:

Electronic Supplementary Material (ESI) for Nanoscale. This journal is © The Royal Society of Chemistry 2020

Electronic Supplementary Information (ESI) for

Insight into atomically dispersed porous M-N-C single site catalysts for electrochemical CO₂ reduction

Leta Takele Menisa $a,b\ddagger$, Ping Cheng c,\ddagger , Chang Long a,b,d, Xueying Qiu a,b,d, Yonglong Zheng a,b, Jianyu Han a,b, Yin Zhang a,b, Yan Gao a,b,* and Zhiyong Tang a,b,d,*

^aCAS Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence i n Nanoscience, National Center for Nanoscience and Technology, Beijing, 100190, P. R. China.

^bSchool of Nanoscience and Technology, University of Chinese Academy of Sciences, Beijing 10 0049, P. R. China

^cCollege of Science, University of Shanghai for Science and Technology, Shanghai 200093, China

^dSchool of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150080, China

*Corresponding Author. E-mail: gaoyan@nanoctr.cn ; zytang@nanoctr.cn

Experimental Section

Preparation of M-N-C Catalyst: In 4 round bottom flask 1gm of carbon black was well dispersed and sonicated in 6M HNO₃ for 10 min. Then 3ml of 2mg/ml solutions of M^{2+} salts (Ni(NO₃)₂, Fe(NO₃)₂, Co(NO₃)₂ or Cu(NO₃)₂) was added to each flux to form Ni-C, Fe-C, Co-C and Cu-C respectively. The flask was refluxed overnight in order to immobilize metals on the matrix of carbon. Then the solid was washed several times with ultra-pure water to remove all the possible residual acid or other impurities by repeated centrifugation and sonication. The refluxed samples were dried at 60 °C and grinded in mortar. Afterwards the as prepared samples were mixed with urea as N source and pyrolyzed at 700-1000 °C for 1 hr under argon atmosphere with ramp rate of 5°C/min.

Preparation of N-C catalysts: 1g of carbon black was well dispersed with sonication in 6M HNO₃ and refluxed at 80 °C for 12hrs. Then the solid was washed several times with ultra-pure water to remove all the possible residual acid or other impurities by repeated centrifugation and sonication. The refluxed carbon was dried up in vacuum at 60 °C and grinded in mortar. After wards the as prepared samples were mixed with urea as N source and pyrolyzed at 1000 °C for 1 hr under argon atmosphere with ramp rate of 5°C/min.

Preparation of Carbon catalysts: 1gof carbon black was well dispersed with sonication in 6M HNO₃ and refluxed at 80 °C for 12hrs. Then the solid was washed several times with ultra-pure water to remove all the possible residual acid or other impurities by repeated centrifugation and sonication. The refluxed carbon was dried up in vacuum at 60 °C and grinded in mortar. Then, pyrolyzed at 1000 °C for 1 hr under argon atmosphere with ramp rate of 5°C/min.

Characterization: TEM images and EDX elemental mapping were performed on Tecnai G2 F20 S-TWIN with an acceleration voltage of 200 kV. HAADF-STEM images were obtained on a Cscorrected FEI Titan G2 60-300 Microscope operated at 300 kV. Probe Cs corrector was applied to get better spatial resolution. X-ray diffraction (XRD) patterns were recorded on D/MAX-TTRIII (CBO) (Rigaku Corporation) with Cu K α radiation (λ =1.54 Å) at a scanning rate of 5° min⁻¹. The microstructure was studied by Raman spectra using Renishaw in Via Raman microscope with 514 nm laser excitation. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Scientific ESCALAB 250 Xi XPS system, in which the analysis chamber pressure was 1.5×10^{-9} mbar and the size of the X-ray spot was 500 um. Specific surface area was measured at -196 °C with a Micromeritics ASAP 2010 analyzer and calculated based on a Brunauer-Emmett-Teller (BET) method. The inductively coupled plasma mass spectrometry (ICP-MS) data were taken from NexION 300X (PerkinElmer). X-ray absorption spectra were acquired in vacuum at beamline 4B7B of the Beijing Synchrotron Radiation Facility (BSRF), the ex-situ Co K-edge X-ray absorption spectra were acquired under ambient condition in florescence mode at beamline 1W1B of BSRF, using a Si (111) double-crystal monochromator. The storage ring of BSRF was operated at 2.5 GeV with a maximum current of 250 mA in decay mode. The energy was calibrated using respective metal foil, and the intensity of the incident and transmitted X-rays was monitored by standard N2-filled ion chambers. The powder samples were pressed to a pellet to maintain the best signal. The XAS raw data were normalized, and Fourier transformed by the standard procedures with the ATHENA program. Fitting analysis of the EXAFS (k) data was carried out using the ARTEMIS program.

Electrochemical Measurements: All electrochemical measurements were carried out using a CHI 660E potentiostat in three-electrode configuration using platinum electrode as a counter

electrode and Ag/AgCl as a reference electrode. Potentials measured were converted to RHE reference scale by E (vs. RHE) = E (vs. Ag/AgCl) + 0.197 + 0.059 * pH. Catalyst ink was prepared by well dispersing 4 mg of catalyst in 1 mL of ethanol and 80 µL of 5 wt% Nafion solutions using ultra sonication. Then 50 μ L catalyst inks were uniformly loaded on 1×1 cm² carbon paper electrode. The electrochemical measurements for CO₂ reduction were performed in a gas-tight two-component H-cell separated by Nafion 117 cation-exchange membranes. A CO₂saturated 0.1 M KHCO3 electrolyte (pH 6.8) was used as electrolyte. A CO2 flow of (${\approx}30$ mL/min), generated from a constant stream bubbling in the cell solution, was purged into the KHCO₃ solution during the measurement to remove residual air and ensure continuous CO₂ saturation. The gas products of CO₂ electrochemical reduction were detected by an online GC equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID) equipped with Mol sieve 5 Å column once every 12. After 30 min continuous electrolysis, 0.9 mL of KHCO₃ solution was collected and mixed with 0.1 mL D₂O in an NMR tube. The mixture was analyzed on a Bruker 600 MHz ¹H NMR spectrometer with water suppression to identify the liquid products. The LSV measurements were carried out in the potential range of 0.10 to -1.2 V (vs RHE) with scan rate of 5 mV s^{-1}

DFT Simulation: Spin-polarized First-principle density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP)^[1–3] and the projector augmented wave (PAW) method.^[4] The exchange-correlation effects were treated in generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) potential.^[5] The kinetic energy cutoff was chosen to be 550 eV. Gaussian smearing method^[6] was employed to determine electron occupancies with a width of 0.2 eV. Graphene with 42 carbon atoms were used as the initial model, and two C atoms were removed to build a defect. Then four C atoms at the defect

were replaced by the N atoms and one metal atom was located in the center of the defect four coordinating with the N atoms. This model was placed in a 24×24×16 Å³ super cell with the unsaturated edges C atoms were saturated with H atoms. Only the gamma point in the Brillouin zone (BZ) was used for the BZ integration. The structures were relaxed before attaching any molecules. For COOH and CO adsorption on Co system, all possible sites were considered. We found that both COOH and CO prefer the Co sites. Therefore, only the metal sites were considered for the other three systems. No atom was fixed during the relaxation. The energy and fore convergence criteria were set as 10⁻⁵ eV and 0.03 eV/Å, respectively. DFT-D3 correction of Grimme was used to describe the role of van der Waals (vdW) dispersion forces.^[7] The Gibbs free energy diagrams were calculated using the computational hydrogen electrode (CHE). In the potential CHE, the chemical of а proton-electron pair was defined as $G(H^+ + e^-) = \frac{1}{2}G(H_2) - eU$ where U is the electrochemical potential relative to RHE. The

Gibbs free energy of a species is calculated according to $G = E_{DFT} + E_{ZPE} + \int C_p dT - TS$ where E_{DFT} is the electronic energy calculated by DFT, E_{ZPE} is the zero point energy obtained from the vibrational frequencies of adsorbates or molecules as calculated within DFT. For an adsorbate, the changes in $\int C_p dt$ and TS are much smaller compared to the variations in E_{DFT} and E_{ZPE} . Therefore, $\int C_p dt$ and TS were assumed constant for *COOH and *CO. The $\int C_p dt$ and TS for *COOH were used as 0.096 and -0.178 eV.^[8] For chemical adsorbed CO, the $\int C_p dt$ and TS were used as 0.076 and -0.153 eV^[8], and for physical adsorbed CO, they were used the value of gas-phase CO, since the properties of physical adsorbed CO is more closer to those of gas-phase CO. For gas-phase molecules, the $\int C_p dt$ and TS at 298.15K were used. To account for the gasphase errors encountered with PBE exchange-correlation functional, -0.51, +0.13, -0.08 eV correction are added to the CO, CO₂, and H₂ electronic energy, respectively. ^[8] The solvation effect has been considered for *COOH and chemical adsorbed *CO by stabilizing 0.25 eV and 0.1 eV respectively.^[8]

Product Quantification

CO₂ gas was delivered into the cathodic compartment of the cell. Then the gas phase composition vented into gas chromatograph (GC, Shimadzu GC-2014C). The gas products were analyzed by GC every 15 min. The gas concentration was averaged over three measurements. Liquid product was characterized by ¹H NMR on Bruker AVANCE III HD 400 using a presaturation sequence. Liquid product concentration was quantified using dimethyl sulfoxide (DMSO) as the internal standard.

The faradic efficiency and turnover frequency are calculated by the equations as follows:

Faradic efficiency (FE):

$$FE_{CO} = \frac{J_{CO}}{J_{total}} = \frac{v_{co} \times N \times F}{J_{total}}$$

 FE_{CO} : Faradic efficiency for CO formation;

J_{CO}: Current density for CO formation;

J_{total}: Total Current density;

 v_{co} : Production rate of CO (measured by GC);

N: Number of electron transferred for product formation, which is 2 for CO;

F: 96485.3 C mol⁻¹ (Faraday constant);

Turnover frequency (TOF, h⁻¹)^[9]:

$$TOF = \frac{I_{product}/NF}{m_{cat} \times \frac{\omega}{M_{\chi}}} \times 3600$$

TOF: Turnover frequency of CO;

Iproduct: Current of CO formation;

N: Number of electron transferred for product formation, which is 2 for CO;

F: 96485.3 C mol⁻¹ (Faraday constant);

 m_{cat} : Catalyst loading on carbon fiber paper, 0.25 mg;

 ω : Ni loading in the catalyst;

M_x: Atomic mass.



Figure S1. SEM images of (a) Ni-N-C, (b) Fe-N-C, (c) Co-N-C and (d) Cu-N-C annealed at 1000 0 C.



Figure S2. TEM images of (a) Ni-N-C, (b) Fe-N-C, (c) Co-N-C and (d) Cu-N-C annealed at $1000 \ ^{0}$ C.



Figure S3. Powder XRD patterns of N-C, Ni-N-C, Fe-N-C, Co-N-C and Cu-N-C catalysts



Figure S4. STEM images and elemental maps for a Ni-N-C, b) Fe-N-C, c) Co-N-C and d) Cu-N-C.



Figure S5. CO₂ physisorption isotherm at 273 K

We performed gas adsorption experiments for all M–N-C catalysts in order to better understand their gas capturing capacity, based on this 40–45 cm³ g⁻¹ capacity for CO_2 capture at atmospheric pressure has been recorded, this indicates the potential of this family of catalyst to trap CO_2 molecules despite the low CO_2 solubility in the electrolyte.



Figure S6. Brunauer-Emmett-Teller (BET) N2 specific ad/desorption isotherm profile and pore distribution statistics for M-N-C family.

N2 physisorption isotherms collected for four of M-N-C catalysts indicated the microporosity of the materials with a little mesopores. The specific surface area based on Brunauer–Emmett–Teller (BET) theory is in range of 215–235 m² g⁻¹, Fe–N-C and Cu–N-C show the lowest and the highest BET surface area, respectively, while Ni-N-C and Co-N-C are in between (**Table S1**).



Figure S7. Raman spectra of this family of M-N-C electrocatalysts. ID/IG ratio is based on peak fitting. As shown, the ratio is very close from one to another, indicating the density of defect sites of M-N-C is very similar.



Figure S8. High-resolution metal 2p of Ni-N-C (a), Fe-N-C (b), Co-N-C (c) and Cu-N-C (d) and their corresponding shake-up satellites.



Figure S9. N1S XPS fitting of N-C sample.



Figure S10. Ni K-edge XANES spectra of Ni-N-C (a) the expanded pre-edge region (b): the grey shaded areas show the intensity of the $1s \rightarrow 3d$ transition. And Fe K-edge XANES spectra of Fe-N-C (c) the expanded pre-edge region (d).



Figure S11. R-space (a,c) and k-space(b,d) of Ni and Fe K-edge fitting EXAFS Spectrum (black) and the fitting curves (red).



Figure S12. Ni K-edge XANES spectra of Co-N-C and Cu-N-C (a and c) and k3-weighted $\chi(k)$ function of the EXAFS spectra of Co-N-C and Cu-N-C (b and d) . e) Comparison between the K-edge XANES experimental spectrum of Cu-N-C (magneto line) and Cu(II) phthalocyanine (black line). f) Comparison between Cu-N-C before and after 15 min reactions at -0.7V vs RHE. The Cu-N-C catalysts was exposed to air for more than 24 hrs after electrolysis until EXAFs measurements, this makes disappearance of the metallic copper phase and the restoration of the original spectra. This is in agreement with previous report.^[9]



Figure S13. Temperature optimization of Ni-N-C and Fe-N-C catalysts based on CO_2RR performance for LSV curves at a cathodic sweeping rate of 5 mV s⁻¹ in CO_2 saturated 0.1 M KHCO₃ solution with the same mass loading.



Figure S14. LSV comparison of Ni-N-C and Fe-N-C with N-C and bare carbon at a cathodic sweeping rate of 5 mV s⁻¹ in CO_2 saturated 0.1 M KHCO₃ solution with the same mass loading.



Figure S15. Cyclic voltammetry of a) Fe-N-C, b) Ni-N-C , c) Cu-N-C and d) Co-N-C catalysts conducted in CO₂-saturated 0.1M KHCO₃ (pH=6.8) solution at scan rate 20 mV s⁻¹, 50 mV s⁻¹, 80 mV s⁻¹, 100 mV s⁻¹ and 120 mV s⁻¹ to determine the double layer capacity. Cyclic voltammetry was performed between 0.3 and 0.55 V vs. RHE to avoid the interference of the faradaic process.



Figure S16. ECSA comparison among of Fe-N-C, Ni-N-C, Cu-N-C and Co-N-C catalysts.

ECSA=R_fS, in which S stands for the real surface area of the smooth metal electrode, which was generally equal to the geometric area of electrode (in this work, S=1 cm⁻²). The roughness factor R_f was estimated from the ratio of double-layer capacitance C_{dl} for the working electrode and the corresponding smooth metal electrode (Specific capacitance for carbon was reported as 27.50 μ F cm⁻²), that is, R_f= C_{dl}/27.5 μ F cm⁻². The C_{dl} was determined by measuring the capacitive current associated with double-layer charging from the scan-rate dependence of cyclic voltammetric stripping. For this, the potential window of cyclic voltammetric stripping was 0.3 V to 0.55 V versus RHE (0.1 M KHCO₃ solution). The scan rates were 20 mV s⁻¹, 50 mV s⁻¹, 80 mV s⁻¹, 100 mV s⁻¹ and 120 mV s⁻¹. The C_{dl} was estimated by plotting the $\Delta j = (ja- jc)$ at 0.45 V (where jc and ja are the cathodic and anodic current densities, respectively) versus RHE against the scan rate, in which the slope was twice that of C_{dl}.



Figure S17. HRTEM images of Ni-N-C after 12 h (a) and 24 h(b) CO_2RR at -0.8V vs RHE . Fe-N-C after 12 h (c) and 24h (d) CO_2RR at -0.5V vs RHE. XPS spectra of Ni-N-C after 12h(e) and 24h(f) CO_2RR at -0.8V vs RHE and Fe-N-C after 12h(g) and 24h(h) CO_2RR at -0.5V vs RHE



Figure S18. TOF of Ni-C-N and Fe-N-C compared with some reported heterogeneous electrocatalysts for electroreduction of CO_2 to CO.



Figure S19. DFT-calculated free energy diagram for the CO_2 reduction reaction (CO_2RR) (a,b) and hydrogen evolution reaction (HER) (c,d) at 0 V vs RHE (a,c) and -0.6 V vs RHE (b,d).



Figure S20. DFT-calculated free energy diagram for the CO_2 reduction reaction (CO_2RR) over three coordinated metal system

Sample	ICP	S _{BET}	Nitroge	I _D /I _G	F	ies/atom ^e	%		
	%wt	(m²g- 1)	n % ^a	b	pyridinic	pyrrolic	M- Nx	N-Ox	quaterna ry
Ni-N-C	1.25	228	1.46	1.02	29.1	34.2	12.6	10.3	13.5
Fe-N-C	1.33	217	1.38	1.03	25.9	34.1	14.6	8.8	15.5
Co-N-C	1.46	227	1.4	1.04	34.1	35.5	13.1	5.6	11.5
Cu-N-C	1.34	230	1.1	1.01	29.2	35.5	10.1	11.6	15.5

Table S1. Surface area, nitrogen content and assignment of different N species of the M-N-C CO₂RR electrocatalysts

(a) The nitrogen content was determined by XPS;

(b) ID/IG determined by Raman spectra.

Table S2. Fitting details of XPS spectra for Ni- N-C and Fe-N-C after CO2RR at -0.8 V and - 0.5V for 12 h and 24 h

Sample	Fittings of N moieties/atom%							
	pyridinic	pyrrolic	M-Nx	N-Ox	quaternary			
Ni-N-C after 12h	15.4	27.8	11.2	10.9	34.4			
Ni-N-C after 24h	10.2	26.7	10.5	11.4	40.9			
Fe-N-C after 12h	9	28.3	13.2	14.3	33.8			
Fe-N-C after 24h	8	28.1	11.7	8.9	39.7			

Catalysts	Cathode	DE	jco	Potential	TOF (h ⁻¹)	Ref.
	Loading $(mg \ am^{-2})$	FE _{CO}	$(mA \cdot cm^{-2})$	(V) VS. DHF	Ref.	
N; N C	$(\operatorname{Ing}\operatorname{cm})$	070/	17.6		20.769	This work
<u>NI-N-C</u>	0.38	9/%	17.0	-0.8	20,708	This work
Fe-N-C	0.58	86.7%	2.7	0.5	2881	This work
<u>(Cl, N)-Mn/G a</u>	0.5	97%	9.2	-0.6	38347	10
_	1	95%	1~	-0.43	1416	11
ZnNx/C ^a	1	85%	6	-0.63	8390	
Fe-N4 ^a	1	80%	2.7	-0.6 -	-	12
COF-367-Co ^a	-	91%	3.3	0.67	1908	13
CoPc/CNT ^a	0.4	92%	~10	-0.63	-	14
CoPPc/CNT ^a	1	90%	~8	-0.5	-	15
Co-N2 ^a	0.8	94%	17	-0.63	18200	16
Ni SAs/N-C ^a	0.1	71.9%	7.5	-1	5273	17
Ni-N4-C ^a	0.2(GC) ^c	99%	~15	-0.81	-	18
	0.2(GC) ^a	98%	~9	-0.6	-	
SE-Ni	0.4	95%	~2	-0.6	4006	19
SAs@PNC ^a	0.4	88%	18.3	-1	47805	
NC-CNTs (Ni)	0.1	90%	9.25	-1	11648	20
N-based silver ^b	0.1	90%	90	-1.6	2000	21
Nanoporous	-	92%	8.7	-0.5	7.2	21
Silver ^a						
Pdnanoparticles	2.0	91%	9.76	-0.89	576	22
a						
Ultrathin Au	-	94%	8.16	-0.35	72	23
NWs ^b						

Table S3. Performance comparison of various reported CO₂RR electrocatalysts

 $^{a}0.5$ M KHCO₃ was used as electrolyte $^{b}0.1$ M KHCO3, and calculated on the Glassy Carbon Electrode (GC).

Table S4. EXAFS fitting result of the Ni-C-N catalyst.

The data range adopted for data fitting in k-space (Δk) and R space (ΔR) are 2-11.426 Å⁻¹and 1-3 Å, respectively.

Sample	Shell	N	R/Å (EXAFS)	Debye-Waller factor $\Delta \sigma^2 (\times 10^{-3}$ Å ²)	$\Delta E_0(eV)$	R factor
Ni-C-N	Ni-N	3.4 <u>+</u> 0.5	1.847	7±0.59	4.47	0.00002
Fe-C-N	Fe-N	3.6 <u>+</u> 0.5	1.971	9±0.59	-9.8	8.6

N, coordination number; R, interatomic distance; EXAFS, extended X-ray absorption fine structure.

Table S4. The adsorption energy values of CO₂ reduction intermediate on 4-coordinated and 3coordinated metal center of nitrogen-doped graphene. All results are in eV units.

Free energy	Co-N4	Co-N3	Fe-N4	Fe-N3	Cu-N4	Cu-N3	Ni-N4	Ni-N3
$\Delta G_{\rm COOH}$	0.365	1.070	0.604	0.910	1.740	1.562	1.932	1.161
$\Delta G_{\rm CO}$	-0.263	0.165	-1.193	0.047	-0.106	0.171	-0.140	0.269

From the table, the binding of the COOH on 3-coordinated Co and Fe systems are much weaker than those on 4-coordinated (Δ G 1.070 eV vs 0.365 eV; 0.910 eV vs 0.604 eV). " to "For all the systems, the binding of CO on 3-coordinated metal center is weaker than their corresponding 4-coordinated metal center, indicting the desorption of CO on the 3-coordinated metal center is much easier for all the systems we studied.

References

- 1. G. Kresse and J. Hafner, *Phys. Rev. B*, **1993**, 47, 558.
- 2. G. Kresse and J. Furthmüller, Comput. Mater. Sci., 1996, 6, 15.
- 3. G. Kresse and J. Hafner, Phys. Rev. B, 1994, 49, 14251.
- 4. G. Kresse and D. Joubert, *Phys. Rev. B*, **1999**, 59, 1758.
- 5. J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865.
- 6. M. Methfessel and A. T. Paxton, *Phys. Rev. B*, **1989**, 40, 3616.
- 7. S. Grimme, J. Antony, S. Ehrlich, and S. Krieg, J. Chem. Phys. 2010, 132, 154104
- 8. A. A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl, J. K. Norskov, *Energy Environ*. *Sci.* **2010**, 3, 1311.
- D. Karapinar, N.T. Huan, N. R. Sahraie, J. Li, D. Wakerley, N. Touati, S. Zanna, D. Taverna, L. H. G. Tizei, A.Zitolo, F. Jaouen, V.Mougel, and M. Fontecave, *Angew. Chem.*, *Int. Ed.* 2019, 58, 15098
- 10. C. Zhao, X. Dai, T. Yao, W. Chen, X. Wang, J. Wang, J. Yang, S. Wei, Y. Wu, Y. Li, J. *Am. Chem. Soc.* **2017**, *139*, 8078
- 11. B. Zhang, J. Zhang, J. Shi, D. Tan, L. Liu, F. Zhang, C. Lu, Z. Su, X. Tan, X. Cheng, B.Han, L. Zheng and J. Zhang, *Nat. Commun.* **2019**, *10*, *2980*.
- 12. F. Yang, P. Song, X. Liu, B. Mei, W. Xing, Z. Jiang, L. Gu, and W. Xu, Angew. Chem., Int. Ed. 2018, 57, 12303
- 13. C. Zhang, S. Yang, J. Wu, M. Liu, S. Yazdi, M. Ren, J. Sha, J. Zhong, K.Nie, A.S. Jalilov, Z. Li, H. Li, B. I. Yakobson, Q. Wu, E. Ringe, H. Xu, P. M. Ajayan, and J. M. Tour, Adv. Energy Mater. 2018, 8, 1703487.
- S. Lin, C. S. Diercks, Y.-B. Zhang, N. Kornienko, E. M. Nichols, Y. Zhao, A. R. Paris, D. Kim, P. Yang, O. M. Yaghi, C. J. Chang, *Science* 2015, 349, 1208.
- 15. X. Zhang, Z. Wu, X. Zhang, L. Li1, Y. Li, H. Xu, X. Li, X. Yu, Z. Zhang, Y. Liang and H. Wang, *Nat. Commun.* **2017**, *8*, *14675*.
- 16. N. Han, Y. Wang, L. Ma, J. Wen, J. Li, H. Zheng, K. Nie, X. Wang, F. Zhao, Y. Li, J. Fan, J. Zhong, T. Wu, D. J. Miller, J. Lu, S. T. Lee and Y. Li, *Chem.* 2017, 3, 652-664.
- 17. X. Wang, Z. Chen, X. Zhao, T. Yao, W. Chen, R. You, C. Zhao, G. Wu, J. Wang, W. Huang, J. Yang, X. Hong, S. Wei, Y. Wu, Y. Li, *Angew. Chem.*, *Int. Ed.* **2018**, 57, 1944.
- 18. X. Li, W. Bi, M. Chen, Y. Sun, H. Ju, W. Yan, J. Zhu, X. Wu, W. Chu, C. Wu, Y. Xie, J. Am. Chem. Soc. 2017, 139, 14889.
- 19. Z. Q. Jian Yang, C. Zhao, W. Wei, W. Chen, Y. Qu, J. Dong, J. Luo, Z. Li, *Angew. Chem.*, *Int. Ed.* **2018**, 57, 14095.
- Q. Fan, P. Hou, C. Choi, T.S.Wu, S. Hong, F. Li, Y.L. Soo, P. Kang, Y. Jung, and Z. Sun, *Adv. Energy Mater.* 2019, 1903068.

- 21. C. E. Tornow, M. R. Thorson, S. Ma, A. A. Gewirth, P. J. A. Kenis, J. Am. Chem. Soc. 2012, 134, 19520.
- 22. Q. Lu, J. Rosen, Y. Zhou, G. S. Hutchings, Y. C. Kimmel, J. G. Chen, F. Jiao, *Nat. Commun.* 2014, 5, 3242.
- 23. D. Gao, H. Zhou, J. Wang, S. Miao, F. Yang, G. Wang, J. Wang, X. Bao, J. Am. Chem. Soc. 2015, 137, 4288.
- 24. W. Zhu, Y. J. Zhang, H. Zhang, H. Lv, Q. Li, R. Michalsky, A. A. Peterson, S. Sun, *J. Am. Chem. Soc.* **2014**, 136, 16132.