Electronic Supplementary Information

Enhancing Selectivity through Decrypting the Uncoordinated Zirconium Sites in MOF Electrocatalysts

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Contents

Section S1. Chemicals and Equipment

Materials. The following chemicals were used without further purification. Zirconium(IV) tetrachloride ($ZrCl_4$, anhydrous), cobalt(II) chloride hexahydrate ($CoCl_2$ $6H_2O$), propionic acid, methyl p-formylbenzoate, pyrrole, benzoic acid, sodium hydroxide, tetrahydrofuran, ethyl acetate, acetone, ethanol, N, N-dimethylformamide and hydrochloric acid were purchased from Aladdin. Benzoic acid (BA), formic acid (FA), and acetic acid (AA) were purchased from Alfa Aesar. Nafion 117 proton exchange membrane and Nafion D-521 dispersion (5 wt% in lower aliphatic alcohols and water) were purchased from Shanghai Hesen Electric Co. Ltd. Toray Carbon Paper (TGP-H-60, 19×19 cm) was purchased from Shanghai feishier experimental equipment co., LTD. 5, 10, 15, 20-tetrakis (4-carboxyphenyl) porphyrin (H_2TCPP) was synthesized according to the literature with minor adjustments. The ultrapure water (18.4 MΩ cm) was prepared by an ELGA purification system (Veolia Water Solutions & Technologies, UK).

Equipment. Powder X-ray diffraction (PXRD) patterns were recorded with a Rigaku SmartLab 9 Kw instrument (Tokyo, Japan) D/MAX-2500 diffractometer equipped with a Cu K_α radiation (λ=1.54056 Å). The scanning electron microscope (SEM) images were obtained from a JSM-7600 scanning electron microscope (JEOL Ltd.). The gaseous product of electroreduction was online analyzed and collected by gas chromatography (GC, SRI, 8610C) equipped with helium ionization detector (HID) and thermal conductivity detector (TCD). Meanwhile, the gas was separated with packed MolSieve 13X column and Silica Gel column. High purity helium (99.999%) was used as the carrier gas. The gaseous product was quantified by automatic integration of peak area referring to standard curve. Electrochemical data was recorded by electrochemical workstation (CHI 660e).

Section S2. Synthesis of Materials [1]

Synthesis of H$_2$TCPP. Methyl p-formylbenzoate (6.9 g, 0.042 mol) was dissolved in the propionic acid (100 mL) in a 500-ml three-necked flask, and pyrrole (3.0 g, 0.043 mol) were added dropwise into the solution, then the mixture was refluxed for 12 h at 135 ^{o}C. The reaction mixture was cooled to room temperature afterwards, and purple powder (TPPCOOMe) was obtained by filtration and vacuum drying. the obtained ester was dissolved in the mixed solvent of THF (65 mL) and MeOH (65 mL), then a solution of KOH (6.82 g, 121.79 mmol) and H$_2$O (65 mL) was added. The mixture was refluxed for 12 h at 85 ^{o}C. After cooling to room temperature, the THF and MeOH were evaporated. Additional water fully dissolved the mixture under heating. Then 1 M HCl was added to acidify the homogeneous solution until no further precipitate was generated. The precipitate was washed by water and dried in vacuum overnight. Finally, dark red powder was obtained.

Synthesis of (5, 10, 15, 20)-tetrakis(4-carboxyphenyl)porphyrin-Co(II) (TCPP(Co)). DMF (100 mL) dissolved TPPCOOMe (1.60 g, 1.87 mmol) and CoCl$_2$·6H$_2$O (5.70 g, 23.98 mmol) in a 500-ml three-necked flask, and the mixture was refluxed for 6 h at 125 ^{o}C. 150 mL of H$_2$O was added after cooling down to room temperature. The obtained precipitate was filtered and washed with H$_2$O (100 mL) for two times. Moderate CHCl$_3$ dissolved the resultant solid, then the mixture was washed with 1 M HCl and water for three times. The organic layer was dried by anhydrous magnesium sulfate and evaporated to collect crimson powder afterwards. The obtained ester (1.95 g) was dissolved the mixed solvent of THF (65 mL), MeOH (65 mL), then a solution of KOH (6.82 g, 121.79 mmol) and H$_2$O (50 mL) was added. This mixture was refluxed for 12 h at 85 ^{o}C. The THF and MeOH were evaporated after cooling to room temperature. Additional water fully dissolved the mixture under heating. Then 1 M HCl was added to acidify the homogeneous solution until no further precipitate was generated. Then the precipitate was washed by water and dried in vacuum overnight. Finally, dark red powder was obtained.

Synthesis of PCN-223-BA. ZrCl$_4$ (5 mg) and TCPP(Co) (30 mg) were mixed in DMF (10 ml) in a Pyrex vial, then benzoic acid (400 mg) was added to the solution. The mixture was heated in 90 ℃ oven for 72 h. After cooling down to room temperature, the precipitate was washed with DMF and ethyl alcohol for three times and dried in vacuum overnight. Finally, dark red powder was obtained.

Synthesis of PCN-223-AA. ZrCl$_4$ (4.19 mg) and TCPP(Co) (30 mg) were mixed in DMF (10 ml) in a Pyrex vial, then acetic acid (600 μL) was added to the solution. The mixture was heated in 90 ℃ oven for 72 h. After cooling down to room temperature, the precipitate was washed with DMF and ethyl alcohol for three times and dried in vacuum overnight. Finally, dark red powder was obtained.

Synthesis of PCN-223-AA-1. The synthesized mothed was the same as PCN-223-AA, except that the volume of AA is 900 μL.

Synthesis of PCN-223-FA. ZrCl$_4$ (7 mg) and TCPP(Co) (10 mg) were mixed in DMF (10 ml) in a Pyrex vial, then formic acid (550 μl) was added to the solution. The mixture was heated in 120 ℃ oven for 16 h. After cooling down to room temperature, the precipitate was washed with DMF and ethyl alcohol for three times and dried in vacuum overnight. Finally, dark red powder was obtained.

Synthesis of PCN-223-FA-1. The synthesized mothed was the same as PCN-223-FA, except that the volume of FA is 700 μL.
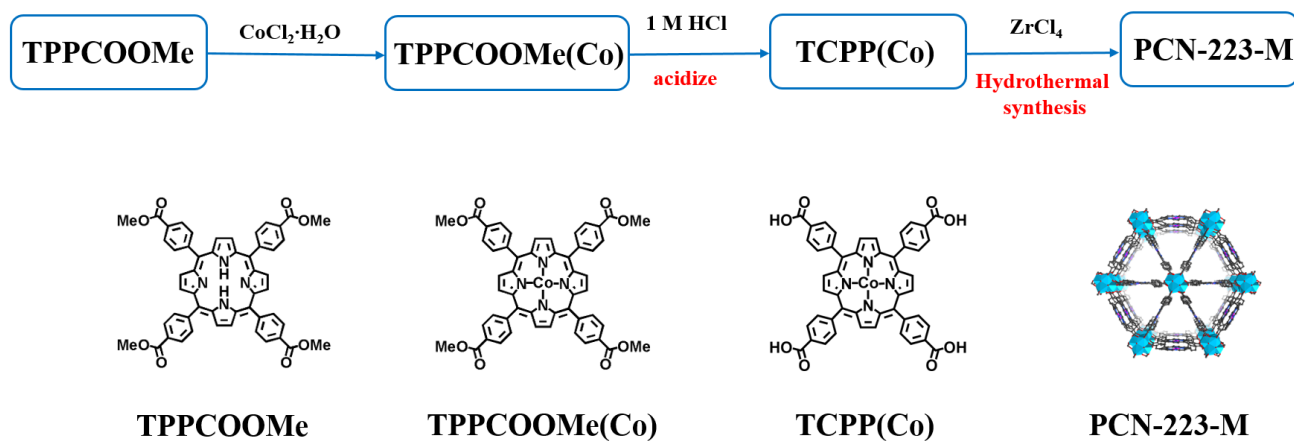
Scheme S1. The synthesized processes of ligands and PCN-223-AA.

Section S3. Electrochemical Measurements

Preparation of working electrode. A mixed solution including 100 μL of ethanol and 10 μL of Nafion D-521 dispersion (5 wt%), in which catalyst (0.5 mg) was dispersed to form a homogeneous ink after 1 h of ultrasonication. Next, 110 μL of the catalyst ink was spread onto a carbon paper surface (1×1 cm^2) using a micropipette and then dried in 100 ^{o}C oven overnight. The loading of catalyst was 0.5 mg/cm^2.

Electrochemical testing. All the data of electrochemical testing was collected from electrochemical workstation (CHI 660E, Shanghai CH Instruments Co., China), operating in a H-type cell equipped with three-electrode configuration consisting of working electrode (catalyst electrode), auxiliary electrode (platinum sheet), and reference electrode (Ag/AgCl). The cathode and anode compartments were separated by a Nafion 117 proton exchange membrane. The electrolyte (0.5 M KHCO$_3$) was bubbled with N$_2$ or CO$_2$ for more than 30 min to form N$_2$ or CO$_2$-saturated solution. The LSV and CV measurement was accomplished in the potential range of 0.5 to -1.8 V vs. Ag/AgCl at a scan rate of 10 mV/s in gas-saturated electrolyte. The experiment of CO$_2$ electroreduction was conducted with continuous CO$_2$ flow (13.4 mL/min) in CO$_2$-saturated electrolyte at room temperature.

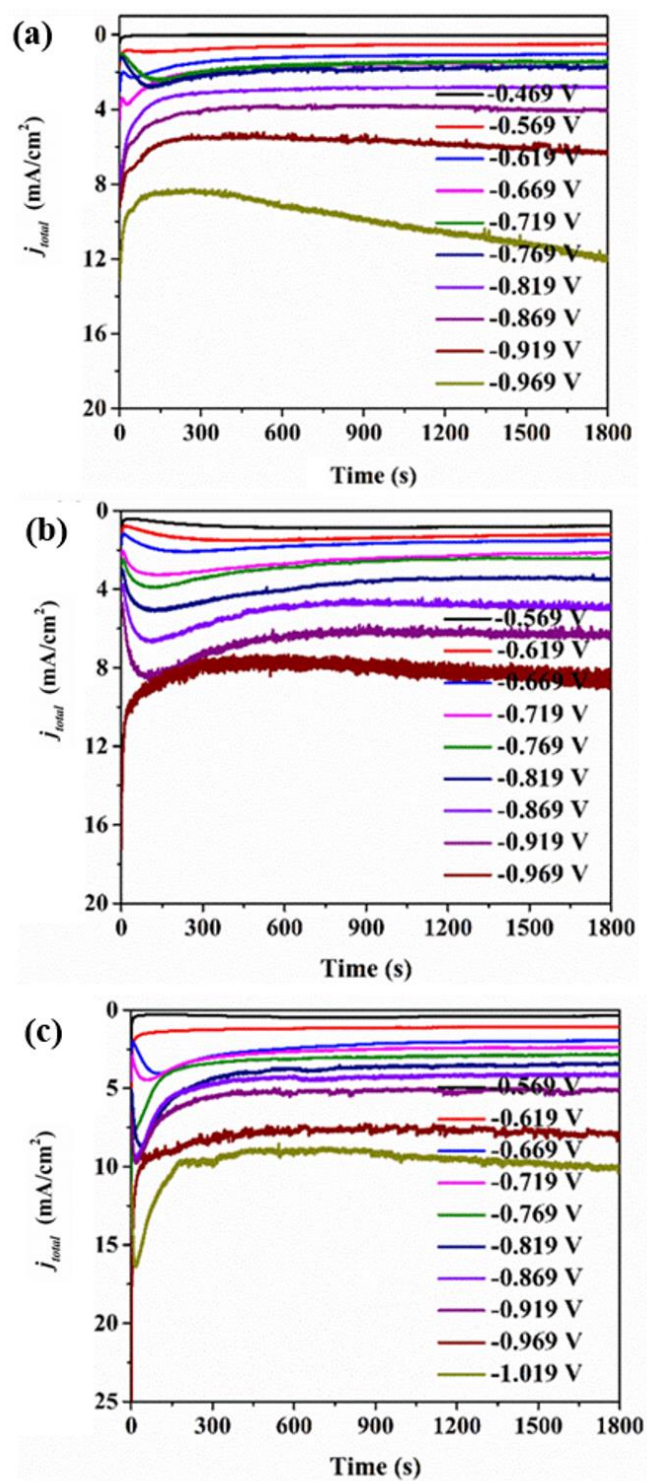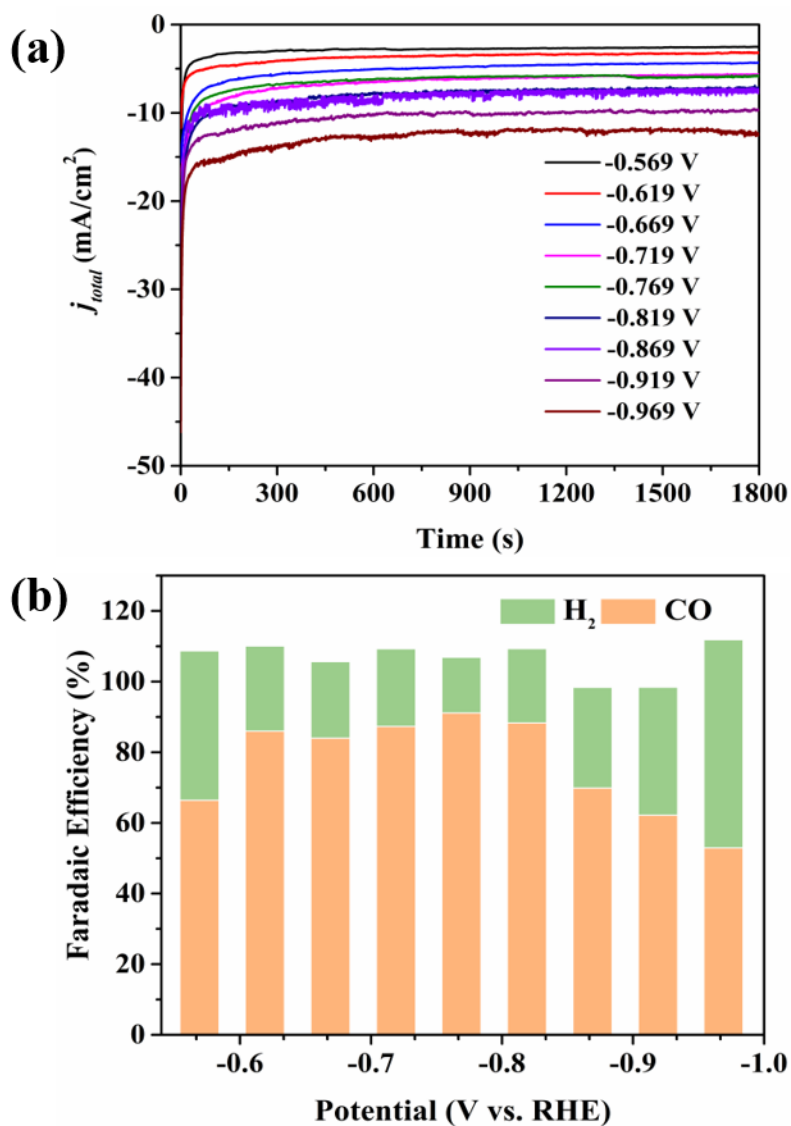# Section S4. Electrocatalytic Performance

**Figure S1. Total current density of three samples.** (a) PCN-223-BA, (b) PCN-223-FA, (c) PCN-223-AA.

Figure S2. Catalytic performance of PCN-223-AA-1. (a) Total current density. (b) Faradaic efficiency at different potential. The maximum FE_{CO} was 91.2%, and catalytic performance of PCN-223-AA-1 with 900 µL acetic acid was similar to PCN-223-AA with 600 µL acetic acid.
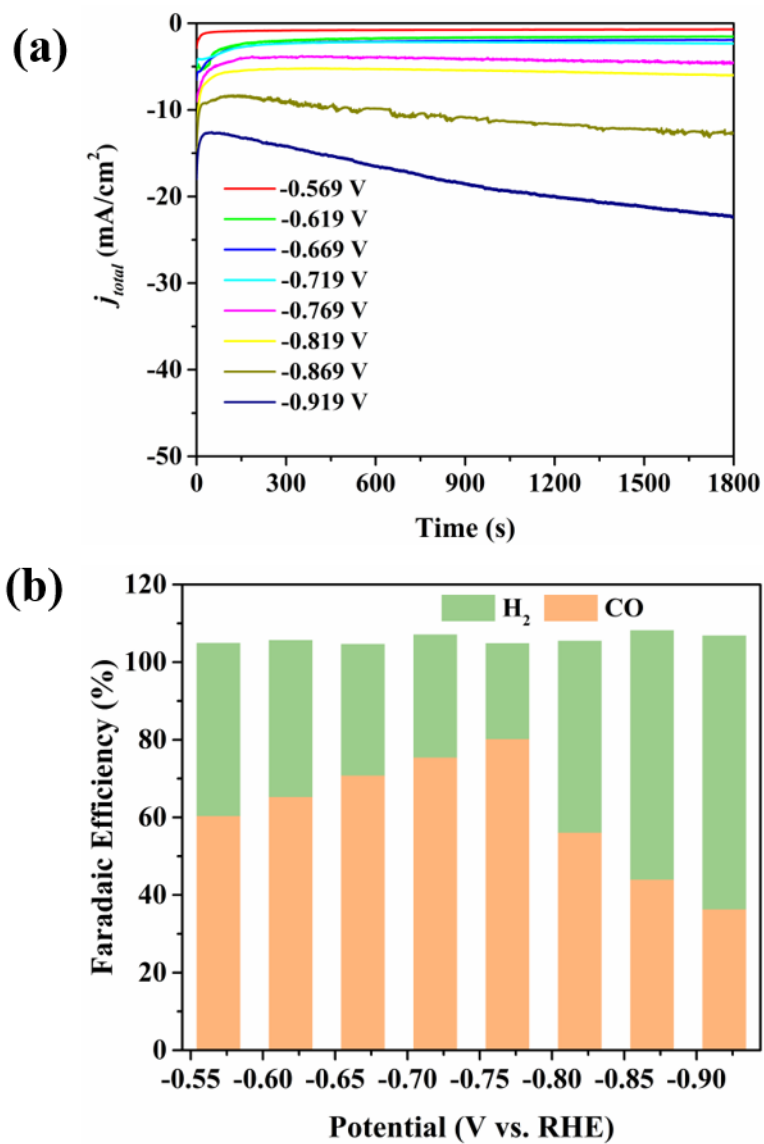
Figure S3. Catalytic performance of PCN-223-FA-1. (a) Total current density. (b) Faradaic efficiency at different potential. The maximum FE_{CO} was 80.2%, and catalytic performance of PCN-223-FA-1 with 700 µL was similar to PCN-223-FA with 550 µL formic acid.
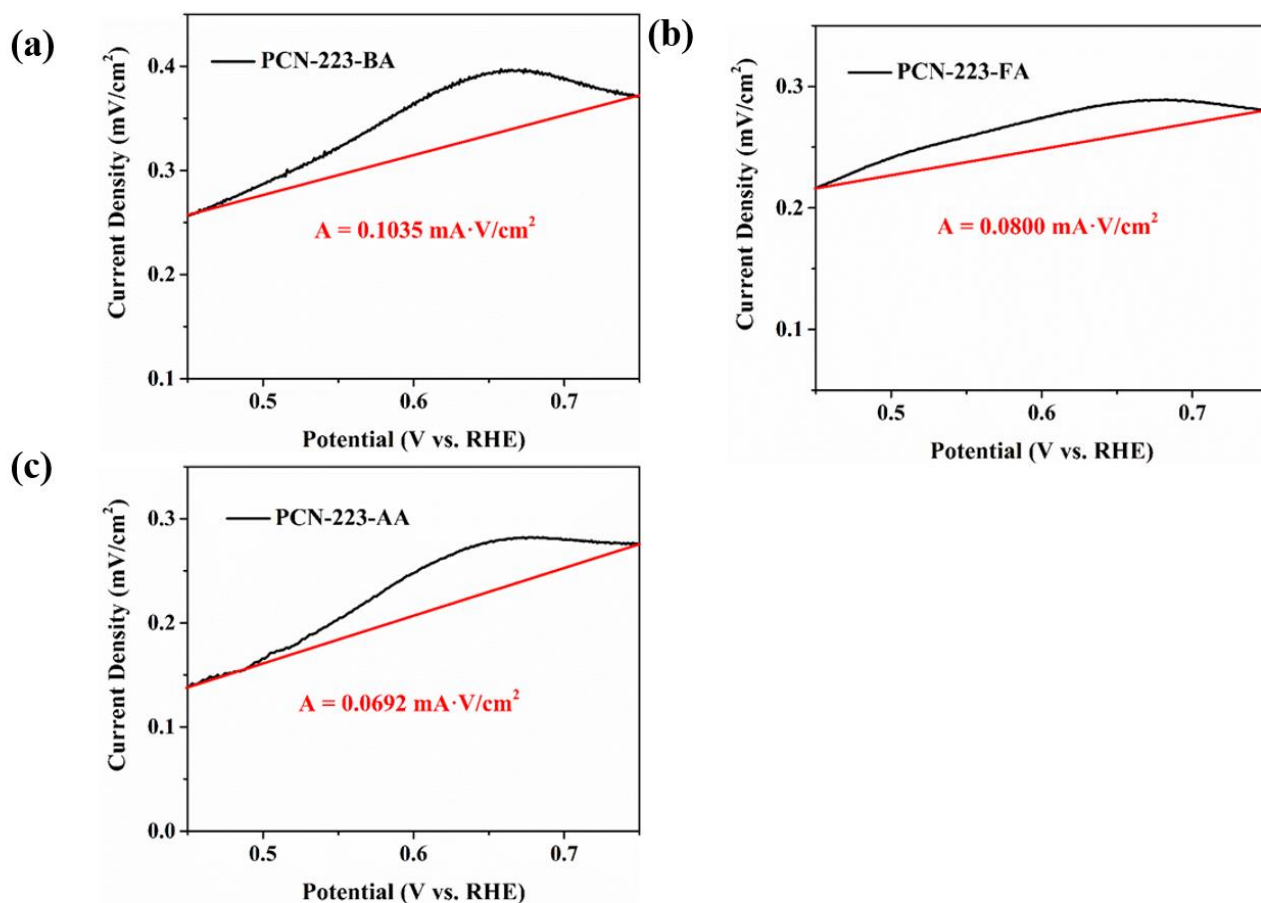
Figure S4. Total charge integrated from the Co^{1+} / Co^{2+} anodic wave of three samples. Using CV value at 10 mV/s, which was in N_2 - saturated 0.5 M $KHCO_3$, we further estimated the number of surface active sites as described in Section S3. The amount of surface active Co.
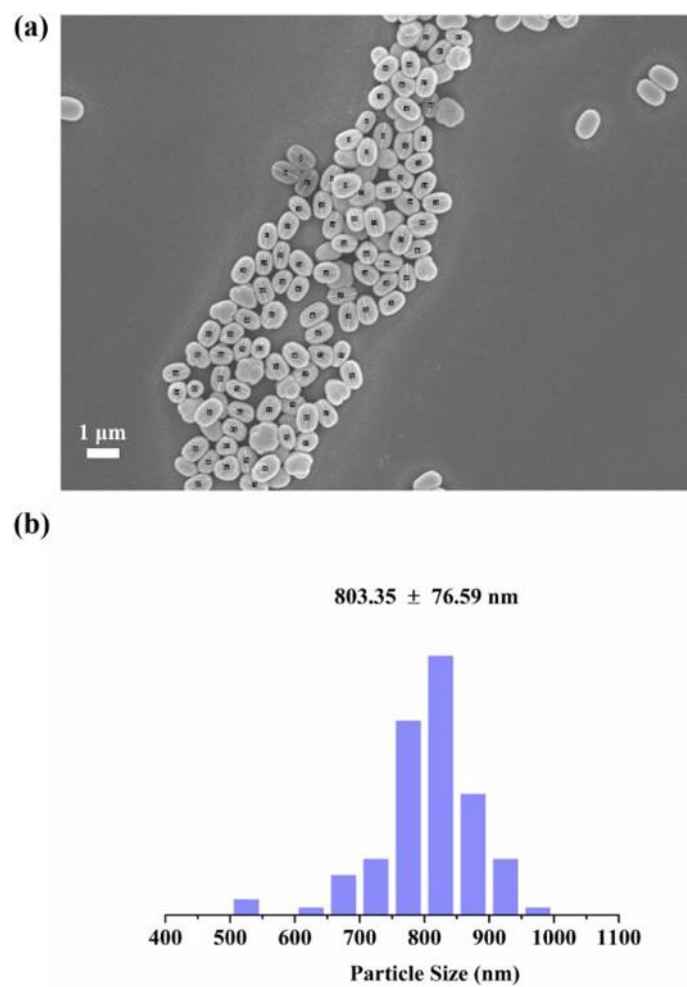
(a) PCN-223-BA (Co) = [0.1035 (mA·V/cm^2)/10 (mV/s)/96485 C/mol = 1.073×10^{-7} mol/cm^2.

(b) PCN-223-FA (Co) = [0.08 (mA·V/cm^2)/10 (mV/s)]/96485 C/mol = 8.291×10^{-8} mol/cm^2.

(c) PCN-223-AA (Co) = [0.0692 (mA·V/cm^2)/10 (mV/s)]/96485 C/mol = 7.172×10^{-8} mol/cm^2.
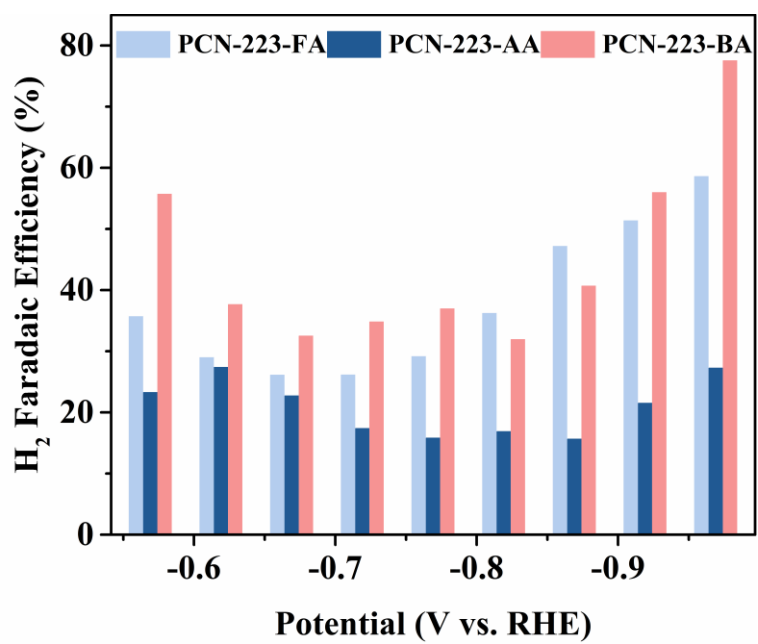
Figure S 5. Faradaic efficiency of PCN-223-FA, PCN-223-AA, and PCN-223-BA.

(a)

1 μm

(b)

803.35 ± 76.59 nm

Particle Size (nm)

Figure S6. (a) SEM image of PCN-223-AA with 600 μL acetic acid. (b) The chart of particle size.

(a)

1 µm

(b)

1 µm

(c)

1362.12 ± 291.08 nm
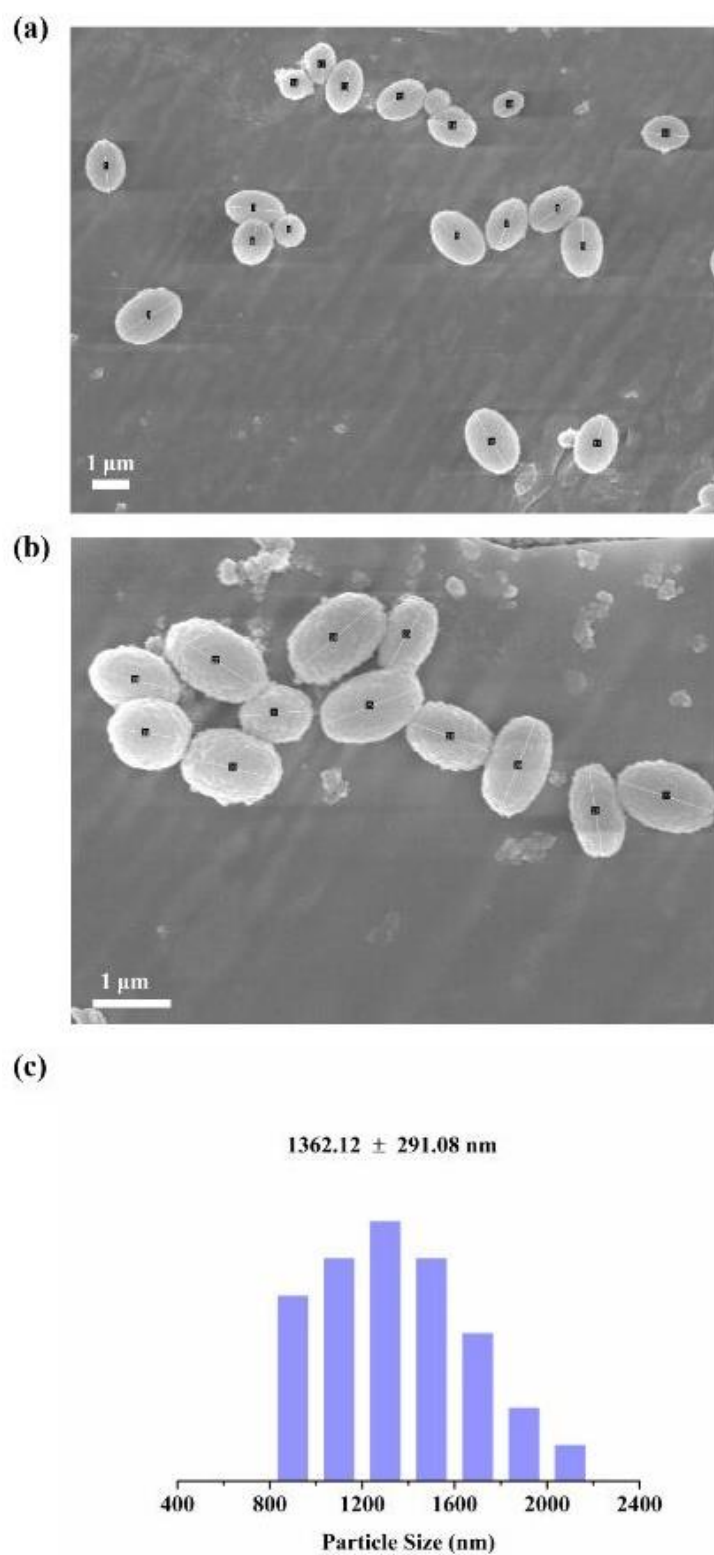
Particle Size (nm)

Figure S7. (a-b) SEM images of PCN-223-AA with 900 µL acetic acid. (b) The chart of particle size.

13
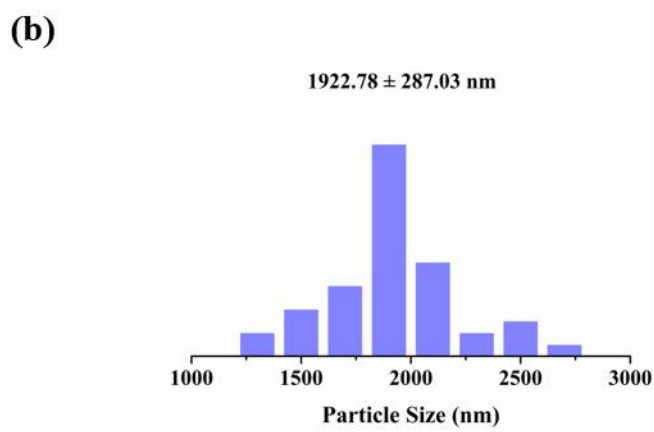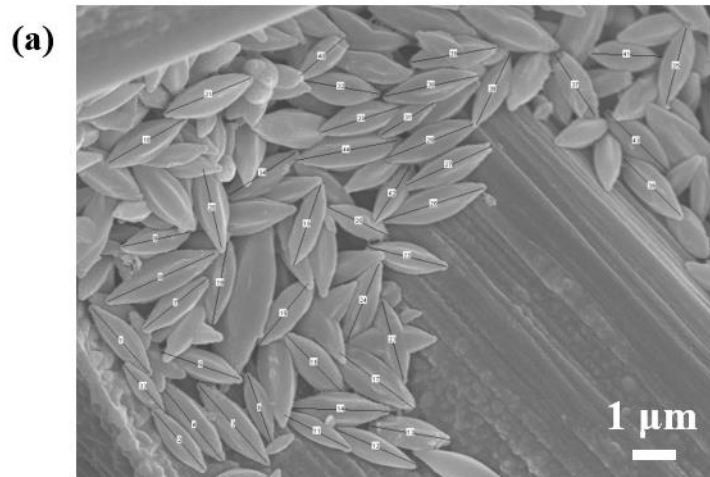
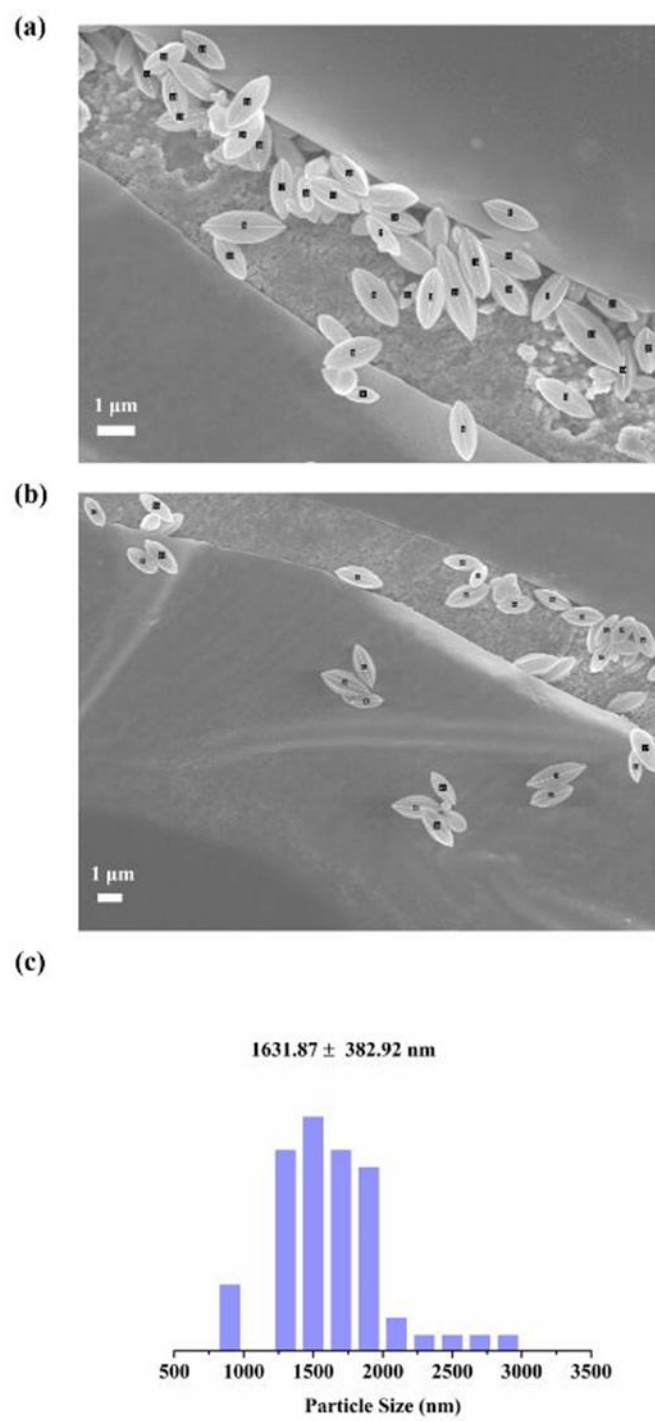**Figure S8.** (a-b) SEM image of PCN-223-FA with 550 μL formic acid. (b) The chart of particle size.

Figure S 9. (a-b) SEM image of PCN-223-FA with 700 μL formic acid. (b) The chart of particle size.
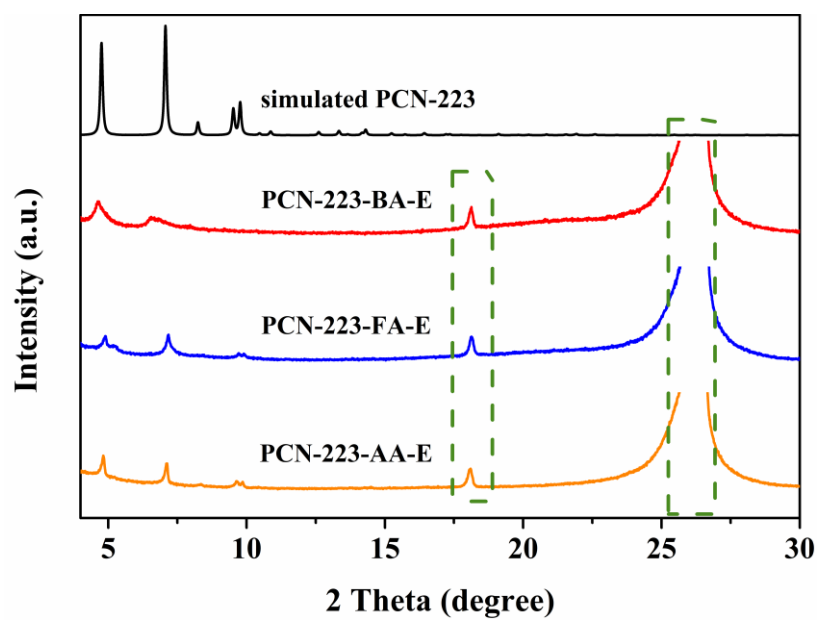
Figure S10. PXRD patterns of PCN-223-M after electrolysis. The peaks of 18.1° and 26.1° are carbon paper.
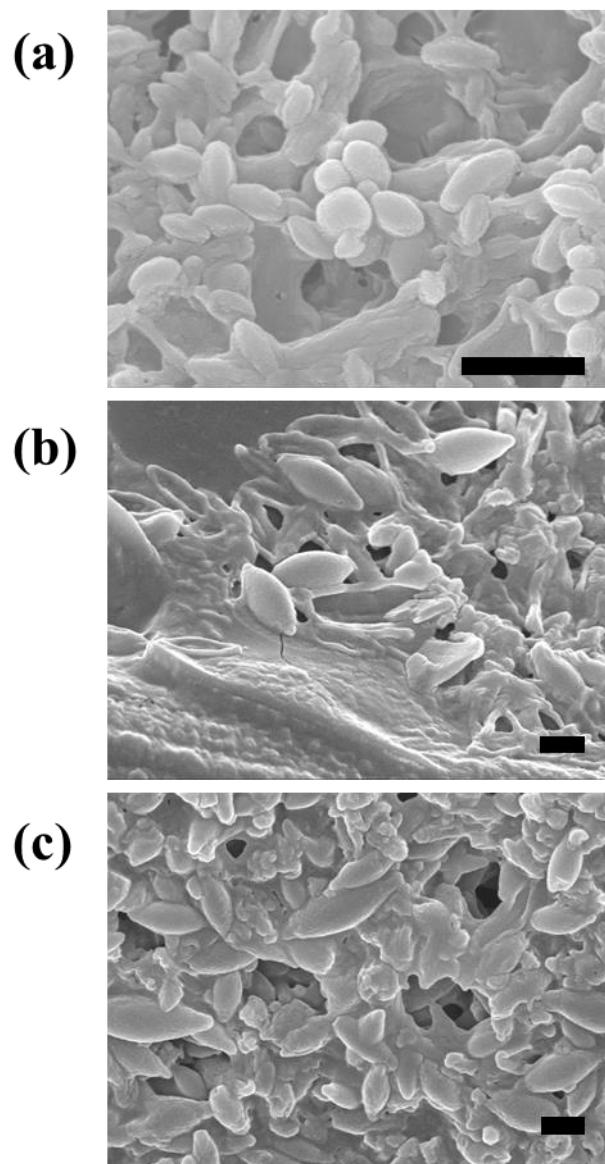
Figure S11. SEM images of PCN-223-M after electrolysis with scale bar of 1 μm.
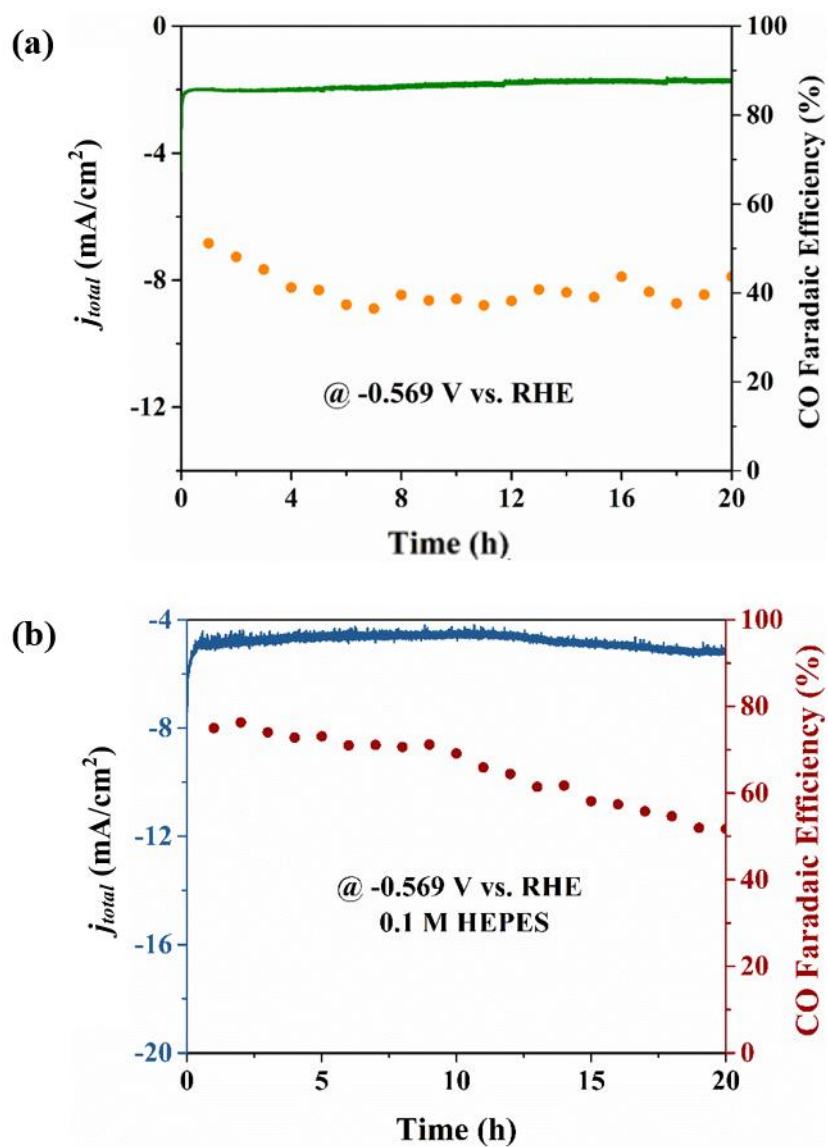
Figure S12. Long-term durability of PCN-223-AA in 0.5 M KHCO₃ solution at -0.569 V vs. RHE. (a) No buffer. (b) 0.1 M HEPES.
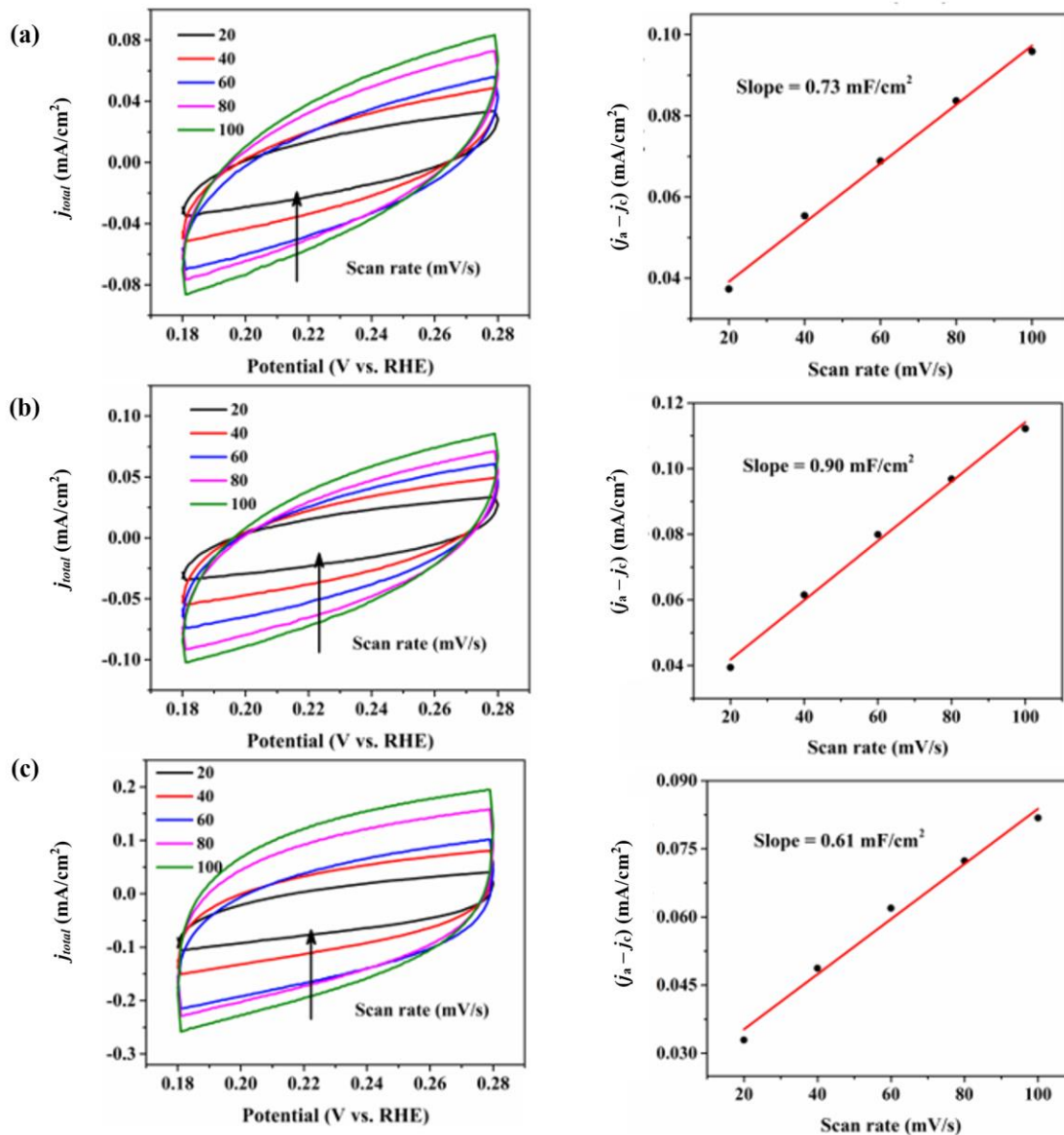
Figure S13. Electrical double layer capacitance of three samples. CV measurements in a non-faradic current region (0.18-0.28 V vs. RHE) at scan rates of 20, 40, 60, 80, and 100 mV/s, (right). Current density ($\Delta j = j_a - j_c$ at 0.23 V vs. RHE) as a function of scan rate, (left). The linear slope represents the double layer capacitance. (a) PCN-223-BA, (b) PCN-223-FA, (c) PCN-223-AA.

Section S5. Calculation Methods of Catalytic Performance[2]

1. Calculation of faradaic efficiency (FE)

Generally, at different working potentials, the faradaic efficiency was calculated as follows:

$$\text{FE}(\%) = \frac{Q_{gas}}{Q_{tot}} \times 100\% = \frac{(\frac{v}{60\,s/min}) \times (\frac{x}{24000\,cm^3/mol}) \times N \times F}{j} \times 100\%$$

Where $v = 13.4\,mL/min$ is the volume flow rate of CO_2, x is the measured concentration of gas product in 1 mL sample loop referring to standard curve, N is the number of transferred electrons for one molecule product, F=96485 C/mol, and j is the recorded current.

2. Calculation of turnover frequency (TOF)

We integrated the anodic wave in CV curve of electrocatalyst at the N_2 atmosphere. Then we calculated the integrated charge of the anodic wave (Q):

$$Q = \frac{S}{v}$$

Where S is the oxidation peak area of the cyclic voltammetry curve and v is the sweep speed.

Assuming a one-electron redox process, then we calculated the amount of surface active Co by:

$$n = \frac{Q}{F}$$

where n is the amount of surface active Co on the working electrode, Q is the integrated charge of the anodic wave, and F=96485 C/mol.

The total amount of Co was calculated as follows:

$$n_{tot} = \frac{m_{cat}}{M_{Co}} \times w_{Co}$$

where n_{tot} is the total molar amount of Co on the working electrode, m_{cat} is the mass of the electrocatalyst loaded on the working electrode, w_{Co} is the weight fraction of Co in the electrocatalyst, and M_{Co} is the atomic weight of Co.

Then, the surface fraction of electrochemically active Co sites was calculated as follows:

$$f = \frac{n}{n_{tot}}$$

Turnover frequency (TOF) is defined as the mole of reduction product generated per electrocatalytic active site per unit time. In reality, only surface Co sites Surface atom acted as catalysts in CO_2RR. So we collected TOF by:

$$\text{TOF} = \frac{j_{tot} \times FE_{product}}{nNF} \times 3600$$

where n is the amount of surface active Co on the working electrode, N is the number of transferred electrons for one molecule product, F=96485 C/mol, and j_{tot} is the recorded current.

Section S6. Calculation Methods of Uncoordinated Zr Sites[3]

Pretreatment of PCN-223-M (PCN-223-BA, PCN-223-FA, and PCN-223-AA). 5.00 mg PCN-223-M was break by 0.1 M K_3PO_4. After centrifugation, the dark red solution was obtained, in which TCPP-Co and modifiers were dissolved. Then, TCPP-Co was quantified by Ultraviolet–visible spectroscopy (UV-Vis) and modifiers quantified by high performance liquid chromatography (HPLC). All measurements were conducted three times.

Quantification of TCPP-Co by UV-Vis. The mole of TCPP-Co ($n_{TCPP-Co}$) was measured at maximum wavelength (427.5 nm) according to standard curve of TCPP-Co (Fig. S5). The results were showed in Table S1.

Table S1. The mole of TCPP-Co ($n_{TCPP-Co}$) for 5.00 mg PCN-223-M.

PCN-223-M	Average absorbance	$n_{TCPP-Co} \times 10^{-6}$ (mol)	$m_{TCPP-Co}$ (mg)
PCN-223-BA	0.80	3.99	3.46
PCN-223-FA	0.82	4.09	3.54
PCN-223-AA	0.88	4.36	3.78

Quantification of modifiers by HPLC. At first, the TCPP-Co was filtrated by acidification with 6 M HCl. Then, the formate and acetate was measured in its acidic form after eluting through a C18 column (250 $\times$ 4.6 mm i.d., 5 μm) with 1 mM sulfuric acid and 8 mM sodium sulfate (pH 2.8) solution as the mobile phase at a flow rate of 1 mL·min^{-1}, the concentration of formate and acetate was evaluated at maximum wavelength (210 nm) according standard curves (Fig. S7). The results were showed in Table S2.

Table S2. The mole of modifier ($n_{modifier}$) for 5.00 mg PCN-223-M.

PCN-223-M	Average peak area	$n_{modifier} \times 10^{-6}$ (mol)	$m_{modifier}$ (mg)
PCN-223-BA	7252258	0.82	0.10
PCN-223-FA	27012	0.65	0.03
PCN-223-AA	36005	0.97	0.06

Quantification mole of Zr cluster [$Zr_6O_4(OH)_4$]. According previous researches, we knew the molecular formula of PCN-223-M was $Zr_6O_4(OH)_4(TCPP-Co)_x(M)_y(H_2O/OH)_z$. Therefore, the mole of $Zr_6O_4(OH)_4$ could be calculated with the flowing equation.

$$n(Zr_6O_4(OH)_4) = \frac{5.00 - m(TCPP\text{-}Co) - m(modifier) - m(H_2O/OH)}{M(Zr_6O_4(OH)_4)}$$

Calculation of uncoordinated Zr sites. The coordination bond between modifier and Zr_6 cluster was strong, but coordination bond between the group of OH/H_2O and Zr_6 cluster was vulnerable to be attacked by proton, which possibly affected CO_2RR. Therefore, we defined the group of OH/H_2O as uncoordinated Zr sites. At first, we hypothesized the mole of H_2O/OH to obtain the $n(Zr_6O_4(OH)_4)$. Then, the total coordination number (N_{total}) of PCN-223-M was calculated with the flowing equation.

$$N_{total} = \frac{4n(TCPP\text{-}Co) + n(modifier) + n(H_2O/OH)}{n(Zr_6O_4(OH)_4)}$$

Herein, the N_{total} should be close to 12. The results were showed in Table S3.

Table S3. The uncoordinated Zr sites of PCN-223-M (per $Zr_6O_4(OH)_4$).

PCN-223-M	Hypothetic n(H2O/OH)	n(TCPP-Co)	n(modifier)	n(Zr6O4(OH)4)	N_{total}	Uncoordinated Zr sites
	5.30			1.89	11.91	2.86
PCN-223-BA	5.40	3.94	0.82	1.88	**12.00**	**2.92**
	5.50			1.88	12.08	2.98
	5.00			1.84	11.94	2.71
PCN-223-FA	5.10	4.09	0.65	1.84	**12.03**	**2.77**
	5.20			1.83	12.11	2.84
	1.20			1.65	11.93	0.73
PCN-223-AA	1.30	4.36	0.97	1.64	**12.02**	**0.79**
	1.40			1.64	12.12	0.86

Conclusion of Calculation details. "PCN-223-M is a repeating network structure that Zr clusters $[Zr_6O_4(OH)_4]$ connected by the square ligands cobalt porphyrin (TCPP-Co) and modifier ((BA, FA, and AA), and uncoordinated site (H_2O/OH^-) (Please see the structure in Scheme 1a). For per Zr cluster, the total coordinate number is 12. And the coordinate number of TCPP-Co, modifiers, and H_2O/OH^- was 4, 1, and 1, respectively. In order to quantify the uncoordinated number (the group of H_2O/OH^-), we explored the combined quantified method of Ultraviolet–visible spectroscopy (UV-Vis) and high performance liquid chromatography (HPLC). Taking PCN-223-AA as an example. Firstly, 5.00 mg PCN-223-AA was accurately weighed, and then destructed by 0.1 M K_3PO_4 to obtain the mixed solution of TCPP-Co and

AA, and sediment of $Zr_3(PO_4)_4$. Secondly, after centrifugal process, the mixed solution was detected by UV-Vis and HPLC. According the standard curves of TCPP-Co and AA, we can calculate that the mole of TCPP-Co was 4.36×10^{-6} mol (3.78 mg) and AA was 9.7×10^{-7} mol (0.06 mg). Thirdly, we hypothesized the mole of H_2O/OH^- as $n(H_2O/OH^-)$. Therefore, the rest was Zr clusters $[Zr_6O_4(OH)_4]$. According to the equation (A) $n(Zr_6O_4(OH)_4) = \frac{5.00 - m(\text{TCPP-Co}) - m(\text{modifier}) - m(H_2O/OH)}{M(Zr_6O_4(OH)_4)}$, we can calculate the mole of Zr cluster. Meanwhile, the total coordination number should be exactly 12, according to the equation (B) $N_{total} = \frac{4n(\text{TCPP-Co}) + n(\text{modifier}) + n(H_2O/OH)}{n(Zr_6O_4(OH)_4)}$. The last, according to simultaneous equations (A) and (B), we can obtain the uncoordinated site number (the group of H_2O/OH^-)."

Section S7. Standard Curve
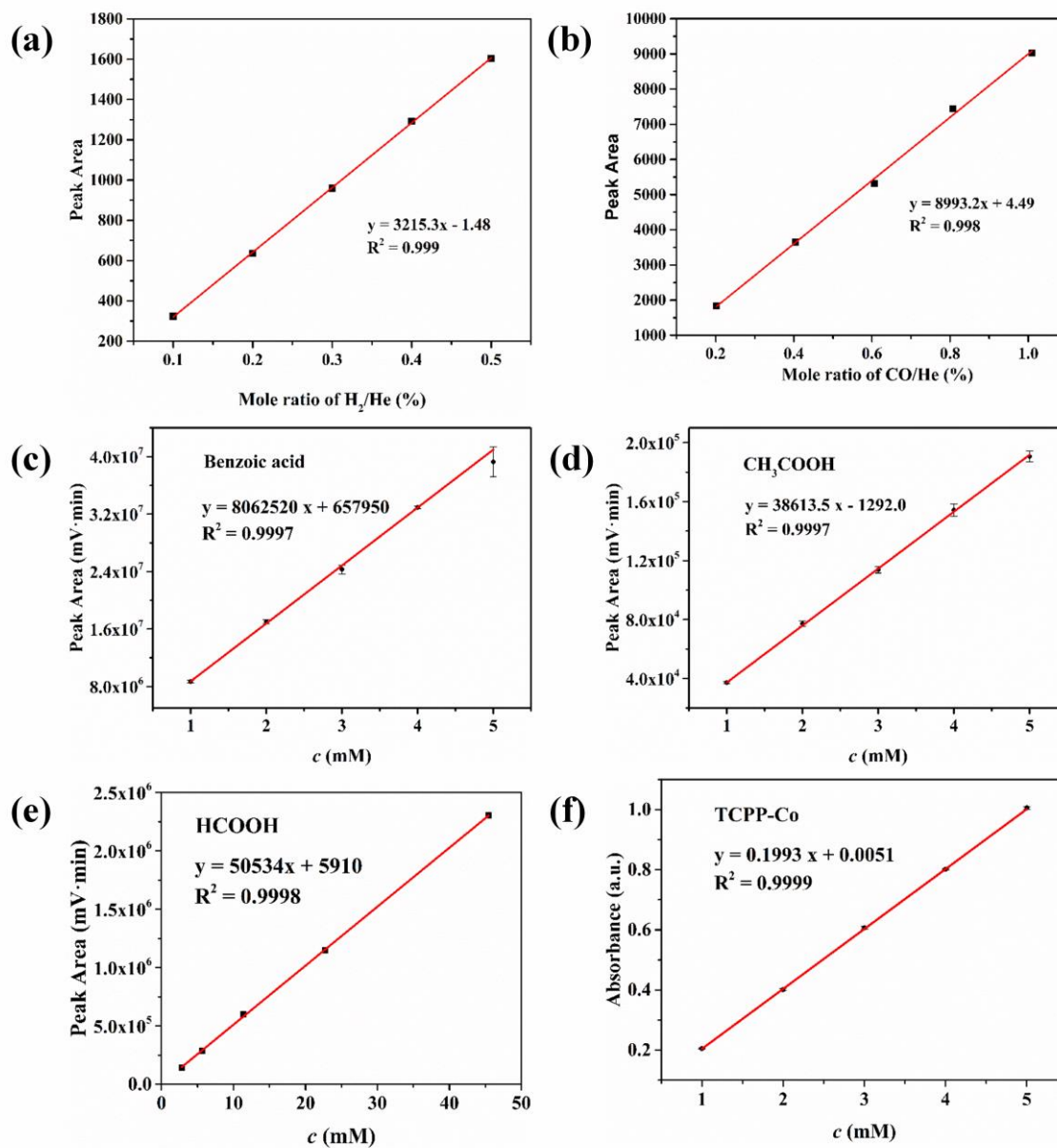
Figure S 14. Standard curve. (a) H_2. (b) CO. (c) Benzoic acid. (d) Acetic acid. (e) Formic acid. (f) TCPP (Co).

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2. J.-X. Wu, S.-Z. Hou, X.-D. Zhang, M. Xu, H.-F. Yang, P.-S. Cao and Z.-Y. Gu, *Chem Sci*, 2019, **10**, 2199-2205.

3. M. Xu, L. Feng, L.-N. Yan, S.-S. Meng, S. Yuan, M.-J. He, H. Liang, X.-Y. Chen, H.-Y. Wei, Z.-Y. Gu and H.-C. Zhou, *Nanoscale*, 2019, **11**, 11270-11278.