Hollow CoFe-layered double hydroxide polyhedrons for highly efficient CO₂ electrolysis

Miaosen Yang^{1,2}, Jiaqiang Sun³, Yongji Qin^{4*}, Hui Yang^{5*}, Shusheng Zhang⁶, Xijun Liu^{7*} and Jun Luo⁴

Over the past several decades, the utilization of fossil fuels is responsible for mainly excessive atmospheric carbon dioxide (CO₂) [1–3]. Increased concentration of CO₂ contributes to the major portion of the critical issues faced worldwide, such as global warming and drastic changes in climate. Therefore, it is imperative to develop an alternative technology that is capable of providing an efficient and sustainable pathway to target the neutralization of CO₂ level in the atmosphere. In this regard, both the photoreduction and electroreduction of CO₂ powered by renewable energy to value-added chemicals are eco-friendly and promising approaches for the integrated utilization of CO₂ [4–11]. Till date, the precious metal catalysts have been used to catalyze CO₂ reduction reaction (CO₂RR); nonetheless, their high cost and low earth-abundance significantly impede their wide applications [12–15]. Therefore, various alternative nanostructured catalysts through engineering strategies are highly desirable to boost CO₂RR performance. Among these catalysts, hollow and porous structures, possessing unique advantages such as low density, large specific surface area, and low diffusion resistance, have been developed to efficiently enhance the catalytic performance [16–19]. This is attributed to the fact that their hierarchical porous structures can significantly enhance the diffusion of reactants with small diffusion blockage and short diffusion pathway [20,21].

In particular, hollow structured layered double hydroxides (LDHs) have emerged as potentially promising catalyst candidates, owing to their unique tunable architecture, compositional flexibility, low manufacturing cost, and ease of scale-up [22,23]. However, previous reports on hollow structured LDHs mainly demonstrated their use in the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) for water splitting and other reactions [24–27]. For the CO₂RR, hollow structured LDHs have been only established and successfully used as the photocatalysts [28–30] to capture solar energy in the presence of water vapor and light excitation, and the type of metal cations in LDH nanosheets strongly influenced the product of CO₂ photoreduction. However, to the best of our knowledge, the application of hollow structured LDHs for the electroreduction

of CO₂ has not been reported till date, which is due to their severe hydrogen evolution reaction (HER) [31,32]. In general, LDHs are composed of M–OH layers containing octahedrally coordinated M1 and M2 cations with hydroxyl-terminated lamellae [33,34]. Thus, LDHs offer a lower barrier for producing H₂, rather than that for CO₂ electroreduction.

Ionic liquids (ILs), an environmentally friendly media with low volatility and high ionic conductivity, have attracted significant research attention as novel electrolytes in the CO₂RR field [35,36]. This is attributed to the fact that IL electrolyte can benefit the ionic conductivity and accelerate the electron transport. Moreover, fluorine-functionalized ILs exhibit strong interaction with CO₂, which facilitates the chemisorption of CO₂ followed by its conversion to CO₂^{•−} intermediates, eventually inhibiting HER and effectively improving the electroreduction reaction [37,38]. Motivated by the above-mentioned advantages, a CoFe-LDH hollow polyhedron (denoted as CoFe-LDH/HP) electrode/IL electrolyte system was innovatively constructed in this study for the electroreduction of CO₂. The as-prepared CoFe-LDH/HP catalyst exhibited a Faradaic efficiency (FE) of 86% ± 3% at a moderate applied potential of −0.9 V vs. reversible hydrogen electrode (RHE) for CO production in the [Bmim]BF₄ IL-water electrolyte system (4 wt% water). Moreover, CoFe-LDH/HP could constantly produce CO for more than 30 h with an FE of greater than 85%, indicating its favorable stability. Experimental analyses evidenced that the unique architecture could provide more exposed active sites and faster CO₂RR kinetics, both of which are beneficial for the electrocatalytic improvement. Theoretical calculations further confirmed that the Co–O–Fe moiety in CoFe-LDH/HP not only stabilizes the key intermediate (*COOH), but also decreases the corresponding activation barrier.

The CoFe-LDH/HP electrocatalysts were synthesized by *in situ* etching of self-templated metal-organic frameworks (MOFs) to form hollow structures with simultaneous generation of LDHs, according to the procedure mentioned in our previous reports [39,40] and the schematic illustration of the preparation process is shown in Fig. 1a (see Supplementary information for

¹ School of Chemical Engineering, Northeast Electric Power University, Jilin 132012, China

² Nanchang Institute of Technology, Nanchang 330044, China

³ State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

⁴ Institute for New Energy Materials and Low-Carbon Technologies, Tianjin Key Lab for Photoelectric Materials & Devices, School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China

⁵ School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China

⁶ College of Chemistry, Zhengzhou University, Zhengzhou 450000, China

⁷ MOE Key Laboratory of New Processing Technology for Non-Ferrous Metals and Materials, and Guangxi Key Laboratory of Processing for Non-Ferrous Metals and Featured Materials, School of Physical Science and Technology, Guangxi University, Nanning 530004, China

* Corresponding authors (emails: 383151026@qq.com (Qin Y); y.hui1021@tjut.edu.cn (Yang H); xjliu@tjut.edu.cn (Liu X))

Figure 1 Synthesis and characterization: (a) Schematic illustration of the synthesis procedure of CoFe-LDH/HP, (b) XRD pattern, (c, d) TEM images, (e) HRTEM image, and (f, g) EDX elemental mapping images of CoFe-LDH/HP.

more details). Moreover, the reference sample of CoFe LDH sheet powder (namely CoFe-LDH/SP) was prepared *via* a facile hydrothermal method (Figs S1 and S2). The crystalline structure of the as-obtained CoFe-LDH/HP was characterized by X-ray diffraction (XRD) and the corresponding patterns are shown in Fig. 1b. The diffraction peaks at 10.2° , 34.1° , and 60.2° are ascribed to the (003), (009), and (110) facets of CoFe LDH structure (JCPDS No. 89-0460). Fig. 1c exhibits the transmission electron microscopy (TEM) image of CoFe-LDH/HP, showing its morphological characteristics. Notably, several dispersed polyhedron nanoparticles with the hollow structure are observed from the different contrast in this image. The size of the CoFe-LDH/HP nanoparticle is estimated to be 600 nm with the shell thickness of ~ 40 nm as shown in Fig. 1d.

High-resolution TEM (HRTEM) image reveals the lattice fringes with an interplanar distance of 0.25 nm, which is indexed to the d -spacing of the (009) plane of CoFe LDH (Fig. 1e), further confirming the formation of the CoFe-LDH in these HP nanoparticles. High-angle annular dark-field scanning TEM (HAADF-STEM) and the corresponding energy-dispersive X-ray spectroscopy (EDX) mapping images were recorded to confirm the composition of the CoFe-LDH/HP nanoparticles (Fig. 1f, g). A homogeneous spatial distribution of Co and Fe was observed over a single nanoparticle. Moreover, some regions exhibit the significant concentration of Co and Fe, indicating the presence of eight thick shells for the hollow nanoparticle, further confirming the structure nature of HPs.

To further confirm the chemical states of CoFe-LDH/HP, X-

ray photoelectron spectroscopy (XPS) was utilized. In the high-resolution Co 2p and Fe 2p spectra, Co 2p_{1/2} and Co 2p_{3/2} peaks were observed at 798.5 and 782.5 eV, respectively. [41,42] The fitting peaks at 799 and 783.5 eV correspond to the Co 2p_{1/2} and Co 2p_{3/2} signals of Co³⁺ of Co–O bonds in CoFe-LDH/HP (Fig. 2a), because some Co²⁺ was oxidized to Co³⁺ by the dissolved O₂ and NO₃[−] ions in the solution. The Fe 2p_{1/2} peak was observed at 724.5 eV and deconvoluted into two peaks corresponding to the Fe²⁺ and Fe³⁺ of Fe–O bonds [41,42] in CoFe-LDH/HP (Fig. 2b). Some shoulder peaks corresponding to the satellite peaks of main peaks are also present. The co-existence of the redox pairs of Co²⁺/Co³⁺ and Fe²⁺/Fe³⁺ confirmed the LDH construction in CoFe-LDH/HP [39,40].

The electrocatalytic CO₂ performance of the obtained CoFe-LDH/HP was evaluated in a typical three-electrode setup with CO₂-saturated [Bmim]BF₄-H₂O electrolyte (4 wt% water), as previously reported by our group [43]. Moreover, the CO₂RR activity of CoFe-LDH/SP was measured for comparative analysis. All potentials were reported with respect to the RHE in this study, and each current density was normalized by the geometric area of the electrode. Fig. 3a exhibits the linear sweep voltammetry (LSV) curves, presenting that the CoFe-LDH/HP electrode shows a higher reduction current density of −12.6 mA cm^{−2} at −0.9 V vs. RHE compared with the CoFe-LDH/SP counterpart, indicating better electrocatalytic activity for these HP CoFe-LDHs. The CoFe-LDH/HP achieved the current density of 10 mA cm^{−2} at a potential of −0.85 V vs. RHE (an overpotential of 0.74 V), which is 100 mV lower than that for CoFe-LDH/SP. Compared with Ar-saturated electrolyte (Fig. S3), the higher current density achieved in the CO₂-saturated case reveals that CO₂RR electrolysis severely suppresses the competitive HER. Furthermore, the CO₂RR performance of the CoFe-LDH/HP and CoFe-LDH/SP electrode in 0.1 mol L^{−1} KHCO₃ solution (Fig. S4) was also investigated in this study. Clearly, CoFe-LDH/HP showed a superior selectivity with a high FE ≥ 89% observed for H₂ production in the potential range, thus further confirming that the ILs are essential for achieving efficient CO₂RR and play a key role in producing CO. In contrast, for CoFe-LDH/SP in 0.1 mol L^{−1} KHCO₃, the FE of CO₂RR corresponds to the production of nearly 100-percentage of H₂ without the formation of CO product, indicating CoFe-LDH/SP served as a better HER catalyst in aqueous solution. It confirmed the uniqueness and superiority of this HP structure. These results also demonstrate that the CoFe-LDH/HP cathode and the IL ([Bmim]BF₄) constitute an excellent combination for pro-

ducing CO from electrochemical reduction of CO₂. As discussed above, both CoFe-LDH/HP cathodes and IL ([Bmim]BF₄) electrolytes are crucial for the high yield of CO.

Furthermore, gas chromatography (GC) and ¹H nuclear magnetic resonance (NMR) spectrometry were employed for the quantitative analysis of the CO₂RR products after electrolysis for 2 h at each working potential. Noteworthily, no liquid product was detected (Fig. S5). Fig. 3b shows the dependence of FE for CO selectivity on the applied potentials for both CoFe-LDH/HP and CoFe-LDH/SP. At a low applied potential of −0.6 V vs. RHE, an FE of 41% ± 4% for CO production was observed over the CoFe-LDH/HP electrode. It further increased as the potential became more negative, and the maximum FE (FE_{max}) of 86% ± 3% was achieved at −0.9 V vs. RHE. This performance is comparable to the recently reported best value achieved using transition metal/noble metal-based electrocatalysts (Table S1), such as Co-N-Ni bimetallic sites supported on N-doped porous carbon (96.4% at −0.58 V vs. RHE) [44]; Ag₁-N₃ anchored on porous concave N-doped carbon (95% at −0.37 V vs. RHE) [45] in aqueous solution, and Mo₂C (90% at −2.24 V vs. saturated calomel electrode (SCE)) [46] in IL electrolyte. In contrast, for the CoFe-LDH/SP reference, the FE_{max} of the CO production was 32% ± 3% and this value is significantly less than that of CoFe-LDH/HP. This contrast between the two electrodes with the HP and sheet powder morphology, respectively, clearly indicates that CoFe-LDH/HP serves as a better CO₂RR catalyst, corresponding to the fact that HP structure provides increased number of the catalytically active sites, thereby promoting the CO₂RR performance. It further confirms the unique structural feature of HP and its superiority in CO₂RR toward CO production for CoFe-LDH/HP. To confirm this viewpoint, electrochemically active surface areas of the two electrodes were systematically investigated by the double-layer capacitance (C_{dl}) method [43,47]. The calculated C_{dl} of the CoFe-LDH/HP was 24 mF cm^{−2}, approximately double of that for the CoFe-LDH/SP counterpart (11 mF cm^{−2}) (Fig. 3c), which confirms the exposure of an increased number of catalytically active sites in CoFe-LDH/HP, and thus, promoted the electroreduction activity. Fig. 3d shows the volumetric CO₂ adsorption results for CoFe-LDH/HP and CoFe-LDH/SP, which demonstrate the enhancement of CO₂ adsorption capacity on CoFe-LDH/HP. This favors the CO₂RR, indicating that the CO₂ adsorption is the prerequisite behavior before the CO₂ reduction. Furthermore, CoFe-LDH/HP also showed a higher selectivity toward CO₂ molecules compared with N₂ molecules (Fig. S6). Moreover, the

Figure 2 XPS analysis of CoFe-LDH/HP. (a, b) HRXPS spectra of Co 2p and Fe 2p.

Figure 3 CO₂RR performance of CoFe-LDH/HP in a CO₂-saturated [Bmim]BF₄-H₂O electrolyte. (a) LSV curves at a scan rate of 10 mV s⁻¹, (b) Faradaic efficiencies for CO at various applied potentials, (c) plots of charging current density differences *versus* scan rates, (d) CO₂ adsorption isotherms, (e) Tafel slopes, and (f) stability test at -0.9 V *vs.* RHE and the corresponding FE variation for CO production.

IL electrolyte with fluorine benefits the ionic conductivity and interaction with CO₂ [35–38], which facilitates the activation and the conversion of CO₂ to CO₂^{•-} intermediates and eventually leads to the effective improvement in the electroreduction reaction. The IL [Bmim]BF₄ containing fluorine shows strong interaction with CO₂; therefore, the IL can serve as both robust electrolyte and CO₂ activation promoter. Furthermore, chemical calculations [39] were performed to confirm the strong interaction in the intermediates formed between the cation of the IL and CO₂ after receiving one electron.

In order to further disclose the kinetic mechanism for the enhanced CO₂RR performance on both catalysts, Tafel slope analysis was carried out and shown in Fig. 3e. The CoFe-LDH/HP exhibited a Tafel slope of 140 mV dec⁻¹, which is obviously lower than that of CoFe-LDH/SP (248 mV dec⁻¹), manifesting

faster CO₂RR kinetics on CoFe-LDH/HP. Nyquist plots further evidenced such a rapid electron transfer process (Fig. S7), which clearly showed that CoFe-LDH/HP had the lower interfacial charge-transfer resistance than CoFe-LDH/SP. Further, the obtained Tafel slope of CoFe-LDH/HP is close to a theoretical value (118 mV dec⁻¹), which indicates that the first single-electron transfer from CO₂ to produce *COOH moiety is the rate-determining step (RDS) for the CO₂RR on CoFe-LDH/HP [48,49].

The stability under long-term electrolysis was also examined for evaluating the CO₂ reduction performance (Fig. 3f). The current density of CoFe-LDH/HP was relatively stable at -0.9 V *vs.* RHE even after 30 h. Notably, the corresponding FE for CO production remained persistently greater than 85% during the electrocatalysis. To the best of our knowledge, in an aqueous

Figure 4 DFT calculations: (a) a possible reaction pathway for CO₂RR to CO on CoFe-LDH/HP, (b) differential charge diagrams, and (c) free energy profiles of CO₂RR to CO.

solution, the CoFe-LDH/HP-based catalysts have been reported to be only applied in OER [25–27] and HER [31,32] in the literature. Moreover, herein, CoFe-LDH/HP after the 30-h electrolysis was further characterized and the TEM image clearly showed that CoFe-LDH/HP still maintained the HP morphology (Fig. S8). Furthermore, the XPS analysis of CoFe-LDH/HP confirmed a negligible change for the samples before and after the long-term electrolysis, as shown in Fig. S9, indicating good structural stability of CoFe-LDH/HP. The above-mentioned electrochemical results confirmed that the designed CoFe-LDH/HP catalyst simultaneously owns the high-activity for CO₂RR, excellent selectivity toward CO, and good durability.

Based on the above-mentioned results and the previously reported studies [48,49], the mechanism for CO₂ electroreduction to CO on the CoFe-LDH/HP electrode was proposed (Fig. 4a). The overall process proceeds as follows: initially, the CO₂ molecule adsorbs on the O atom binding with Co and Fe of CoFe-LDH/HP surface and converts to *CO₂, and then couples with a proton and electron to form *COOH intermediate and this step is identified as the RDS. Finally, the *COOH intermediate leaves off H₂O to produce CO.

In order to further provide mechanistic insights into the promoted CO₂RR activity, density-functional-theory (DFT) calculations were performed to obtain the differential charge density and the Gibbs free energy profile of CoFe-LDH/HP and analyze the kinetics of elementary steps in the CO₂RR. The differential charge density of Co–O–Fe bonds in CoFe-LDH/HP

(Fig. 4b) reveals that the charges accumulate around Co–O–Fe bonds and the electrons exchange between the *COOH and Co–O–Fe is notable, indicating that CoFe-LDH/HP favors the stabilization of *COOH intermediate. From the free energy diagrams (Fig. 4c), the *COOH formation was the RDS on CoFe-LDH surface, showing a free energy change of 0.56 eV, in line with Tafel slope analysis. When an extra potential was applied, the RDS energy barrier decreased, indicating an energetic-favorable pathway proceeded on CoFe-LDH to form CO product. Furthermore, the free energy change of CoFe-LDH/HP for the HER was calculated to be –0.18 eV (Fig. S10), which is much lower than that for the CO₂RR, further indicating the key role of the usage of ILs-based electrolyte. Therefore, the relatively low free-energy barrier for the formation of key *COOH species, the large specific surface area from the hollow structure, and the strong chemisorption of CO₂ facilitated by IL confirm the superior CO₂RR performance over CoFe-LDH/HP.

In this study, an active and robust electrocatalyst composed of CoFe LDH HPs was first reported towards CO₂RR in IL electrolyte. It exhibited an improved performance toward CO₂RR with a maximum CO FE of 86% ± 3% at –0.9 V vs. RHE and promising durability (30 h). Systematic characterizations demonstrated that such a unique architecture could expose more electrocatalytic active sites and promote interfacial charge/mass transfer, simultaneously. Theoretical calculations further reveal that the Co–O–Fe moiety not only favors the stabilization of the key *COOH intermediate, but also owns a small activation

barrier for the RDS. This attempt presented herein sheds a bright light on the development of LDH HPs for CO₂ fixation, and other electrocatalytic processes such as water splitting, CO reduction, and nitrogen reduction.

Received 16 August 2021; accepted 3 November 2021;
published online 13 December 2021

- 1 Zheng Y, Vasileff A, Zhou X, *et al.* Understanding the roadmap for electrochemical reduction of CO₂ to multi-carbon oxygenates and hydrocarbons on copper-based catalysts. *J Am Chem Soc*, 2019, 141: 7646–7659
- 2 Yang H, Han N, Deng J, *et al.* Selective CO₂ reduction on 2D mesoporous Bi nanosheets. *Adv Energy Mater*, 2018, 8: 1801536
- 3 Gao T, Xie T, Han N, *et al.* Electronic structure engineering of 2D carbon nanosheets by evolutionary nitrogen modulation for synergizing CO₂ electroreduction. *ACS Appl Energy Mater*, 2019, 2: 3151–3159
- 4 Wang L, Chen W, Zhang D, *et al.* Surface strategies for catalytic CO₂ reduction: From two-dimensional materials to nanoclusters to single atoms. *Chem Soc Rev*, 2019, 48: 5310–5349
- 5 Yang C, Wang Y, Qian L, *et al.* Heterogeneous electrocatalysts for CO₂ reduction. *ACS Appl Energy Mater*, 2021, 4: 1034–1044
- 6 Wang X, Chen Z, Zhao X, *et al.* Regulation of coordination number over single Co sites: Triggering the efficient electroreduction of CO₂. *Angew Chem Int Ed*, 2018, 57: 1944–1948
- 7 Ji S, Qu Y, Wang T, *et al.* Rare-earth single erbium atoms for enhanced photocatalytic CO₂ reduction. *Angew Chem Int Ed*, 2020, 59: 10651–10657
- 8 Li Y. Hybrid atomic layers based electrocatalyst converts waste CO₂ into liquid fuel. *Sci China Mater*, 2016, 59: 1–3
- 9 Li Y. Photosynthetic conversion of CO₂ to acetic acid by an inorganic-biological hybrid system. *Sci China Mater*, 2016, 59: 93–94
- 10 Ji Y, Shi Y, Liu C, *et al.* Plasma-regulated N-doped carbon nanotube arrays for efficient electrosynthesis of syngas with a wide CO/H₂ ratio. *Sci China Mater*, 2020, 63: 2351–2357
- 11 Yang D, Wang G, Wang X. Photo- and thermo-coupled electrocatalysis in carbon dioxide and methane conversion. *Sci China Mater*, 2019, 62: 1369–1373
- 12 Cai Z, Zhang Y, Zhao Y, *et al.* Selectivity regulation of CO₂ electroreduction through contact interface engineering on superwetting Cu nanoarray electrodes. *Nano Res*, 2019, 12: 345–349
- 13 Zhou Y, Zhou R, Zhu X, *et al.* Mesoporous PdAg nanospheres for stable electrochemical CO₂ reduction to formate. *Adv Mater*, 2020, 32: 2000992
- 14 Pan Y, Lin R, Chen Y, *et al.* Design of single-atom Co–N₅ catalytic site: A robust electrocatalyst for CO₂ reduction with nearly 100% CO selectivity and remarkable stability. *J Am Chem Soc*, 2018, 140: 4218–4221
- 15 Yang H, Wu Y, Li G, *et al.* Scalable production of efficient single-atom copper decorated carbon membranes for CO₂ electroreduction to methanol. *J Am Chem Soc*, 2019, 141: 12717–12723
- 16 Zhang P, Wang S, Guan BY, *et al.* Fabrication of CdS hierarchical multi-cavity hollow nanofibers for efficient visible light CO₂ reduction. *Energy Environ Sci*, 2019, 12: 164–168
- 17 Li D, Liu T, Yan Z, *et al.* MOF-derived Cu₂O/Cu nanospheres anchored in nitrogen-doped hollow porous carbon framework for increasing the selectivity and activity of electrochemical CO₂-to-formate conversion. *ACS Appl Mater Interfaces*, 2020, 12: 7030–7037
- 18 Tan D, Lee W, Kim YE, *et al.* SnO₂/ZnO composite hollow nanofiber electrocatalyst for efficient CO₂ reduction to formate. *ACS Sustain Chem Eng*, 2020, 8: 10639–10645
- 19 Huo H, Liu D, Feng H, *et al.* Double-shelled Cu₂O/MnO_x mesoporous hollow structure for CO₂ photoreduction with enhanced stability and activity. *Nanoscale*, 2020, 12: 13912–13917
- 20 Qin Y, Han X, Li Y, *et al.* Hollow mesoporous metal-organic frameworks with enhanced diffusion for highly efficient catalysis. *ACS Catal*, 2020, 10: 5973–5978
- 21 Lin X, Wang S, Tu W, *et al.* MOF-derived hierarchical hollow spheres composed of carbon-confined Ni nanoparticles for efficient CO₂ methanation. *Catal Sci Technol*, 2019, 9: 731–738
- 22 Li P, Wang M, Duan X, *et al.* Boosting oxygen evolution of single-atomic ruthenium through electronic coupling with cobalt-iron layered double hydroxides. *Nat Commun*, 2019, 10: 1711
- 23 Cai M, Liu Q, Xue Z, *et al.* Constructing 2D MOFs from 2D LDHs: A highly efficient and durable electrocatalyst for water oxidation. *J Mater Chem A*, 2020, 8: 190–195
- 24 Chen S, Duan J, Jaroniec M, *et al.* Three-dimensional N-doped graphene hydrogel/NiCo double hydroxide electrocatalysts for highly efficient oxygen evolution. *Angew Chem Int Ed*, 2013, 52: 13567–13570
- 25 Gu H, Shi G, Chen HC, *et al.* Strong catalyst-support interactions in electrochemical oxygen evolution on Ni-Fe layered double hydroxide. *ACS Energy Lett*, 2020, 5: 3185–3194
- 26 Fagiolarì L, Bini M, Costantino F, *et al.* Iridium-doped nanosized Zn-Al layered double hydroxides as efficient water oxidation catalysts. *ACS Appl Mater Interfaces*, 2020, 12: 32736–32745
- 27 Jung E, Kim JK, Choi H, *et al.* Aqueous-phase synthesis of layered double hydroxide nanoplates as catalysts for the oxygen evolution reaction. *Dalton Trans*, 2018, 47: 17342–17348
- 28 Xiong X, Zhao Y, Shi R, *et al.* Selective photocatalytic CO₂ reduction over Zn-based layered double hydroxides containing tri or tetravalent metals. *Sci Bull*, 2020, 65: 987–994
- 29 Dewangan N, Hui WM, Jayaprakash S, *et al.* Recent progress on layered double hydroxide (LDH) derived metal-based catalysts for CO₂ conversion to valuable chemicals. *Catal Today*, 2020, 356: 490–513
- 30 Chen G, Gao R, Zhao Y, *et al.* Alumina-supported CoFe alloy catalysts derived from layered-double-hydroxide nanosheets for efficient photothermal CO₂ hydrogenation to hydrocarbons. *Adv Mater*, 2018, 30: 1704663
- 31 Jia X, Zhao Y, Chen G, *et al.* Ni₃FeN nanoparticles derived from ultrathin NiFe-layered double hydroxide nanosheets: An efficient overall water splitting electrocatalyst. *Adv Energy Mater*, 2016, 6: 1502585
- 32 Yang H, Chen Z, Guo P, *et al.* B-doping-induced amorphization of LDH for large-current-density hydrogen evolution reaction. *Appl Catal B-Environ*, 2020, 261: 118240
- 33 Mohapatra L, Parida K. A review on the recent progress, challenges and perspective of layered double hydroxides as promising photocatalysts. *J Mater Chem A*, 2016, 4: 10744–10766
- 34 Tran NV, Tieu AK, Zhu H. First-principles molecular dynamics study on the surface chemistry and nanotribological properties of MgAl layered double hydroxides. *Nanoscale*, 2021, 13: 5014–5025
- 35 Zhang Z, Song J, Han B. Catalytic transformation of lignocellulose into chemicals and fuel products in ionic liquids. *Chem Rev*, 2017, 117: 6834–6880
- 36 Ren W, Tan X, Chen X, *et al.* Confinement of ionic liquids at single-Ni-sites boost electroreduction of CO₂ in aqueous electrolytes. *ACS Catal*, 2020, 10: 13171–13178
- 37 Sun X, Lu L, Zhu Q, *et al.* MoP nanoparticles supported on indium-doped porous carbon: Outstanding catalysts for highly efficient CO₂ electroreduction. *Angew Chem Int Ed*, 2018, 57: 2427–2431
- 38 Huan TN, Simon P, Rousse G, *et al.* Porous dendritic copper: an electrocatalyst for highly selective CO₂ reduction to formate in water/ionic liquid electrolyte. *Chem Sci*, 2017, 8: 742–747
- 39 Qin Y, Wang F, Shang J, *et al.* Ternary NiCoFe-layered double hydroxide hollow polyhedrons as highly efficient electrocatalysts for oxygen evolution reaction. *J Energy Chem*, 2020, 43: 104–107
- 40 Qin Y, Wang B, Qiu Y, *et al.* Multi-shelled hollow layered double hydroxides with enhanced performance for the oxygen evolution reaction. *Chem Commun*, 2021, 57: 2752–2755
- 41 Yang Y, Ou Y, Yang Y, *et al.* Modulated transition metal-oxygen covalency in the octahedral sites of CoFe layered double hydroxides with vanadium doping leading to highly efficient electrocatalysts. *Nanoscale*, 2019, 11: 23296–23303
- 42 Xu H, Yuan Y, Liao Y, *et al.* [MoS₄]²⁻ cluster bridges in Co-Fe layered double hydroxides for mercury uptake from S-Hg mixed flue gas. *Environ Sci Technol*, 2017, 51: 10109–10116
- 43 Liu X, Yang H, He J, *et al.* Highly active, durable ultrathin MoTe₂ layers for the electroreduction of CO₂ to CH₄. *Small*, 2018, 14: 1704049

- 44 Sui R, Pei J, Fang J, *et al.* Engineering Ag-N_x single-atom sites on porous concave N-doped carbon for boosting CO₂ electroreduction. *ACS Appl Mater Interfaces*, 2021, 13: 17736–17744
- 45 Pei J, Wang T, Sui R, *et al.* N-bridged Co-N-Ni: New bimetallic sites for promoting electrochemical CO₂ reduction. *Energy Environ Sci*, 2021, 14: 3019–3028
- 46 Attanayake NH, Banjade HR, Thenuwara AC, *et al.* Electrocatalytic CO₂ reduction on earth abundant 2D Mo₂C and Ti₃C₂ MXenes. *Chem Commun*, 2021, 57: 1675–1678
- 47 Gao S, Lin Y, Jiao X, *et al.* Partially oxidized atomic cobalt layers for carbon dioxide electroreduction to liquid fuel. *Nature*, 2016, 529: 68–71
- 48 Xu J, Lai S, Hu M, *et al.* Semimetal 1H-SnS₂ enables high-efficiency electroreduction of CO₂ to CO. *Small Methods*, 2020, 4: 2000567
- 49 Hsieh YC, Senanayake SD, Zhang Y, *et al.* Effect of chloride anions on the synthesis and enhanced catalytic activity of silver nanocoral electrodes for CO₂ electroreduction. *ACS Catal*, 2015, 5: 5349–5356

Acknowledgements This work was supported by the Research Fund of State Key Laboratory for Marine Corrosion and Protection of Luoyang Ship Material Research Institute (LSMRI) (KF190411), and Tianjin Natural Science Foundation (18JCQNJC77100). The authors also acknowledge Beijing PARATERA Tech CO., Ltd. for providing HPC resources that have contributed to the research results reported in this paper.

Author contributions Liu X and Qin Y designed the project. Yang M and Sun J performed the main experiments and Yang H wrote this manuscript. Zhang S and Luo J helped to analyze the data, discussed the results and contributed to the theoretical analysis. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

Miaosen Yang received her PhD degree in chemical engineering and technology from Beijing University of Chemical Technology in 2012. Her current scientific interests focus on the design, preparation and application of inorganic functional materials and organic-inorganic composite materials.

Hui Yang received her PhD degree in materials science in 2013 from the South China University of Technology (SCUT). She currently conducts scientific research at Tianjin University of Technology. Her current research mainly focuses on the synthesis of advanced nanomaterials for catalytic applications.

Xijun Liu received his PhD degree from the College of Science, Beijing University of Chemical Technology in 2014. His current scientific interests focus on nanomaterials, heterogeneous catalysis, and materials design for catalysts and energy conversion/storage.

钴铁层状双金属氢氧化物空心多面体用于高效电催化二氧化碳还原

杨淼森^{1,2}, 孙甲强³, 秦永吉^{4*}, 杨慧^{5*}, 张书胜⁶, 刘熙俊^{7*}, 罗俊⁴

摘要 可再生能源驱动电催化二氧化碳还原制备高附加值化学燃料, 是一种实现二氧化碳资源化的有效途径. 以金属有机骨架(MOF)为模板制备的层状双金属氢氧化物空心多面体已成为当前电催化领域的热门材料. 然而, 该类材料的高析氢活性严重阻碍了其在电催化二氧化碳还原中的应用. 基于此, 本文报道了一种在离子液体电解液中可高效稳定电催化二氧化碳还原的钴铁层状双金属氢氧化物空心多面体(CoFe LDH/HP), 其最大法拉第转换效率可达86% ± 3% (−0.9 V相对于可逆氢电极), 且可连续电解30 h. 实验结果表明此CoFe LDH/HP因其独特的空心结构可暴露更多的活性位点, 从而具有更快的电催化二氧化碳还原动力学; 理论计算表明CoFe LDH/HP中Co–O–Fe键有利于稳定关键中间体(*COOH)并降低相应的活化势垒. 本研究可为其他层状双金属氢氧化物用于二氧化碳固定的设计提供参考.