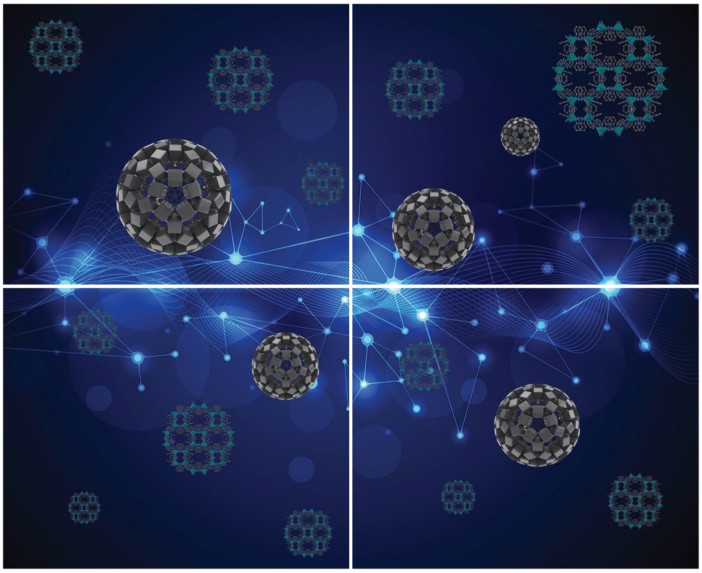
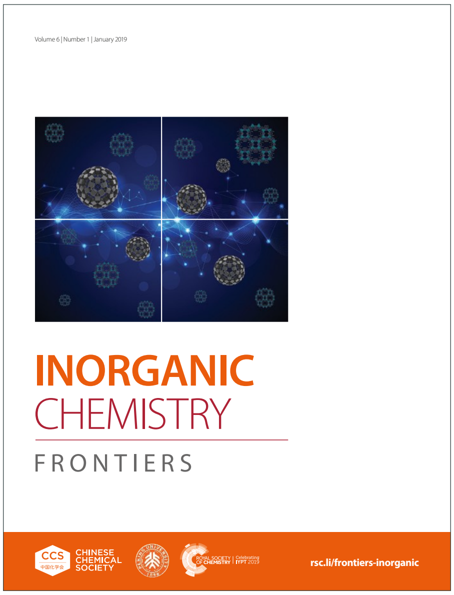
INORGANIC CHEMISTRY

FRONTIERS

Accepted Manuscript





CHINESE CHEMICAL SOCIETY
ROYAL SOCIETY OF CHEMISTRY
rsc.li/frontiers-inorganic

Cu-Ni Alloy Decorating N-Doped Carbon Nanosheets toward High-performance Electrocatalysis of Mildly Acidic CO_2 Reduction

Weifan Pan[a,b], Peng Wang[a], Linfeng Fan[a], Kai Chen[a], Luocai Yi[a], Junheng Huang[a], Pingwei Cai[a], Xi Liu[a], Qingsong Chen[a], Genxiang Wang[a*], Zhenhai Wen[a*]

[a] *CAS Key Laboratory of Design and Assembly of Functional Nanostructures, and Fujian Provincial Key Laboratory of Materials and Techniques toward Hydrogen Energy, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, China*

[b] *University of Chinese Academy of Sciences, Bejing 100049, China*

Abstract

Electrochemical CO_2 reduction to value-added chemicals or fuels is a prospective strategy for facilitating closing carbon loop. However, there still exist challenges in developing efficient catalysts and optimizing the electrolyzer components to meet industrial applications. Herein, a nitrogen-doped "willow leaf" shaped carbon nanosheets modified with Cu-Ni alloy (CuNi-N-CNS) is designed for electrochemical CO_2 reduction reaction (CO_2RR), which shows high faradaic efficiency for CO of almost 90% at a wide potential window ranging from -0.8 V to -1.0 V, and robust durability with almost 100% of its initial selectivity after 36 hours of electrolysis in H-type cell. Moreover, we evaluate its electrocatalytic activity in a self-assembly flow cell in mildly acid catholyte (CO_2-saturated 3 M KCl solution, pH = 4.25), which can achieve a commercially viable current density of 420 mA cm^{-2} at -1.0 V *versus* reversible hydrogen electrode (*vs.* RHE) with CO selectivity above 95%. Experimental characterization and electrochemical analysis reveal that the synergistic effects of ultra-thin "willow leaf" structure and bimetallic alloy modification can not only increase electron transport efficiency, but also decrease the reaction energy barrier of COOH* and promote the formation of CO.

Keywords: Electrocatalysts, Carbon nanosheets, Cu-Ni alloy, CO_2 reduction, Acid media

Introduction

Massive carbon dioxide emissions from excessive utilization of fossil fuels have led to widespread environment issues.[1-3] Up to now, many approaches has been adequately investigated to reduce the concentration of carbon dioxide in the atmosphere, among which, electrocatalytic CO_2 reduction reaction (CO_2RR) driven by renewable electrical energy represents a realizable and convenient carbon-neutral pathway for producing valuable carbon-based chemical feedstocks.[4-6] However, the extremely stable C=O bond (806 KJ mol^{-1}) in CO_2 and the competing hydrogen evolution reaction in the aqueous phase hinder the activation of $CO_{2.}$[7,8] Besides, owing to the complex multiple protons and electrons transfer processes during CO_2 reduction, the variety of the products from CO_2 reduction adds extra difficulties for controlling its selectivity.[9-11] Among these possible products, CO is a more accessible product ($CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$, -0.11 V *vs.* RHE) than other multi-carbon products in terms of reaction kinetics and is also an important raw material in industrial production.[12-14] Thus, elevating the conversion efficiency of CO_2 reduction into CO is crucial to promote the actual applications of CO_2RR.[15,16]

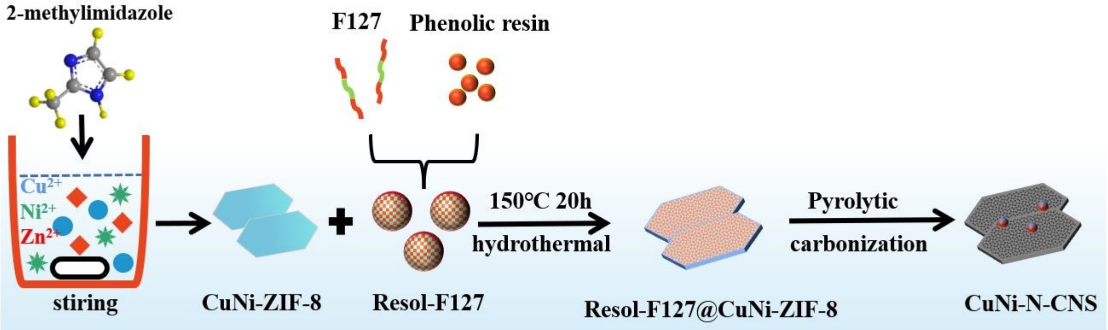
On one hand, designing effective catalysts for CO_2RR is still at the center of promoting the conversion efficiency of CO_2RR.[17,18] The electrocatalytic performance of catalysts is largely affected by their structure, crystal surface, and number of active sites.[19-21] In earlier times, a variety of nano-structured Ag, Au and Pd-based electrocatalysts have been studied due to their high selectivity and relatively low overpotential for CO_2 to CO in aqueous solution.[22-25] But the scarcity of noble metal always limits their practical use. In this regard, replacing noble metal catalysts with non-noble carbon-based metal materials is a promising way towards sustainable CO_2RR.[26] Metal-organic Framework derived carbon-based materials hold great promise for applications in CO_2RR due to the exceptionally high surface areas, flexible electronic structure, multiple active sites and designable morphology.[27,28] The single metal atom sites anchored on carbon materials derived from MOF templates were widely prepared for CO_2RR and display excellent activity and selectivity for CO_2 reduction.[29] Compared with these carbon-based materials anchored with single sites, carbon-based materials modified with metal alloys receives less attention but are still worthy of being studied owing to their rich components with tunable electronic structure and multicomponent cooperative effect.[30] For instance, Liu [31] reported an ultrathin porous g-C_3N_4 nanosheets modified with AuCu alloy NPs catalyst. The charge transfer from Au to Cu in the alloy enriches Cu with excessive negative charges, which promotes the formation of intermediates *CO on the surface, thus increasing the yield of C_2 products. And Roy's [32] group found that the carbon supported PtZn nano-alloy can efficiently convert CO_2 to CH_3OH, resulting from the intermetallic alloy's ability to fine-tune electron transport properties and structures. Though desirable performance has been achieved on these reported carbon-based alloy catalysts, there is still room for designing other novel carbon-based catalysts with excellent catalytic performance.

On the other hand, the CO_2RR performance of catalysts are mainly investigated in H-cells or flow cell in neutral or alkaline electrolytes at present time, which exist problems like CO_2 mass transport limitation, carbonatation, and poor stability.[33] In these H-cells, the limited solubility and mass diffusion of CO_2 seriously limit its conversion rate.[15,34-36]. In the widely reported gas diffusion electrode (GDE) based flow cells, the mass transport limitation problem can be avoided by constructing a gas-liquid-solid three-phase reaction interface and the reaction rate are greatly improved.[37] However, the commonly used alkaline electrolyte and the high local pH of the reaction interface at large current density accelerate the carbonation and flooding of the flow cell, leading to poor stability and rather low CO_2 utilization.[38,39] In comparison, the CO_2RR performed in acid media has been emerged as a promising strategy to circumvent the carbonation and its induced problems. Though hydrogen evolution reaction may be more favorable in acidic conditions， it can be suppressed by suitable adjusting the reaction interface of electrode and the pH of catholyte. For example, Sargent [40] carried out CO_2RR over copper in electrolyte with pH <1, which achieved a single-pass CO_2 utilization of 77% and a conversion efficiency of 50% toward multi-carbon products at a current density of 1.2 A cm^{-2}. Besides, Monteiro [41] investigated the feasibility of CO_2 electrolysis with 10 cm^2 gold gas diffusion electrodes at pH of 2-4, which can obtain CO faradaic efficiencies between 80-90%, with a 30% improvement of the overall process energy efficiency in comparison with neutral media. The research of CO_2RR in acidic electrolyte open up unique routine for CO_2RR, and studying the CO_2RR performance of various catalysts in acidic electrolyte provides references for solving practical application of CO_2RR. [42-46].

Herein, we strategically design a nitrogen-doped “willow leaf” shaped carbon nanosheets modified with Cu-Ni alloy (CuNi-N-CNS) through a facile solvothermal-evaporation-pyrolysis process. The Cu-Ni alloy nanoparticles are encapsulated in the *in situ* formed carbon layers on the ultra-thin lancet nanosheets. Such unique composite structure can greatly improve the catalytic activity for CO_2RR, which achieves a high CO faradaic efficiency over 90% for the CO_2 electroreduction at a potential window of -0.8 V to -1.0 V *vs.* RHE in H-Cell. Besides, the CO_2RR performance of the prepared catalyst was further investigated in a home-made flow cell with CO_2-saturated 3 M KCl solution as catholyte (pH = 4.25), which can provide a mildly acidic environment to prevent carbonation and achieve high current density (420 mA cm^{-2}) at -1.0 V with FE_{CO} above 95%. Consequently, our study affords an innovative idea of designing metal-based catalysts for CO_2RR and provides the possibility for its industrialization.

Results and Discussion

Catalyst preparation and characterization. As shown in scheme 1, the catalyst was synthesized by a metal-organic framework (MOF) assisted method. The CuNi doped zeolitic imidazolate framework-8 (CuNi-ZIF-8) suspension was first fabricated by mixing zinc nitrate, copper nitrate, nickel nitrate and 2-methylimidazole in DI water *via* vigorously stirring, and Resol-F127 solution was synthesized by heating phenolic resin and surfactant F127. Then, the nitrogen-doped ultra-thin carbon nanosheets modified with Cu-Ni alloy, named as CuNi-N-CNS, was obtained *via* two steps of hydrothermal and pyrolysis reactions (for synthesis details see supporting information and Figure S1 and S2). Remarkably, gram-scale catalyst can be obtained *via* simply increasing feeding reagents (Figure S3) during synthetic processes, indicating the feasibility of scalable synthesis. For comparison, we probed the effect of raw material ratios on the structure of CuNi-N-CNS catalyst to determine the optimal one. And the Ni-N-CNS, Cu-N-CNS and N-CNS were also synthesized as controlled samples through the similar method (Figure S2).



Scheme 1. Schematic representation for the synthetic method of the CuNi-N-CNS samples.

The morphology characterizations of CuNi-N-CNS were conducted by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As displayed in Figure 1a-c, the as-prepared catalyst maintains the uniform structure of ultra-thin "willow leaf" shaped nanosheets. In contrast, samples without Resol-F127 composite would lose the "willow leaf" structure and agglomerate after pyrolysis (Figure S4). It could be inferred that Resol-F127 plays a crucial role in the whole reaction process. Specifically, in the hydrothermal process, Resol-F127 would attach to CuNi-ZIF-8 nanosheets due to the surface induction effect and cure with increasing temperature. Then it *in situ* formed a carbon layer after undergoing the pyrolysis at 900 ℃, which encapsulates Cu-Ni alloy nanoparticles as revealed by the TEM images (Figure 1d). And in the HRTEM images of the calcined sample (Figure e-f), the well-defined lattice streaks with d-spacing of 2.24 and 1.96 Å could be safely indexed to the (111) and (200) planes of Cu-Ni alloy, respectively. From the element mapping images (Figure 1g), it can be demonstrated that Cu, Ni, C and N species are homogeneously distributed in the carbon substrate and CuNi alloy was clearly distributed on the surface. Complementally, as revealed by the inductively coupled plasma optical emission spectrometry (ICP-OES), the Cu and Ni contents of CuNi-N-CNS are determined to be 2.60 and 2.39

wt%, respectively. (Table S1). EDS and XPS data are further used to assist in the determination of Cu and Ni contents (Figure S5-S12). And the N_2 sorption isotherms (Figure S13a) furtherly verify that the CuNi-N-CNS possesses a porous structure with large specific surface area of 984.21 m^2g^{-1}. The pore size distribution (Figure S13b) peaks of the CuNi-N-CNS at ca. 0.68 nm (~2.1 times of the dynamic diameter of CO_2 molecules) reveal its micropores structure which could enhance the capture of CO_2, resulting in CO_2 enrichment around the active sites.

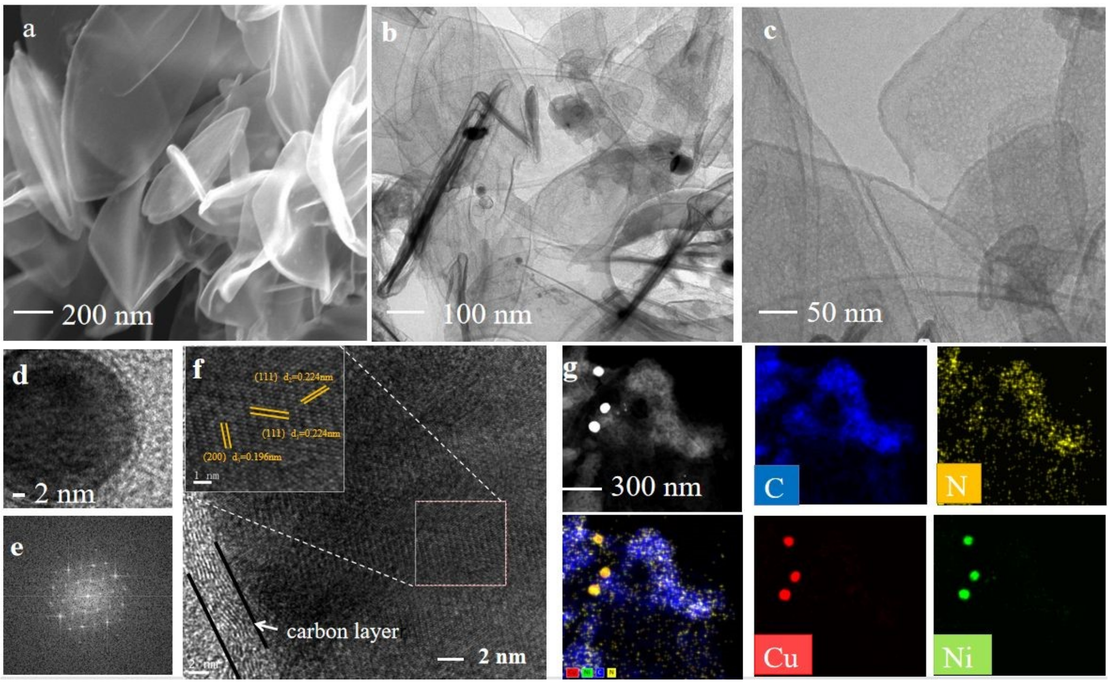


Figure 1. (a) High-resolution SEM patterns of CuNi-N-CNS. (b-f) TEM images of CuNi-N-CNS at different resolutions. (g) EDS mapping of C, N, Cu and Ni elements.

The X-ray diffraction (XRD) patterns exhibit that all as-prepared catalysts contain the characteristic peak of carbon at 22° and 44° (Figure S13d). More concretely, for CuNi-N-CNS, another three existing diffraction peaks at 43.6°, 50.8°, 74.7°, which corresponded to the (111), (200) and (220) facets of $Cu_{0.81}Ni_{0.19}$ alloy (JCPSD no. 47-1406), respectively. For Ni-N-CNS and Cu-N-CNS, there are metallic Ni and Cu in the corresponding XRD patterns (Figure S13d). X-ray photoelectron spectroscopy (XPS) was then carried out to characterize the catalyst composition and elemental states on the surface (Figure 2b). The high-resolution XPS N1s spectrum can be deconvoluted into pydidinic (~398.43 eV), M-N (~399.26 eV), pyrrolic (~400.92 eV), graphitic (~402.40 eV), and oxidized (~404.62 eV) species (Figure 2c). In the high-resolution Ni 2p spectrum (Figure 2d), the Ni $2p_{3/2}$ peak of CuNi-N-CNS can be fitted into the Ni^0 (855.03 eV) peak and Ni^{2+} (856.39 eV) peak.[1,10-13] Moreover, the Cu 2p XPS spectrum in Figure 2e reveals that the Cu $2p_{3/2}$ peak of CuNi-N-CNS can be fitted into Cu/Cu^+ (932.26 eV) peak and Cu^{2+} (934.82 eV) peak.[1,13,17] Besides, the energy shift in the spectrum of CuNi-N-CNS compared with the single-metal and non-metal counterparts suggest the strong electronic effect between Cu and Ni atoms (Figure S14-17). In Figure 2f, Raman spectroscopy confirms the ratio of the defects and graphitization (I_D/I_G) with a D peak at 1351 cm^{-1} and a G peak at 1580 cm^{-1}, respectively. The intensity ratio I_D/I_G was widely used to indicate the activity and conductivity of the catalyst. Obviously, CuNi-C-CNS shows a relatively higher I_D/I_G ratio of 1.08 in comparison with those of other counterparts. The higher D peak in CuNi-N-CNS could be essentially ascribed to the plentiful O cavities and high level of defects, which resulted in increased active sites for improving CO_2RR performance.

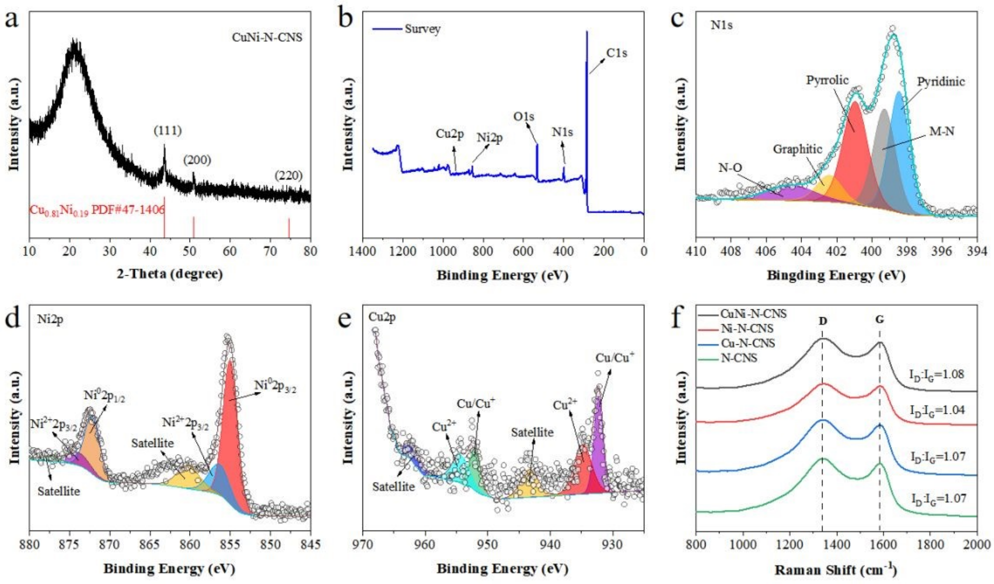


Figure 2. (a) X-ray diffraction patterns of CuNi-N-CNS. (b) The survey XPS spectrums of CuNi-N-CNS. (c-e) High-resolution spectrums of N1s, Ni2p and Cu2p of CuNi-N-CNS. (f) Raman spectrums of CuNi-N-CNS, Ni-N-CNS, Cu-N-CNS and N-CNS samples.

These above characterization results reveal that the composite structure is carbon nanosheets with abundant Cu-Ni alloys wrapped in Cu/Ni-N_x-carbon (N-C@CuNi alloy) structure at the surface. For these CuNi-N-CNS catalysts, the Cu-Ni alloys cannot be effectively removed by acid etch due to the covering of carbon layer. Although these embedded Cu-Ni alloys cannot directly involve the CO_2RR, the electronic interaction between Cu-Ni alloys and carbon nanosheets can enhance the activity of Cu/Ni-N_x-C_y coordination for CO_2RR. Furthermore, recent reported works have suggested that the secondary metal Cu can not only positively shift the Ni 3d orbital energy to the Fermi level and thus accelerate the step of *COOH formation, but also cause a considerable reaction barrier for water dissociation and thus decelerate the competing hydrogen evolution reaction.[1,13]

Electrochemical performance for CO_2RR in H-cell. The electrocatalytic CO_2RR activity of the developed

CuNi-N-CNS catalyst was firstly investigated in a typical H-cell with CO_2 saturated 0.5 M $KHCO_3$ solution as the electrolyte. For comparison, the CO_2RR activities of Ni-N-CNS, Cu-N-CNS and N-CNS were also evaluated. As revealed by linear sweep voltammetry (LSV) curves in Figure 3a, the CuNi-N-CNS exhibits a remarkably higher current density from -0.18 to -1.18 V *vs.* RHE compared with these controlled sample, giving current densities of 18 mA cm^{-2} at -0.78 V and 42 mA cm^{-2} at -1.18 V. Notably, the current density of CuNi-N-CNS increases faster than that of Ni-N-CNS at high potential, indicating the CuNi alloy may play key role in elevating conductivity of the CuNi-N-CNS. Furthermore, the catalytic selectivity of these catalysts was also examined by chronoamperometry technique. The gas and liquid products were monitored by gas chromatography (GC) and nuclear magnetic resonance (NMR), which indicated that CO and H_2 were the only two products of the reduction and there was almost no liquid product (Figure S18). Figure 3b compares the Faradaic efficiency of CO (FE_{CO}) for these prepared catalysts in the potential range from -0.6 V to -1.1 V. Among them, CuNi-N-CNS exhibits impressively high selectivity (> 90%) for CO product at a wide potential window (-0.8 V to -1.0 V). While the peak FE_{CO} of Cu-N-CNS and N-CNS are 58% and 10% at -0.7 V, far lower than that of CuNi-N-CNS. Figure 3c shows the dependence of the CO partial current density (j_{CO}) on applied potential. The CuNi-N-CNS delivers much higher j_{CO} with respect to the other catalysts, and achieves a current density of 11mA cm^{-2} at -0.8 V, which is 1.2, 5, 3 times higher than those of Ni-N-CNS, Cu-N-CNS and N-CNS, respectively. The Turnover frequency (TOF) of CO production for the developed CuNi-N-C catalyst was calculated based on the current density of CO_2RR and FE_{CO}, which exhibits an exceptionally high TOF of 879 h^{-1} at -1.1 V, indicating the highly enhanced activity of bimetal-nitrogen sites. And the Nyquist plot of CuNi-N-CNS exhibits the smallest semicircle among the prepared catalysts, which suggests its fast interfacial charge-transfer process during CO_2RR process (Figure 3d). Besides, to further compare the intrinsic activity of these catalysts, cyclic voltammetry (CV) measurements were performed to determine their electrochemical active surface areas (ECSAs) via evaluation of double-layer capacitance (C_{dl}). CuNi-N-CNS showed the highest ECSAs of 244 mF cm^{-2}, which was 1.3, 1.5 and 2.4-fold of Ni-N-CNS, Cu-N-CNS and N-CNS (Figure S19), verifying more active catalytic sites in CuNi-N-CNS. To uncover the reaction kinetics on different catalysts, Tafel plots were further carried out and analyzed. As shown in Figure 3e, Tafel slopes of 73.9, 98.3, 84.2 and 113.1 mV $decade^{-1}$ were found over CuNi-N-CNS, Ni-N-CNS, Cu-N-CNS and N-CNS, respectively. The lowest Tafel slope of CuNi-N-CNS further confirms its accelerated CO_2-to-CO conversion kinetics. Moreover, from the Tafel slope results, one can know that the first electron transfer ($CO_2 + H^+ + e^- \rightarrow *COOH$), which generates surface adsorbed *COOH intermediate, is the rate-determining step for CO_2RR. The significantly lowered Tafel slope of CuNi-N-CNS indicates the kinetics of this step may be greatly enhanced. Beyond that, the CuNi-N-CNS also exhibits excellent durability for CO_2RR, maintaining almost 100% of the initial FE for CO production at -0.8 V after 36 hours of continuous electrolysis in H-type cell (Figure 3f). The stability of the prepared catalyst was further confirmed through checking the SEM and XRD of the catalyst after long-term electrolysis. The XRD patterns of catalysts of the similar mass before and after stability test showed no obvious changes (Figure S20, peaks of $Cu_{0.81}Ni_{0.19}$ are not so observable owing to the very small amount of samples). The SEM images of the sample after electrolysis also display the morphology is well preserved, and the element mapping of the post-reaction sample shows the homogeneous distribution of elements and the preservation of CuNi alloy particles (Figure S20 and S21). The above results confirmed the excellent stability of the prepared catalyst. The fact that the CuNi-N-CNS catalyst outperformed the counterparts clearly points out the crucial role of the bimetallic alloy in the reaction.

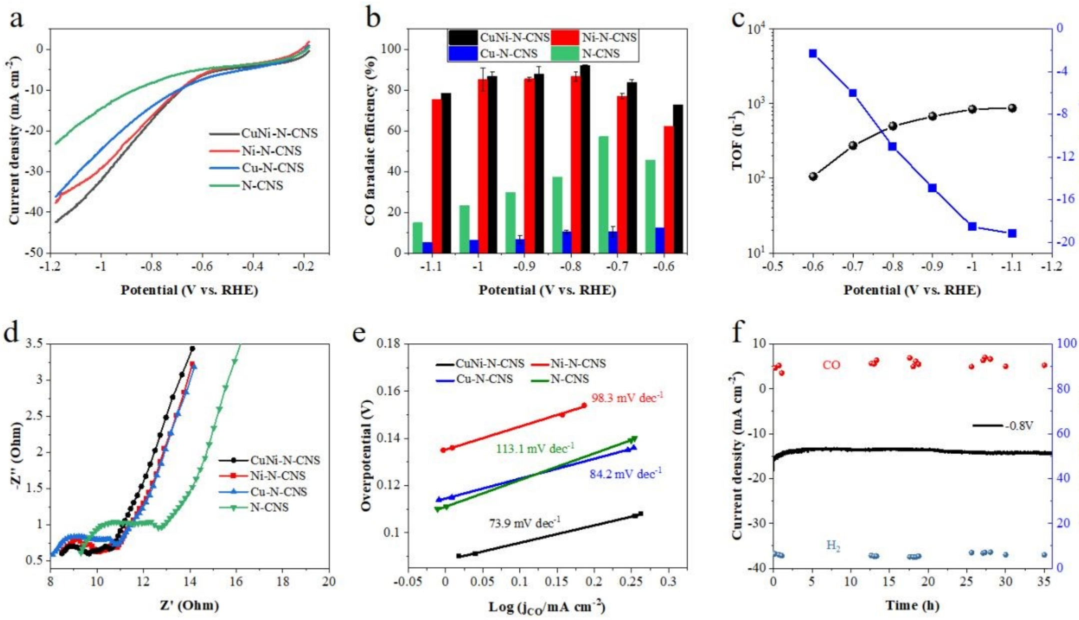


Figure 3. (a) LSV curves obtained in CO_2-saturated 0.5 M $KHCO_3$ solution (pH=7.2) in H-type cell. (b) Faradaic efficiency for CO production at various applied potentials. (c) TOF of CuNi-N-CNS at various applied potentials. The blue curve is j_{CO}. (d) Nyquist plots. (e) Tafel plots of the samples. (f) Current-time response of CuNi-N-CNS on carbon paper for CO_2RR and the corresponding Faradaic efficiency for CO/H_2 production at a fixed potential of -0.80 V (versus RHE).

Electrochemical performance in flow cell. Given the CO_2 mass transfer limitation in H-type cell as well as the adverse impact of carbonatation of CO_2RR in neutral or alkaline electrolytes, the CO_2RR performance of CuNi-N-CNS was further evaluated in a home-made flow cell with CO_2-saturated KCl aqueous as the cathode electrolyte to verify its practical application (Figure 4a and Figure S22). The assembled flow cell is set up with CuNi-N-CNS as the cathode in CO_2-saturated 3M KCl, a commercial RuIrTi mesh as the anode in 1M KOH, an

Ag/AgCl (saturated KCl aqueous solution) as the reference electrode in cathode chamber, and the Nafion 117 membrane as the separator. The use of gas diffusion electrode can circumvent the transport limitation of CO_2, leading to much higher current density of CuNi-N-CNS in the flow cell. To shed light on how electrolyte influence CO_2RR, the effects of different catholytes and concentrations on the flow cell performance were firstly explored.

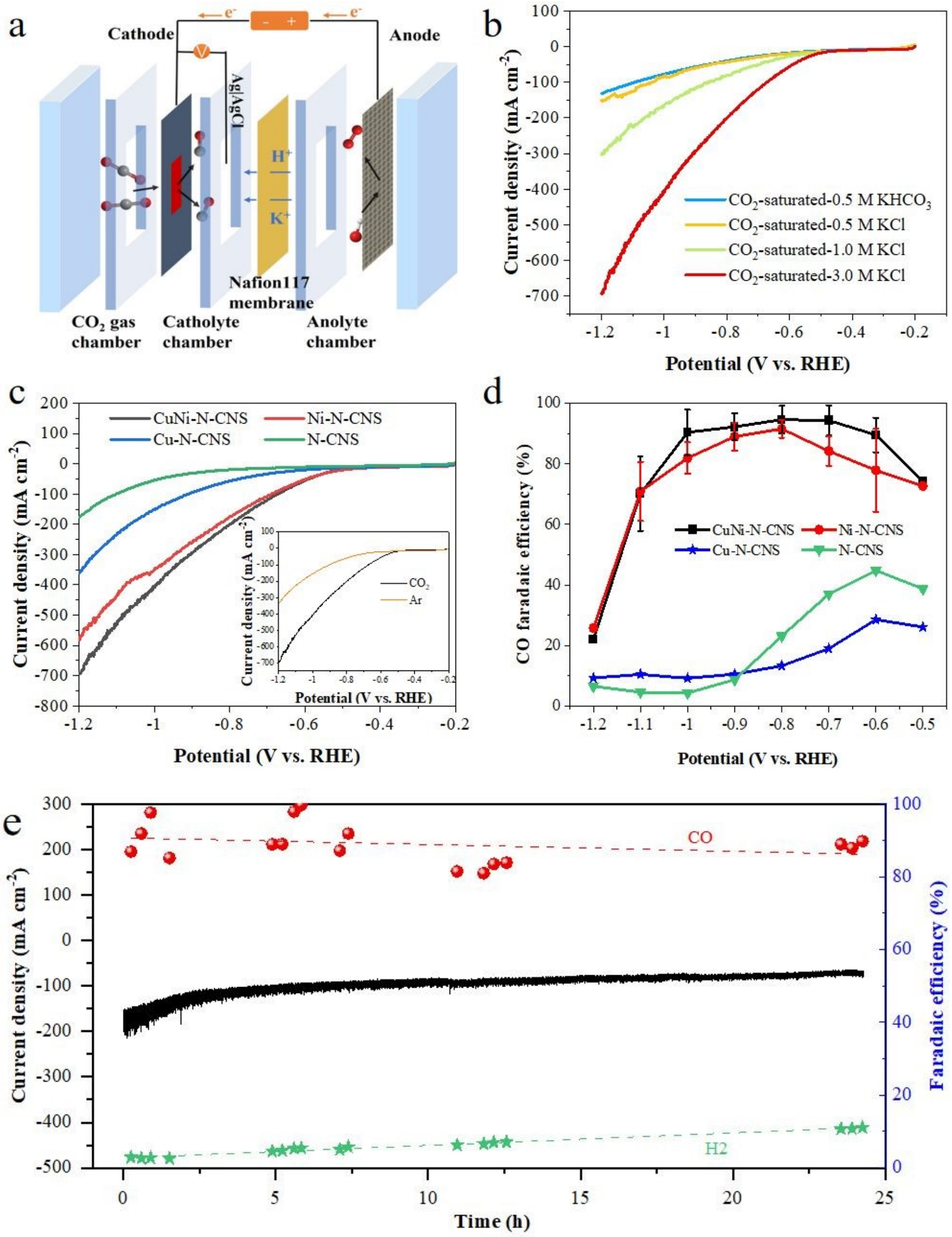


Figure 4. (a) Schematic diagram showing the basic structure of the flow cell that employs a gas diffusion electrode with the cathode electrolyte of 3 M KCl and the anode electrolyte of 1 M KOH. (b) LSV curves at a scan rate of 10 mV s^{-1} with different cathode electrolyte. (c) LSV comparison for CuNi-N-CNS, Ni-N-CNS, Cu-N-CNS and N-CNS. Inset: the LSV comparison for CuNi-N-CNS in Ar- and CO_2-saturated 3 M KCl solution. (d) FE_{CO} as a function of potentials for CuNi-N-CNS, Ni-N-CNS, Cu-N-CNS and N-CNS in the flow cell. (e) Stability assessment for CuNi-N-CNS at -0.8 V in the flow cell.

As Figure 4b displays, the CuNi-N-CNS in CO_2-saturted 0.5 M $KHCO_3$ aqueous solution presents similar current density with that of in 0.5 M KCl, and the current density significantly escalates from -152 mA cm^{-2} to -700 mA cm^{-2} with the KCl concentration increasing from 0.5 M to 3 M, which possibly results from that the high-concentration K^+ cations can promote ion exchange. Besides, the selectivity of the reaction products is regulated by the electrolyte (Figure S23). It is found that the Cl^- is much better at converting CO_2-to-CO than HCO_3^- at the same concentration of K^+, and a highly concentrated solution of KCl can markedly improve the faradaic efficiency of CO while inhibiting hydrogen evolution.[47] More importantly, a mildly acidic environment that can efficiently avoid carbonatation is formed by saturating KCl aqueous with CO_2. As shown in the inset of Figure 4c, CuNi-N-CNS conveys a much smaller current density and higher onset potential in Ar-saturated KCl electrolyte compared with that in CO_2 saturated KCl, indicating a promising CO_2RR performance of CuNi-N-CNS in KCl electrolyte. The CO_2RR performance of the controlled catalysts are also studied in the flow cell. The LSV curves trend of each sample in the flow cell are similar to those of in H-cell. To be specific, the CuNi-N-CNS achieves a current density of 700 mA cm^{-2} at -1.2 V *vs.* RHE, which is 1.2-fold, 2.0-fold and 3.7-fold those of Ni-N-CNS (570 mA cm^{-2}), Cu-N-CNS (355 mA cm^{-2}) and N-CNS (190 mA cm^{-2}), respectively (Figure 4c). Besides, CuNi-N-CNS exhibits FE_{CO} value over 90% in a wide potential range from -0.6 to -1.0 V, obviously superior to other counterparts (Figure 4d). Moreover, we tested the long-term operation stability at -0.80 V as shown in Figure 4e, the current density can maintain at above 100 mA cm^{-2} during 24 h constant electrolysis with FE_{CO} over 90%, which proves the satisfying performance under industrial high current density. Besides, when tested at 250 mA cm^{-2}, it can still maintain the perfect performance (Figure S24). And it can be observed through the device diagram after long-term test, the back of the carbon paper does not appear serious flooding and salting out phenomenon, compared with that in $KHCO_3$ electrolyte (Figure S25). Moreover, the existence of carbonate in the electrolyte is confirmed by the phenomenon of precipitation experiment which shows a very small amount of precipitation occurred in the electrolyte after long-term electrolysis when the $BaCl_2$ solution was dropped into (Figure S26). We also tested the catalyst performance in the flow cell of a two-electrode system. The LSV curve showed that the current density can reached 1260 mA cm^{-2} at 3.8 V, of course, under this condition, hydrogen production was preferred (Figure S27-28). While under a smaller cell voltage, CO_2RR was dominated, which exhibited a maximum FE_{CO} 94.14% at 2.2 V with a total current density of 180 mA cm^{-2} (Figure S29), thus enable CO_2 electrolysis at commercially relevant conditions ($j_{CO} > 100$ mA cm^{-2}, and $E_{Cell} < 3$ V).

Conclusion

In summary, we have successfully designed a Cu-Ni alloy modified carbon nanosheets catalyst for CO_2RR

through a facile pyrolysis route, which owns a special “willow leaf” shaped structure. Multiple characterizations and experiments uncovered that the intermetallic CuNi alloy encapsulated with N-C layer played an important role in regulating the electronic properties, thus accelerate *COOH adsorption and increase the formation of CO. Benefiting from this, CuNi-N-CNS showed a high FE for CO of about 95% and a partial current density of about 400 mA cm^{-2} at -1.0 V *vs.* RHE in a self-assembly flow cell using CO_2-saturated 3 M KCl solution as catholyte (pH = 4.25), which can also maintain good stability. This work not only affords new insights for the design of high performance catalysts toward CO_2RR, but also provides a reference for industrial application through optimizing the electrolyzer component parameters, especially by changing the electrolyte.

Acknowledgements

This work was financially supported by the National key Research & Development Program of China (2022YFE0115900, 2021YFA1501500), the National Natural Science Foundation of China (No. 22225902, U22A20436, 22209183), the CAS-Commonwealth Scientific and Industrial Research Organization (CSIRO) Joint Research Projects (121835KYSB20200039), and the Joint Fund of the Yulin University and the Dalian National Laboratory for Clean Energy (Grant. YLU-DNL Fund 2021011), Fujian Province Central Government Guides to Science and Technology Development Special Project (No. 2022L3024), Fujian Natural Science Foundation (2021J01210293).

Declaration of Competing Interest

There are no conflicts to declare.

References

1 J. Zhu, M. Xiao, D. Ren, R. Gao, X. Liu, Z. Zhang, D. Luo, W. Xing, D. Su, A. Yu and Z. Chen, Quasi-Covalently Coupled Ni-Cu Atomic Pair for Synergistic Electroreduction of CO_2, *J .Am. Chem. Soc.*, 2022, **144**, 9661-9671.

2 Ding, H. Zhao, T. Li, Y. Luo, G. Fan, G. Chen, S. Gao, X. Shi, S. Lu and X. Sun, Metal-based electrocatalytic conversion of CO_2 to formic acid/formate, *J. Mater. Chem. A*, 2020, **8**, 21947-21960.

3 G. Wang, J. Chen, K. Li, J. Huang, Y. Huang, Y. Liu, X. Hu, B. Zhao, L. Yi, T. W. Jones and Z. Wen, Cost-effective and durable electrocatalysts for Co-electrolysis of CO_2 conversion and glycerol upgrading, *Nano Energy*, 2022, **92**.

4 M. Chen, S. Wan, L. Zhong, D. Liu, H. Yang, C. Li, Z. Huang, C. Liu, J. Chen, H. Pan, D. S. Li, S. Li, Q. Yan and B. Liu, Dynamic Restructuring of Cu-Doped SnS_2 Nanoflowers for Highly Selective Electrochemical CO_2 Reduction to Formate, *Angew. Chem., Int. Ed.*, 2021, **60**, 26233-26237.

5 J. Li, A. Ozden, M. Wan, Y. Hu, F. Li, Y. Wang, R. R. Zamani, D. Ren, Z. Wang, Y. Xu, D. H. Nam, J. Wicks, B. Chen, X. Wang, M. Luo, M. Graetzel, F. Che, E. H. Sargent and D. Sinton, Silica-copper catalyst interfaces enable carbon-carbon coupling towards ethylene electrosynthesis, *Nat. Commun*., 2021, **12**, 2808.

6 K. Li, J. Xu, T. Zheng, Y. Yuan, S. Liu, C. Shen, T. Jiang, J. Sun, Z. Liu, Y. Xu, M. Chuai, C. Xia and W. Chen, In Situ Dynamic Construction of a Copper Tin Sulfide Catalyst for High-Performance Electrochemical CO_2 Conversion to Formate, *ACS Catal.*, 2022, **12**, 9922-9932.

7 H. B. Yang, S.-F. Hung, S. Liu, K. Yuan, S. Miao, L. Zhang, X. Huang, H.-Y. Wang, W. Cai, R. Chen, J. Gao, X. Yang, W. Chen, Y. Huang, H. M. Chen, C. M. Li, T. Zhang and B. Liu, Atomically dispersed Ni(i) as the active site for electrochemical CO_2 reduction, *Nat. Energy.*, 2018, **3**, 140-147.

8 T. Ahmad, S. Liu, M. Sajid, K. Li, M. Ali, L. Liu and W. Chen, Electrochemical CO_2 reduction to C2+ products using Cu-based electrocatalysts: A review, *Nano Res*. Energy, 2022, **1**.

9 W. Liu, S. Wei, P. Bai, C. Yang and L. Xu, Robust coal matrix intensifies electron/substrate interaction of nickel-nitrogen (Ni-N) active sites for efficient CO_2 electroreduction at industrial current density, *Appl. Catal. B Environ.*, 2021, **299**.

10 Y. Niu, C. Zhang, Y. Wang, D. Fang, L. Zhang and C. Wang, Confining Chainmail-Bearing Ni Nanoparticles in N-doped Carbon Nanotubes for Robust and Efficient Electroreduction of CO_2, *ChemSusChem*, 2021, **14**, 1140-1154.

11 L. Ji, L. Li, X. Ji, Y. Zhang, S. Mou, T. Wu, Q. Liu, B. Li, X. Zhu, Y. Luo, X. Shi, A. M. Asiri and X. Sun, Highly Selective Electrochemical Reduction of $CO_{(2)}$ to Alcohols on an FeP Nanoarray, *Angew. Chem., Int. Ed.*, 2020, **59**, 758-762.

12 W. Zhu, J. Fu, J. Liu, Y. Chen, X. Li, K. Huang, Y. Cai, Y. He, Y. Zhou, D. Su, J.-J. Zhu and Y. Lin, Tuning single atom-nanoparticle ratios of Ni-based catalysts for synthesis gas production from CO_2, *Appl. Catal. B Environ.*, 2020, **264**.

13 H. Cheng, X. Wu, M. Feng, X. Li, G. Lei, Z. Fan, D. Pan, F. Cui and G. He, Atomically Dispersed Ni/Cu Dual Sites for Boosting the CO_2 Reduction Reaction, *ACS Catal.*, 2021, **11**, 12673-12681.

14 H. Li, N. Zhang, S. Bai, L. Zhang, F. Lai, Y. Chen, X. Zhu and T. Liu, Strain-Regulated Pd/Cu Core/Shell Icosahedra for Tunable Syngas Electrosynthesis from CO_2, *Chem. Mater.*, 2022.

15 Z.-Z. Niu, L.-P. Chi, R. Liu, Z. Chen and M.-R. Gao, Rigorous assessment of CO_2 electroreduction products in a flow cell, *Energy Environ. Sci.*, 2021, **14**, 4169-4176.

16 H. Yang, Y. Wu, Q. Lin, L. Fan, X. Chai, Q. Zhang, J. Liu, C. He and Z. Lin, Composition Tailoring via N and

S Co-doping and Structure Tuning by Constructing Hierarchical Pores: Metal-Free Catalysts for High-Performance Electrochemical Reduction of CO_2, *Angew. Chem., Int. Ed.*, 2018, **57**, 15476-15480.

17 Z. Yin, H. Peng, X. Wei, H. Zhou, J. Gong, M. Huai, L. Xiao, G. Wang, J. Lu and L. Zhuang, An alkaline polymer electrolyte CO_2 electrolyzer operated with pure water, *Energy Environ. Sci.*, 2019, **12**, 2455-2462.

18 T. K. Todorova, M. W. Schreiber and M. Fontecave, Mechanistic Understanding of CO_2 Reduction Reaction (CO_2RR) Toward Multicarbon Products by Heterogeneous Copper-Based Catalysts, *ACS Catal.*, 2019, **10**, 1754-1768.

19 Q. Chen, K. Liu, Y. Zhou, X. Wang, K. Wu, H. Li, E. Pensa, J. Fu, M. Miyauchi, E. Cortes and M. Liu, Ordered Ag Nanoneedle Arrays with Enhanced Electrocatalytic CO_2 Reduction via Structure-Induced Inhibition of Hydrogen Evolution, *Nano Lett.*, 2022, **22**, 6276-6284.

20 H. Huo, J. Wang, Q. Fan, Y. Hu and J. Yang, Cu-MOFs Derived Porous Cu Nanoribbons with Strengthened Electric Field for Selective CO_2 Electroreduction to C2+ Fuels, *Adv. Energy Mater.*, 2021, **11**.

21 W. Wang, J. Han, Y. Sun, M. Zhang, S. Zhou, K. Zhao and J. Yuan, Metal-Free SeBN Ternary-Doped Porous Carbon as Efficient Electrocatalysts for CO_2 Reduction Reaction, *ACS Appl. Energy Mater.*, 2022.

22 R. Zhao, P. Ding, P. Wei, L. Zhang, Q. Liu, Y. Luo, T. Li, S. Lu, X. Shi, S. Gao, A. M. Asiri, Z. Wang and X. Sun, Recent Progress in Electrocatalytic Methanation of CO_2 at Ambient Conditions, *Adv. Funct. Mater.*, 2021, **31**.

23 Q. Chang, Y. Liu, J. H. Lee, D. Ologunagba, S. Hwang, Z. Xie, S. Kattel, J. H. Lee and J. G. Chen, Metal-Coordinated Phthalocyanines as Platform Molecules for Understanding Isolated Metal Sites in the Electrochemical Reduction of CO_2, *J. Am. Chem. Soc.*, 2022.

24 R. Sui, J. Pei, J. Fang, X. Zhang, Y. Zhang, F. Wei, W. Chen, Z. Hu, S. Hu, W. Zhu and Z. Zhuang, Engineering Ag-Nx Single-Atom Sites on Porous Concave N-Doped Carbon for Boosting CO_2 Electroreduction, *ACS Appl. Mater. Interfaces*, 2021, **13**, 17736-17744.

25 S. Mou, Y. Li, L. Yue, J. Liang, Y. Luo, Q. Liu, T. Li, S. Lu, A. M. Asiri, X. Xiong, D. Ma and X. Sun, Cu_2Sb decorated Cu nanowire arrays for selective electrocatalytic CO_2 to CO conversion, *Nano Res.*, 2021, **14**, 2831-2836.

26 Y. Cheng, S. Yang, S. P. Jiang and S. Wang, Supported Single Atoms as New Class of Catalysts for Electrochemical Reduction of Carbon Dioxide, *Small Methods*, 2019, **3**.

27 Y. Zhao, L. Zheng, D. Jiang, W. Xia, X. Xu, Y. Yamauchi, J. Ge and J. Tang, Nanoengineering Metal-Organic Framework-Based Materials for Use in Electrochemical CO_2 Reduction Reactions, *Small*, 2021, **17**, e2006590.

28 Y. Zhu, X. Yang, C. Peng, C. Priest, Y. Mei and G. Wu, Carbon-Supported Single Metal Site Catalysts for

Electrochemical CO_2 Reduction to CO and Beyond, *Small*, 2021, **17**, e2005148.

29 G. Wang, J. Chen, Y. Ding, P. Cai, L. Yi, Y. Li, C. Tu, Y. Hou, Z. Wen and L. Dai, Electrocatalysis for $CO_{(2)}$ conversion: from fundamentals to value-added products, *Chem. Soc. Rev.*, 2021, **50**, 4993-5061.

30 A. Jedidi, S. Rasul, D. Masih, L. Cavallo and K. Takanabe, Generation of Cu–In alloy surfaces from CuInO2as selective catalytic sites for CO_2 electroreduction, *J. Mater. Chem. A*, 2015, **3**, 19085-19092.

31 P. Li, L. Liu, W. An, H. Wang, H. Guo, Y. Liang and W. Cui, Ultrathin porous g-C_3N_4 nanosheets modified with AuCu alloy nanoparticles and C-C coupling photothermal catalytic reduction of CO to ethanol, *Appl. Catal. B Environ.*, 2020, **266**.

32 S. Payra, S. Shenoy, C. Chakraborty, K. Tarafder and S. Roy, Structure-Sensitive Electrocatalytic Reduction of CO_2 to Methanol over Carbon-Supported Intermetallic PtZn Nano-Alloys, *ACS Appl. Mater. Interfaces*, 2020, **12**, 19402-19414.

33 T. N. Nguyen and C. T. Dinh, Gas diffusion electrode design for electrochemical carbon dioxide reduction, *Chem. Soc. Rev.*, 2020, **49**, 7488-7504.

34 H. Yang, Q. Lin, C. Zhang, X. Yu, Z. Cheng, G. Li, Q. Hu, X. Ren, Q. Zhang, J. Liu and C. He, Carbon dioxide electroreduction on single-atom nickel decorated carbon membranes with industry compatible current densities, *Nat. Commun.*, 2020, **11**, 593.

35 Z. Xing, L. Hu, D. S. Ripatti, X. Hu and X. Feng, Enhancing carbon dioxide gas-diffusion electrolysis by creating a hydrophobic catalyst microenvironment, *Nat. Commun.*, 2021, **12**, 136.

36 K. Jiang, S. Siahrostami, T. Zheng, Y. Hu, S. Hwang, E. Stavitski, Y. Peng, J. Dynes, M. Gangisetty, D. Su, K. Attenkofer and H. Wang, Isolated Ni single atoms in graphene nanosheets for high-performance CO_2 reduction, *Energy Environ. Sci.*, 2018, **11**, 893-903.

37 C. Chen, X. Yan, Y. Wu, S. Liu, X. Zhang, X. Sun, Q. Zhu, H. Wu and B. Han, Boosting the Productivity of Electrochemical CO_2 Reduction to Multi-Carbon Products by Enhancing CO_2 Diffusion through Porous Organic Cage, *Angew. Chem., Int. Ed.*, 2022.

38 Z. Chen, G. Yu, B. Li, X. Zhang, M. Jiao, N. Wang, X. Zhang and L. Liu, In Situ Carbon Encapsulation Confined Nickel-Doped Indium Oxide Nanocrystals for Boosting CO_2 Electroreduction to the Industrial Level, *ACS Catal.*, 2021, **11**, 14596-14604.

39 J. E. Huang, F. Li, A. Ozden, A. S. Rasouli, S. Zhang, M. Luo, X. Wang, D. Sinton and E. H. Sargent, CO_2 electrolysis to multicarbon products in strong acid, *Science*, 2021, **372**, 1074-1078.

40 M. C. O. Monteiro, M. F. Philips, K. J. P. Schouten and M. T. M. Koper, Efficiency and selectivity of CO_2

reduction to CO on gold gas diffusion electrodes in acidic media, *Nat. Commun.*, 2021, **12**, 4943.

41 J. Gu, S. Liu, W. Ni, W. Ren, S. Haussener and X. Hu, Modulating electric field distribution by alkali cations for CO_2 electroreduction in strongly acidic medium, *Nat. Catal.*, 2022, **5**, 268-276.

42 H. Li, N. Zhang, S. Bai, L. Zhang, F. Lai, Y. Chen, X. Zhu and T. Liu, Strain-Regulated Pd/Cu Core/Shell Icosahedra for Tunable Syngas Electrosynthesis from CO_2, *Chem. Mater.*, 2022.

43 X. Zheng, P. De Luna, F. P. García de Arquer, B. Zhang, N. Becknell, M. B. Ross, Y. Li, M. N. Banis, Y. Li, M. Liu, O. Voznyy, C. T. Dinh, T. Zhuang, P. Stadler, Y. Cui, X. Du, P. Yang and E. H. Sargent, Sulfur-Modulated Tin Sites Enable Highly Selective Electrochemical Reduction of CO_2 to Formate, *Joule*, 2017, **1**, 794-805.

44 F. P. G. Arquer, C. T. Dinh, A. Ozden, J. Wicks, C. McCallum, D. Sinton, E. H. Sargent, CO_2 electrolysis to multicarbon products at activities greater than 1 A cm^{-2}, *Science*, 2020, **367**, 661-666.

45 H. Yano, T. Tanaka, M. Nakayama and K. Ogura, Selective electrochemical reduction of CO_2 to ethylene at a three-phase interface on copper(I) halide-confined Cu-mesh electrodes in acidic solutions of potassium halides, *J. Electroanal. Chem.*, 2004, **565**, 287-293.

46 Z. Wang, P. Hou, Y. Wang, X. Xiang and P. Kang, Acidic Electrochemical Reduction of CO_2 Using Nickel Nitride on Multiwalled Carbon Nanotube as Selective Catalyst, *ACS Sustain. Chem. Eng.*, 2019, **7**, 6106-6112.

47 Z. Zhao, J. Zhang, M. Lei and Y. Lum, Reviewing the impact of halides on electrochemical CO2 reduction, *Nano Res. Energy*, 2022, DOI: 10.26599/nre.2023.9120044.