Supporting Information

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Ligand Engineering in Nickel Phthalocyanine to Boost the Electrocatalytic Reduction of CO₂

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Experimental methods

Synthesis of substituted NiPc. 4 mmol of 4-Aminophthalonitrile and 1 mmol of nickel acetate tetrahydrate were dissolved into 30 mL of ethanol with the help of ultrasonic treatment. The reaction mixture was transferred into a 50 mL Teflon-lined stainless-steel autoclave and then heated at 160 °C for 6 h. The strong bases produced during the solvothermal reaction perform a nucleophilic attack at the cyano group of phthalonitrile to form metal phthalocyanines.[1-2] The obtained sample was washed with hot ethanol and the 1 M hydrogen chloride solution for several times. After that, a black sample of NiTAPc was dried in a vacuum oven at 60 °C for 10 h. NiTHPc and NiTBPc were synthesized by employing 4-Hydroxyphthalonitrile and 4-tert-Butylphthalonitrile to replace 4-Aminophthalonitrile in a similar fashion, respectively.

Preparation of carbon nanotube supported molecule catalysts. NiPc and H2Pc were obtained from Alfa Aesar. Carbon nanotube (Tanfeng Tech. Inc.) was treated with the concentrated nitric acid at 90 °C overnight to remove the nickel nanoparticles. The purified carbon nanotube was obtained after washing with the water and drying at 60 °C for 12 h. Molecule catalysts (0.01 mmol) including the NiPc, NiTBPc, NiTHPc and NiTAPc were dispersed into 50 mL of DMF, respectively. The prepared suspension was sonicated for 30 min, and then 100 mg of purified carbon nanotube was added. The mixed suspension was further sonicated for another 30 min and stirred for 24 h at room temperature. Finally, the carbon nanotube supported molecule catalysts (NiPc/CNT, NiTBPc/CNT, NiTHPc/CNT and NiTAPc/CNT) was obtained by suction filtration and dried in a vacuum oven at 80 °C for 10 h.

Materials characterizations. UV-Vis spectra were measured by Shimadzu UV-2600. MALDI-TOF-MS of substituted NiPc were analyzed by AB SCIEX MALDI-TOF/TOF 5800. FTIR spectra were measured by Thermo iS50. 1HNMR spectra were achieved using a Bruker
AVANCE III 500M spectrometer. Powder XRD patterns were carried out on a RIGAKU Rint-2000 X-ray diffractometer equipped with graphite monochromatized Cu-Kα radiation (λ = 1.54184 Å). Raman spectra were performed by a Laser Micro-Raman Spectrometer (Renishaw InVia, UK). Inductively coupled plasma optical emission spectrometry (ICP-OES) was carried out on PerkinElmer Optima 8300. XPS was tested by Thermo ESCALAB 250XI. SEM was conducted by TESCAN MAIA3. HAADF-STEM experiments were conducted on a Cs-corrected FEI Titan Cube transmission electron microscope at an acceleration voltage of 300 kV. The thermogravimetric experiments were measured on TG 209 F3 Tarsus under the high-purity Ar atmosphere from the room temperature to 600 °C with a heating rate of 10 °C min⁻¹. The CO₂-TPD of the samples was measured using a BIAODE PCA-1200 apparatus equipped with a thermal conductivity detector. The molecule catalysts (100 mg) were pretreated at 150 °C and purged with high-purity Ar for 2 h, and cooled down to the room temperature. And then, the catalyst was purged high-purity CO₂ (99.999%) with at 25 °C for 12 h. Moreover, CO₂ adsorption saturated catalyst was further purged with the high-purity Ar for 1 h. Finally, the desorption signal of CO₂ was recorded online under the atmosphere of high-purity Ar.

Electrochemical measurements. All the electrochemical tests were implemented on an electrochemical station of Auto Lab at room temperature.

In the H-type cell, two chambers were separated by the proton exchange membrane of Nafion 117. The three-electrode system consisted of a modified carbon paper (Toray, TGP-H-060) as a working electrode, a platinum plate as a counter electrode and an Ag/AgCl filled with saturated KCl electrode as a reference electrode. To prepare the working electrode, 4 mg of catalyst was dispersed into 1 mL of aqueous alcohol (50 vol%) and 60 μL of Nafion (5 wt%) was employed as the binder. The prepared ink was dropped onto carbon paper with a loading of 0.4 mg cm⁻². The 0.5 M KHCO₃ saturated with high-purity CO₂ (99.999%) was
used as the electrolyte for electrocatalytic CO₂ reduction. The flow rate of high-purity CO₂ was set at 20 sccm. The potentials in H-cell were transformed to the RHE with $iR$ compensations by the equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0592 \times \text{pH} + 0.197 - iR_u$$  \hspace{1cm} (1)

where $i$ is the current and $R_u$ is the solution resistance. The pH of CO₂-saturated 0.5 M KHCO₃ and Ar-saturated 0.5 M KHCO₃ are 7.2 and 8.45, respectively.

The products of CO₂RR in cathodic were analyzed by an on-line gas chromatograph (Shimadzu, 2014C) and $^1$HNMR. High-purity N₂ (99.999%) was used as the carrier gas. A thermal conductivity detector was employed to measure the H₂ fraction and a flame ionization detector was equipped with a nickel conversion furnace to analyze the CO fraction. The faradaic efficiency of products was calculated from gas chromatograph chromatogram peak according to the flowing equation:

$$FE_{\text{CO or H}_2} = x \times V \times \frac{2FP_0}{iRT}$$  \hspace{1cm} (2)

where $x$ is the fraction, $V$ is the flow rate of CO₂, $F$ is faraday constant (96485 C mol⁻¹), $P_0$ is the normal atmosphere (101325 Pa), $i$ is the applied current, $R$ is the gas constant (8.314 J·mol⁻¹·K⁻¹) and $T$ is the room temperature (298 K).

The flow cell measurements were performed on a home-made cell including sandwich of flow frames, gaskets and an anion-exchange membrane (Selecion DSVN). The window for electrolysis is set at 0.5 × 2 cm². 6 mg of carbon nanotube supported molecule catalysts can be dispersed into 2 mL ethanol with 100 μL of Nafion (5 wt%) and 300 μL of 1.0 wt% PTFE solution, forming a homogenous suspension. A 1 × 3 cm² gas diffusion layer (GDL, SGL29BC) with a catalyst loading of 1 mg cm⁻² was heated at 300 °C for 1 h under nitrogen and used as the working electrode. The GDL for long-term measurements before loading catalysts was modified by the PTFE with loading of 0.5 mg cm⁻² to further improve its hydrophobicity. The IrO₂–coating titanium sheet was employed as the counter electrode and...
an Ag/AgCl (with saturated KCl) electrode as a reference electrode. The flow rate of the electrolyte (1 M KHCO₃, pH = 8.63) was set at 10 mL min⁻¹ in both of cathodic and anodic chambers. The potentials in flow-cell were transformed to the RHE with iR compensations (resistance of ~4 Ω).

Operando attenuated total reflection-infrared spectroscopy (ATR-IR) and Raman spectroscopy. ATR-IR was measured by a Nicolet iS50 FT-IR spectrometer. The Au-coated Si semi-cylindrical prism (20 mm in diameter) was employed as the conductive substrate for catalysts and the IR reflection element. The catalyst suspension was dropped on the Au/Si surface as the working electrode. The mass loading of the catalyst was controlled about 1 mg cm⁻² and the electrolyte was 0.5 M KHCO₃ saturated with CO₂. As for operando Raman measurements, the suspension of catalysts were respectively dropped on the glassy carbon electrode with loading of 0.4 mg cm⁻². Raman measurements were measured by the laser of 532 nm. Operando ATR-IR and Raman spectra were recorded during stepping the applied electrode potential.

Computational methods. All density functional theory calculations on nickel phthalocyanines in this work were conducted by using the Gaussian 09 program. A PBE0 functional with D3 correction (Becke–Johnson damping) was employed for the dispersion and robustness corrections, which can achieve the proper function to investigate the reactions of transition nickel complexes. The double-ζ valence basis set and Stuttgart–Dresden pseudopotential were used for nickel atom. The all-electron 6–31G* basis set was used for the other elements (C, H, O, N). The geometry optimization and frequencies calculations were performed. Kohn–Sham molecular orbital analysis and atomic charge analysis by Mulliken atom population and Hirshfeld atomic charge were carried out via using Multiwfn 3.8 software. The 3D models of all the reaction intermediates were visualized by using the VMD 1.9 program.

The pathways for reduction of CO₂ into CO are listed as the following elementary steps:

\[ *+\text{CO}_2 + \text{H}^+ + e^- \rightarrow *\text{COOH} \]

(4)
\[ ^*\text{COOH} + \text{H}^+ + e^- \rightarrow ^*\text{CO} \quad (5) \]
\[ ^*\text{CO} \rightarrow \text{CO} + ^* \quad (6) \]

where * is the active site of the catalyst surface and \(^*\text{COOH}\) and \(^*\text{CO}\) were two key intermediates during CO\(_2\)RR. The computational hydrogen electrode (CHE) model was used to describe the free energy of proton-electron pairs in the proton-electron transfer steps by using the free energy of hydrogen at the potential of 0 V. The effect of applied bias on a proton-electron transfer step is represented by adding a \(-eU\) term to the standard \(\Delta G\).
Supplementary Figures

**Figure S1.** Calculation models. (a) NiPc. (b) NiTHPc. (c) NiTAPc.

**Figure S2.** CO$_2$ adsorption configurations. (a) NiPc. (b) NiTHPc. (c) NiTAPc.
**Figure S3.** Proposed reaction pathways for electrochemical reduction of CO$_2$ to CO.

**Figure S4.** The optimized structural models of *COOH on Ni site of NiPc, NiTHPc and NiTAPc.
Figure S5. The orbital energy level of Ni $d_{z^2}$ and LUMO (COOH).

Figure S6. Scheme for synthesis of NiTAPc and NiTHPc.
Figure S7. $^1$HNMR spectra of (a) NiTAPc and (b) NiTHPc in DMSO-$d_6$.

Figure S8. FTIR spectra of phthalonitrile, 4-Hydroxyphthalonitrile and 4-Aminophthalonitrile.
**Figure S9.** UV-Vis spectrum of nickel acetate tetrahydrate in dimethyl formamide.

**Figure S10.** The HOMO and LUMO orbital energies of NiPc, NiTHPc and NiTAPc.
**Figure S11.** The XRD patterns of NiPc, NiTHPc and NiTAPc.

**Figure S12.** Raman spectra of NiPc, NiTHPc and NiTAPc.
Figure S13. (a) XPS survey and (b) high-resolution XPS N 1s spectra of NiPc, NiTHPc and NiTAPc.

Figure S14. XAS spectra of (a) C and (b) N K-edge in NiPc, NiTHPc and NiTAPc.
Figure S15. The wavelet transform plot of (a) NiPc, (b) NiTHPc and (c) NiTAPc.

Figure S16. R space fitting of FT-EXAFS spectra for (a) NiPc; (b) NiTHPc; (c) NiTAPc.
Figure S17. SEM images of (a) NiPc, (b) NiTHPc, (c) NiTAPc, (d) NiPc/CNT, (e) NiTBpC/CNT, (f) NiTHPc/CNT and (g) NiTAPc/CNT. Scale bar, 1 μm.
Figure S18. HAADF-STEM images and corresponding EDX elemental mapping of Ni and N in (a-c) NiPc/CNT, (d-f) NiTHPc/CNT and (g-i) NiTAPc/CNT.
**Figure S19.** (a) XRD patterns and (b) Raman spectra of the pristine CNT, NiPc/CNT, NiTHPc/CNT and NiTAPc/CNT.

**Figure S20.** (a) XANES spectra of Ni K-edge in NiPc and NiPc/CNT. (b) XANES spectra of Ni K-edge in NiTHPc and NiTHPc/CNT. (c) XANES spectra of Ni K-edge in NiTAPc and NiTAPc/CNT. (d) EXAFS spectra of Ni K-edge in NiO, Ni powder, NiPc/CNT, NiTHPc/CNT and NiTAPc/CNT.
Figure S21. (a) TGA curves in Ar atmosphere. (b) TPD profile of CO$_2$ desorption on NiPc.

Figure S22. Schematic illustration of the CO$_2$ adsorption responses measurements.
Figure S23. LSV curve of blank carbon nanotube in the CO$_2$-saturated 0.5 M KHCO$_3$ electrolyte.

Figure S24. (a) The structure of H$_2$Pc. (b) LSV curve, (c) I-T curves and (d) FE of H$_2$ and CO in the CO$_2$-saturated 0.5 M KHCO$_3$ electrolyte.
**Figure S25. Optimized structural models.** The structural models of *COOH on substituent site of a NiTHPc and b NiTAPc.

**Figure S26.** CV of the NiPc/CNT, NiTHPc/CNT and NiTAPc/CNT in Ar-saturated 0.5 M KHCO₃ electrolyte for ECSA measurements. Scan rate: 400 mV s⁻¹.
Figure S27. Tafel plots of NiPc/CNT, NiTHPc/CNT and NiTAPc/CNT.

Figure S28. Chronoamperometry of (a) NiPc/CNT, (b) NiTHPc/CNT and (c) NiTAPc/CNT at different potentials in CO$_2$-saturated 0.5 M KHCO$_3$ electrolyte.
**Figure S29.** The gas chromatograph traces of gaseous products of NiTAPc/CNT from flame ionization detector (FID) channel.

**Figure S30.** $^1$HNMR spectrum of the electrolyte of NiTAPc/CNT after 2 h electrochemical CO$_2$RR in H-cell.
Figure S31. FE$_{H_2}$ of catalysts at different applied potential.

Figure S32. Schematic illustration of flow cell for CO$_2$RR.
Figure S33. Electrochemistry tests of NiPc/CNT in flow cell. (a) The LSV of catalyst without $iR$ corrections in CO$_2$ including the pristine of NiPc/CNT and the NiPc/CNT after the LSV measurement for 5 times in the Ar atmosphere. (b) FE of NiPc/CNT for CO$_2$RR after the LSV measurement for 5 times in the Ar atmosphere. (c) The NiPc/CNT for CO$_2$RR electrolysis at the current density of $-60$ mA cm$^{-2}$.

Figure S34. EIS spectra of NiTAPc/CNT after chronopotentiometry at different current density for 20 min.
Figure S35. (a-c) Operando Raman spectra of different molecule catalysts in CO$_2$-satureated KHCO$_3$ at various applied potentials (vs. RHE). (d) The Ni 2p XPS spectra of catalysts after chronoamperometry measurements for CO$_2$RR at $-0.65$ V for 1 h. The Ni 2p XPS shows a satellite peak due to the presence of C–F in Nafion or carbon paper.

Figure S36. Operando FTIR spectra of NiTAPc/CNT in CO$_2$-satureated KHCO$_3$ at various applied potentials (vs. RHE).
Figure S37. The CO$_2$RR electrolysis of NiTAPc/CNT at the current density of $-100$ mA cm$^{-2}$ (a) and $-400$ mA cm$^{-2}$ (b).

Figure S38. Molecular formula of NiTBPC.
Figure S39. Structure characterization of NiTBPc. (a) MALDI-TOF MS spectrum. (b) FTIR spectra. (c) UV-Vis spectrum in dimethyl formamide. (d) Raman spectrum.

Figure S40. SEM and HAADF-STEM characterizations. SEM images of (a) NiTBPc and (b) NiTBPc/CNT, Scale bar, 1 µm. (c-e) HAADF-STEM images and corresponding EDX elemental mapping of Ni and N in NiTBPc/CNT.
Figure S41. Electronic density characterizations. (a) High-resolution XPS Ni 2p spectra of NiPc and NiTBPc. (b) XAS spectra of Ni L-edge NiPc and NiTBPc. (c) XANES spectra of Ni K-edge from NiPc and NiTBPc. (d) XANES spectra of Ni K-edge from NiPc/CNT and NiTBPc/CNT.

Figure S42. (a) EXAFS spectrum of Ni K-edge from NiTBPc. (b) The wavelet transform plot of NiTBPc.
Figure S43. CO₂RR performance of NiTBPC in H-cell. (a) LSV profile in 0.5 M CO₂-saturated KHCO₃ electrolyte. (b) Chronoamperometry of NiTBPC/CNT at −0.68 V. (c) Chronoamperometry of NiTBPC/CNT at different potentials in CO₂-saturated 0.5 M KHCO₃ electrolyte. (d) FE(CO)s of NiTBPC/CNT at the according potentials.
Figure S44. CO₂RR performance of NiTBPC in flow cell. (a) Current densities of NiTBPC/CNT at different potentials in 1 M KHCO₃ electrolyte. (b) FE(CO) of NiTBPC/CNT.
Table S1. Structural parameters extracted from the EXAFS fitting.

| Samples  | N   | R (Å)     | σ²(Å²)   | ΔE₀ (eV) | R-factor |
|----------|-----|-----------|----------|----------|----------|
| NiPc     | 4   | 1.88674   | 0.00045  | 5.166    | 0.019723 |
| NiTHPc   | 3.762256 | 1.87925    | 0.00074  | 5.034    | 0.018676 |
| NiTAPc   | 3.671492 | 1.88573    | 0.00057  | 5.688    | 0.012139 |

*N, coordination number; R, bonding distance; σ², Debye-Waller factor; ΔE₀, inner potential shift. K²-weighting; fitting range: 2.0-13.25.
**Table S2.** The ICP-OES results of prepared molecular catalysts and carbon nanotubes.

| Samples        | Nickel content  |
|----------------|----------------|
| NiPc/CNT       | 0.4553 wt%     |
| NiTHPc/CNT     | 0.4234 wt%     |
| NiTAPc/CNT     | 0.3474 wt%     |
| CNT            | 0.0030 wt%     |
Table S3. Comparison of CO₂RR performance between the prepared catalysts and the reported molecule catalysts for conversion CO₂ into CO in H-cell with KHCO₃ electrolyte.

| Catalysts               | E vs. RHE (V) | J (mA cm⁻²) | FE(CO)       | Reference |
|-------------------------|---------------|-------------|--------------|-----------|
| NiTAPc/CNT              | -0.58         | 12.2        | Almost 100%  | This work |
| NiPc-OMe-MDE            | -0.62         | 16.7        | Almost 100%  |           |
| Co−N₃/HNPCSs            | -0.73         | 6.2         | 99.2%        | [12]      |
| Ni-CNT-CC               | -0.60         | 10          | 99%          | [13]      |
| Co(II)CPY/CNT           | -0.70         | 10.73       | 96%          | [14]      |
| CoPc2@MWCNTS            | -0.576        | 9.23        | 84%          | [15]      |
| NiPc/NC                 | -0.7          | 4.43        | 96%          | [16]      |
| NiPcTFFPN COF           | -0.9          | 14.1        | 99.8%        | [17]      |
| NiPc-NiO₄               | -0.85         | ~8.0        | 86%          | [18]      |
| N₃NiPc–CNT              | -0.68         | 12          | Almost 100%  | [19]      |
| PyNiPc/CNT              | -0.68         | ~10         | 99.5%        | [20]      |
| NiPc–Cu–O               | -0.74         | ~8          | ~55%         | [21]      |
| CoPc                    | -0.8          | ~7.2        | 90%          | [22]      |
| CCG/CoPc-A              | -0.69         | ~4          | ~85%         | [23]      |
Table S4. Comparison of CO₂RR performance between the prepared catalysts and the reported catalysts with gas-diffusion electrodes.

| Catalysts        | Electrolyte | J (mA cm⁻²) | FE(CO) | Reference |
|------------------|-------------|-------------|--------|-----------|
| NiTAPe/CNT       | 1 M KHCO₃  | 150         | 99.9%  | This work |
|                  | 1 M KHCO₃  | 500         | 94.6%  |           |
| NiPc-OMe-MDE     | 1 M KHCO₃  | 150         | 99.6%  | [12]      |
| CoPc2@MWCNTS     | 1 M KOH    | 116         | ~96%   | [16]      |
| Fe³⁺-N-C         | 0.5 M KHCO₃| ~50         | ~90%   | [25]      |
| CoPc+phenol      | 1 M KOH    | 200         | ~88%   | [26]      |
| CoPc©Fe-N-C      | 0.5 M KOH  | 275.6       | ~90%   | [27]      |
| Ni-N-C           | 1 M KHCO₃  | ~200        | ~89%   | [28]      |
| C/Ag/PTFE        | 1 M KOH    | ~160        | >90%   | [29]      |
| MWNT/PyPBI/Au    | 2 M KOH    | ~100        | >90%   | [30]      |
| Ag/MPL-3C        | MEA         | 300         | 99%    | [31]      |
| Ag-D             | 1 M KOH    | ~180        | >92%   | [32]      |
Supplementary Discussion

Discussion S1. The XPS survey (Figure S13a) indicates the molecule catalysts comprised by the C, N and Ni. The NiTHPc has a pronounced O signal from the periphery substituent of hydroxyl. The high-resolution XPS of N 1s (Figure S13b) can be well deconvoluted with a Lorentzian-Gaussian fit into three peaks. The peaks at around 397.9 eV can be assigned to the pyridinic-N, and the peaks locates at 399.5 eV belongs to the pyrrolic-N of Ni–N. In addition, the binding energy of N from the NH$_2$ falls in between that of pyridinic-N and pyrrolic-N at 398.5 eV. On the basis of these results, the amino and hydroxyl are successfully substituted in NiTAPc and NiTHPc, respectively.

Discussion S2. Figure S14a presents the C K-edge XANES spectra of the three investigated NiPc in this work. The prominent peaks of NiPc-base molecules at about 285.8 eV can be assigned to π* excitation of C–C bonds in the phthalocyanines ring, and the modern intensity peaks located at 288.1 eV can be attributed to C–H bonding and π* states. Figure S14b display the N K-edge XANES spectra of samples. The absorption edge among 397 and 403 eV is indexed to the π* resonance, and the absorption peaks at about 406.6 and 409 eV are belonged to σ* feature. The electron-donating substituents of amino and hydroxyl have great influence on the electronic structure of N to further tune the electron density catalytic site of Ni.
Supplementary References

[1] H. Tomoda, S. Saito, S. Shiraishi, *Chem. Lett.* **1983**, *12*, 313-316.

[2] B. I. Kharisov, U. Ortiz Méndez, J. L. Almaraz Garza, J. R. Almaguer Rodríguez, *New J. Chem.* **2005**, *29*, 686-692.

[3] G. Version, *Inc.: Wallingford, CT* **2009**.

[4] C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158-6170.

[5] P. C. Hariharan, J. A. Pople, *Theor.Chim. Acta* **1973**, *28*, 213-222.

[6] M. S. Gordon, *Chem. Phys. Lett.* **1980**, *76*, 163-168.

[7] R. C. Binning Jr, L. A. Curtiss, *J. Comput. Chem.* **1990**, *11*, 1206-1216.

[8] F. L. Hirshfeld, *Theor.Chim. Acta* **1977**, *44*, 129-138.

[9] I. Mayer, *Chem. Phys. Lett.* **1983**, *97*, 270-274.

[10] T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580-592.

[11] Ltd, P. o. V. P., Persistence of Vision Raytracer (Version 3.6). Persistence of Vision Pty. Ltd. Williamstown, Australia: 2004.

[12] X. Zhang, Y. Wang, M. Gu, M. Wang, Z. Zhang, W. Pan, Z. Jiang, H. Zheng, M. Lucero, H. Wang, *Nat. Energy* **2020**, *5*, 684-692.

[13] Y. Pan, R. Lin, Y. Chen, S. Liu, W. Zhu, X. Cao, W. Chen, K. Wu, W.-C. Cheong, Y. Wang, *J. Am. Chem. Soc.* **2018**, *140*, 4218-4221.

[14] S. Liu, H. B. Yang, S. F. Hung, J. Ding, W. Cai, L. Liu, J. Gao, X. Li, X. Ren, Z. Kuang, *Angew. Chem. Int. Ed.* **2020**, *59*, 798-803.

[15] L. Sun, Z. Huang, V. Reddu, T. Su, A. C. Fisher, X. Wang, *Angew. Chem. Int. Ed.* **2020**, *59*, 17104-17109.

[16] M. Wang, K. Torbensen, D. Salvatore, S. Ren, D. Joulié, F. Dumoulin, D. Mendoza, B. Lassalle-Kaiser, U. Işçi, C. P. Berlinguette, *Nat. Commun.* **2019**, *10*, 1-8.

[17] X. Yang, J. Cheng, X. Xuan, N. Liu, J. Liu, *ACS Sustain. Chem. Eng.* **2020**, *8*, 10536-
10543.

[18] M. Lu, M. Zhang, C.-G. Liu, J. Liu, L.-J. Shang, M. Wang, J.-N. Chang, S.-L. Li, Y.-Q. Lan, *Angew. Chem. Int. Ed.* **2021**, *60*, 4864-4871.

[19] J.-D. Yi, D.-H. Si, R. Xie, Q. Yin, M.-D. Zhang, Q. Wu, G.-L. Chai, Y.-B. Huang, R. Cao, *Angew. Chem. Int. Ed.* **2021**, *60*, 17108-17114.

[20] D.-D. Ma, S.-G. Han, C. Cao, W. Wei, X. Li, B. Chen, X.-T. Wu, Q.-L. Zhu, *Energy Environ. Sci.* **2021**, *14*, 1544-1552.

[21] D.-D. Ma, S.-G. Han, C. Cao, X. Li, X.-T. Wu, Q.-L. Zhu, *Appl. Catal. B.* **2020**, *264*, 118530.

[22] Z. Meng, J. Luo, W. Li, K. A. Mirica, *J. Am. Chem. Soc.* **2020**, *142*, 21656-21669.

[23] Z. Zhang, J. Xiao, X.-J. Chen, S. Yu, L. Yu, R. Si, Y. Wang, S. Wang, X. Meng, Y. Wang, Z.-Q. Tian, D. Deng, *Angew. Chem. Int. Ed.* **2018**, *57*, 16339-16342.

[24] J. Choi, P. Wagner, S. Gambhir, R. Jalili, D. R. MacFarlane, G. G. Wallace, D. L. Officer, *ACS Energy Lett.* **2019**, *4*, 666-672.

[25] J. Gu, C.-S. Hsu, L. Bai, H. M. Chen, X. Hu, *Science* **2019**, *364*, 1091-1094.

[26] S. Ren, D. Joulié, D. Salvatore, K. Torbensen, M. Wang, M. Robert, C. P. Berlinguette, *Science* **2019**, *365*, 367-369.

[27] L. Lin, H. Li, C. Yan, H. Li, R. Si, M. Li, J. Xiao, G. Wang, X. Bao, *Adv. Mater.* **2019**, *31*, 1903470.

[28] T. Möller, W. Ju, A. Bagger, X. Wang, F. Luo, T. N. Thanh, A. S. Varela, J. Rossmeisl, P. Strasser, *Energy Environ. Sci.* **2019**, *12*, 640-647.

[29] C.-T. Dinh, F. P. García de Arquer, D. Sinton, E. H. Sargent, *ACS Energy Lett.* **2018**, *3*, 2835-2840.

[30] S. Verma, Y. Hamasaki, C. Kim, W. Huang, S. Lu, H.-R. M. Jhong, A. A. Gewirth, T. Fujigaya, N. Nakashima, P. J. A. Kenis, *ACS Energy Lett.* **2018**, *3*, 193-198.

[31] R. Wang, H. Haspel, A. Pustovarenko, A. Dikhtiarenko, A. Russkikh, G. Shterk, D.
Osadchii, S. Ould-Chikh, M. Ma, W. A. Smith, K. Takanabe, F. Kapteijn, J. Gascon, *ACS Energy Lett.* **2019**, *4*, 2024-2031.

[32] X. Wu, Y. Guo, Z. Sun, F. Xie, D. Guan, J. Dai, F. Yu, Z. Hu, Y.-C. Huang, C.-W. Pao, J.-L. Chen, W. Zhou, Z. Shao, *Nat. Commun.* **2021**, *12*, 660.

[33] J. Fu, K. Liu, K. Jiang, H. Li, P. An, W. Li, N. Zhang, H. Li, X. Xu, H. Zhou, *Adv. Sci.* **2019**, *6*, 1900796.

[34] J. Zhong, J.-J. Deng, B.-H. Mao, T. Xie, X.-H. Sun, Z.-G. Mou, C.-H. Hong, P. Yang, S.-D. Wang, *Carbon* **2012**, *50*, 335-338.

[35] T. M. Willey, M. Bagge-Hansen, J. R. I. Lee, R. Call, L. Landt, T. van Buuren, C. Colesniuc, C. Monton, I. Valmianski, I. K. Schuller, *J. Chem. Phys.* **2013**, *139*, 034701.