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Cu–Ni alloy decorating N-doped carbon nanosheets toward high-performance electrocatalysis of mildly acidic CO_2 reduction†

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Electrochemical CO_2 reduction to value-added chemicals or fuels is a prospective strategy for facilitating the closing of the carbon loop. However, there still exist challenges in developing efficient catalysts and optimizing the electrolyzer components to meet industrial applications. Herein, 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 over 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 h of electrolysis in H-type cell. Moreover, we evaluate its electrocatalytic activity in a self-assembly flow cell in a mildly acidic 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.

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Introduction

Massive carbon dioxide emissions from excessive utilization of fossil fuels have led to widespread environmental issues.[1–3] To date, many approaches have 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 proton and electron transfer processes during CO_2 reduction, the variety of products from CO_2 reduction adds extra difficulties in 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] Earlier, 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 solutions.[22–25] But the scarcity of noble metals 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 have been 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,

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carbon-based materials modified with metal alloys have received 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 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 intermediate *CO on the surface, thus increasing the yield of C_2 products. 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 is mainly investigated in H-cells or flow cells in neutral or alkaline electrolytes currently, where problems like CO_2 mass transport limitation, carbonation, and poor stability exist.[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 rates 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 acidic media has emerged as a promising strategy to circumvent carbonation and its induced problems. Though hydrogen evolution reaction may be more favorable in acidic conditions, it can be suppressed by suitably adjusting the reaction interface of electrodes and the pH of the catholyte. For example, Sargent[40] carried out CO_2RR over copper in an 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, obtaining 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 electrolytes opens up a unique routine for CO_2RR, and studying the CO_2RR performance of various catalysts in acidic electrolytes provides references for solving problems in practical applications 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 encapsulated in the *in situ* formed carbon layers decorate on the ultra-thin lancet nanosheets. Such a unique composite structure can greatly improve the catalytic activity for CO_2RR, which achieves a high CO faradaic efficiency of over 90% for 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 CuNi-N-CNS, were obtained *via* two steps of hydrothermal and pyrolysis reactions (for synthesis details, see ESI and Fig. S1, S2†). Remarkably, a gram-scale catalyst can be obtained *via* simply increasing feeding reagents (Fig. S3†) during synthetic processes, indicating the feasibility of scalable synthesis. For comparison, we probed the effect of raw material ratios on the structure of the CuNi-N-CNS catalyst to determine the optimal one. Ni-N-CNS, Cu-N-CNS, and N-CNS were also synthesized as controlled samples through a similar method (Fig. S2†).

The morphology characterizations of CuNi-N-CNS were conducted by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As displayed in Fig. 1a–c, the as-prepared catalyst maintained 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 (Fig. S4†). It could be inferred that Resol-F127 played 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 °C, which encapsulated Cu–Ni alloy nanoparticles, as revealed by the TEM images (Fig. 1d). In the HRTEM images of the calcined sample (Fig. 1e and f), the well-defined lattice streaks with *d*-spacings 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 (Fig. 1g), it can be demonstrated that Cu, Ni, C, and N species are homogeneously distributed in the carbon substrate, and CuNi alloy is 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

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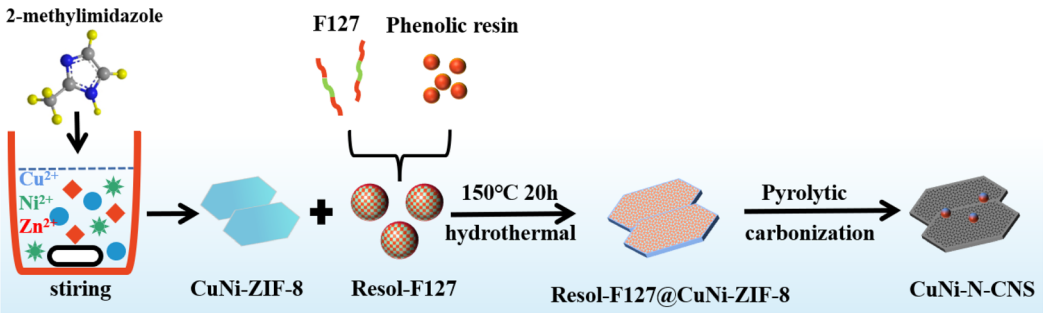

Scheme 1 Schematic representation of the synthetic method of CuNi-N-CNS samples.

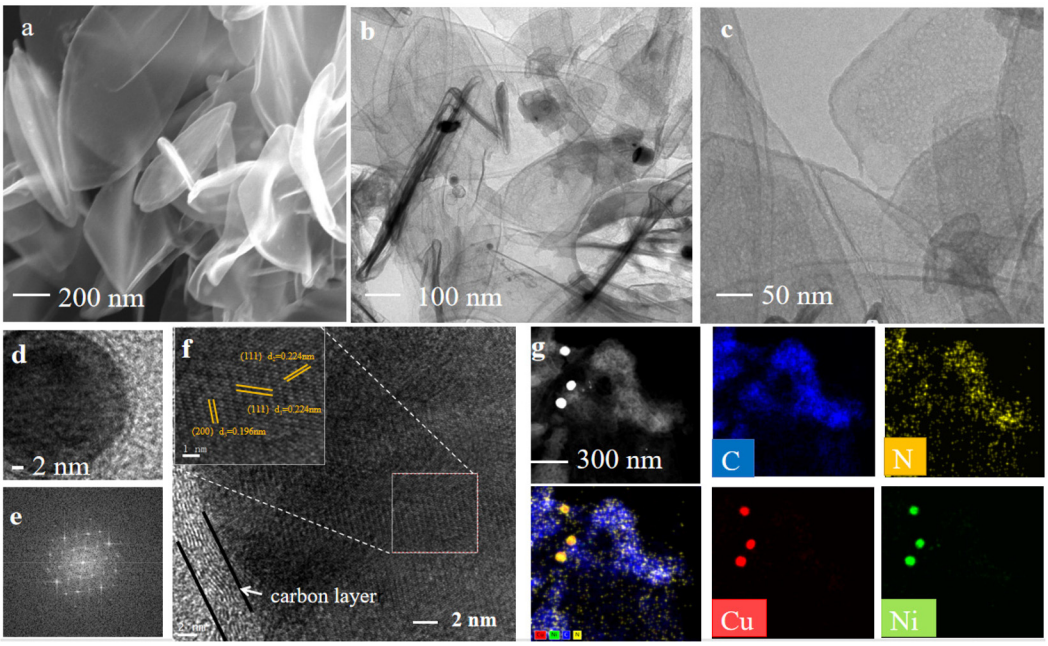

Fig. 1 (a) High-resolution SEM patterns of CuNi-N-CNS. (b–c) TEM images of CuNi-N-CNS at different resolutions, and (d) CuNi@C in CuNi-N-CNS. (e) Corresponding FFT patterns. (f) HRTEM image and the enlarged image (g) EDS mapping of C, N, Cu, and Ni elements.

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

The X-ray diffraction (XRD) patterns exhibit that all as-prepared catalysts contain the characteristic peaks of carbon at 22° and 44° (Fig. S13d†). More concretely, CuNi-N-CNS display another three diffraction peaks at 43.6°, 50.8°, and 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 (Fig. S13d†). X-ray photoelectron spectroscopy (XPS) was then carried out to characterize the catalyst composition and elemental states on the surface (Fig. 2b). The high-resolution XPS N1s spectrum can be deconvoluted into pyridinic (~398.43 eV), M-N (~399.26 eV), pyrrolic (~400.92 eV), graphitic (~402.40 eV), and oxidized (~404.62 eV) species (Fig. 2c). In the high-resolution Ni 2p spectrum (Fig. 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 Fig. 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 (Fig. S14–S17†). In Fig. 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 is widely used to indicate the activity and conductivity of the catalyst. Obviously, CuNi-C-CNS shows a relatively higher I_D/I_G

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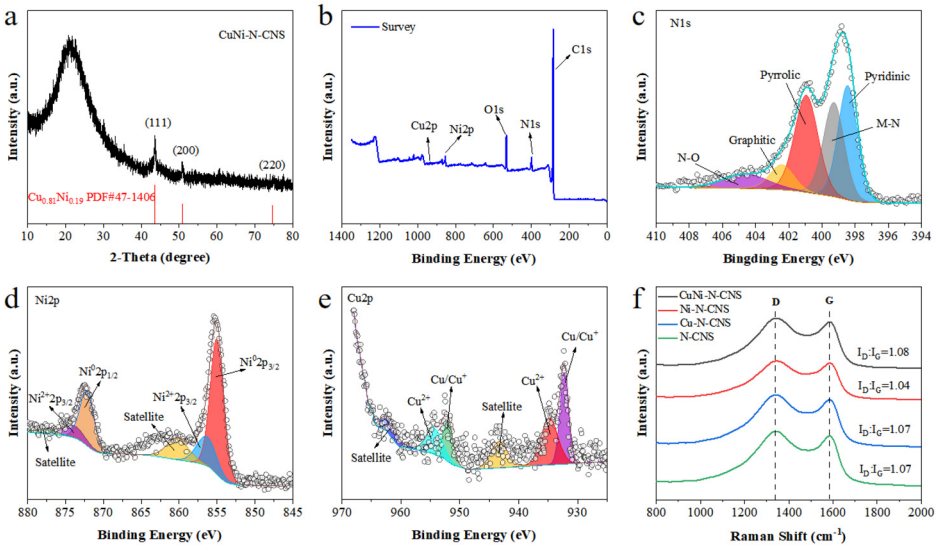

Fig. 2 (a) X-ray diffraction patterns of CuNi-N-CNS. (b) The survey XPS spectrum of CuNi-N-CNS. (c–e) High-resolution spectra of N1s, Ni2p, and Cu2p of CuNi-N-CNS. (f) Raman spectra of CuNi-N-CNS, Ni-N-CNS, Cu-N-CNS, and N-CNS samples.

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 a high level of defects, which resulted in increased active sites for improving CO_2RR performance.

These above characterization results reveal that the composite structure corresponds to 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 etching due to the covering of the 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, recently 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 first 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 Fig. 3a, the CuNi-N-CNS exhibits a remarkably higher current density from −0.18 to −1.18 V *vs.* RHE compared with these controlled samples, 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 a key role in elevating the conductivity of CuNi-N-CNS. Furthermore, the catalytic selectivity of these catalysts was also examined by the 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 gas products of the reduction, and there was almost no liquid product (Fig. S18†). Fig. 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 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. Fig. 3c shows the dependence of the CO partial current density (j_{CO}) on the applied potential. CuNi-N-CNS delivers much higher j_{CO} with respect to the other catalysts and achieves a current density of 11 mA cm^{-2} at −0.8 V, which is 1.2, 5, and 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. The Nyquist plot of CuNi-N-CNS exhibits the smallest semicircle among the prepared catalysts, which suggests its fast interfacial charge-transfer process during the CO_2RR process (Fig. 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* the evaluation of double-layer capacitance (C_{dl}). CuNi-N-CNS showed the highest C_{dl} 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, respectively (Fig. S19†), verifying more active catalytic sites in CuNi-N-CNS. To uncover the reaction kinetics on different catalysts, Tafel plots were further determined and

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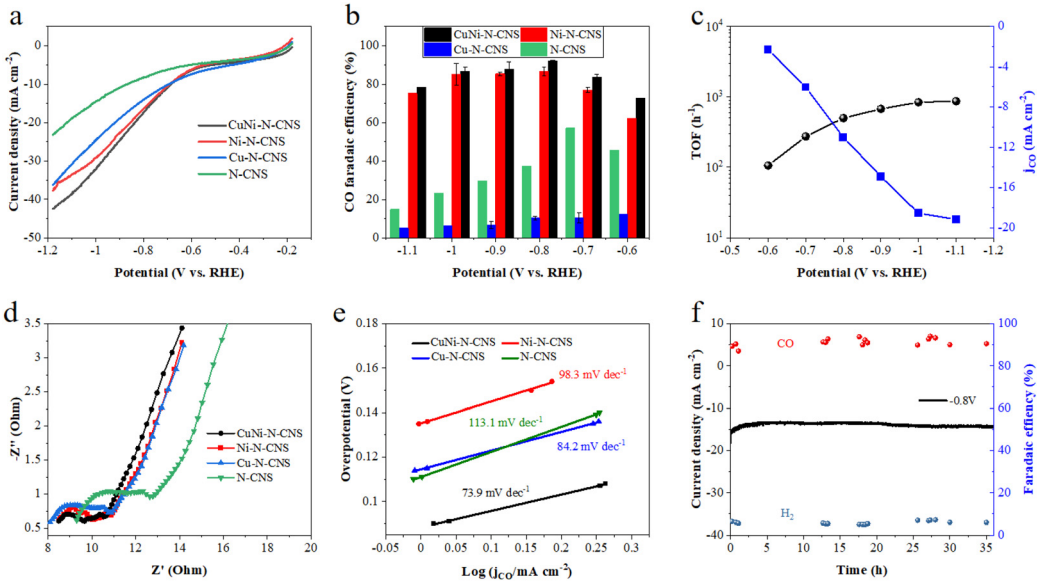

Fig. 3 (a) LSV curves obtained in CO_2-saturated 0.5 M $KHCO_3$ solution (pH = 7.2) in the H-type cell. (b) faradaic efficiency for CO production at various applied potentials. (c) TOF of CuNi-N-CNS at various applied potentials. The blue curve is j_{CO}. (d) Nyquist plots. (e) Tafel plots of the samples. (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).

analyzed. As shown in Fig. 3e, Tafel slopes of 73.9, 98.3, 84.2, and 113.1 mV decade^{-1} are 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 h of continuous electrolysis in an H-type cell (Fig. 3f). The stability of the prepared catalyst was further confirmed by checking the SEM and XRD of the catalyst after long-term electrolysis. The XRD patterns of catalysts of similar mass before and after the stability test showed no obvious changes (Fig. S20,† peaks of $Cu_{0.81}Ni_{0.19}$ are not so observable owing to the very small amounts 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 (Fig. 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.

Electrochemical performance in the flow cell

Given the CO_2 mass transfer limitation in H-type cells as well as the adverse impact of carbonation 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 potential (Fig. 4a and Fig. S22†). The assembled flow cell is set up with CuNi-N-CNS as the cathode in CO_2-saturated 3 M KCl, a commercial RuIrTi mesh as the anode in 1 M 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 a gas diffusion electrode can circumvent the transport limitation of CO_2, leading to a much higher current density of CuNi-N-CNS in the flow cell. To shed light on how electrolytes influence CO_2RR, the effects of different catholytes and concentrations on the flow cell performance were first explored.

As Fig. 4b displays, the CuNi-N-CNS in CO_2-saturated 0.5 M $KHCO_3$ aqueous solution presents a similar current density to that 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 (Fig. S23†). It is found that 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 carbonation is formed by saturating KCl aqueous with CO_2. As shown in the inset of Fig. 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

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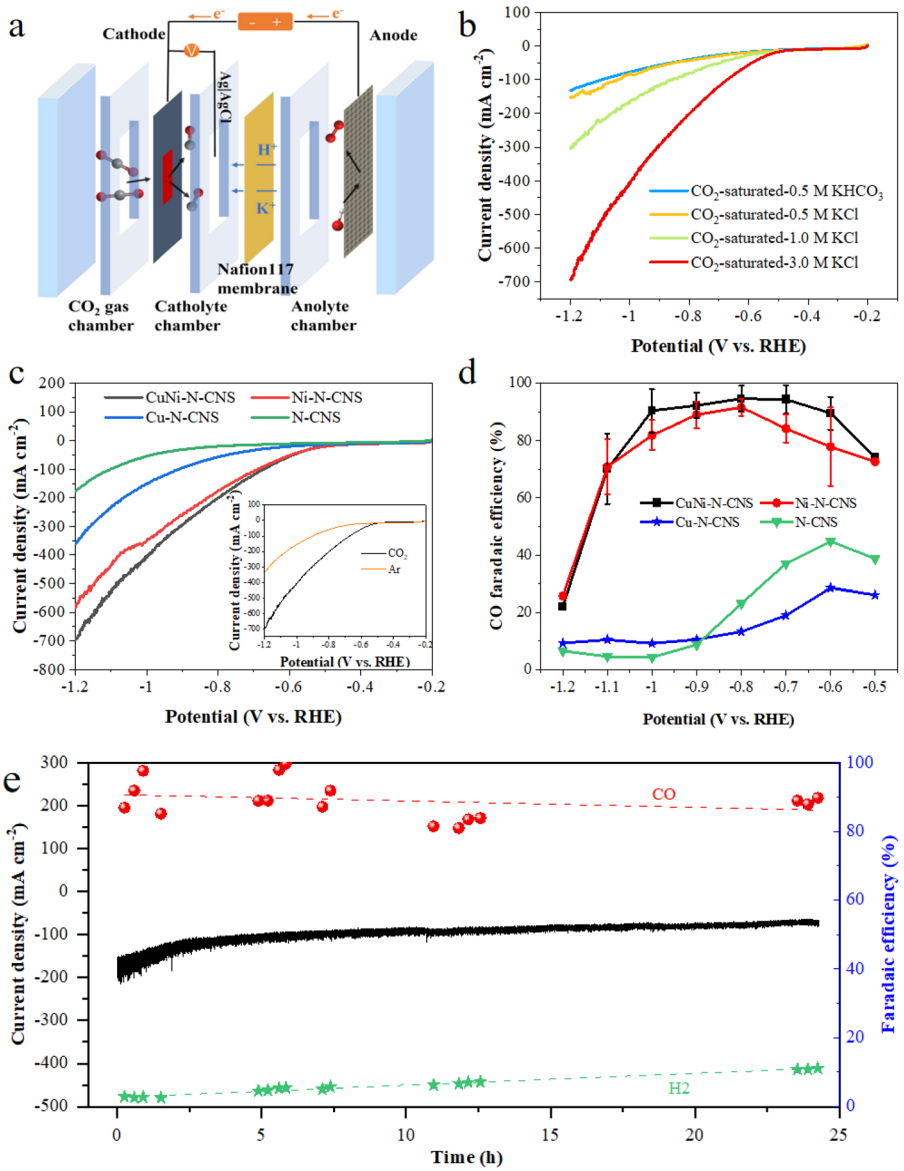

Fig. 4 (a) Schematic diagram showing the basic structure of the flow cell that employs a gas diffusion electrode with the cathode electrolyte of 3 M KCl and the anode electrolyte of 1 M KOH. (b) LSV curves at a scan rate of 10 mV s^{-1} with different cathode electrolytes. (c) LSV comparison for CuNi-N-CNS, 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.

electrolyte. The CO_2RR performances of the controlled catalysts are also studied in the flow cell. The LSV curve trend of each sample in the flow cell is similar to those 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 of Ni-N-CNS (570 mA cm^{-2}), Cu-N-CNS (355 mA cm^{-2}), and N-CNS (190 mA cm^{-2}), respectively (Fig. 4c). Besides, CuNi-N-CNS exhibits FE_{CO} value over 90% in a wide potential ranging from −0.6 to −1.0 V, obviously superior to other counterparts (Fig. 4d). Moreover, we tested the long-term operation stability at −0.80 V as shown in Fig. 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 (Fig. S24†). It can be observed through the device diagram after a long-term test that the back of the carbon paper does not display serious flooding and salting out phenomenon, compared with that in the $KHCO_3$ electrolyte (Fig. 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 occurring in the electrolyte after long-term electrolysis when the $BaCl_2$ solution was dropped into (Fig. S26†). We also tested the

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catalyst performance in the flow cell of a two-electrode system. The LSV curve showed that the current density could reach 1260 mA cm^{-2} at 3.8 V. Of course, under this condition, hydrogen production was preferred (Fig. S27 and S28†). While under a smaller cell voltage, CO_2RR was dominant, which exhibited a maximum FE_{CO} of 94.14% at 2.2 V with a total current density of 180 mA cm^{-2} (Fig. S29†), thus enabling 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 nanosheet 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 the N–C layer played an important role in regulating the electronic properties, thus accelerating *COOH adsorption and increasing 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.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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