

Supplementary Information

Atomically dispersed Co-N-C electrocatalysts synthesized by a low-speed ball milling method for proton exchange membrane fuel cells

*Tao Liu^a, Feng Sun^a, Meihua Huang^{*a}, Lunhui Guan^{*a}*

a. CAS Key Laboratory of Design and Assembly of Functional Nanostructures, and Fujian Provincial Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P.R. China

† Corresponding Author: meihuahuang@fjirsm.ac.cn; guanlh@fjirsm.ac.cn

Experimental section

Chemicals: Zinc oxide (ZnO, A.R. grade), Cobalt chloride hexahydrate (CoCl₂·6H₂O, A.R. grade), 2-methylimidazole (C₄H₆N₂, A.R. grade), and N,N-dimethylformamide (DMF, G.C. grade) were bought from Shanghai Aladdin Biochemical Technology Co., Ltd. Perchloric acid (HClO₄) and Nafion solution (5.0 wt.%) were bought from Sigma-Aldrich. 2-Propanol ((CH₃)₂CHOH, 99+% grade) and Pt/C (20.0 wt.%) were bought from AlfaAesar. All reagents are used directly without further treatment.

Preparation of Co-120 material: The Co-120 precursor was synthesized via method following the high-energy ball milling method, which has been optimized accordingly. In detail, 0.5g ZnO, and 1g 2-methylimidazole were mixed in a Nylon

ball mill can (volume 50 mL). And 3 mL of DMF and 1 mL of 0.504mmol/L (120 mg) cobalt chloride hexahydrate aqueous solution were added to the ball mill can, then the agate beads which accounted for 50% of the can's volume were added rapidly. The ball mill can was then placed in a planetary ball mill and run for 800 minutes at 250 rpm, and the MOF-Co-120 is obtained as seeing in Fig. S8. The slurry product was washed with ethanol for three times, by vacuum filtration and dried at 80°C overnight. The dried precursor was ground in agate mortar and heated to 950°C for 2 h with a heating rate of 3 °C min⁻¹ under N₂ flow protection. The black powder was stirred in 1 mol/L of hydrochloric acid at 60°C for 3 hours, then washed and dried. The dried powder was heated to 950°C for 2 h with a heating rate of 3 °C min⁻¹ under N₂ flow protection. Finally, the obtained powder was denoted as the Co-120 samples. The Co-40&Co-200 was synthesized adding 1 mL of 0.168mmol/L (40mg) & 0.84 mmol/L (200mg) cobalt chloride hexahydrate aqueous solution, and NC was prepared without adding cobalt chloride hexahydrate aqueous solution.

Characterization

The morphologies and structures of the materials were characterized by scanning electron microscopy (SEM) with a HITACHI SU-8010 scanning electron microanalyzer at an accelerating voltage, Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), high-annular dark-field scanning transmission electron microscopy (STEM) and element mapping analysis were taken on FEI Talos F200X electron microscope operating at 200 kV.

X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo ESCALAB 250 spectrometer. X-ray diffraction (XRD) measurements were performed with a Miniflex600 diffractometer using a Cu K α ($\lambda = 1.5405 \text{ \AA}$) radiation source. Raman spectra were taken on a LabRAM HR800 spectrometer with 532 nm wavelength incident laser light. The pore structures of the samples were analyzed by using an Autosorb-iQ2 (Quantachrome Instruments) physical absorber.

Electrochemical measurements

Rotating Disk Electrode tests: All electrocatalytic measurements were performed in a three-electrode cell using a rotating disk electrode (RDE, PINE Research Instrumentation) of 5.0 mm in diameter with an electrochemical workstation (CHI 760E, Shanghai Chenhua, China) in 0.1M HClO₄ electrolyte. A platinum gauze electrode and Ag/AgCl (saturated KCl) electrode were used as the counter and reference electrodes, respectively. All potentials in this study are referenced to reversible hydrogen electrode (RHE), $E_{(\text{RHE})} = E_{(\text{Ag}/\text{AgCl})} + 0.059\text{pH} + 0.197$. The catalyst ink is prepared by dispersing the catalyst (5 mg) in solution (1 mL) containing isopropanol (960 μL) and 5 wt% Nafion solution (40 μL), followed by ultrasonication for 3 hours. Then, a certain volume of catalyst ink was pipetted onto the GC surface to give a 0.8 mg cm⁻² loading for all samples.

The loading of commercial Pt/C (20 wt%) was 20 $\mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$. The perchloric acid electrolyte is fully aerated with oxygen prior to the electrochemical test until oxygen saturation is reached, and the flow of O₂ was maintained on the electrolyte

during the measurement. The cyclic voltammetry (CV) and linear sweep voltammetry (LSV) curves of the catalyst under N₂ saturated computational electrolyte were also measured. The scan rate of LSV was 10 mV s⁻¹ and the rotating speed was varied from 500 to 2500 rpm. The electron-transfer number (n) of Co-120 at different potentials was calculated according to the Koutecky-Levich equation.

$$1/j_d = 1/j_k + 1/B\omega^{1/2} \quad (1)$$

$$B = 0.2nFC_0(D_0)^{2/3}\nu^{-1/6} \quad (2)$$

where j_d and j_k are the kinetic- and diffusion-limited current densities of ORR; B is the theoretical value of the Levich slope B and can be calculated via equation of (2). n is the overall number of electrons transferred during the ORR, F is the Faraday constant, C_0 is the bulk concentration of oxygen, D_0 is the molecular diffusion coefficient of oxygen. ν is the kinematic viscosity of the electrolyte. The coefficient 0.2 is adopted when the rotating speed is expressed in rpm. (In 0.1 M HClO₄, $C_0 = 1.6 \times 10^{-3} \text{ mol L}^{-1}$, $D_0 = 1.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $\nu = 0.01 \text{ cm}^2 \text{ s}^{-1}$)¹. Long-term operation stability of Co-120 were performed at room temperature in oxygen saturated 0.1 M HClO₄ solutions by applying cyclic potential sweeps between 0.6 and 1.0 V versus reversible hydrogen electrode (RHE) at a sweep rate of 100 mV s⁻¹ for 10000 cycles.

Preparation of membrane electrode (MEA): The anode part was Pt/C 40 wt.% (JM) and the cathode part uses the catalyst in this paper. 80 mg of catalyst was ultrasonically dispersed in 4 mL of deionized water, and 36 mL of isopropanol was

added for ultrasonic treatment for 1 h. Then, Nafion5% solution was added for ultrasonic treatment for 1 h to obtain 2 mg mL⁻¹ ink. Prepare the Nafion proton exchange membrane and anode spray paste to be tested. Automatic ultrasonic spraying apparatus was used to operate the anode and cathode respectively. Allow the membrane to cool to room temperature, remove it carefully, place it in a clean place and level it off, and wait for the next test.

Single cell assembly and performance test method

Single cell assembly and performance test method: Single cell tests were conducted with a PEM station (SMART2, WonA-Tech). The catalyst ink was directly sprayed onto a Nafion 211 membrane until the catalyst loading at the cathode reached 3mg cm⁻² for Co-120, Co-40. The geometric active area of the MEA was 5 cm². For the anode side, commercial Pt/C (40 wt.%) was used with a Pt loading of 0.1mg_{Pt} cm⁻². The cell temperature was kept at 80C° and H₂/O₂ with 80% relative humidity were flowed to the anode and cathode. The flow rates of H₂/O₂ were 200 sccm and 500 sccm with 1.5 bar backpressure. The durability in a single cell setup was tested by repeating 10000 CV cycles at 50 mV s⁻¹ between 0.6V and 1.0V with humidified H₂ (200 sccm) at the anode and N₂ (75 sccm) at the cathode.

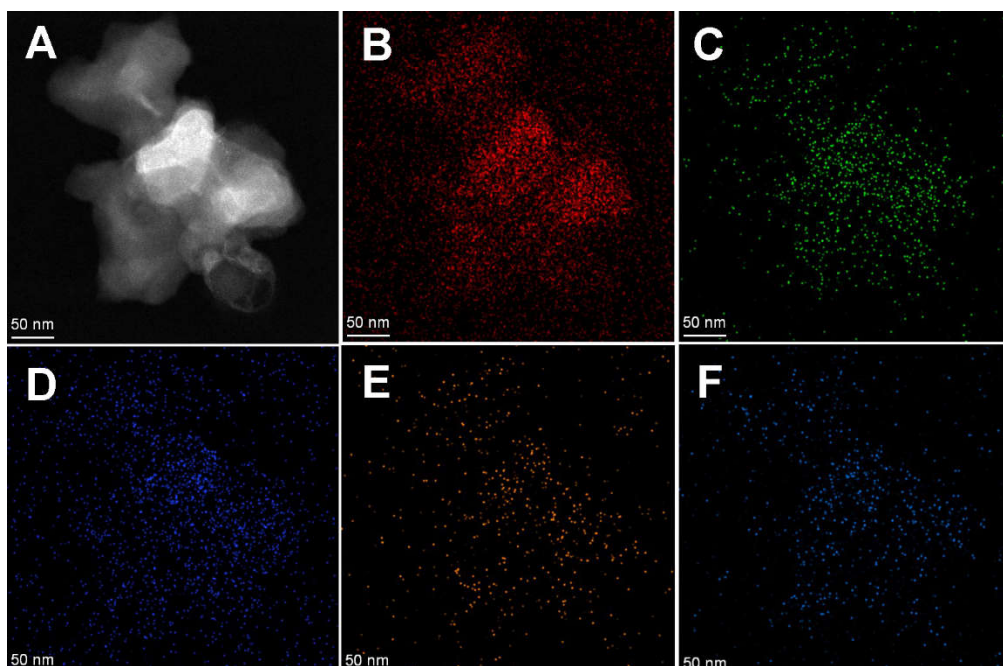


Fig. S1 (A) STEM image of Co-40. (B-F) HAADF-STEM-EDS elemental mappings.

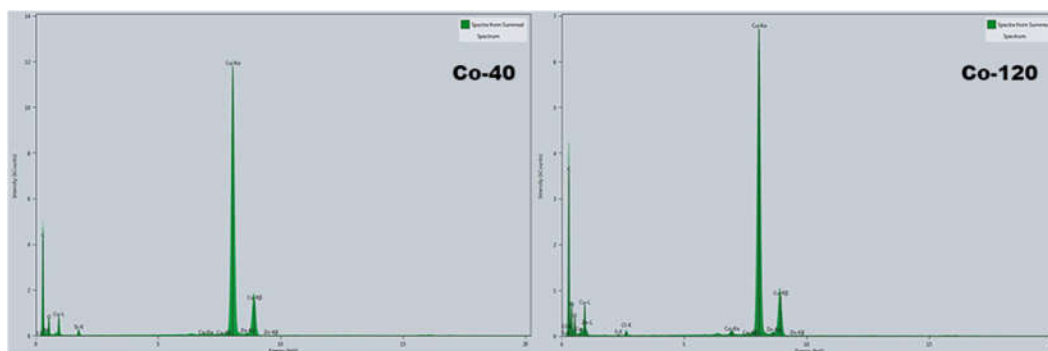


Fig. S2 Spectrum EDS of Co-40 and Co-120.

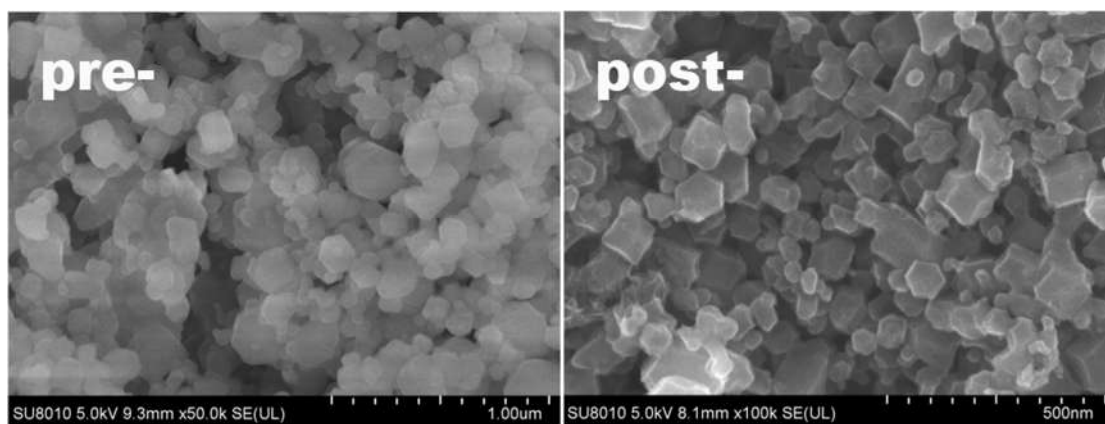


Fig. S3 SEM of Co-120 on a large scale.

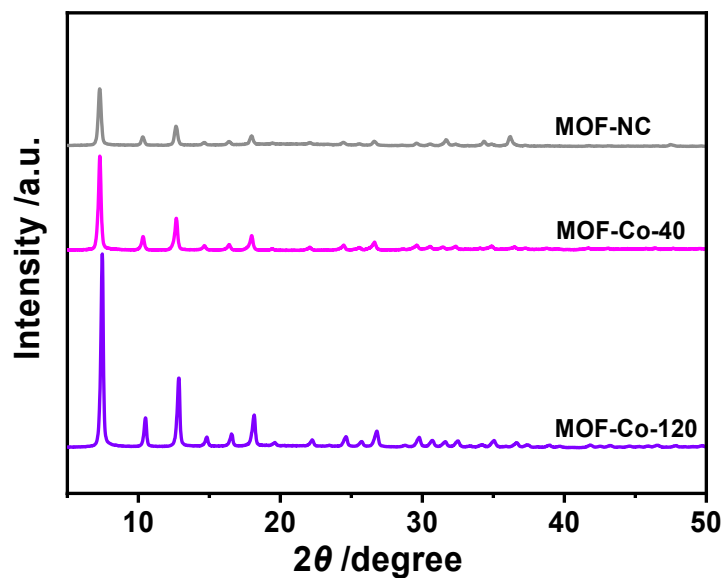


Fig. S4 XRD patterns of the MOF-NC, MOF-CO-40 and MOF-Co-120

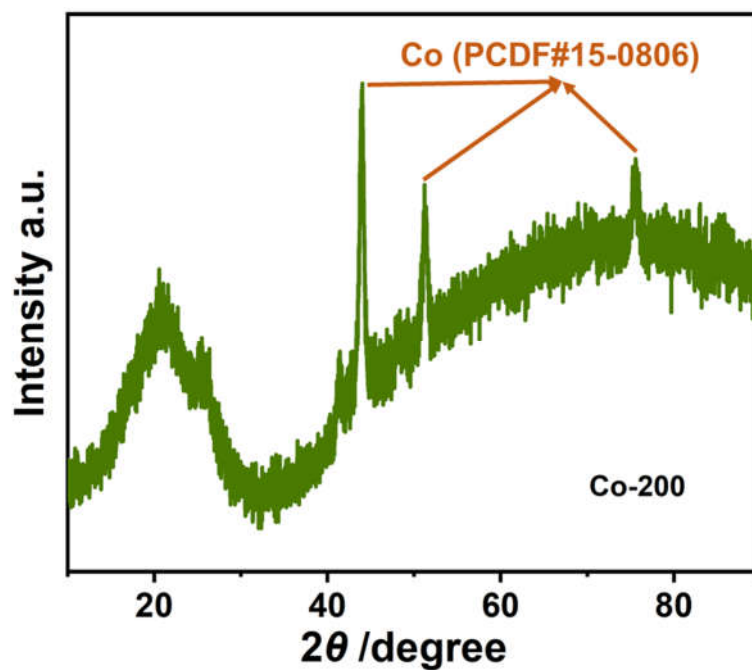


Fig. S5 XRD patterns of the Co-200

Table S1 Pore volume and BET surface areas of Co-40 and Co-120.

Catalysts	Specific surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)
Co-40	700.06	0.421
Co-120	956.9	0.745

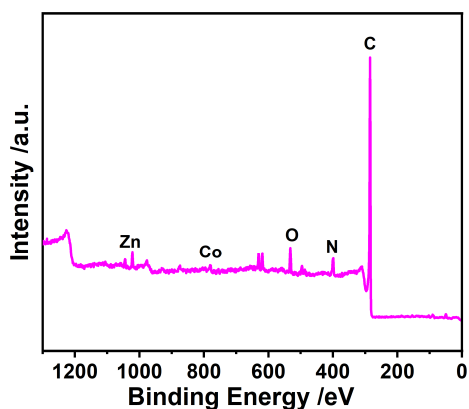


Fig. S6 XPS spectrum of the Co-40.

Table S2 Elemental quantification determined by XPS for different materials (at. %).

	C	N	O	Zn	Co
Co-120	82.23%	7.46%	9.30%	0.47%	0.54%
Co-40	88.41%	6.32%	4.23%	0.59%	0.44%

Table S3 EXAFS fitting parameters at the Co K-edge various samples (S02=0.77)

Sample	Path	C.N.	R (Å)	$\sigma^2 \times 10^3$ (Å ²)	ΔE (eV)	R factor
Co-foil	Co-Co	12*	2.50±0.01	6.2±0.1	7.9±0.2	0.001
Co-40a	Co-N	3.7±2.4	1.92±0.02	11.8±4.3	-8.2±4.2	0.019
Co-40b	Co-N	3.6±0.9	1.99±0.02	11.4±3.6	2.6±2.3	0.012
	Co-O	2.6±0.9	2.27±0.04			
Co-120a	Co-N	9.4±3.9	1.97±0.03	20.3±6.5	-3.6±3.2	0.018
Co-120b	Co-N	3.9±1.8	1.99±0.04	3.1±8.4	3.9±3.5	0.019
	Co-O	1.6±0.4	2.23±0.08			

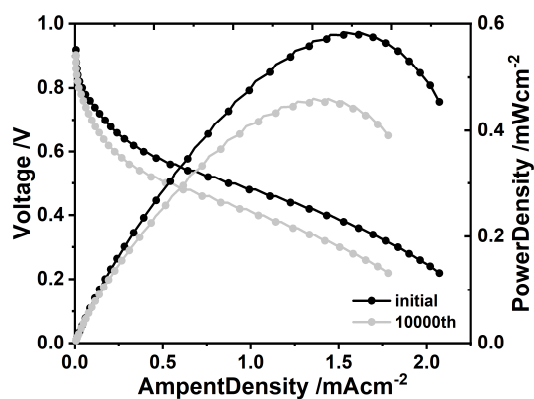


Fig. S7 Polarization and power density plots of PEMFCs in 1.5 bar H₂-O₂ of Pt/C20% 0.1mgPtcm⁻².



Fig. S8 MOF-Co-120

Table S4 Comparison of ORR performance for electrocatalysts in acid

Sample	Electrolyte	E _{1/2} (V)	Year	Reference
PANI-Co-C	0.5 M H ₂ SO ₄	0.75	2011	2
Co/Zn(mlm) ₂ -P	0.1 M HClO ₄	0.76	2016	3
Co-N-C	0.1 M HClO ₄	0.761	2015	4
Co corrole/CNT	0.5 M H ₂ SO ₄	0.78	2019	5
Co-N/CNFs	0.1 M HClO ₄	0.70	2017	6
Co/CNFs (1000)	0.1 M HClO ₄	0.68	2020	7
Fe-N/P-C-700	0.1 M HClO ₄	0.72	2020	8
FeNC-S-MSUFC-2	0.5 M H ₂ SO ₄	0.73	2019	9
p-Fe-NCNF	0.1 M HClO ₄	0.74	2018	10
Co-N-GA	0.5 M H ₂ SO ₄	0.73	2016	11
S-Cu-	0.5 M H ₂ SO ₄	0.74	2020	12

ISA/SNC				
Co-120	0.1 M HClO ₄	0.78	2021	This work

Table S5 Comparison of the proton exchange membrane based fuel cell performance of the present system with literature reports.

Sample	H ₂ -O ₂ maximum power density (mW cm ⁻²)	Year	Reference
PANI-Co-C	350	2011	2
Co/Zn(mlm) ₂ -P	374	2016	3
FeCo-EDA-KJ600R	440	2010	13
FeGNT	200	2015	14
Py-Co-corrole/C	275	2012	15
Fe-NSG	225	2015	16
CoFeNx	460	2008	17
Co ₉ S ₈ /NVC-G	245	2020	18
1.5Fe-ZIF	650	2019	19
Co-120	450	2021	This work

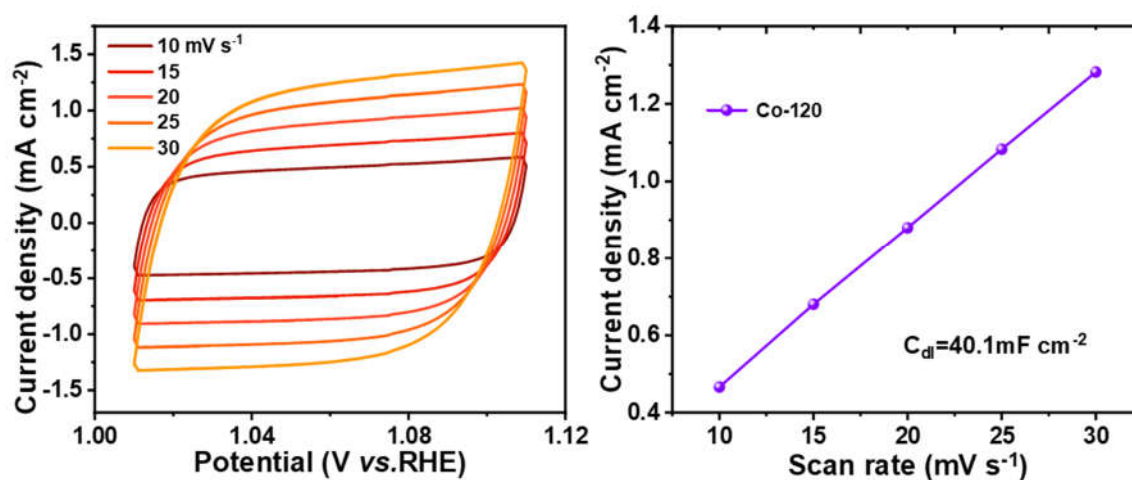


Fig. S 9 ECVS of series of Co-120

References

1. L. Q. Wang, K. X. Liang, L. Deng and Y. N. Liu, *Appl. Catal. B-Environ.*, 2019, **246**, 89-99.
2. G. Wu, K. L. More, C. M. Johnston and P. Zelenay, *Science*, 2011, **332**, 443-447.
3. L. Chong, G. A. Goenaga, K. Williams, H. M. Barkholtz, L. R. Grabstanowicz, J. A. Brooksbank, A. B. Papandrew, R. Elzein, R. Schlaf, T. A. Zawodzinski, Jr., J. Zou, S. Ma and D.-J. Liu, *Chemelectrochem*, 2016, **3**, 1541-1545.
4. B. You, N. Jiang, M. L. Sheng, W. S. Drisdell, J. Yano and Y. J. Sun, *ACS Catal.*, 2015, **5**, 7068-7076.
5. J. Meng, H. T. Lei, X. L. Li, J. Qi, W. Zhang and R. Cao, *ACS Catal.*, 2019, **9**, 4551-4560.
6. Q. Q. Cheng, L. J. Yang, L. L. Zou, Z. Q. Zou, C. Chen, Z. Hu and H. Yang, *ACS Catal.*, 2017, **7**, 6864-6871.
7. Z. Yang, C. Zhao, Y. Qu, H. Zhou, F. Zhou, J. Wang, Y. Wu and Y. Li, *Adv. Mater.*, 2019, **31**, 1808043.
8. K. Yuan, D. Lu[†]tzenkirchen-Hecht, L. Li, L. Shuai, Y. Li, R. Cao, M. Qiu, X. Zhuang, M. K. Leung and Y. Chen, *J. Am. Chem. Soc.*, 2020, **142**, 2404-2412.
9. Y. Mun, S. Lee, K. Kim, S. Kim, S. Lee, J. W. Han and J. Lee, *J. Am. Chem.*

- Soc.*, 2019, **141**, 6254-6262.
10. B.-C. Hu, Z.-Y. Wu, S.-Q. Chu, H.-W. Zhu, H.-W. Liang, J. Zhang and S.-H. Yu, *Energy Environ. Sci.*, 2018, **11**, 2208-2215.
 11. X. Fu, J.-Y. Choi, P. Zamani, G. Jiang, M. A. Hoque, F. M. Hassan and Z. Chen, *ACS applied materials & interfaces*, 2016, **8**, 6488-6495.
 12. H. Shang, X. Zhou, J. Dong, A. Li, X. Zhao, Q. Liu, Y. Lin, J. Pei, Z. Li and Z. Jiang, *Nature communications*, 2020, **11**, 1-11.
 13. J.-Y. Choi, R. S. Hsu and Z. Chen, *The Journal of Physical Chemistry C*, 2010, **114**, 8048-8053.
 14. S. M. Unni, R. Illathvalappil, S. N. Bhange, H. Puthenpediakkal and S. Kurungot, *ACS applied materials & interfaces*, 2015, **7**, 24256-24264.
 15. H. C. Huang, I. Shown, S. T. Chang, H. C. Hsu, H. Y. Du, M. C. Kuo, K. T. Wong, S. F. Wang, C. H. Wang and L. C. Chen, *Advanced Functional Materials*, 2012, **22**, 3500-3508.
 16. B. Vinayan, T. Diemant, R. J. Behm and S. Ramaprabhu, *Rsc Advances*, 2015, **5**, 66494-66501.
 17. V. Nallathambi, J.-W. Lee, S. P. Kumaraguru, G. Wu and B. N. Popov, *J. Power Sources*, 2008, **183**, 34-42.
 18. R. Illathvalappil and S. Kurungot, *ChemElectroChem*, 2020, **7**, 3123-3134.
 19. H. Zhang, H. T. Chung, D. A. Cullen, S. Wagner, U. I. Kramm, K. L. More, P. Zelenay and G. Wu, *Energy Environ. Sci.*, 2019, **12**, 2548-2558.