Electronic Supplementary Information (ESI)

N-donor flexible ligands constructed polyoxometalate-based metal-organic frameworks as multifunctional electrocatalyts

Qian Zhou, Jin-Zhen Yao, Jing Sun,* Xiao Li,* Zhong-Min Su*

[a] School of Chemistry and Environmental Engineering, Changchun University of Science and Technology；Jilin Provincial Science and Technology Innovation Center of Optical Materials and Chemistry；Jilin Provincial International Joint Research Center of Photofunctional Materials and Chemistry ； Changchun130022, China.

* Corresponding author. Tel.: 0431-85583894.

E-mail address: sj-cust@126.com; lix@cust.edu.cn; zmsu@nenu.edu.cn

1.Experimental section

1.1. Materials and general methods

All chemicals were commercially purchased and used without purification. Crystal data were collected using a Bruker APEX II CCD diffractometer in Germany. Powder X-ray diffraction (PXRD) patterns were measured on a powder X-ray diffractometer (DRIC Y-2000) using Cu Kα radiation. EVO2G-TG-08 analyzer was used for testing under air at a heating rate of 10 ℃/min. FT-IR spectra were recorded from KBr pellets from 4000-500 cm^{-1} with a Nicolet Magna750 spectrometer. CHI760E electrochemical workstation was used for control of the electrochemical measurements and data collection. A conventional three-electrode system was used, with a carbon paste electrode (CPE) as a working electrode, a commercial Ag/AgCl as reference electrode and graphite carbon as counter electrode.

1.2. Synthesis of CUST-631 and CUST-632

A mixture of $Ni(NO_3)_2·6H_2O$ (0.06 g, 0.21 mmol), $H_4SiW_{12}O_{40}·xH_2O$ (0.06 g, 0.02 mmol), btbu (0.20 mmol) and 8 mL H_2O under ultrasonic treatment at room temperature for 30 min, then several drops of HNO_3 were added and stirred evenly. This mixture was transferred to a 25 mL Teflon-lined reactor 130 °C for 3 days. After the reactor was slowly cooled to room temperature, green block crystals of **CUST-631** were obtained. The crystals were picked out, washed and dried at room temperature (62% yield based on W).The CCDC number of **CUST-631** is 2132631. Anal.Calcd. for **CUST-631**: H, 0.05; C, 10.08; N, 8.82; O,

19.33, Ni, 3.08; Si, 0.74, W, 57.93 (%). Found: H, 0.07; C, 10.04; N, 8.72; O, 19.35,Ni, 3.05; Si, 0.76, W, 58.01 (%).

CUST-632was prepared similarly to **CUST-631,** a mixture of $Co(NO_3)_2·6H_2O$ (0.06 g, 0.34 mmol), $H_4SiW_{12}O_{40}·xH_2O$ (0.06 g, 0.02 mmol), btbu (0.20 mmol) and 8 mL H_2O under ultrasonic treatment at room temperature for 30 min, then several drops of HNO_3 were added. After the reactor was slowly cooled to room temperature, red block crystals of **CUST-632** were obtained (65 yield based on W). The CCDC number of **CUST-632** is 2132630. Anal.Calcd. for **CUST-632**: H, 0.02; C, 9.79; N, 8.85; O, 19.39, Co, 3.10; Si, 0.74, W, 58.11 (%). Found:H, 0.05; C, 9.81; N, 8.81; O, 19.33,Co, 3.08; Si, 0.76, W, 58.16 (%).

1.3. Preparation of CPEs

Carbon paste electrodes (CPEs) were fabricated as follows: First, suitable proportions of **CUST-631**or **CUST-632** with acetylene black were weighed and grinded for 30 minutes. Then, electrocatalyst inks were prepared by dispersing the mixture in deionized water, ethanol, and 5 wt % Nafion solution by ultra sonication for at least 30 min. 5 μL of the ink was dropped on the surface of precleaned glassy carbon electrode and dried in air.

1.4 Theoretical support

The reactions associated with reduction of $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ in concentrated H_2SO_4 are represented.

$$[\alpha\text{-}SiW_{12}O_{40}]^{4-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\alpha\text{-}SiW_{12}O_{40}]^{5-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\alpha\text{-}SiW_{12}O_{40}]^{6-} \quad \text{(I)}$$

$$[\alpha\text{-}SiW_{12}O_{40}]^{6-} \underset{-2e^-\,-4H^+}{\overset{+2e^-\,+4H^+}{\rightleftharpoons}} [\alpha\text{-}H_2SiW_{12}O_{40}]^{6-} \quad \text{(II)}$$

Take the reduction of nitrite as an example, HNO_2 can disproportionate to form NO and NO_3^-, then $[\alpha\text{-}SiW_{12}O_{40}]^{5-}$ is oxidized by HNO_2 in sulfuric acid media to reform $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$,

$$\mathbf{3HNO_2 \rightarrow H^+ + 2NO + NO_3^- + H_2O} \quad \text{(III)}$$

$$\mathbf{H^+ + HNO_2 + [\alpha\text{-}SiW_{12}O_{40}]^{5-} \rightarrow NO + H_2O + [\alpha\text{-}SiW_{12}O_{40}]^{4-}} \quad \text{(IV)}$$

Table S1. Crystal data and structure refinement for CUST-631.

Empirical formula	$C_{32}H_{54}N_{24}Ni_2O_{42}SiW_{12}$
Formula weight	3798.70
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.438(2)
b/Å	16.716(3)
c/Å	17.383(3)
α/°	90
β/°	102.122(3)
γ/°	90
Volume/Å^3	3533.7(12)
Z	2
density (calculated)	3.570 g/cm^3
absorption coefficient	20.086 mm^{-1}
F(000)	3416.0
2Θ range for data collection/°	3.418 to 50.216
Index ranges	$-14 \le h \le 14$, $-16 \le k \le 19$, $-20 \le l \le 20$
Reflections collected	20127
Independent reflections	6274 [R_{int} = 0.0438, R_{sigma} = 0.0459]
Data/restraints/parameters	6274/210/530
Goodness-of-fit on F^2	1.254
R_1 [I>=2σ (I)] [a]	0.0578
wR_2[I>=2σ (I)] [b]	0.1084
R_1 [all data] [a]	0.0690
wR_2[all data] [b]	0.1119
Largest diff. peak/hole / e Å^{-3}	2.14/-1.60

[a]$R1 = \sum||F_0| - |F_c||/\sum|F_0|$. [b]$wR_2 = [\sum w(F_0^2 - F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$

Table S2. Bond Lengths for CUST-631.

Atom Atom	Length/Å	Atom Atom	Length/Å
Ni1-N1	2.100(16)	W4-O2	1.685(11)

Ni1-O1	2.133(14)	W4-O5	1.885(17)
Ni1-N2	2.080(17)	W4-O9	1.854(18)
Ni1-N3	2.103(16)	W4-O10	1.898(14)
Ni1-O2	2.177(12)	W4-O17	2.41(2)
Ni1-N8	2.077(15)	W4-O18	2.34(2)
Si08-O17[1]	1.61(2)	W4-O23	1.912(17)
Si08-O18	1.67(2)	W5-O5	1.916(15)
Si08-O20	1.608(19)	W5-O11[1]	1.917(15)
Si08-O21[1]	1.59(2)	W5-O13	1.913(17)
W3-O3	1.861(16)	W5-O16	1.664(14)
W3-O7	1.639(14)	W5-O18	2.40(2)
W3-O9	1.927(15)	W5-O20[1]	2.44(2)
W3-O14[1]	1.892(15)	W5-O22	1.866(16)
W3-O15	1.864(17)	W6-O3[1]	1.926(15)
W3-O17	2.38(2)	W6-O8	1.889(16)
W3-O21[1]	2.41(2)	W6-O18	2.38(2)
W1-O6	1.653(14)	W6-O19	1.671(14)
W1-O8	1.926(15)	W6-O21	2.43(2)
W1-O12	1.869(15)	W6-O22	1.914(16)
W1-O13[1]	1.866(16)	W6-O23	1.881(16)
W1-O14	1.866(14)	W2-O4	1.669(13)
W1-O20	2.36(2)	W2-O10	1.879(15)
W1-O21	2.39(2)	W2-O11	1.878(15)
		W2-O12	1.894(15)
		W2-O15	1.933(18)
		W2-O17	2.38(2)
		W2-O20	2.412(19)

[1]1-X,1-Y,1-Z; [2]5/2-X,-1/2+Y,1/2-Z; [3]-1/2+X,3/2-Y,-1/2+Z

Table S3. Bond Angles for CUST-631.

Atom Atom Atom	Angle/°	Atom Atom Atom	Angle/°
N1-Ni1-O1	85.1(6)	O17[1]-Si08-O20	109.3(10)
N1-Ni1-N3	91.2(6)	O17[1]-Si08-O20[1]	70.7(10)

N1-Ni1-O2	86.7(6)	O17-Si08-O20[1]	109.3(10)
O1-Ni1-O2	83.5(5)	O18-Si08-O18[1]	180.0(16)
N2-Ni1-N1	100.5(6)	O20[1]-Si08-O18[1]	107.5(11)
N2-Ni1-O1	169.6(6)	O20-Si08-O18[1]	72.5(11)
N2-Ni1-N3	92.8(7)	O20-Si08-O18	107.5(11)
N2-Ni1-O2	88.1(6)	O20-Si08-O20[1]	180.0
N3-Ni1-O1	95.8(6)	O21-Si08-O17[1]	71.0(11)
N3-Ni1-O2	177.8(6)	O21-Si08-O17	109.0(11)
N8-Ni1-N1	167.0(6)	O21[1]-Si08-O18	109.4(11)
N8-Ni1-O1	82.3(6)	O21-Si08-O18	70.6(11)
N8-Ni1-N2	91.4(6)	O21[1]-Si08-O20[1]	67.6(10)
N8-Ni1-N3	93.4(6)	O21-Si08-O20[1]	112.4(10)
N8-Ni1-O2	88.5(6)	O21[1]-Si08-O21	180.0
O17[1]-Si08-O17	180.0		
O17[1]-Si08-O18	109.2(11)		
O17[1]-Si08-O18[1]	70.8(11)		

[1]1-X,1-Y,1-Z;[2]5/2-X,-1/2+Y,1/2-Z;[3]-1/2+X,3/2-Y,-1/2+Z;[4]1/2+X,3/2-Y,1/2+Z

Table S4. Crystal data and structure refinement for CUST-632.

Empirical formula	$C_{32}H_{52}N_{24}Co_2O_{42}SiW_{12}$
Formula weight	3797.12
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.407(10)
b/Å	16.723(13)
c/Å	17.478(14)
α/°	90
β/°	102.562(14)
γ/°	90
Volume/Å^3	3540(5)
Z	2

density (calculated)	3.563 g/cm^3
absorption coefficient	19.990 mm^{-1}
F(000)	3408.0
2Θ range for data collection/°	3.41 to 50.814
Index ranges	-14 ≤ h ≤ 14, -19 ≤ k ≤ 12, -20≤ l ≤ 21
Reflections collected	20195
Independent reflections	6391 [R_{int} = 0.0650, R_{sigma} = 0.0687]
Data/restraints/parameters	6391/617/548
Goodness-of-fit on F^2	1.168
R_1 [I>=2σ (I)] [a]	0.0672
wR_2[I>=2σ (I)] [b]	0.1322
R_1 [all data] [a]	0.0829
wR_2[all data] [b]	0.1386
Largest diff. peak/hole / e Å^{-3}	1.89/-1.78

[a]$R1 = \sum||F_0| - |F_c||/\sum|F_0|$. [b]$wR_2 = [\sum w(F_0^2 - F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$

Table S5. Bond Lengths for CUST-632.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co07	O1	2.220(17)	W3	O18	1.673(17)
Co07	O4	2.168(15)	W3	O22	1.878(17)
Co07	N1	2.116(18)	W3	O2	2.42(3)
Co07	N2	2.11(2)	W3	O9[1]	2.41(3)
Co07	N3	2.15(2)	W3	O11	1.928(17)
Co07	N4	2.135(19)	W4	O10	1.915(17)
Si1	O2	1.60(3)	W4	O12	1.847(16)
Si1	O9[1]	1.61(3)	W4	O23	1.942(17)
Si1	O5	1.59(3)	W4	O17	1.669(16)
Si1	O21[1]	1.63(3)	W4	O9	2.41(3)
W1	O6[1]	1.878(18)	W4	O21[1]	2.40(3)
W1	O10	1.846(17)	W4	O11[1]	1.883(19)
W1	O3[1]	1.920(17)	W5	O8	1.656(15)
W1	O13	1.859(17)	W5	O14	1.905(17)

W1-O7	1.647(16)	W5-O20	1.895(17)
W1-O9	2.38(3)	W5-O13	1.951(18)
W1-O5[1]	2.40(3)	W5-O15	1.871(17)
W2-O1	1.669(15)	W5-O2	2.38(3)
W2-O12	1.961(17)	W5-O5[1]	2.42(3)
W2-O16	1.864(16)	W6-O16	1.901(17)
W2-O3	1.851(17)	W6-O20	1.860(17)
W2-O15[1]	1.901(16)	W6-O22	1.888(18)
W2-O5	2.37(3)	W6-O23	1.868(18)
W2-O21[1]	2.37(3)	W6-O2	2.42(3)
W3-O6	1.864(17)	W6-O19	1.651(16)
W3-O14	1.861(17)	W6-O21[1]	2.41(3)

[1]1-X,1-Y,1-Z; [2]1/2+X,3/2-Y,1/2+Z; [3]-1/2-X,-1/2+Y,3/2-Z

Table S6. Bond Angles for CUST-632.

Atom Atom Atom	Angle/°	Atom Atom Atom	Angle/°
O4-Co07-O1	81.2(6)	O2[1]-Si1-O21	70.9(15)
N1-Co07-O1	87.2(7)	O21-Si1-O21[1]	180.0
N1-Co07-O4	84.1(7)	O9-Si1-O9[1]	180.0
N1-Co07-N3	91.7(8)	O9[1]-Si1-O21	70.2(15)
N1-Co07-N4	165.9(8)	O9-Si1-O21	109.8(15)
N2-Co07-O1	87.8(7)	O9-Si1-O21[1]	70.1(18)
N2-Co07-O4	166.7(7)	O5[1]-Si1-O2[1]	109.2(17)
N2-Co07-N1	103.0(8)	O5[1]-Si1-O2	70.8(17)
N2-Co07-N3	93.4(8)	O5-Si1-O9	109.4(16)
N2-Co07-N4	90.1(7)	O5[1]-Si1-O9	70.6(16)
N3-Co07-O1	178.6(7)	O5[1]-Si1-O5	180.0(13)
N3-Co07-O4	97.8(7)	O5-Si1-O21	110.4(15)
N4-Co07-O1	87.9(7)	O5[1]-Si1-O21	69.6(15)
N4-Co07-O4	82.1(7)		
N4-Co07-N3	93.0(8)		
O2[1]-Si1-O2	180.0		
O2-Si1-O9	109.0(16)		

O2[1]-Si1-O9	71.0(16)
O2-Si1-O21	109.1(15)

[1]1-X,1-Y,1-Z;[2]1/2+X,3/2-Y,1/2+Z;[3]-1/2+X,3/2-Y,-1/2+Z;[4]-1/2-X,-1/2+Y,3/2-Z;[5]-1/2-X,1/2+Y,3/2-Z

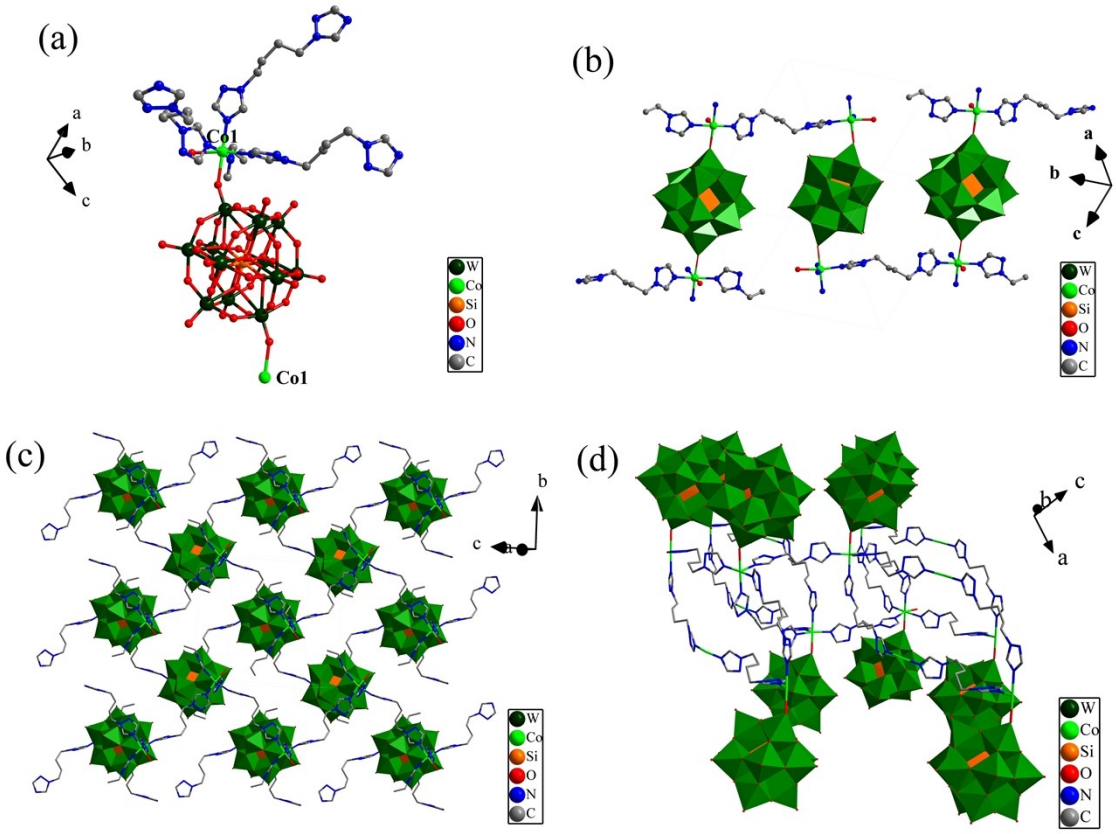

Figure S1 (a) Asymmetric unit of CUST-632. (All hydrogens are omitted for clarity); (b) The 1D Co-{SiW_{12}} inorganic chain of CUST-632; (c) The {SiW_{12}}-based 2D network of CUST-632 along a-axis; (d) The diagram of the 3D fabric of CUST-632.

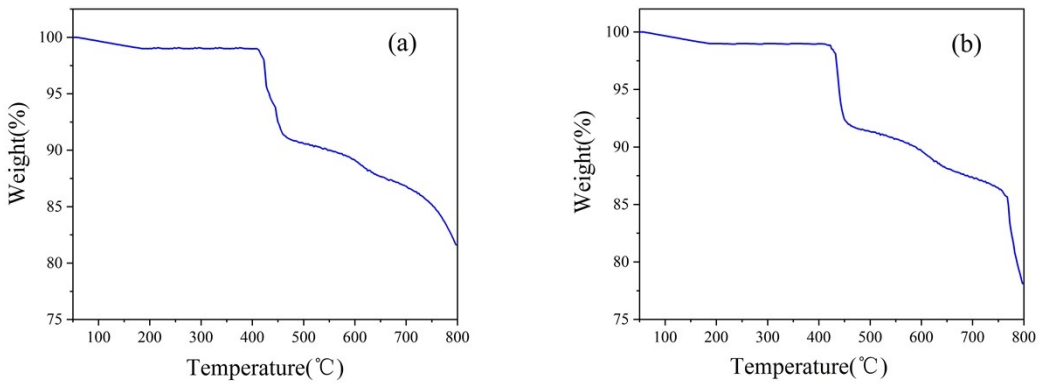

Figure S2 TG curves of (a) CUST-631 and (b) CUST-632.

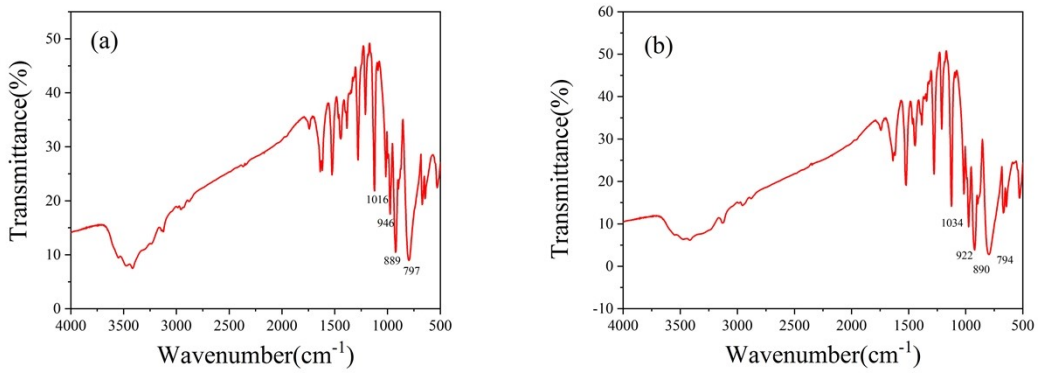

Figure S3 IR spectra of (a) CUST-631and (b) CUST-632.

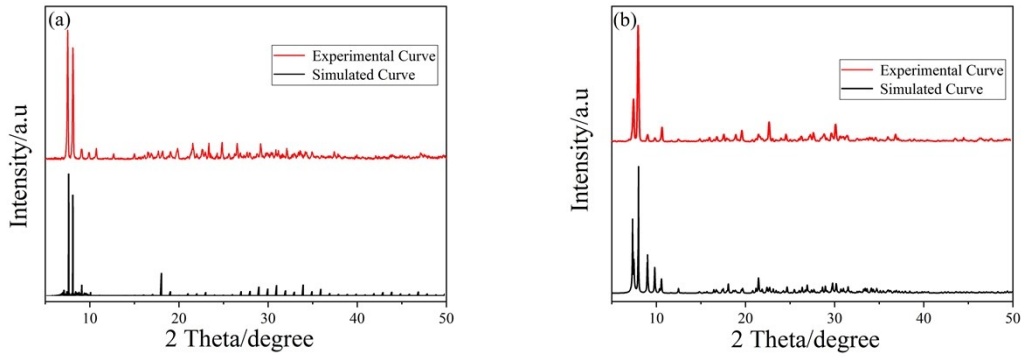

Figure S4 The PXRD patterns of (a) CUST-631 and (b) CUST-632.

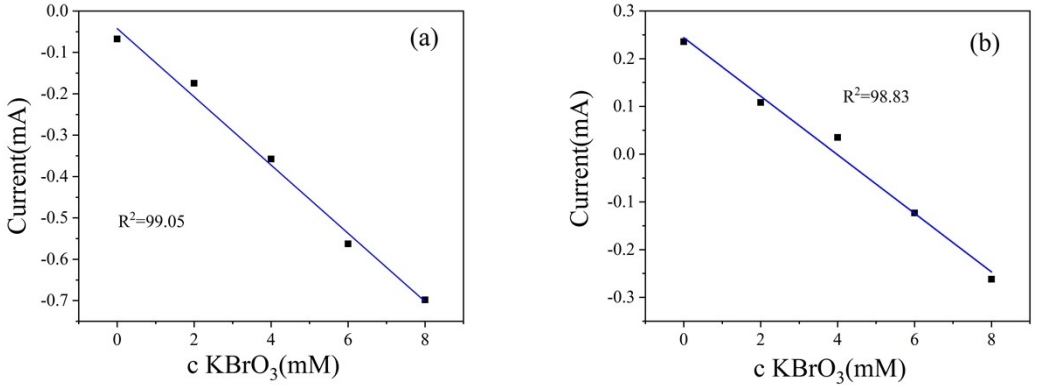

Figure S5 The plot of the cathodic peak currents vs. concentrations of $KBrO_3$ of (a) CUST-631 and (b) CUST-632.

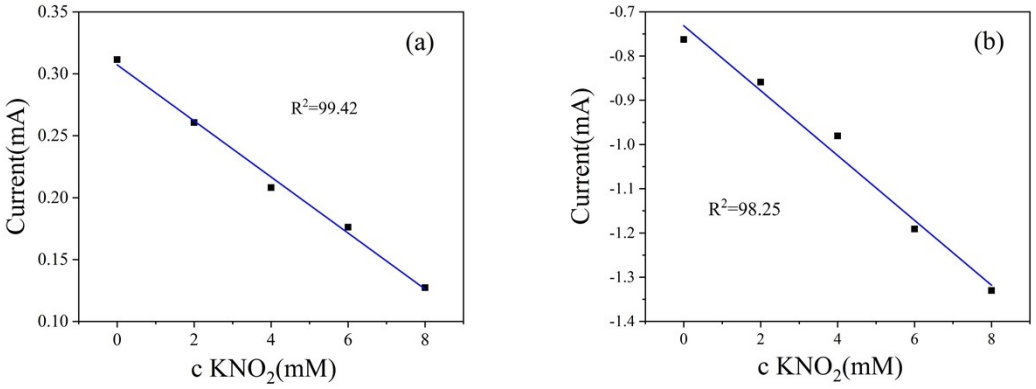

Figure S6 The plot of the cathodic peak currents vs. concentrations of KNO_2 of (a) CUST-631 and (b) CUST-632.

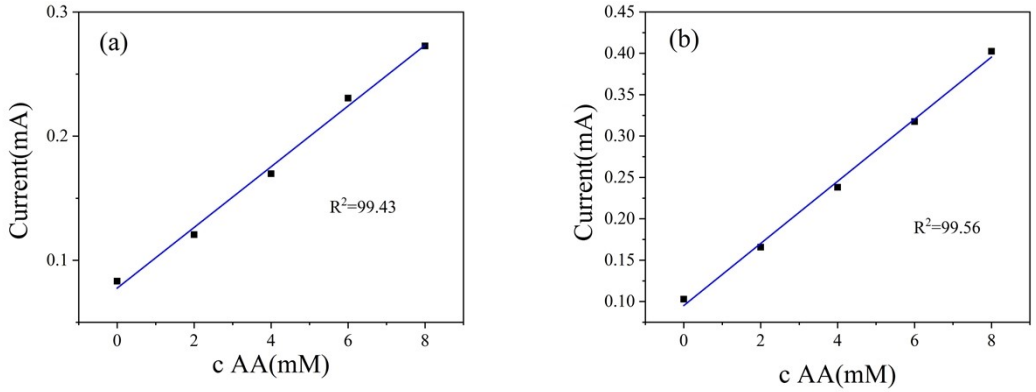

Figure S7 The plot of the anodic peak currents vs. concentrations of AA of (a) CUST-631 and (b) CUST-632.