure,* University of Göttingen, Germany, **1997**.

S2 *Software packages SMART and SAINT*, Siemens Energy & Automation Inc., Madison, Wisconsin, **1996**.

S3 Sheldrick, G. M. *SADABS Absorption Correction Program*, University of Göttingen, Germany, **1996**.

S4 P. Garrido-Barros, D. Moonshiram, M. Gil-Sepulcre, P. Pelosin, C. Gimbert-Surinach, J. Benet-Buchholz, and A. Llobet, *J. Am. Chem. Soc.*, 2020, **142**, 17434

S5 M.-C. Kafentzi, R. Papadakis, F.Gennarini, A. Kochem, O. Iranzo, Y. L. Mest, N. L. Poul, T. Tron, B. Faure, A. J. Simaan and M. Réglier, *Chem. Eur. J.*, 2018, **24**, 5213.

S6 Y. Liu, Y. Han, Z. Zhang, W. Zhang, W. Lai, Y. Wang and R. Cao, *Chem. Sci.*, 2019, **10**, 2613.

S7 A. M. Geer, C. Musgrave III, C. Webber, R. J. Nielsen, B. A. McKeown, C. Liu, P. P. M. Schleker, P. Jakes, X. Jia, D. A. Dickie, J. Granwehr, S. Zhang, C. W. Machan, W. A. Goddard III, and T. B. Gunnoe, *ACS Catal.*, 2021, **11**, 7223

S8 J. Lin, X. Chen, N. Wang, S. Liu, Z. Ruan and Y. Chen, *Catal. Sci. Technol.*, 2021, **11**, 6470.

S9 H. Kuilya, N. Alam, D. Sarma, D. Choudhury and A. Kalita, *Chem. Commun.*, 2019, **55**, 5483.

S10 H.-H. Huang, J.-W. Wang, P. Sahoo, D.-C. Zhong and T.-B. Lu, *Chem. Commun.* 2017, **53**, 9324.

S11 F. Yu, F. Li, J. Hu, L. Bai, Y. Zhu, L. Sun, *Chem. Commun.* 2016, **52**, 10377.

S12 A. Prevedello, I. Bazzan, N. D. Carbonare, A. Giuliani, S. Bhardwaj, C. Africh, C. Cepek, R. Argazzi, M. Bonchio, S. Caramori, M. Robert and A. Sartorel, *Chem. Asian J.* 2016, **11**, 1281.

S13 T.-T. Li and Y.-Q. Zheng, *Dalton Trans.* 2016, **45**, 12685.

S14 X.-J. Su, M. Gao, L. Jiao, R.-Z. Liao, P. E. M. Siegbahn, J.-P. Cheng and M.-T. Zhang, *Angew. Chem. Int. Ed.*, 2015, **54**, 4909.

S15 X.-J. Su, C. Zheng, Q.-Q. Hu, H.-Y. Du, R.-Z. Liao and M.-T. Zhang, *Dalton Trans.*, 2018, **47**, 8670.