

Electrochemical water oxidation catalyzed by a mononuclear cobalt complex of pentadentate ligand: the critical effect of borate anion

Haixia Zheng^{a,b}, Hui Ye^b, Tao Xu^b, Kaibo Zheng^{a*}, Xinyi Xie^c, Binghui Zhu^c, Xichao Wang^b, Junqi Lin^{b*} and Zhijun Ruan^{a,b*}

^a College of Materials and Chemical Engineering, Key laboratory of inorganic nonmetallic crystalline and energy conversion materials, China Three Gorges University, Yichang, 443002, China. Email: zhengkbo@126.com

^b Hubei Key Laboratory of Processing and Application of Catalytic Materials, College of Chemistry and Chemical Engineering, Huanggang Normal University, Huanggang, 438000, China. Email: linjunqi@hgnu.edu.cn; ruanzhijun@hgnu.edu.cn

^c Institute for New Energy Materials & Low Carbon Technologies, School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China.

Table S1 Crystallographic data and processing parameters for complex **1**

Crystal data	
Chemical formula	C ₁₉ H ₃₁ CoN ₅ O·2(ClO ₄)
<i>M_r</i>	603.32

Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	273
a, b, c (Å)	9.0629 (18), 33.221 (8), 8.842 (2)
β (°)	104.732 (9)
V (Å ³)	2574.6 (11)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.93
Crystal size (mm)	0.22 x 0.20 x 0.17
Data collection	
Diffractometer	Bruker <i>APEX-II</i> CCD
Absorption correction	—
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	29858, 5876, 4110
R_{int}	0.069
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.064, 0.203, 1.04
No. of reflections	5876
No. of parameters	329
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	1.35, -0.64

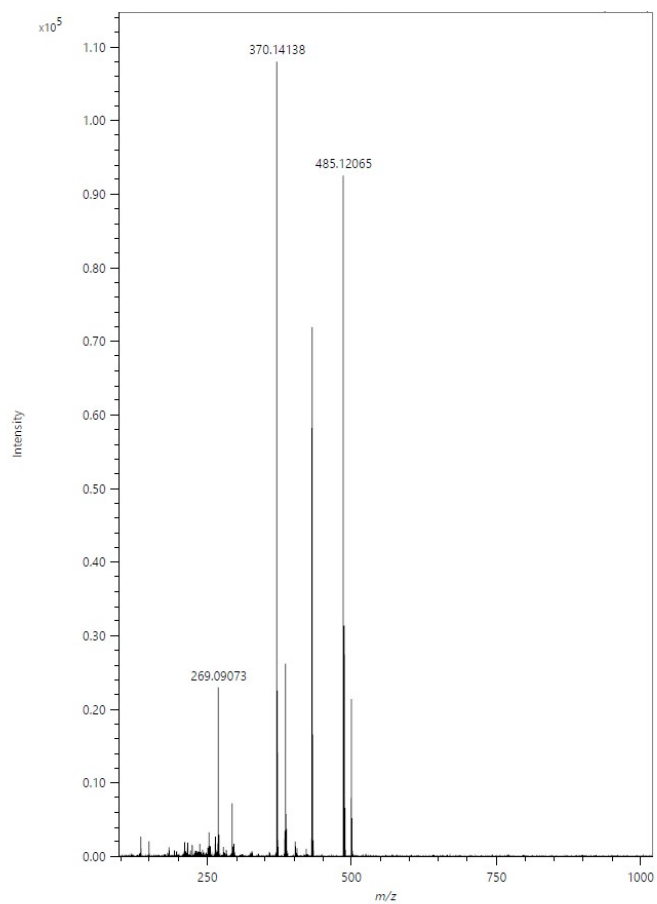


Fig. S1 High-resolution mass spectrum of complex **1** in pure water, the $m/z = 485.12065$ is ascribed to $[\text{Co}(\text{N}3\text{Py}2)(\text{ClO}_4)]^+$ (calc. 485.12).

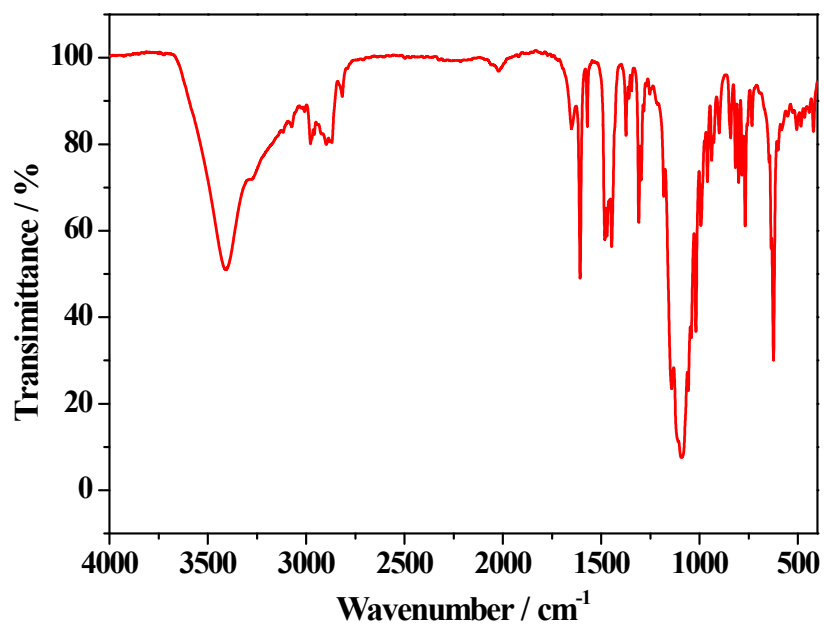


Fig. S2 Infrared spectrum of complex **1**.

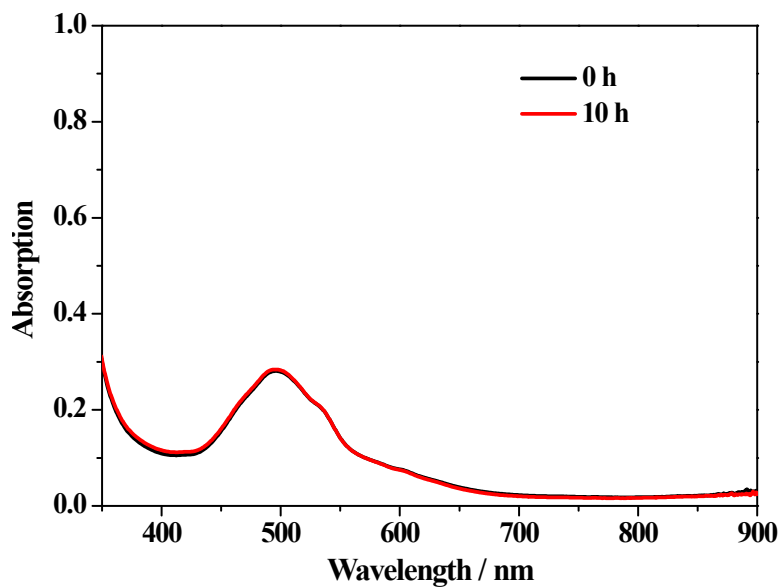


Fig. S3 The absorption spectrum of 10 mM of **1** before and after 10 h aging in 0.1 M borate buffer solution at pH 9.0.

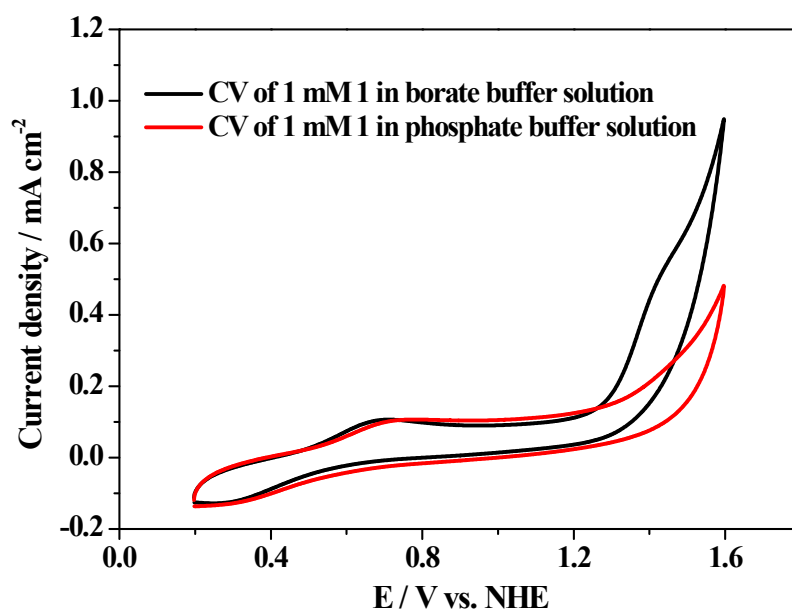


Fig. S4 CV curves of 1 mM of **1** in 0.1 M borate buffer solution at pH 9.0 (black) and 0.1 M phosphate buffer solution at pH 9.0 (red). GC electrode as working electrode, scan rate = 100 mV/s.

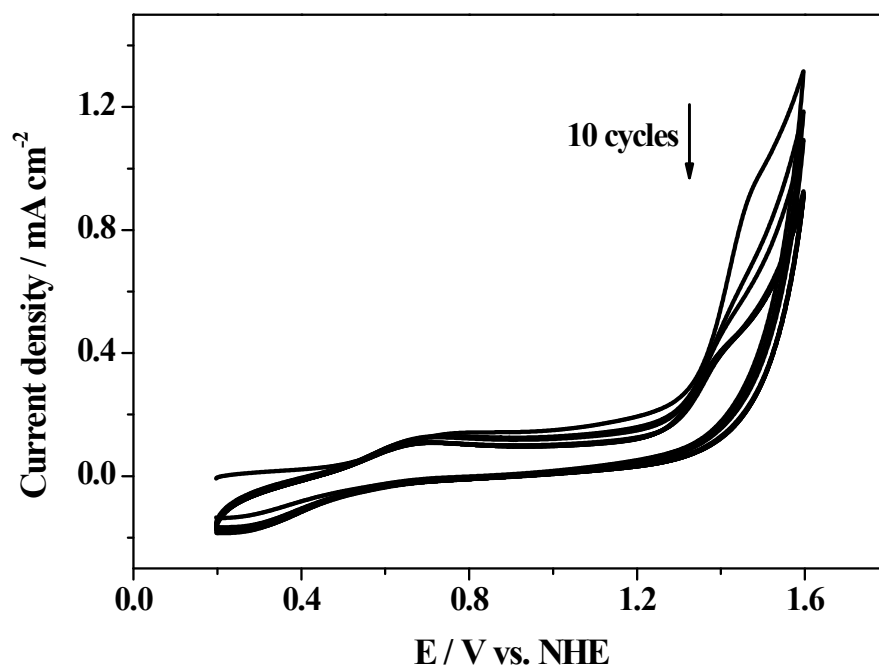


Fig. S5 Ten consecutive CV cyclic scan curves of 1 mM complex 1 in borate buffer solution.

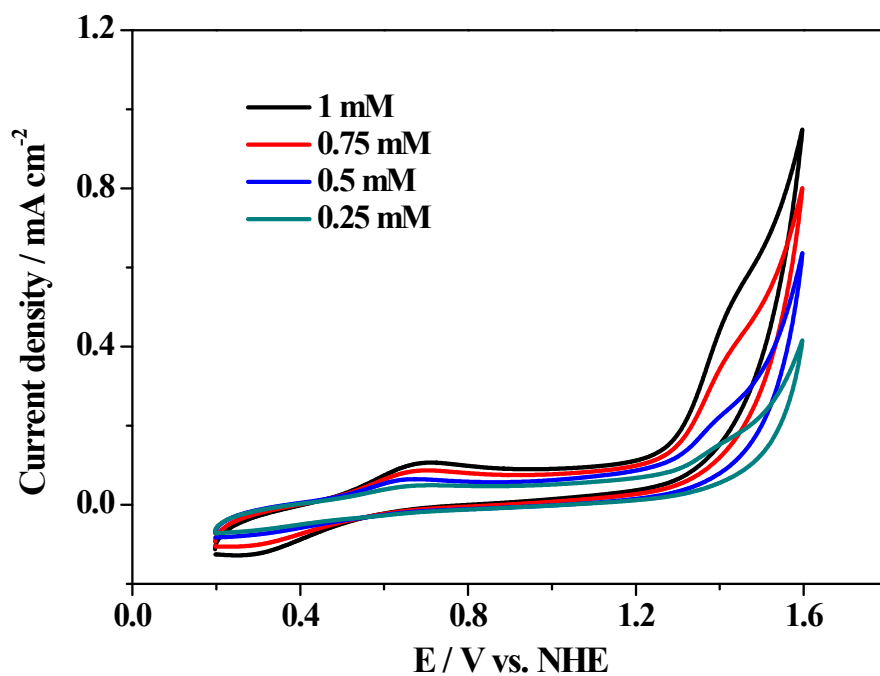


Fig. S6 CV of complex 1 with various concentrations in borate buffer solution at pH 9.0.

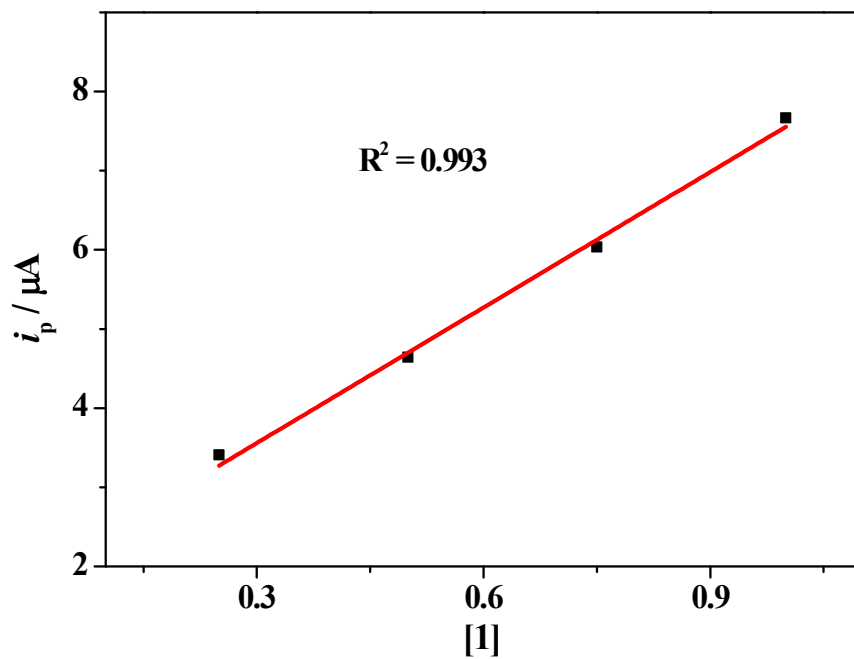


Fig. S7 Relationship between current of anodic wave and concentration of complex **1**, scan rate = 100 mV/s, 0.1 M borate buffer solution at pH 9.0 as electrolyte.

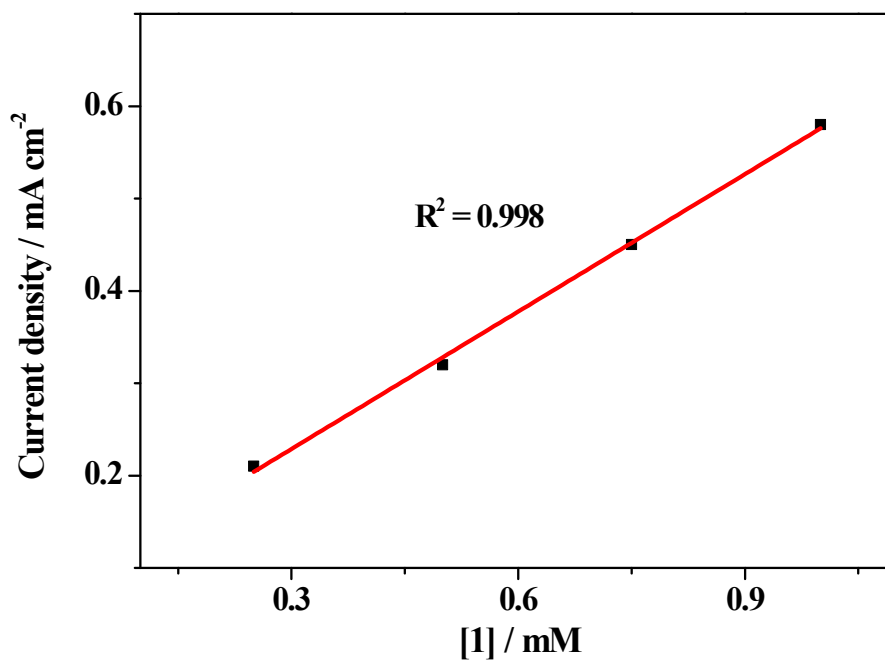


Fig. S8 Relationship between current density at 1.45 V vs. NHE and concentration of complex **1**, scan rate = 100 mV/s, 0.1 M borate buffer solution at pH 9.0 as electrolyte.

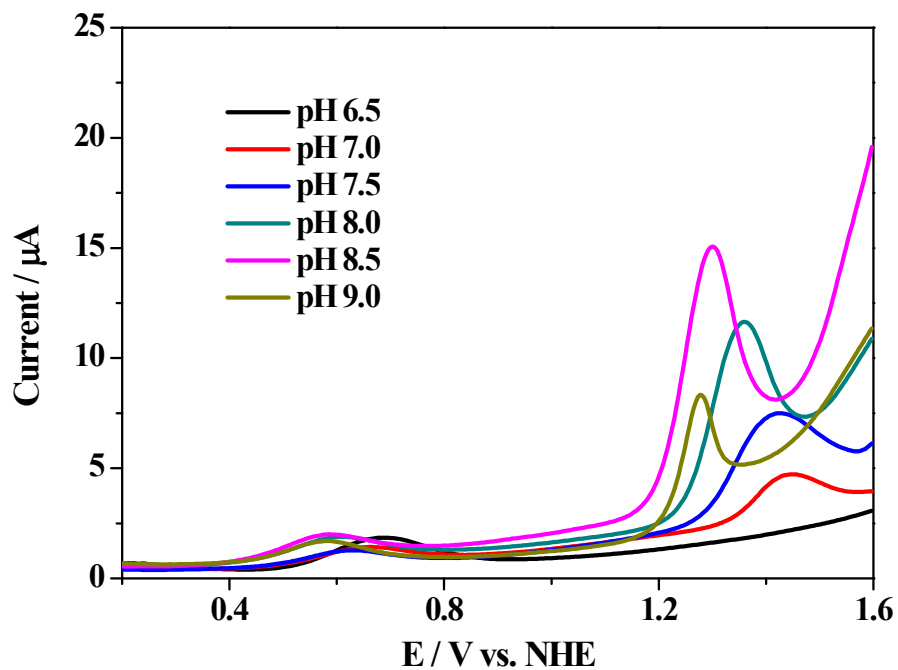


Fig. S9 Differential pulse voltammetry (DPV) examination of 1 mM complex **1** in 0.1 M borate buffer solution at various pH values.

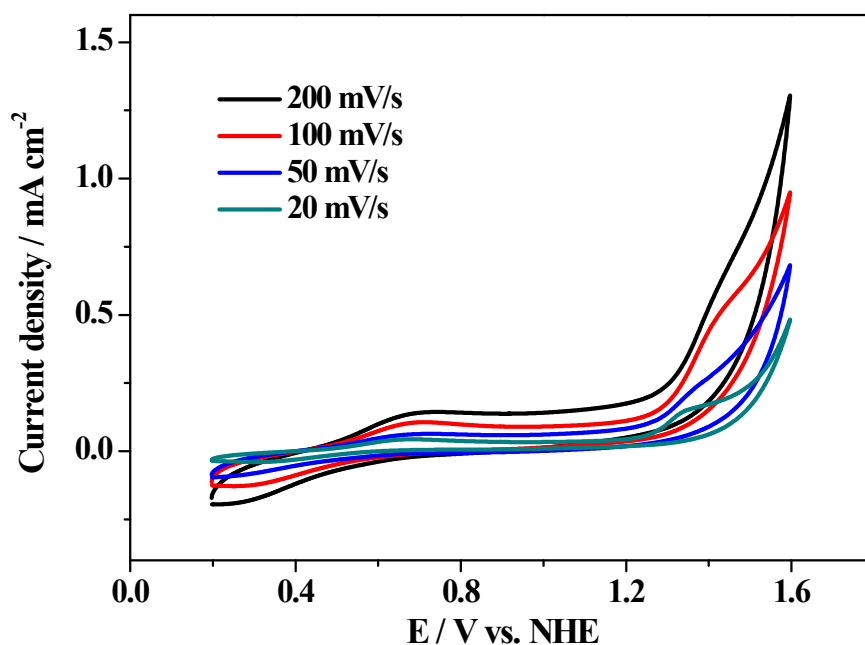


Fig. S10 CV of 1.0 mM of **1** with various scan rates, 0.1 M borate buffer solution as electrolyte.

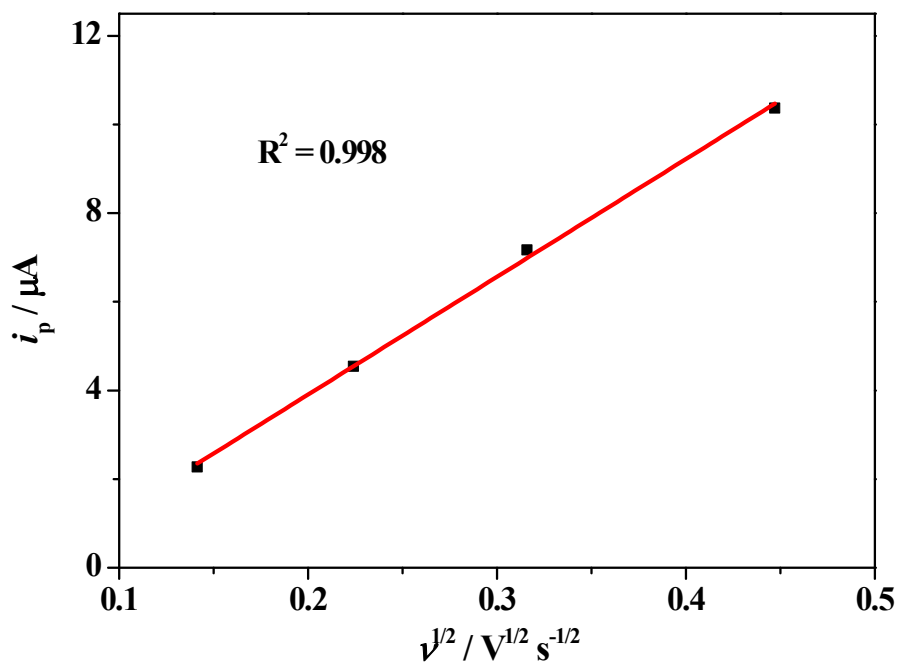


Fig. S11 Dependence of oxidation wave current density of the non-catalytic process of 1 mM of **1** on the square root of scan rates, 0.1 M borate buffer solution as electrolyte.

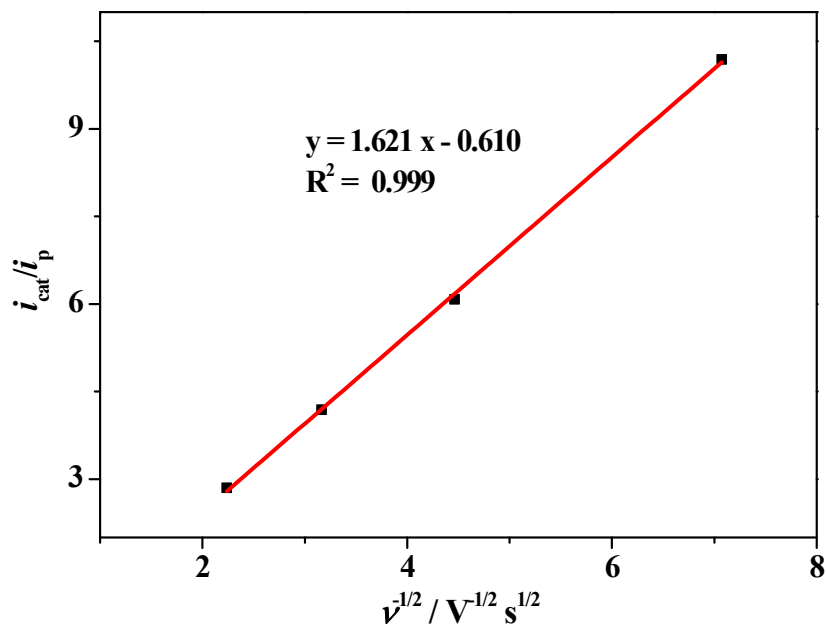


Fig. S12 Plots of the ratio of i_{cat} to i_d of complex **1** versus the reciprocal of the square root of scan rate.

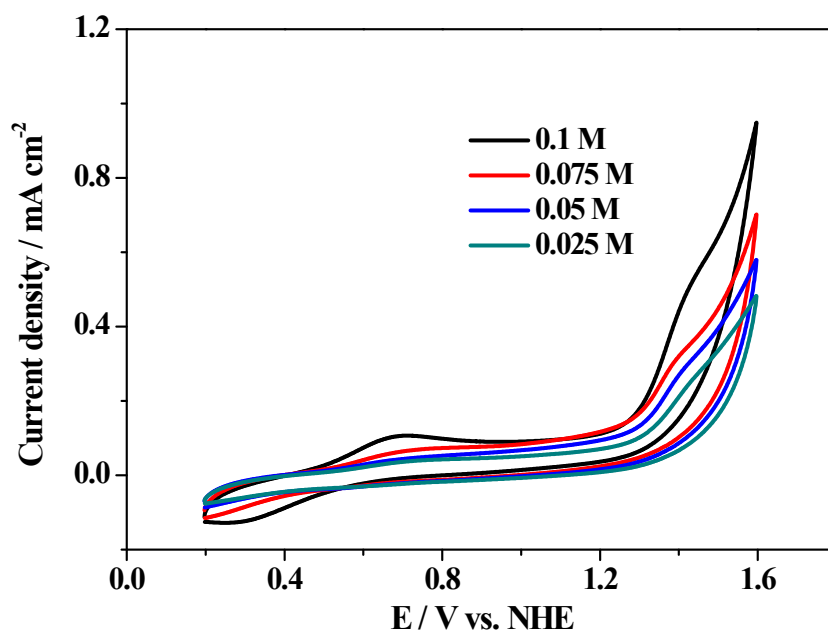


Fig. S13 CV of 1.0 mM of **1** in borate buffer solution with various concentrations as electrolyte (pH 9.0). The ionic strength of electrolyte was maintained with the addition of NaClO₄.

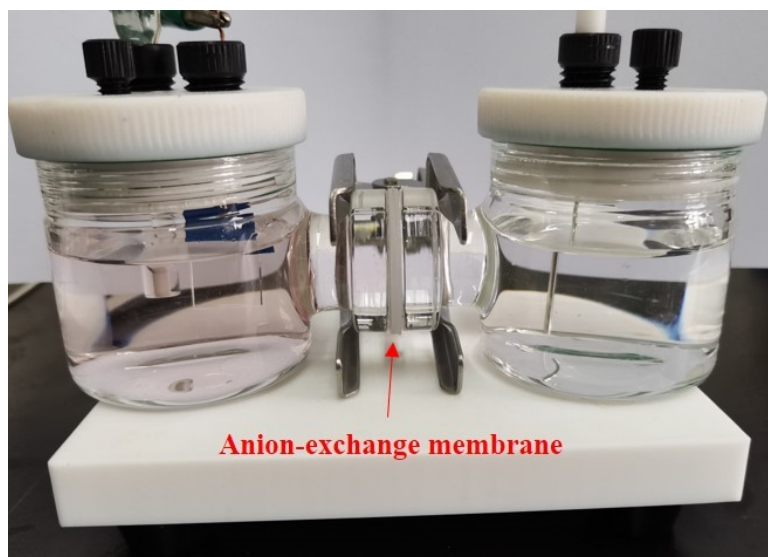


Fig. S14 Picture of the two-compartment cell used for CPE experiments; 0.1 M borate buffer solution containing 1 mM complex **1** was used as electrolyte and potential was controlled at 1.45 V vs. NHE.

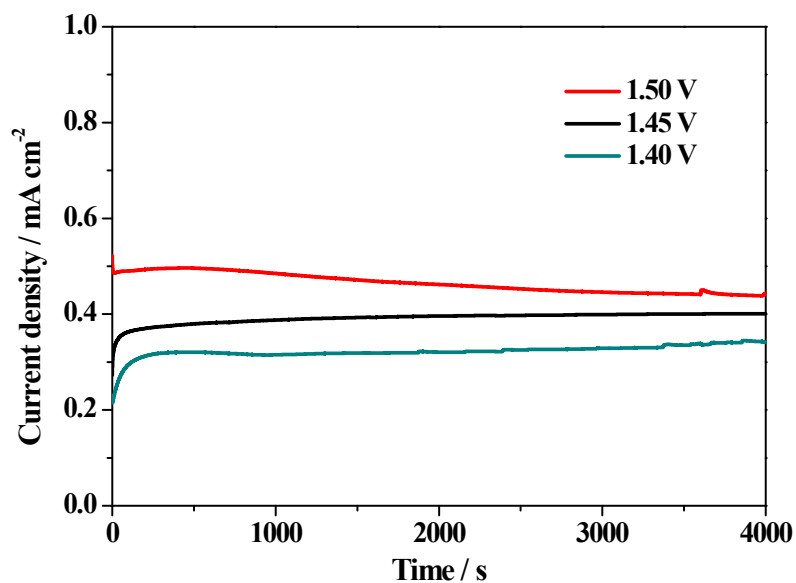


Fig. S15 The i - t curves obtained in CPE experiment of 1 mM of complex **1** at different potential (vs. NHE) using 0.1 M borate buffer at pH 9.0 as electrolyte and ITO electrode ($1\text{ cm} \times 2\text{ cm}$ with 1 cm^2 immersed in electrolyte).

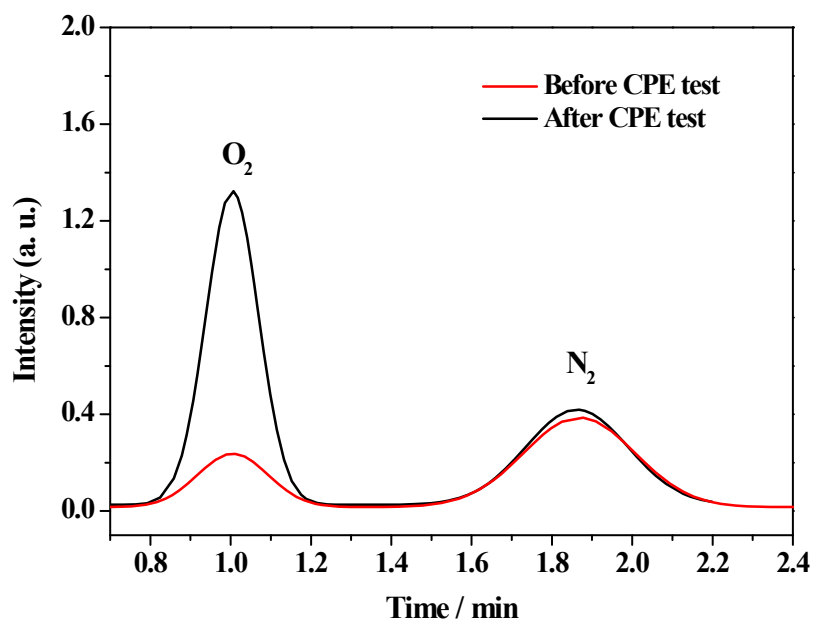


Fig. S16 Gas chromatographic trace before and after CPE test at 1.45 V vs. NHE.

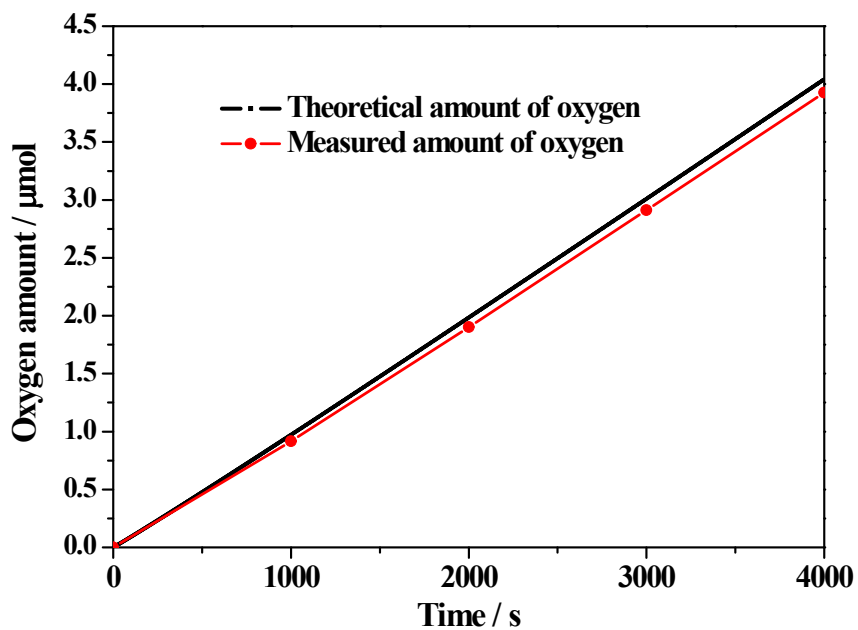


Fig. S17 Faradaic efficiency of O₂ evolution for complex **1** under electrolysis of 4000 s at 1.45 V (vs. NHE) in 0.1 M borate buffer solution at pH 9.0.

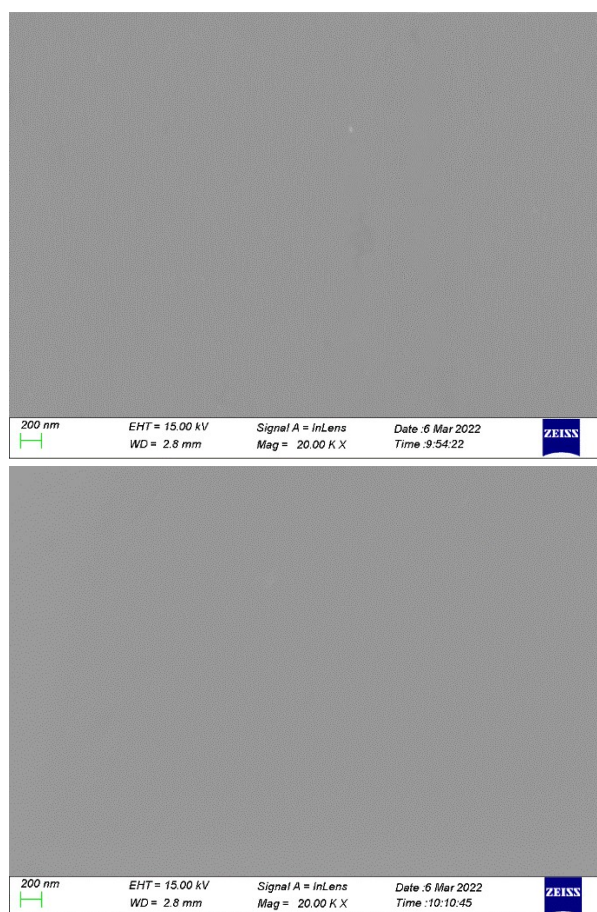


Fig. S18 SEM images of the surface of ITO electrode before (top) and after (bottom) 4 h CPE experiments (1.45 V vs. NHE) of 1 mM of **1** in 0.1 M borate buffer solution at pH 9.0.

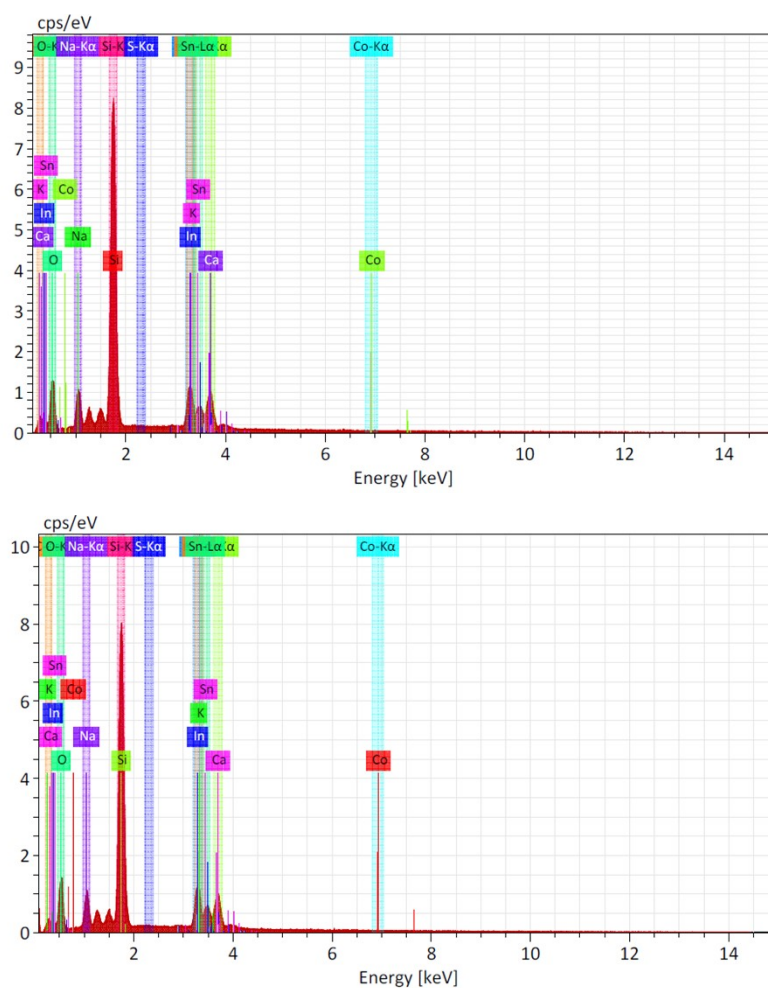


Fig. S19 EDX analysis of the surface of ITO electrode before (top) and after (bottom) 4 h CPE experiments of 1 mM of **1** in 0.1 M borate buffer solution at pH 9.0.

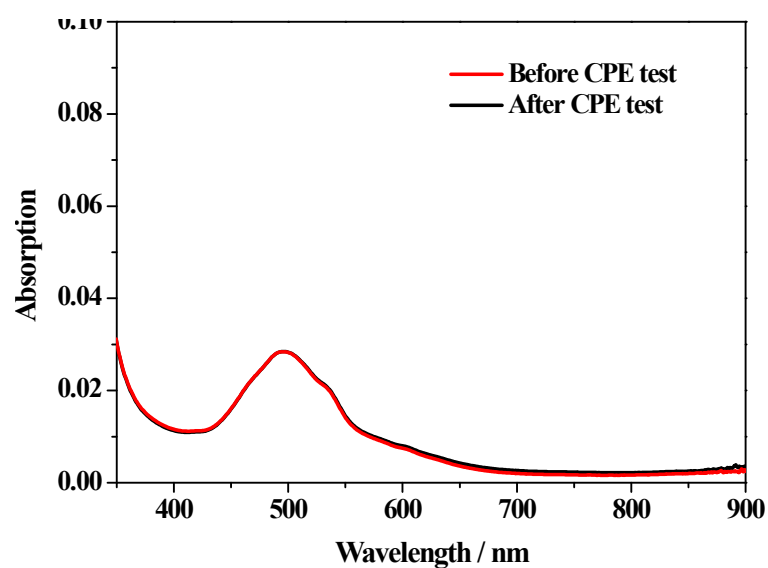


Fig. S20 UV-vis absorption spectra of 1 mM of **1** before and after the CPE test at 1.45 V vs. NHE.