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Supporting Information for

# Highly active atomically dispersed CoN<sub>4</sub> fuel cell cathode catalysts derived from surfactant-assisted MOFs: carbon-shell confinement strategy

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# **1. Experimental section**

#### 1.1 Materials and reagent

All chemical reagents including zinc nitrate hexahydrate (99%) (Alfa Aesar), cobalt(II) nitrate hexahydrate (99+%) (ACROS Organics), 2-methylimidazole (99%) (ACROS Organics), sodium dodecyl sulfate (99+%) (Fisher BioReagents), cetyltrimethylammonium bromide (99%) (VWR INTERNATIONAL LLC), Pluronic(R) F-127 (Sigma Andrich), Polyvinylpyrrolidone, M.W. 40,000 (Alfa Aesar), methanol (99.8+%) (Fisher Chemical) were used directly without further purification. The commercial Pt/C catalyst was 20% by weight of ~3 nm Pt nanoparticles on Vulcan XC-72 carbon support purchased from (Cabot Corp.). Nafion was acquired from Sigma-Aldrich.

#### 1.2 Synthesis of Co-N-C@surfactant nanocrystals

Co-ZIF-8@surfactant crystals precursors were synthesized by the same method, but either with different surfactants or without surfactant. In the typical synthesis of Co-ZIF-8@F127 precursor, F127 (1g) was dissolved in methanol (25 ml) to form a clear solution, and then mixed with 25 ml methanolic solution of 2.68 g (9 mmol) of zinc nitrate hexahydrate and 1.16 mg (4 mmol) cobalt(II) nitrate hexahydrate. 50ml of methanol containing 3.2 g (39 mmol) 2-methylimidazole was subsequently injected into the above solution under stirring for 5 minutes at room temperature. After stirring for 30 minutes in 60 °C in a reflux system, pink crystal precipitates were obtained, and they were subsequently collected by centrifugation in fresh ethanol solution, centrifugation was repeated three times. After drying in a vacuum oven at 60 °C for 12 hours, pink solid Co-ZIF-8@F127 particles were obtained as precursor for subsequent processes. To obtain Co-N-C@F127 catalysts, the as-obtained Co-ZIF-8@F127 nanocrystals were directly carbonized at 900 °C for 3 hours under constant nitrogen flow. We applied a quick ramp rate of 30 °C/min. The resulting material was treated with 2 M HCl solution for 5h at 50 °C. The solid material was collected by centrifuge and cleaned with ethanol three times before being dried at 60 °C in a vacuum to obtain the Co-N-C@F127.

#### **1.3 Physical characterization**

The morphology of Co-ZIF-8@surfactant precursors and derived catalysts were studied using scanning electron microscopy (SEM) on a Hitachi SU 70 microscope at a working voltage of 5 kV. The crystal phases present in each sample were identified using X-ray diffraction (XRD) on a Rigaku Ultima IV diffractometer with Cu Ka X-rays. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos AXIS Ultra DLD XPS system equipped with a hemispherical energy analyzer and a monochromatic Al Ka source. The source was operated at 15 keV and 150 W; pass energy was fixed at 40 eV for the high-resolution scans. All samples were prepared as pressed powders supported on a metal bar for the XPS measurements. The N<sub>2</sub> isothermal adsorption/desorption was recorded at 77 K on a Micromeritics TriStar II. Samples were degassed at 150 °C for 5 hours under vacuum prior to nitrogen physisorption measurements. Atomic resolution medium-angle annular dark-field (MAADF) images of dispersed Co over the ZIF framework were captured in a Nion UltraSTEM U100 operated at 60 keV and equipped with a Gatan Enfina electron energy loss spectrometer (EELS) at Oak Ridge National Laboratory. In addition, transmission electron microscopy (TEM), high resolution TEM (HRTEM), high angle annular dark field scanning TEM (HAADF-STEM) were performed on a probe-corrected FEI Titan 80-300 S/TEM at Brookhaven National Laboratory. Co K-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) experiments were carried out at beamline 10BM, Materials Research Collaborative Access Team, Advanced Photon Source (APS), Argonne National Laboratory (ANL). Data reduction, data analysis, and EXAFS fitting were performed with the Athena, Artemis, and IFEFFIT software packages.<sup>1</sup>

#### **1.4 Electrochemical measurements**

Electrochemical measurements were carried out using an electrochemical workstation (CHI760b) coupled with a rotating-ring disc electrode (RRDE, Pine, AFMSRCE 3005) in a three-electrode cell. A graphite rod and a Hg/HgSO<sub>4</sub> ( $K_2SO_4$ -sat.) electrode were used as the counter and reference electrodes, respectively. The reference electrode was calibrated to a reversible hydrogen electrode (RHE) in the same electrolyte before each measurement. A rotating disk electrode with a disk diameter of 5.6 mm covered by a thin film of the catalyst was used as the working electrode. To

prepare the working electrode, 5 mg Co-N-C@surfactant catalysts were ultrasonically dispersed in a 0.51 mL mixture of Isopropyl alcohol and Nafion® (5 wt.%) solution to form an ink. Then the ink was drop-casted on the disk electrode with a designed loading of 0.8 mg cm<sup>-2</sup> and dried at room temperature to yield a thin-film electrode. The catalyst-coated disk working electrode was subjected to cyclic voltammetry (CV) in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at a scan rate of 100 mV/s to activate the catalysts. The electrocatalytic activity for ORR was tested by steady-state measurement using staircase potential control with a step of 0.05 V at intervals of 30 s from 1.0 to 0 V vs. RHE in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at 25°C and a rotation rate of 900 rpm. Fourelectron selectivity during the ORR was determined by measuring the ring current for calculating H<sub>2</sub>O<sub>2</sub> yield. Catalyst stability was studied by potential cycling (0.6 to 1.0 V in O<sub>2</sub> sat. 0.5 M H<sub>2</sub>SO<sub>4</sub>, 50 mV s<sup>-1</sup>) and by holding at constant potential at 0.84 V and 0.7 V during the ORR.

#### 1.5 Fuel cell tests

Catalyst ink was prepared by ultrasonically mixing the catalyst, isopropanol, de-ionized water, and 5% Nafion® suspension (Ion Power). The inks were applied to a GDL by a manual doctor blade technique until the cathode catalyst loading of  $\sim 4.0 \text{ mg cm}^{-2}$  was reached. A commercial Ptcatalyzed gas diffusion electrode (GDE, 0.3 mgPt cm-2, Fuelcelletc) was used at the anode. The cathode and anode are hot-pressed (500 psi) onto a Nafion® 212 membrane at 125°C for 5 minutes. The geometric area of the membrane electrode assembly (MEA) was 5.0 cm<sup>2</sup>. Fuel cell testing was carried out in a single-cell fuel cell (Scribner) with single serpentine flow channels. Pure hydrogen and air/oxygen, humidified at 80 °C, were supplied to the anode and cathode at a flow rate of 200 sccm. Fuel cell polarization plots were recorded using a commercial fuel cell test stations (Scribner) in a voltage control mode. The Fe-N-C catalyst was obtained in our group<sup>2</sup>, and we tested it performance using the protocol as reference. same а

# 2. Characterizations and discussion

### 2.1 Summary of previously reported Co-based-nitrogen-carbon catalysts

Name	Precursors	Carbon supports	Additional nitrogen sources	Pyrolysis temperature (°C)	Half-wave potential	Electrolyte	Stability	Fuel cell performance	Ref.
CoHMTA/ C	cobalt chloride	Acetyle ne black	hexamethyl enetetramin e	600	0.72 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	3
Py-Co- Corrin/C	Vitamin B <sub>12</sub>	carbon black	/	700	0.58 V	0.1 M HClO <sub>4</sub>	/	/	4
Py-Co- Porphyrin/C	CoTMPP (cobalt (II) tetramethoxyphe nylporphyrin)	carbon black	/	700	0.75 V	0.1 M HClO <sub>4</sub>	/	/	4
Py-Co- corrole/C	cobalt(III) (triphenylphosp hine)(5,10,15- triphenylcorrolat o)	carbon black	/	700	0.78 V	0.1 M HClO <sub>4</sub>	/	/	4
Py-B <sub>12</sub> -M/C	vitamin B <sub>12</sub>	Vulcan XC-72R	cyanocobal amin, melamine	700	0.8 V	0.1 M HClO <sub>4</sub>		0.26 W cm <sup>-</sup> <sup>2,</sup> H <sub>2</sub> -O <sub>2</sub> , 6.0 mg/cm <sup>2</sup>	5
Co/N/C	vitamin B <sub>12</sub>	carbon quantum dots	/	700	0.42 V	0.1 M HClO <sub>4</sub>	14% loss for 5h	./	6
(CoePPyeT sOH/C)PeA eP	$Co(Ac)_2 4H_2O$	BP2000 carbon powder	pyrrole	800	0.7 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	7
CoDETA/C	CoCl <sub>2</sub> 6H <sub>2</sub> O	Black	diethylenet	800	0.72 V vs	0.5 M	/	/	8

Table S1. Prepare precursors, pyrolysis conditions, ORR performance and PEM fuel cell performance

		Pearl 2000	riamine		SHE	$H_2SO_4$			
Co/N/C	Co- phthalocyanine	active carbon , formald ehyde	urea	800	0.4 V	0.1 M HClO <sub>4</sub>	/	/	9
CoCl <sub>2</sub> -PPy- TsOH/C	cobalt chloride	BP2000 carbon	pyrrole	800	0.68 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	10
Co(NO <sub>3</sub> ) <sub>2</sub> - PPy- TsOH/C	cobalt nitrate	BP2000 carbon	pyrrole	800	0.63 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	10
Co(OH <sub>2</sub> ) <sub>2</sub> - PPy- TsOH/C	cobalt oxalate	BP2000 carbon	pyrrole	800	0.66 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	10
Co(OAc) <sub>2</sub> - PPy- TsOH/C	cobalt acetate	BP2000 carbon	pyrrole	800	0.7 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	10
CoDETA/B P-800	CoCl <sub>2</sub> 6H <sub>2</sub> O	Black Pearl 2000	diethylenet riamine	800	0.59 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	11
CoDETA/B P-H <sub>2</sub> O <sub>2</sub>	CoCl <sub>2</sub> 6H <sub>2</sub> O	Black Pearl 2000	diethylenet riamine	800	0.64 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	11
CoDETA/B P-KOH	CoCl <sub>2</sub> 6H <sub>2</sub> O	Black Pearl 2000	diethylenet riamine	800	0.64 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	11
CoNC	Co(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O	carbon quantum dots	melamine	800	0.63 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	13% loss after 12000s	/	12
CoDETA/C	CoCl <sub>2</sub>	Black	diethylenet	800	0.68 V	0.5 M	/	/	13

-Ar		Pearls 2000	riamine			$H_2SO_4$			
CoDETA/C -N <sub>2</sub>	CoCl <sub>2</sub>	Black Pearls 2000	diethylenet riamine	800	0.66 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	13
CoDETA/C -CO <sub>2</sub>	CoCl <sub>2</sub>	Black Pearls 2000	diethylenet riamine	800	0.62 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	13
Co-PPy-C	Co(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O	Ketjenbl ack EC 300J	pyrrole	900	0.65 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	0.28 W cm <sup>-</sup> <sup>2</sup> , 2.0 bar H <sub>2</sub> /2.0 bar O <sub>2</sub>	14
Co-PPy-C	Co(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O	Ketjenbl ack EC 300J	pyrrole	900	0.6 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	0.16 W cm <sup>-</sup> <sup>2,</sup> 2.0 bar H <sub>2</sub> /2.0 bar O <sub>2</sub>	14
Co/TETA/C	cobalt (II) chloride hydrate	BP2000	Triethylene tetraamine	1000	0.4 V	0.1 M HClO <sub>4</sub>	/	/	15
Co-CNM	Co <sub>3</sub> O <sub>4</sub>	nitrogen doped multi- walled carbon nanotub es	melamine	800	0.75 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	20mv loss after 10k cycles	0.023 W cm <sup>-2</sup>	16
PANI-Co- CNT+CA	CoCl <sub>2</sub>	CNTs	aniline	/	0.62 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	24% loss for 1500 cycles	/	17
Co-N-GA	Co(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O	graphen e oxide	polyaniline	900	0.73 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	20mv shift after 5000	/	18

							cycles		
Amido-cob alt(III)	cobalt(II) chloride	graphen e	amido- macrocycli c ligand	/	0.12 V	pH=2	/	/	19
Co-Zn- ZIF/GO- 800	Co(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O, Zn(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O	Graphen e oxide (GO), 2- methyli midazol e	2- methylimid azole	800	0.7 V	0.1 M HClO <sub>4</sub>	14% loss for 3h	/	20
CoSe <sub>2</sub> /N- carbon	dicobalt octacarbonyl Co <sub>2</sub> (CO) <sub>8</sub>	nitrogen -doped carbon	nitrogen- doped carbon	400	0.711 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	67mv shift after 1000 cycles	/	21
Co <sub>0.5</sub> Mo <sub>0.5</sub> N <sub>y</sub> /NCNCs	Co(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O, (NH <sub>4</sub> )6Mo <sub>7</sub> O <sub>24</sub> 4H <sub>2</sub> O	N-doped carbon nanocag e	NH <sub>3</sub>	700	0.58 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	16% loss after 100h	/	22
Co(ATZC)	Cobalt meso- tetra-(4- carboxyphenyl)- porphyrin (CoTCPP)	mesopor ous carbon	3-amino- 1,2,4- triazole-5- carboxylic acid	700	0.52 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	23
Co(bis-Me- Im)	Cobalt meso- tetra-(4- carboxyphenyl)- porphyrin (CoTCPP)	mesopor ous carbon	2,20- bis(4,5- dimethylim idazole)	700	0.58 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	23
Co(CO <sub>2</sub> Pz)	Cobalt meso- tetra-(4- carboxyphenyl)- porphyrin	mesopor ous carbon	2- pyrazinecar boxylic acid	700	0.63 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	23

	(CoTCPP)								
Co(phen)	Cobalt meso- tetra-(4- carboxyphenyl)- porphyrin (CoTCPP)	mesopor ous carbon	phenanthro line	700	0.7 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	23
Co <sub>10</sub> – NMCV	Co(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O	mesopor ous carbon vesicles	cyanamide	900	0.5 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	24
Co@NG- acid	cobalt acetate, K <sub>3</sub> [Co(CN) <sub>6</sub> ]	/	/	600	0.63 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	25
C–N–Co	Vitamin B <sub>12</sub>	/	/	700	0.79 V	0.1 M HClO <sub>4</sub>	9mv shift after 10k cycles	/	26
Co-CA-N	cobalt salt	formald ehyde	melamine	700	0.64 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	27
Co(mIm) <sub>2</sub> -P	Co(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O	2- methyl- 1H- imidazol e	NH <sub>3</sub>	750	0.7 V	0.1 M HClO <sub>4</sub>	/	1.6 mg cm <sup>-2</sup> , 0,25 W cm <sup>-2</sup>	28
MDCs	$Co(Ac)_2 4H_2O$	2- methyli midazol e	2- methylimid azole	750	0.7 V	0.1 M HClO <sub>4</sub>	58% loss after 15000s	/	29
Co-NCX	Co(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O	resorcin ol(R)- formald ehyde (F) resin	NH <sub>3</sub>	800	0.69 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	30

Co-OMPC	5,10,15,20- tetrakis(4- methoxyphenyl) -21H, 23H-porphine cobalt(II) (CoTMPP)	/	/	800	0.8 V	0.1 M HClO <sub>4</sub>	/	/	31
CoSe <sub>2</sub> /N- carbon	Co(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O	Formald ehyde	ethylenedia mine	800	0.667 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	21
N/S-Co- HPC	CoSO <sub>4</sub> H <sub>2</sub> O	polyquat ernium- 2	polyquater nium-2	800	/	/	/	/	32
Co <sub>3</sub> O <sub>4</sub> @Ce N	Co <sub>3</sub> O <sub>4</sub>	sugar	Melamine	800	0.36 V	0.1 M HClO <sub>4</sub>	20 mV loss after 1000 cycles	/	33
ISAS- Co/HNCS	Co(OAc) <sub>2</sub> 4H <sub>2</sub> O	5, 10, 15, 20- tetra(4- (imidaz ol-1- yl)phen yl)porph yrindine	5, 10, 15, 20-tetra(4- (imidazol- 1- yl)phenyl)p orphyrindin e	800	0.77 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	7 mV loss after 10000 cycles	/	34
Co-MF- 800-AL	cobalt nitrate hexahydrate	formald ehyde	melamine	800	0.65 V	0.1 M HClO4	almost unchan ged up to 1000th cycle of tests	/	35
Co-N-C	Co(II)-	/	/	800	0.73 V	0.5 M	/	/	36

	phthalocyanine					$H_2SO_4$			
Cu-N-C	Cu(II)- phthalocyanine	/	/	800	0.48 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	36
20CZ	cobalt nitrate hexahydrate, zinc nitrate hexahydrate	hexamet hylenete tramine	hexamethyl enetetramin e	800	0.7 V	0.1 M HClO <sub>4</sub>	/	/	37
Co–N–C	Co(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O	polyacry lonitrile	polyacrylo nitrile	800	0.4 V	0.1 M HClO <sub>4</sub>	/	/	38
ZIF-C	Co(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O	2- Methyli midazol e	2- Methylimid azole	800	0.65 V	1 M HClO <sub>4</sub>	/	/	39
CO-600- 800	cobalt acetate	melamin e	melamine	800	0.7 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	40
Co/N/C	cobalt(II) phthalocyanine	olyacryl onitrile	olyacryloni trile	900	0.5 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	41
Co–Nx–C	cobalt (II) acetate	1,10- phenant hroline	1,10- phenanthro line	900	0.71 V	0.1 M HClO <sub>4</sub>	/	/	42
Co–N/CNF s	Co(Ac) <sub>2</sub>	polyacry lonitrile	4- dimethyla minopyridi ne	900	0.7 V	0.1 M HClO <sub>4</sub>	1mv loss after 10k cycles	0.016 W cm <sup>-2</sup>	43
Co-N-C	Co(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O, Zn(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O	2- methyli midazol e	2- methylimid azole	900	0.76 V	0.1 M HClO <sub>4</sub>	7mv loss after 5000 cycles	/	44
ZIF-67-900	$Co(Ac)_2 4H_2O$	2- methyli midazol	2- methylimid azole	900	0.75 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	45

		e							
ZIF-8-900	Zn(OAc) <sub>2</sub> 2H <sub>2</sub> O	2- methyli midazol e	2- methylimid azole	900	0.58 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	45
Co-NC-900	CoCl <sub>2</sub>	montmo rillonite	aniline	900	0.5 V	0.1 M HClO <sub>4</sub>	30mv loss after 6000 cycles	/	46
Co-N-C	cobalt phthalocyanine	/	/	900	0.5 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	47
Co-N-OMC	CoCl <sub>2</sub>	Furfuryl amine	Furfuryl amine	950	/	/	/	0.018 W/cm <sup>2</sup>	48
CoNPs@N G	CoCl <sub>2</sub>	glucose	dicyandiam ide	1000	0.65 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	4% loss for 30,000s	/	49
Co/Zn(mIm )2- P	Co(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O, Zn(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O	2- methyl- 1H- imidazol e	NH <sub>3</sub>	1000	0.75 V	0.1 M HClO <sub>4</sub>	/	1.6 mg cm <sup>-2</sup> , 0.374 W cm <sup>-2</sup>	28
Co-N-C	Co(II)Ac	Zn(II) zeolitic imidazol ate framew ork	1,10- phenanthro line	1050	0.7 V	0.1 M H <sub>2</sub> SO <sub>4</sub>	/	0.3 W cm-2 H2-O2, 1bar	50
Cr-N-C	Cr(II)Ac	Zn(II) zeolitic imidazol ate framew	1,10- phenanthro line	1050	0.72 V	0.1 M H <sub>2</sub> SO <sub>4</sub>	/	0.42 W cm <sup>-2</sup> H <sub>2</sub> -O <sub>2</sub> , 1bar	50

		ork							
20Co-NC- 1100	cobalt (II) nitrate hexahydrate	2- methyli midazol e	2- methylimid azole	1100	0.8 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	30mV shift after 10k cycles	4.0 mg cm <sup>-2</sup> , H <sub>2</sub> /O <sub>2</sub> : 0.56 W cm <sup>-</sup> <sup>2</sup> ; H <sub>2</sub> /air: 0.28 W cm <sup>-2</sup>	51
Co-N-C	CoCl <sub>2</sub> 6H <sub>2</sub> O	poly(vin ylpyridi ne) resin	poly(vinylp yridine) resin	1200	0.3 V	0.1 M HClO <sub>4</sub>	/	/	52
Co-2D-Co- Ppy	CoCl <sub>2</sub>	sodium modifie d montmo rillonite	pyrrole	/	0.2 V	0.5 M H <sub>2</sub> SO <sub>4</sub>		/	53
PPy/pTS– Co	Co(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O	p- toluenes ulfonate	polypyrrole	/	0.52 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	/	54
Co-N- C@F127	Co(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O, Zn(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O	2- methyli midazol e, F127	2- methylimid azole	900	0.84 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	Around 40 mV loss: 30k cycles; 0.7V and 0.85V hold for 100h	4.0 mg cm <sup>-2</sup> , H <sub>2</sub> /O <sub>2</sub> : 0.87 W cm <sup>-</sup> <sup>2</sup> ; H <sub>2</sub> /air: 0.28 W cm <sup>-2</sup>	This work

#### 2.2 Molecular formula of surfactants



**Figure S1.** Molecular formula of (A) sodium dodecyl sulfate (Mw = 288 g/mol), (B) cetrimonium bromide (Mw = 364 g/mol), (C) Pluronic® F-127 (Mw = 12,600 g/mol), (D) polyvinylpyrrolidone (Mw = 40,000 g/mol).

### 2.3 Morphology and characterization of precursors



Figure S2. SEM images (A and B) of Co-ZIF-8 nanocrystal precursors without surfactants.



Figure S3. SEM images (A and B) of Co-ZIF-8@F127 nanocrystal precursors.



Figure S4. HRTEM and HAADF-STEM images of Co-ZIF-8 precursors without surfactants.



Figure S5. HRTEM and HAADF-STEM images of Co-ZIF-8@F127 precursors.



Figure S6. XRD patterns of Co-ZIF-8@different surfactants precursors.



2.3 Morphology and characterization of carbon catalysts

Figure S7. SEM images of Co-ZIF-8@different surfactants carbon catalysts: (A) Co-N-C, (B) Co-N-C@SDS, (C) Co-N-C@CTAB, (D) Co-N-C@F127 and (E) Co-N-C@PVP.



Figure S8. XRD patterns of various Co-N-C@surfactants carbon catalysts.



Figure S9. Raman spectrum of Co-N-C and Co-N-C@different surfactants carbon catalysts.

	I peak%	D peak%	D" peak%	G peak%	$I_D/I_G$
Co-N-C Surfactant-	7 53	47.60	11.85	33.02	1 44
free	1.55	47.00	11.05	55.02	1.44
Co-N-C@SDS	9.33	46.33	13.24	31.09	1.49
Co-N-C@CTAB	7.93	46.19	15.07	30.82	1.50
Co-N-C@F127	6.45	49.08	12.20	32.28	1.52
Co-N-C@PVP	7.18	49.86	9.24	33.72	1.48

Table S2. Raman fitting results of materials got from different step.

(Fitting result was calculated by peak area;  $I_D/I_G$  was calculated by the intensity at peak center; I peak: sp<sup>2</sup>-C outside graphene; D'' peak: distortion, C5 ring or heteroatoms)



**Figure S10.** N<sub>2</sub> isothermal physisorption at 77K and the pore size distribution for (A-B) different Co-ZIF-8@surfactant precursors and (C-D) resulting Co-N-C catalysts after a thermal treatment at 900 °C.



**Figure S11.** Pore distribution and BET surface areas of (A) Co-ZIF-8 precursors and (B) corresponding Co-N-C catalysts with different surfactants doping.

	V <sub>micro</sub> /cm <sup>3</sup> g <sup>-1</sup>	/%	V <sub>meso</sub> /cm <sup>3</sup> g <sup>-1</sup>	/%	V <sub>macro</sub> /cm <sup>3</sup> g <sup>-1</sup>	/%	V <sub>tot</sub> /cm <sup>3</sup> g <sup>-1</sup>	S <sub>BET</sub> /m <sup>2</sup> g <sup>-1</sup>
Co-ZIF- 8	0.432	100	0	0	0	0	0.432	1068
Co-ZIF- 8 @SDS	0.531	100	0	0	0	0	0.531	1294
Co-ZIF- 8 @CTAB	0.505	96	0	0	0.023	4	0.527	1312
Co-ZIF- 8 @F127	0.562	94	0.009	1	0.030	5	0.601	1366
Co-ZIF- 8 @PVP	0.519	100	0	0	0	0	0.519	1364
Co-N-C	0.123	52	0.083	35	0.029	13	0.235	324
Co-N-C @SDS	0.191	65	0.047	16	0.054	19	0.293	479
Co-N-C @CTAB	0.312	71	0.031	7	0.096	22	0.44	500
Co-N-C @F127	0.443	82	0.037	7	0.059	11	0.54	825
Co-N-C @PVP	0.140	27	0.065	13	0.315	60	0.52	426

**Table S3.** Pore distribution and BET surface areas of Co-ZIF-8 precursors and correspondingCo-N-C catalysts with different surfactants doping

#### 2.4 High-density atomically-dispersed CoN<sub>4</sub> sites

	Pre-edge Energy (eV)	Edge Energy (eV)	S <sub>0</sub> <sup>2</sup> *N	CN	R (Å)	σ <sup>2</sup> (*10 <sup>3</sup> )	Eo (eV)	R- factor (*10 <sup>2</sup> )
								k <sup>1</sup> : 0.03
Co-N-C@F127	7709.4	7718.7	2.4 (Co-N)	3.6±0.6	$1.94{\pm}0.02$	10.8	-9.7	k <sup>2</sup> : 0.1
								k <sup>3</sup> : 0.3
Co(NO <sub>3</sub> ) <sub>2</sub> *6H <sub>2</sub> O	7709.3	7719.3						
								k <sup>1</sup> : 0.3
Co Foil		7708.8	$0.66 (S_0^2)^1$	12	2.49±0.02	5.9	5.8	k <sup>2</sup> : 0.2
								k <sup>3</sup> : 0.2

Table S4. Co K Edge XAS Summary

<sup>1.</sup> The value of  $S_0^2$  determined for the foil was used to estimate the CN of the sample from the fitted value of  $N^*S_0^2$ 

Co content	EELS (wt. %)	XPS (wt. %)	ICP-AES (wt. %)
Co-N-C	0.48	4.2	4.2
Co-N-C@F127	1.38	4.4	6.2

Table S5. Co contents analysis by different methods for Co-N-C and Co-N-C@F127 catalysts

We employed three different techniques (i.e., EELS, XPS, and ICP-AES) to study the Co content in both catalysts with and without the assistance of F127, which is aim to provide a comprehensive understanding. Each technique has its own advantages and limitations. X-ray photoelectron spectroscopy (XPS) is a relatively surface sensitive technique with a detection depth of 10 nm. Due to the highly porous carbon structures of the ZIF-8 derived Co catalysts, the Co content detected using XPS is not very sensitive. That is the reason why the Co content of the catalyst with F127 capping is just slightly higher than that without F127. Different from XPS analysis, electron energy loss spectroscopy (EELS) analysis can focus more on the bulk content of the materials at nanoscale, which is more accurate. After multiple tests at different areas, we clearly identified that the F127 derived Co catalysts contains nearly 3 times higher Co when compare to the one without F127. The average values are listed as below. As for the inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis, it can determine all of Co species in the catalysts, which is the most accurate technique for elemental analysis. The results also indicate that F127-derived catalyst contains nearly 1.5 times higher Co content than that of the one without F127.

			Co-N-C@F12	7		
Image #	С	Ν	0	Со	N : C	Co : N
3	91.31	5.88	2.44	0.36	0.0605	0.05769
6	91.83	5.24	2.75	0.17	0.0540	0.03142
9	91.07	5.18	3.54	0.21	0.0538	0.0390
12	91.36	6.12	2.22	0.3	0.0628	0.0467
15	86.29	8.69	4.6	0.42	0.0915	0.0461
Average	90.37	6.22	3.11	0.29	0.06	0.04
Stdev	2.30	1.44	0.97	0.10	0.02	0.01
			Co-N-C			
Image #	С	Ν	0	Со	N : C	Co : N
3	93.72	3.64	2.45	0.18	0.03739	0.04712
5	94.41	3.39	2.11	0.09	0.03466	0.02586
9	94.6	3.25	2.1	0.05	0.03321	0.01515
12	93.95	3.25	2.28	0.08	0.03779	0.02122
Average	94.17	3.49	2.24	0.10	0.04	0.03
Stdev	0.41	0.21	0.17	0.06	0.00	0.01

Table S6. EELS overall composition

	С	Ν	0	Со	Zn
Co-N-C without surfactant	90.8	6.1	2.1	0.9	0.1
Co-N-C @SDS	84.9	7.4	6.5	1.1	0.1
Co-N-C @CTAB	88.8	4.8	5.5	0.9	0
Co-N-C @F127	87.1	9.1	2.4	1.0	0.4
Co-N-C @PVP	86.2	5.6	7.3	0.9	0.1

 Table S7. Elemental quantification determined by XPS for different materials (at. %)

**Table S8.** Elemental contents determined by XRF for different Co-ZIF-8 precursors and theircorresponding catalysts treated at 900 °C

	C+N+O (wt. %)	Co (wt. %)	Zn (wt. %)
Co-ZIF-8 without surfactant	-	17.2	82.7
Co-ZIF8 @SDS	-	16.1	83.0
Co-ZIF-8 @CTAB	-	16.6	83.0
Co-ZIF-8 @F127	-	16.7	81.6
Co-ZIF-8 @PVP	-	14.9	84.7
Co-N-C without surfactant	99.7	0.23	18 ppm
Co-N-C @SDS	99.2	0.60	105 ppm
Co-N-C @CTAB	99.2	0.70	1.7 ppm
Co-N-C @F127	99.0	0.77	852 ppm
Co-N-C @PVP	99.2	0.66	150 ppm

	C=C	C-N, C-C	С-О	0-C=0	Carbonates	$\pi - \pi^*$
Co-N-C	50.8	20.8	9.7	5.9	4.7	14.0
Co-N-C @SDS	54.2	19.4	9.6	6.7	4.1	6.0
Co-N-C @CTAB	57.4	18.4	8.4	6.1	4.1	5.6
Co-N-C @F127	46.9	23.1	10.8	6.0	6.9	6.3
Co-N-C @PVP	51.0	23.4	9.1	6.2	4.2	6.1

Table S9. The (%) ratio of each contribution in comparison to the total intensity of the C 1s peak

 Table S10. Fitting results for Co 2p XPS spectra for different materials (at. %).

	Co-N <sub>4</sub>	СоО
Co-N-C without surfactant	32.10	32.10
Co-N-C @SDS	35.45	35.45
Co-N-C @CTAB	39.05	39.05
Co-N-C @F127	40.56	40.56
Co-N-C @PVP	37.72	37.72

	Pyridinic-N	Co-N <sub>4</sub>	Graphitic-N	Oxidized pyridinic-N
Co-N-C without surfactant	24.50	12.47	44.53	18.51
Co-N-C @SDS	29.49	15.81	41.22	13.47
Co-N-C @CTAB	26.44	16.78	44.02	12.76
Co-N-C @F127	30.93	17.61	38.29	13.18
Co-N-C @PVP	22.75	16.92	35.96	24.36

Table S11. Fitting results for N 1s XPS spectra for different materials (at. %).

## **3.** Computational section

#### 3.1 Computational method

In this study, we performed spin-polarized DFT<sup>55, 56</sup> calculations using the Vienna ab initio simulation package (VASP) code.<sup>57, 58</sup> Projector augmented wave (PAW) pseudopotential<sup>59, 60</sup> was used to describe the core electrons and a plane wave basis set with a kinetic energy cutoff of 400 eV was used to expand the wave functions. Electronic exchange and correlation was described within the framework of generalized gradient approximation (GGA) of Perdew, Burke and Ernzernhof (PBE) functionals.<sup>61</sup> The Brillouin zone was sampled using a Monkhorst-pack<sup>62</sup>  $4 \times 4 \times 1$  k-point grid for active site CoN<sub>4</sub> and  $4 \times 3 \times 1$  for CoN<sub>2+2</sub>. The atomic positions were optimized until the forces were below 0.02 eV/Å during structural optimization. The transition state of chemical reactions was located using the climbing image nudged elastic band (Cl-NEB) method<sup>63</sup> with a convergence of 0.05 eV/Å for the force components both along and perpendicular to the tangent of the reaction path. Zero-point energy (ZPE) corrections were included in all the energies

reported in this work. ZPE corrections were calculated as  $ZPE = \sum_{i} \frac{1}{2}hv_i$ , where *h* is Planck's constant and  $v_i$  is the frequency of the *i*th vibrational mode of binding molecules.

#### **3.2 Predicted adsorption configuration of ORR species**



Figure S12. Atomistic structures of the optimized configurations of various ORR species, (a) O<sub>2</sub>,
(b) OOH, (c) O, (d) OH, and (e) H<sub>2</sub>O, adsorbed on the CoN<sub>2+2</sub> active sites. In this figure, the gray, blue, yellow, red, and white balls represent C, N, Co, O, and H atoms, respectively. It should be mentioned that the adsorption configurations of ORR species on CoN<sub>4</sub> site are the same as these configurations.

#### 3.3 Predicted adsorption energy of ORR species

**Table S12.** Predicted adsorption energies of various ORR species on the  $CoN_{2+2}$  and  $CoN_4$  active sites of the Co-N-C catalysts. The adsorption energies are calculated as the difference in energy between the adsorption system and the corresponding isolated systems. Hence, negative value of the adsorption energy indicates attractive interaction between the ORR species and ORR active sites.

$E_{ad} (eV)$	$O_2$	ООН	0	OH	H <sub>2</sub> O
CoN <sub>2+2</sub>	- 0.67	- 1.30	- 3.58	- 2.39	- 0.04
CoN <sub>4</sub>	- 0.67	- 1.23	- 3.18	- 2.44	- 0.02

# 4. Electrochemical performance and PEMFC application

### 4.1 ORR activity and stability



**Figure S13**. The comparison of ORR activity between the Co-N-C catalysts and the Pt/C reference determined by using RDE in aqueous electrolytes ( $0.5 \text{ M H}_2\text{SO}_4$  for Co-N-C and  $0.1 \text{ M HClO}_4$  for Pt/C).



**Figure S14.** The ORR activity of Co-N-C catalysts as a function of doped Co contents in ZIF precursor showing a typical "volcano plot". Lower doping yields insufficient density of active  $CoN_4$  sites, while higher doping leads to Co agglomeration and unfavorable carbon structures (i.e., less defect and porosity).



Figure S15. CV curves of the Co-N-C@F127 catalyst during various stability tests.



**Figure S16.** HAADF-STEM images of the best performing Co-N-C@F127 catalysts after 30,000 potential cycles in the range of 0.6-1.0 V, 50 mV s<sup>-1</sup>.



**Figure S17.** HAADF-STEM images of the best performing Co-N-C@F127 catalysts after 100 h chronoamperometry stability test at 0.85 V.



Figure S18. H<sub>2</sub>-O<sub>2</sub> fuel cell polarization plots at 100% RH for various PGM-free catalysts.



Figure S19. H<sub>2</sub>-air fuel cell polarization plots at 100% RH for various PGM-free catalysts.



**Figure S20.** SEM images for the Co-N-C@F127 catalysts within a MEA electrode dispersed with ionomers.



**Figure S21.** (a) Stability test of 100h at 0.7 V in H<sub>2</sub>-air fuel cell, (b)  $H_2-O_2$  and (c)  $H_2$ -air fuel cell polarization plots before and after stability test (BOT: before of the test; EOT: end of the test).

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