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Homogeneous electrocatalytic water oxidation at neutral pH by a robust trinuclear copper (Ⅱ)-substituted polyoxometalate

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Equipments and Apparatus

Infrared spectra (2–4 wt% sample in KBr pellets) were recorded using a Bruker VERTEX 70v FT-IR spectrometer. Elemental analysis of the catalysts was performed on a TJA ICP-atomic emission spectrometer (IRIS Advantage ER/S). Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectrometry (EDX) were obtained by a Hitachi S-4800 with a scanning voltage of 5000 V. Single-crystal X-ray diffraction analyze was performed in a cooled nitrogen gas stream at 100 K on AgilentGemini A Ultra with Mo Kα-radiation (λ = 0.7107 Å). Intensity data were collected by using ω scans with 10 s frame exposure and 1° frame width. Data collection, indexing and initial cell refinements were all carried out using CrysAlis$^{\text{Pro}}$[1].The structure was solved by direct methods and refined by full-matrix least-squares fitting on F^2 with programs SHELXS-97 and SHELXL-97[1] within Olex2.[2]

Electrocatalytic water oxidation

Electrocatalytic activities of the catalysts were tested in 80 mM tris (hydroxymethyl) aminomethane-HCl (Tris-HCl) buffer with the standard three-electrode electrochemical glass flask using a CHI660D electrochemical analyzer at room temperature with glassy carbon (or FTO), Ag/AgCl, and Pt wire electrodes as the working, reference, and auxiliary electrode, respectively.

Faradic efficiency measurement

The oxygen evolution was monitored with a Clark electrode (from Unisence Company) in buffer solution phase. The CPE was carried out at 1.2 V vs Ag/AgCl (3.5 M KCl) using a CHI660D electrochemical analyzer with a FTO, Ag/AgCl and Pt wire electrode as the working, reference and auxiliary electrodes. The Faraday efficiency was determined according to the charge passed during the CPE (recorded by electrochemical analyzer) process and the total mole of generated oxygen by taking into account that water oxidation is a 4 electron reaction.

Synthesis of $Na_9[SbW_9O_{33}]$ ligand

$Na_9[SbW_9O_{33}]$ was synthesized according to reference.[3] Sodium tungstate (40 g, 121 mmol) is dissolved in boiling water (80 mL) and dropwise addition of Sb_2O_3 (1.96 g, 6.72 mmol) dissolved in concentrated HCI (10 mL). The mixture was refluxed for 1 h and allowed to cool slowly. Colourless crystals of $Na_9[SbW_9O_{33}]$ were formed after evaporation of one-third of the solution volume.

Synthesis of $[(\alpha\text{-}SbW_9O_{33})_2Cu_3(H_2O)_3]^{12-}$ (**1**)

1 was synthesized according to reference.[4] A 1.0 g (5.8 mmol) sample of $CuCl_2\cdot 2H_2O$ was dissolved in 50 mL of H_2O, and then, 10.0 g (3.5 mmol) of $Na_9[\alpha\text{-}SbW_9O_{33}]$ was added. The solution was refluxed for 1 h and filtered after it cooled (pH 6.2). Slow evaporation at room temperature led to large green crystals. This resulted in 8.0 g of greenish product, which was isolated and air-dried. IR: 940, 889, 771, 724, 509, 470, 438 cm^{-1}. Anal. Calcd (Found) for **1**: Na 4.7 (4.9), Cu 3.3 (3.5).

Table S1 Crystal data and structure refinement for **1**

Empirical formula	$Cu_3Na_{13}O_{116}Sb_2W_{18}$
Formula weight	5898.29
Temperature/K	173.00(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	14.0354(3)
b/Å	23.3234(5)
c/Å	32.0641(7)
α/°	90
β/°	99.2951(19)
γ/°	90
Volume/Å^3	10358.5(4)
Z	4
ρcalcg/cm^3	3.782
μ/mm^{-1}	21.195
F(000)	10368.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.842 to 57.636
Index ranges	$-18 \le h \le 18$, $-31 \le k \le 27$, $-43 \le l \le 40$
Reflections collected	25604
Independent reflections	11973 [Rint = 0.0589, Rsigma = 0.0834]
Data/restraints/parameters	11973/0/677
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0502, wR_2 = 0.1076
Final R indexes [all data]	R_1 = 0.0634, wR_2 = 0.1176
Largest diff. peak/hole / e Å^{-3}	3.73/-4.18

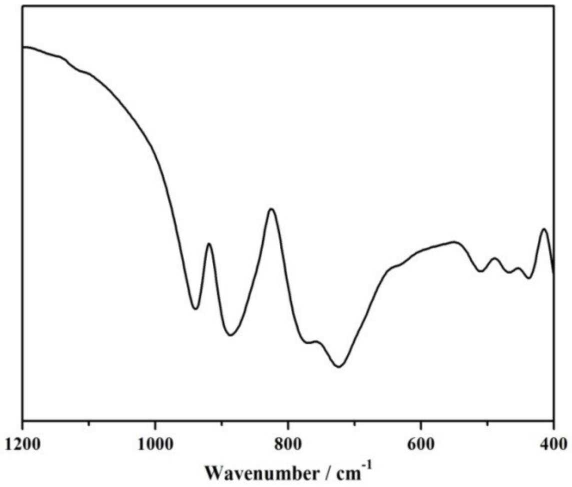

Fig. S1 FT-IR spectrum of **1**.

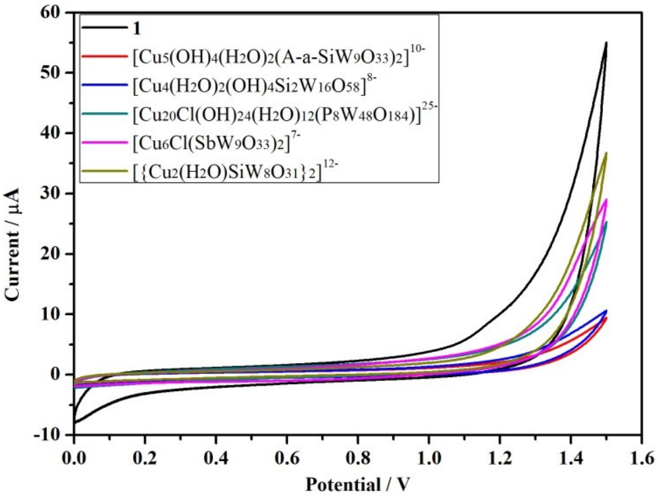

Fig. S2 CVs of different copper-containing POMs (2.0 mM) in 80 mM pH 7.1 Tris-HCl buffer solutions. Conditions: glassy carbon working electrode, Ag/AgCl (3.5 M KCl) reference electrode and Pt wire counter electrode; scan rate 100 mV/s.

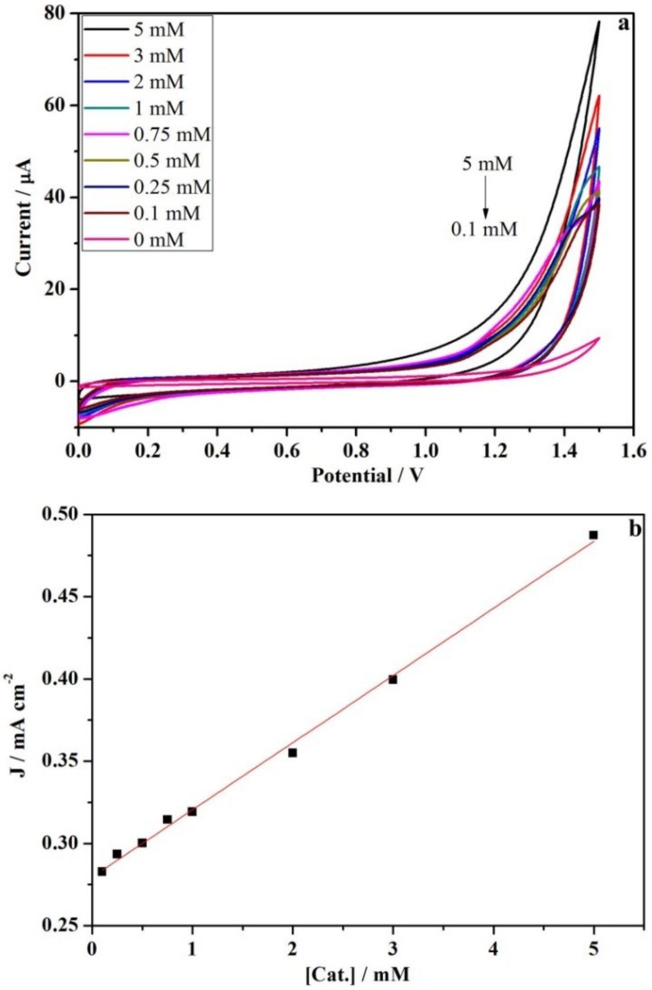

Fig. S3 (a) CVs of different concentrations of **1** (0.1 ~ 5.0 mM) in 80 mM pH 7.1 Tris-HCl buffer solution. Conditions: glassy carbon working electrode, Ag/AgCl (3.5 M KCl) reference electrode and Pt wire counter electrode; scan rate 100 mV/s. (b) Plot of catalytic current density J at ~1.35 V vs Ag/AgCl electrode against the concentrations of **1**.

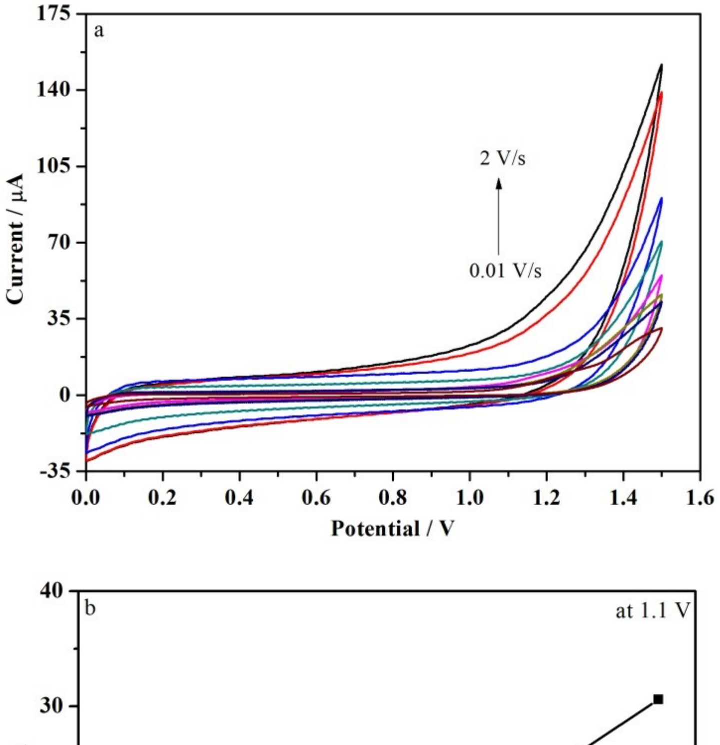

Fig. S4 (a) CV curves of **1** (2.0 mM) in 80 mM Tris-HCl buffer solution at pH 7.1 with a scan rate dependence at 0.01–2 V/s (from bottom to top). (b) Current as a function of $\nu^{1/2}$ for **1** (at 1.1 V). Conditions: glassy carbon working electrode, Ag/AgCl (3.5 M KCl) reference electrode and Pt wire counter electrode.

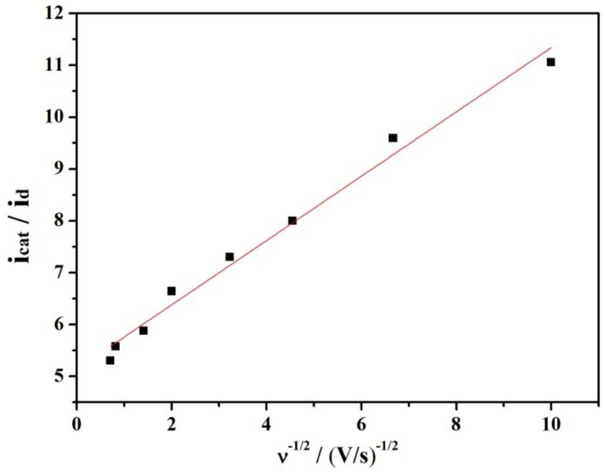

Fig. S5 Linear fitting plot of i_{cat}/i_d vs. $v^{-1/2}$ for TOF calculations. Conditions: glassy carbon working electrode, Ag/AgCl (3.5 M KCl) reference electrode and Pt wire counter electrode.

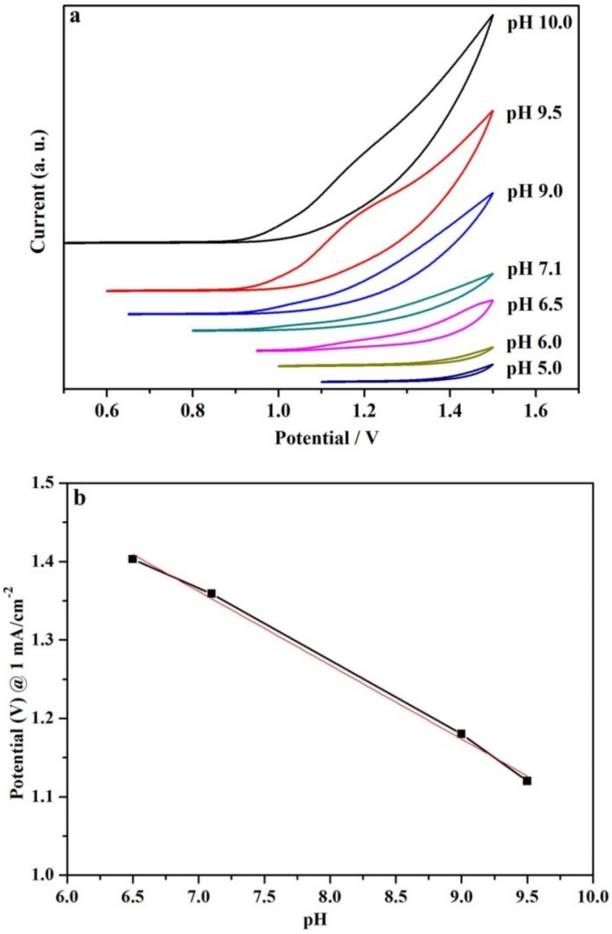

Fig. S6 (a) CV curves of 2.0 mM **1** from pH 5.0 to pH 10.0. (b) pH-dependent potential change at a constant current density of 0.5 mA/cm^2. Conditions: glassy carbon working electrode, Ag/AgCl (3.5 M KCl) reference electrode and Pt wire counter electrode; scan rate 100 mV/s; 80 mM Tris-HCl buffer solution.

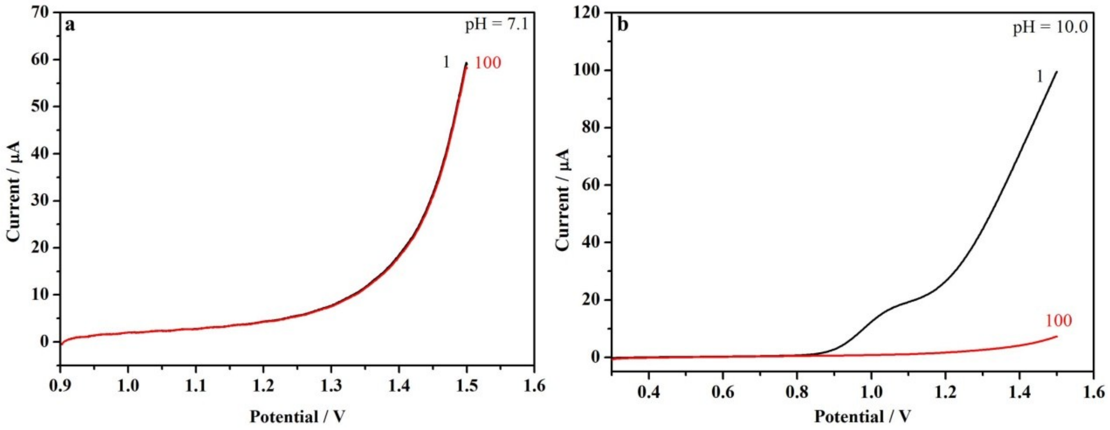

Fig. S7 Linear sweep voltammetry (LSV) curves of 2.0 mM **1** for 100 times of voltammetry cycling in neutral condition at pH 7.1 (a) and 100 cycles under basic condition at pH 10.0 (b). Test conditions: glassy carbon working electrode, Ag/AgCl (3.5 M KCl) reference electrode and Pt wire counter electrode; scan rate 100 mV/s; 80 mM Tris-HCl buffer solution.

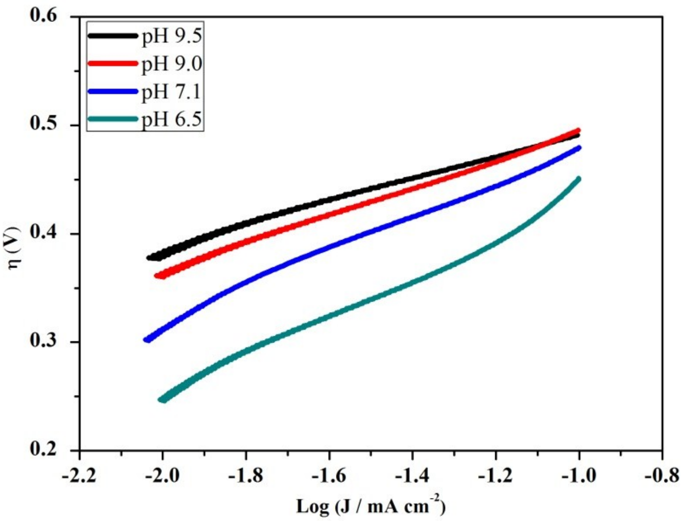

Fig. S8 Tafel plots of **1** from pH 6.5 to pH 9.5. Conditions (LSV): glassy carbon working electrode, Ag/AgCl (3.5 M KCl) reference electrode and Pt wire counter electrode; scan rate 100 mV/s; 2.0 mM catalyst; 80 mM Tris-HCl buffer solution.

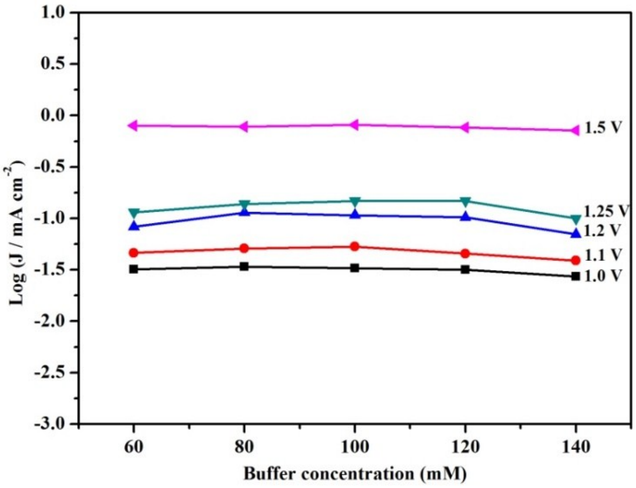

Fig. S9 Tris-HCl buffer concentrations dependency of current at a constant applied potential (1.0, 1.1, 1.2, 1.25 and 1.25 V vs Ag/AgCl) at pH 7.1. Conditions: glassy carbon working electrode, Ag/AgCl (3.5 M KCl) reference electrode and Pt wire counter electrode; scan rate 100 mV/s; 2.0 mM **1**.

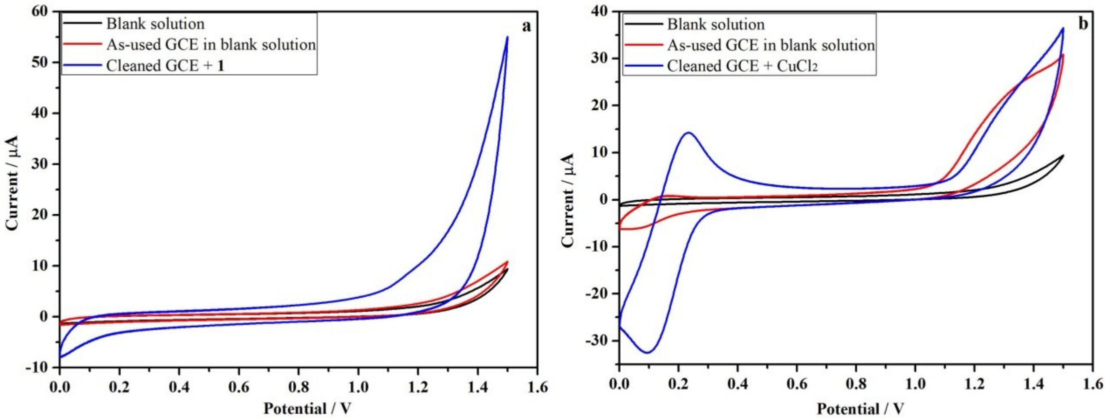

Fig. S10 (a) CV curve of 2.0 mM **1** in 80 mM pH 7.1 Tris-HCl buffer solution (blue curve) with cleaned GCE. Red curve shows the CV curve of the as-used GCE in 80 mM pH 7.1 Tris-HCl buffer without **1**. Black curve shows the CV curve of cleaned GCE in 80 mM pH 7.1 Tris-HCl buffer without **1** (i.e. blank solution). (b) CV curves of 2.0 mM $CuCl_2$ in 80 mM pH 7.1 Tris-HCl buffer solution (blue curve) with cleaned GCE. Red curve shows the CV curve of the as-used GCE in 80 mM pH 7.1 Tris-HCl buffer without $CuCl_2$. Black curve shows the CV curve of cleaned GCE in 80 mM pH 7.1 Tris-HCl buffer without $CuCl_2$ (i.e. blank solution). Conditions: glassy carbon working electrode, Ag/AgCl (3.5 M KCl) reference electrode and Pt wire counter electrode; scan rate 100 mV/s.

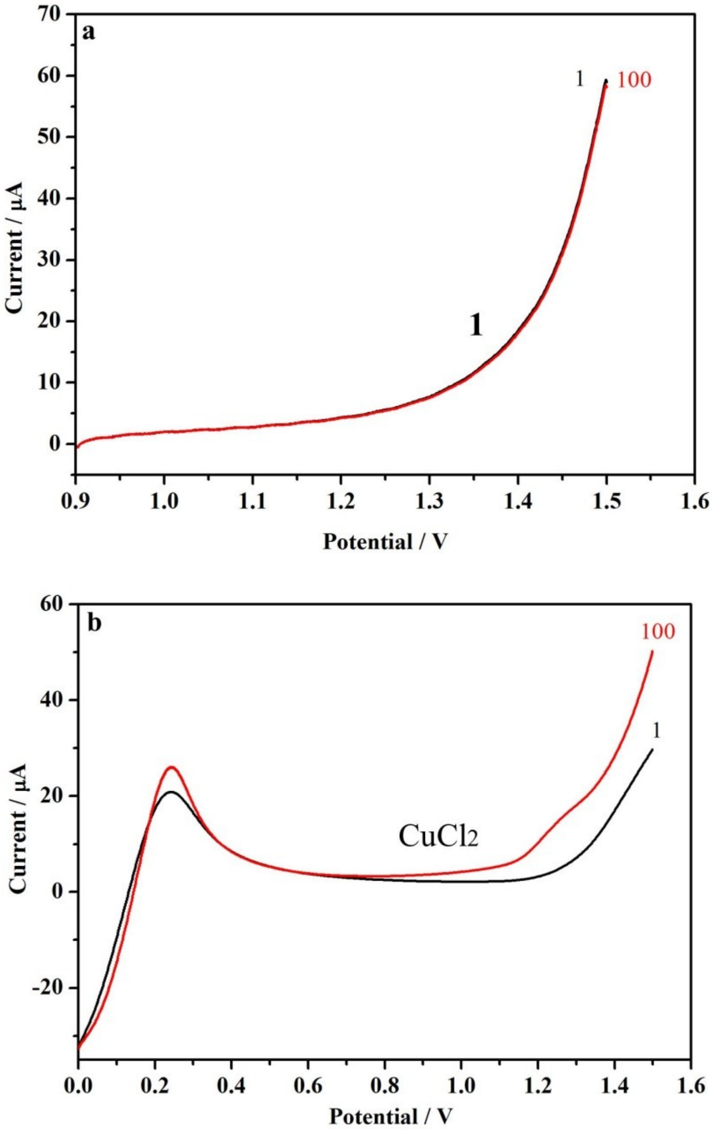

Fig. S11 LSV curves and of **1** (a) and $CuCl_2$ (b) for the 1st and 100th cycle in 80 mM pH 7.1 Tris-HCl buffer. Conditions: glassy carbon working electrode, Ag/AgCl (saturate KCl) reference electrode and Pt wire counter electrode; scan rate 100 mV/s.

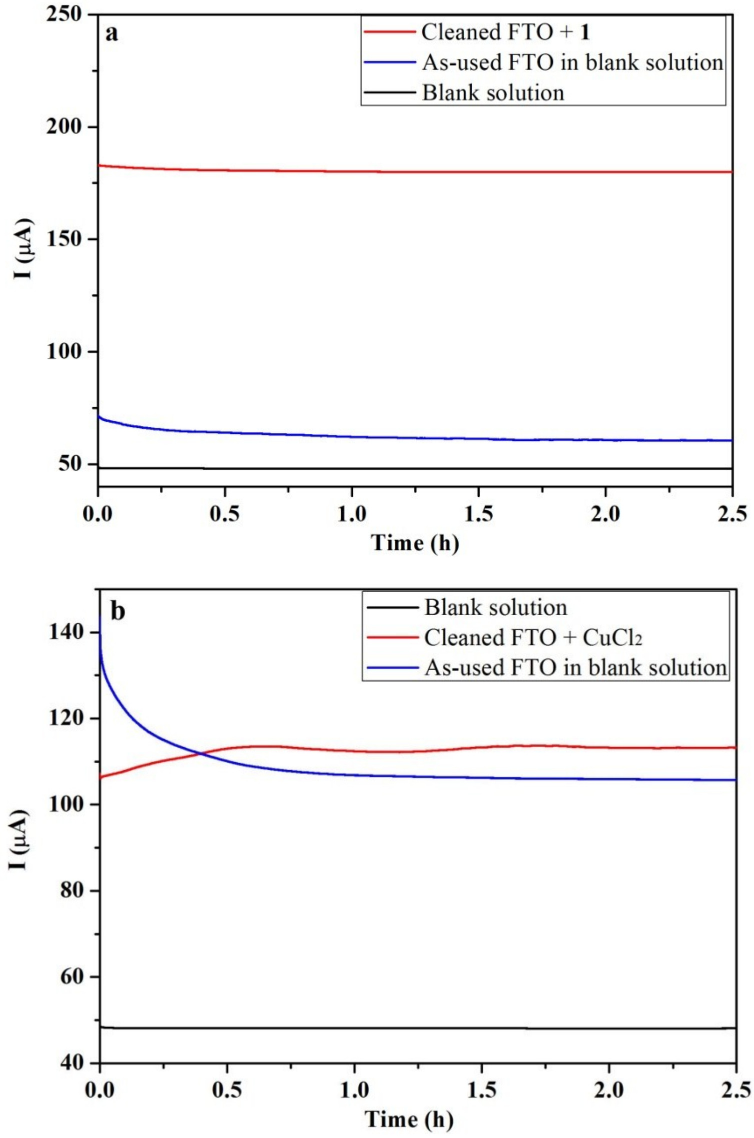

Fig. S12 (a) Water electrolysis under an applied voltage of 1.2 V vs Ag/AgCl electrode in 80 mM pH 7.1 Tris-HCl buffer solution. Initial blank (black line); 2.0 mM **1** (red line); blank after **1**-catalyzed electrolysis (blue line). (b) Water electrolysis under an applied voltage of 1.2 V vs Ag/AgCl electrode in 80 mM pH 7.1 Tris-HCl buffer solution. Initial blank (black line); 2.0 mM $CuCl_2$ (red line); blank after $CuCl_2$-catalyzed electrolysis (blue line). Conditions: FTO glass working electrode, Ag/AgCl (3.5 M KCl) reference electrode and Pt wire counter electrode.

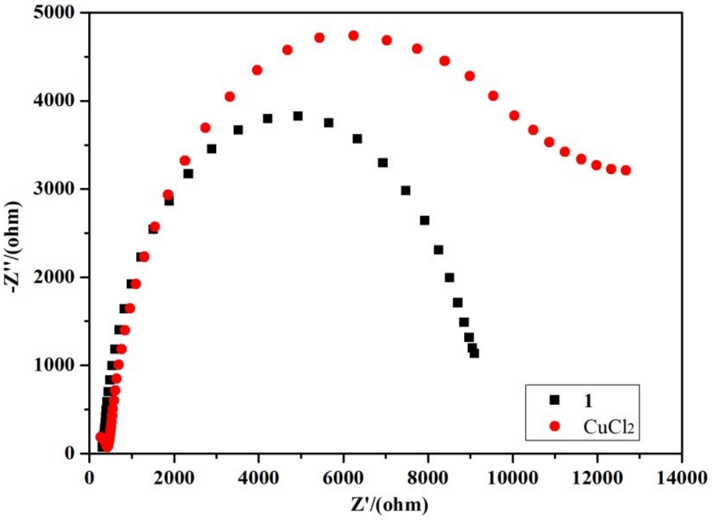

Fig. S13 Nyquist diagrams of EIS for $CuCl_2$ and **1** in 80 mM Tris-HCl buffer solution (pH 7.1). Conditions: glassy carbon working electrode, Ag/AgCl (3.5 M KCl) reference electrode and Pt wire counter electrode.

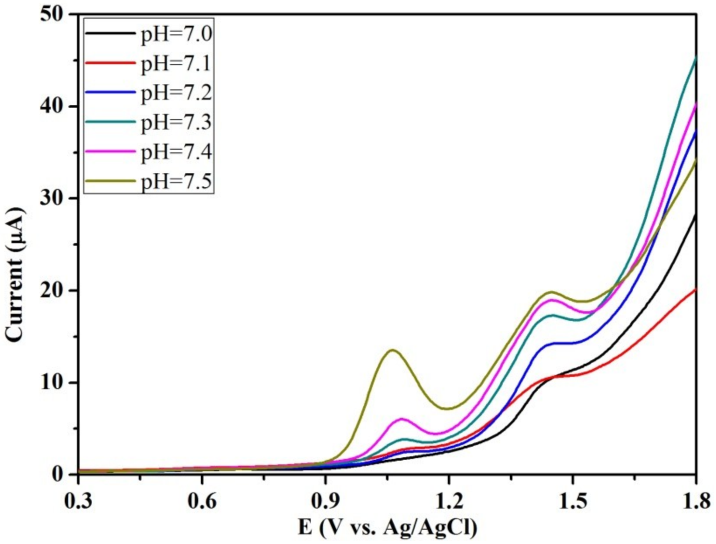

Fig. S14 DPVs of **1** in Tris-HCl buffers (80 mM) with various pH values. Conditions: glassy carbon working electrode, Ag/AgCl (3.5 M KCl) reference electrode and Pt wire counter electrode, 2.0 mM **1**.

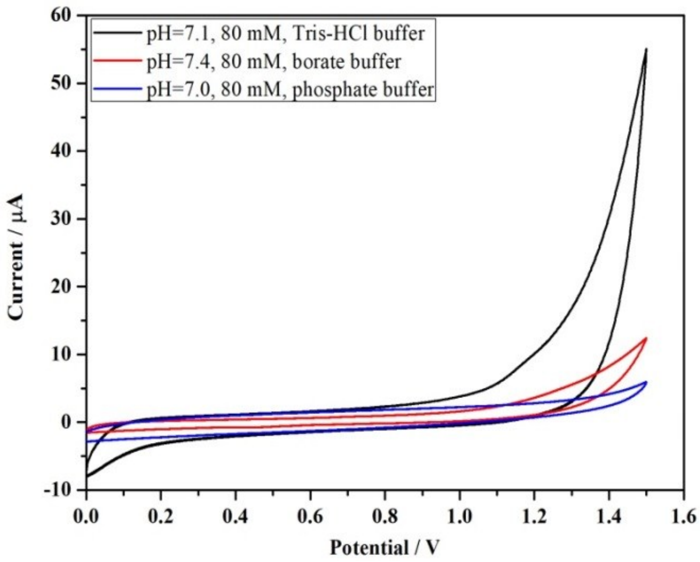

Fig. S15 CV curves of 2.0 mM **1** in different buffers (Tris-HCl buffer, black; borate buffer, red; phosphate buffer, blue). Conditions: glassy carbon working electrode, Ag/AgCl (3.5 M KCl) reference electrode and Pt wire counter electrode; scan rate 100 mV/s.

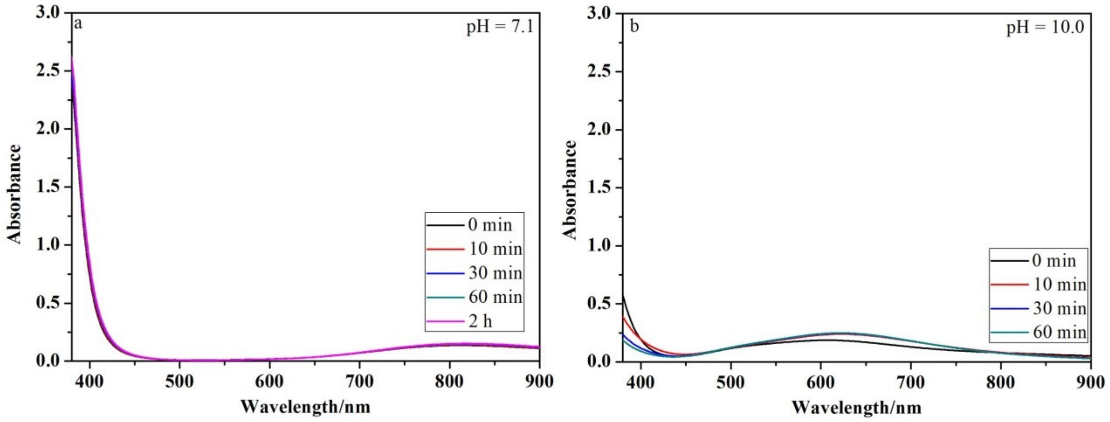

Fig. S16 Time-dependent UV-Vis spectra of 2.0 mM **1** in 80 mM Tris-HCl buffer solution with different pH.

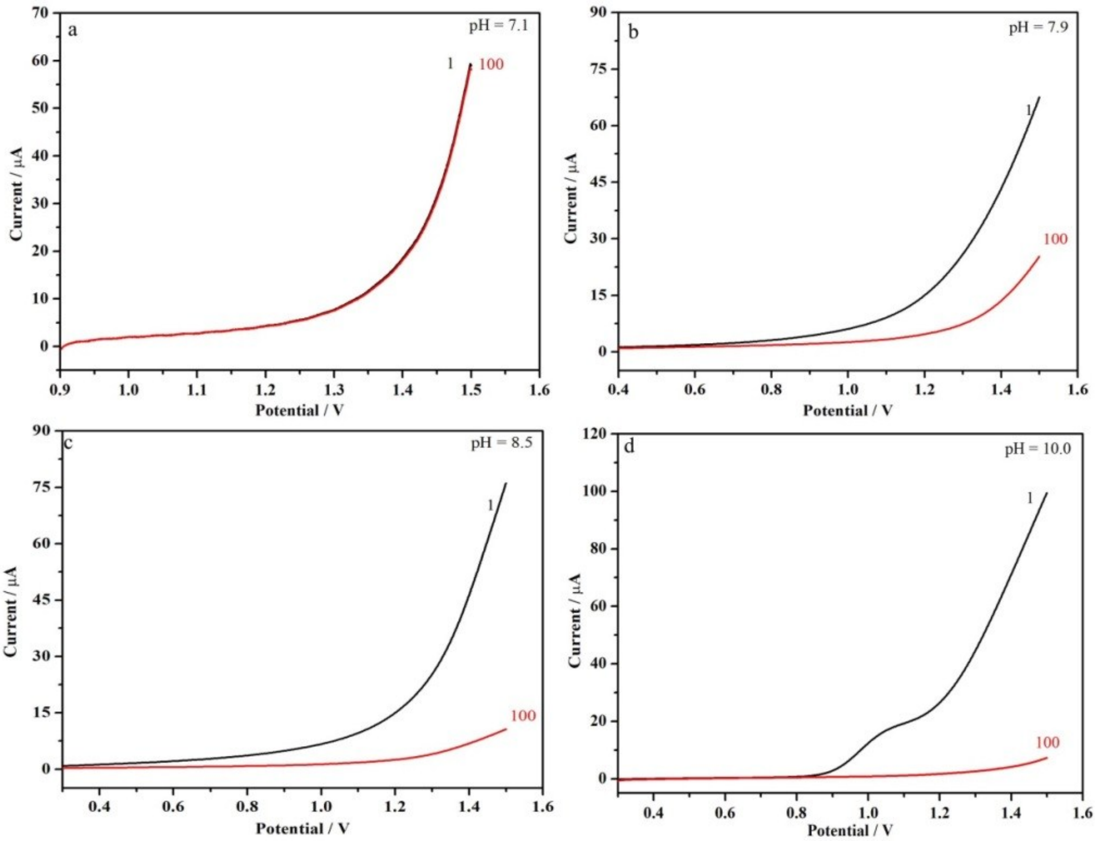

Fig. S17 LSV curves of 2.0 mM **1** for 100 times of voltammetry cycling at different pH from 7.1 to 10.0. Test conditions: glassy carbon working electrode, Ag/AgCl (3.5 M KCl) reference electrode and Pt wire counter electrode; scan rate 100 mV/s; 80 mM Tris-HCl buffer solution.

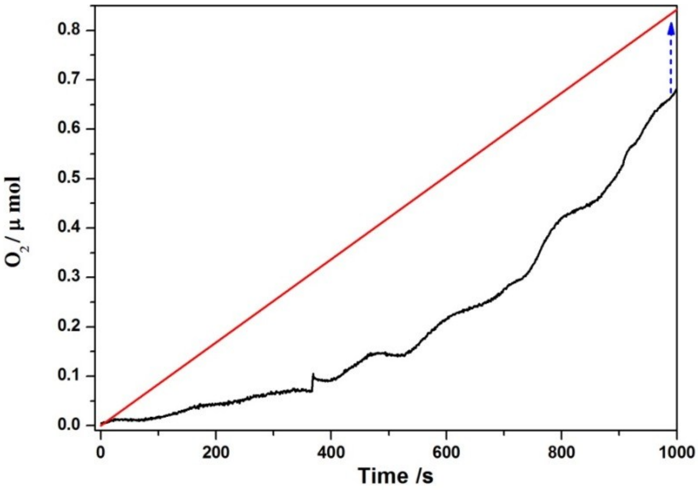

Fig. S18 O_2 production measured by Clark electrode with 2 mM **1** (black line) without stirring using an FTO electrode (1 cm^2) in 80 mM Tris-HCl buffer (pH 7.1) at 1.20 V vs Ag/AgCl. The red line is the theoretical amount of O_2. The arrow indicates termination of electrolysis with a Faradic efficiency of 80.67%.

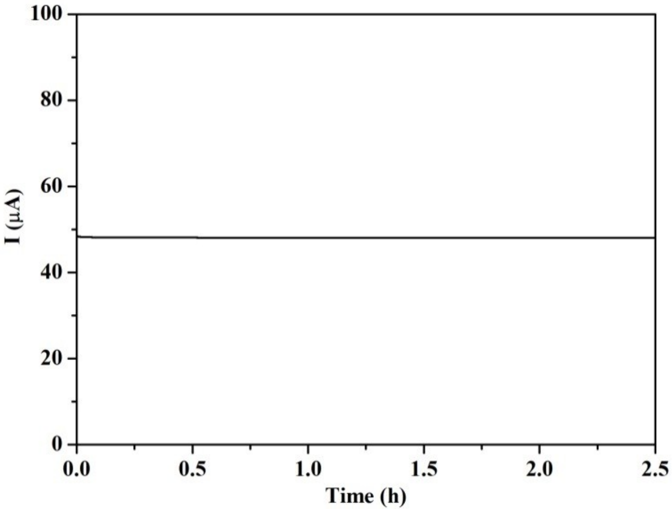

Fig. S19 Water electrolysis under an applied voltage of 1.2 V vs Ag/AgCl electrode in 80 mM pH 7.1 Tris-HCl buffer solution without **1**. Conditions: FTO glass working electrode, Ag/AgCl (3.5 M KCl) reference electrode and Pt wire counter electrode.

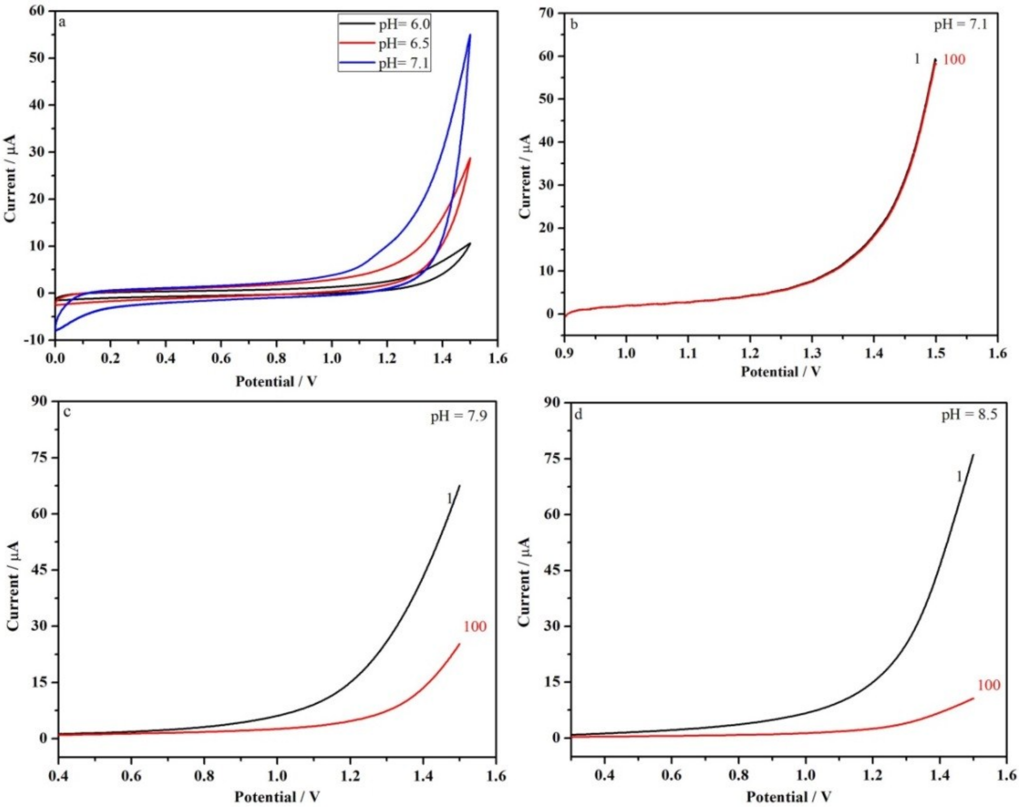

Fig. S20 (a) CV curves of 2.0 mM **1** at different pH from 6.0 to 7.1. (b-d) LSV curves of 2.0 mM **1** for 100 times of voltammetry cycling at different pH from 7.1 to 8.5. Test conditions: glassy carbon working electrode, Ag/AgCl (3.5 M KCl) reference electrode and Pt wire counter electrode; scan rate 100 mV/s; 80 mM Tris-HCl solution.

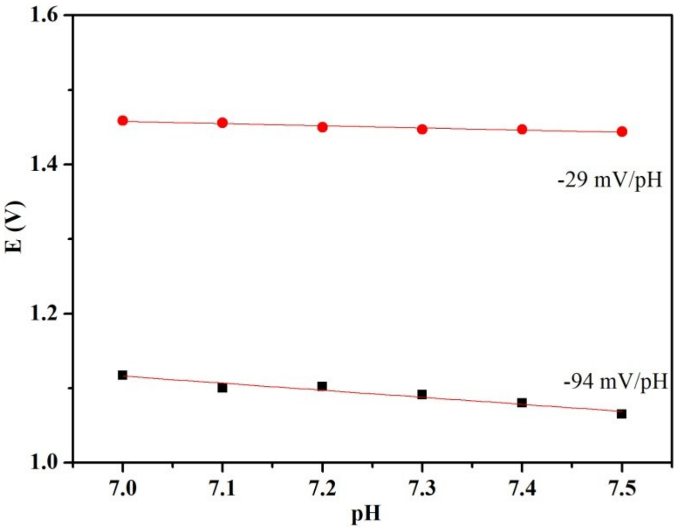

Fig. S21 Pourbaix diagram of **1**. The potential values were obtained from its DPVs at different pH.

Notes and references

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