Sharp Cu@Sn nanocones on Cu foam for highly selective and efficient electrochemical reduction of CO2 to formate†

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Electrochemical reduction of aqueous CO2 into formate is subject to poor selectivity and low current density with conventional Sn-based catalysts owing to the inert nature of CO2 molecules and the low number of active sites. Recently, it has been demonstrated that alkali metal cations could greatly enhance selectivity for CO2 reduction by stabilizing the key intermediates, which leads to an effective solution to this problem by concentrating local metal cations through tailoring the catalyst structure. Herein, we synthesized spiky Cu@Sn nanocones over a macroporous Cu foam, which has a curvature radius of 10 nm, via facile electrochemical coating of a thin layer of Sn over the Cu nanoconic surface. A faradaic efficiency of 90.4% toward formate production was achieved, with a current density of 57.7 mA cm⁻² at –1.1 V vs. a reversible hydrogen electrode, which far exceeds results achieved to date with state-of-the-art Sn catalysts. The performance should be attributed to the combined effects of a sharp conical feature that facilitates the enrichment of surface-adsorbed metal cations and the promotion of the mass transfer and active sites growth favored by the three-dimensional porous network.

Introduction

Electrochemical reduction of CO2 offers a promising approach for its conversion into chemical fuels under ambient conditions. In addition, it can also be used for the storage of excessive renewable electric energy, generated by intermittent wind and solar power, and therefore help to reduce greenhouse gas emissions. Formate (or formic acid), a valuable liquid product from CO2 electroreduction, is in high demand as a promising carrier for hydrogen storage over other options in terms of its relatively high capacity (52 g H₂ per L) and low volatility (40 mmHg in vapor pressure at 20 °C). Furthermore, it can also serve as a heat-transfer medium in oil and gas manufacturing, as an important chemical feedstock in paper manufacturing, or it can be used directly in fuel cells. Motivated by its considerable benefits, efforts to improve the selectivity and current density for CO2 electroreduction into formate have been an active research area in recent years.

Conventionally, two strategies have been used to enhance the electrocatalytic performance of heterogeneous catalysts on CO2 conversion: (1) increasing the intrinsic activity of active sites such as creating a reactive single-atom structure, grain boundaries, and edge sites; (2) increasing the number of active sites through controlling the nanoparticle size or designing a three-dimensional (3D) porous structure to increase the active surface area. It should be noted that, in a recent work by Liu et al., it was discovered that CO2 reduction can be facilitated by surface-adsorbed metal cations (e.g., K⁺), which strengthen the carbon–metal (C–M) bond by reducing C–M distance, and consequently stabilize the CO2 reduction intermediates. Moreover, these authors claimed that the local concentration of the metal cation could be dramatically increased due to the strong electric field induced by a high-curvature structure. Thus, a highly selective catalyst for CO2 electroreduction into formate may be obtained with a specifically designed high-curvature structure. Nevertheless, their work on fabricating a sharp noble-metal catalyst was only achieved with the aid of a fragile carbon paper support, which will be limited in practical applications considering the poor mechanical strength and low physical flexibility of electrodes, in view of the rigorous conditions in reactors.

Among the various earth-abundant metal candidates (Cu, Co, Sn, Bi, and their oxide-derived catalysts), Sn-based...
catalysts are particularly attractive due to their low cost and easy surface modification to support CO₂ electroreduction, giving formate faradaic efficiencies above 80%.17,18 However, they only yield low current densities of approximately 10 mA cm⁻² at the potentials of maximum faradaic efficiency.16,17,19 Therefore, it is of great interest to further enhance the formate production ability of cheap Sn-based catalysts.

We hypothesized that an attractive way to achieve this goal would be the synthesis of an electrocatalyst having a sharp feature in a 3D framework, which would enable enrichment with local metal cations within the 3D porous structure, while the 3D porous structure could provide a large number of active sites as well as excellent mass transfer capacity. Through a facile, duplicatable, and affordable electrodeposition process, we cultivated spiky copper@tin nanocones over a macroporous Cu foam substrate, and achieved an excellent selectivity in formate with a performance superior to those of state-of-the-art Sn catalysts. Furthermore, this strategy provides a simple and efficient way to design effective and inexpensive metal catalysts with Cu nanocones as the template, which provides rich active sites and favorable mass transfer and local metal cation enrichment to favor CO₂ reduction.

Experimental section

Materials

Cu foil (99.98%, 0.5 mm thick) was purchased from Alfa Aesar; potassium bicarbonate (KHCO₃, 99.99%), copper sulfate (CuSO₄·5H₂O, 99.8%), nickel sulfate (NiSO₄·6H₂O, 99.9%), sodium hypophosphite (NaH₂PO₂, 99.0%), sodium citrate (Na₃C₆H₅O₇·2H₂O, 99.0%), orthoboric acid (H₃BO₃, 99.5%), polyethylene glycol, sodium hydroxide (NaOH, 97%) and stannous sulfate (SnSO₄, 99.0%) were purchased from Macklin, and used without further purification. The pH meter (FE28, Mettler Toledo), epoxy polymer (Sigma-Aldrich), Ag/AgCl electrode (CH Instruments), saturated calomel electrode (SCE) electrode (CH instruments), platinum gauze (Tianjin ida), and Cu foam substrate (99.99%, 2 mm thick, JYS company) were directly used without modification. All aqueous solutions were prepared with Hitech-Scientecool water. The bulk pH of the electrolytes after CO₂ saturation is shown in Table S1 (ESI†).

Fabrication of Cu nanocones on Cu foil (Cu nanocones)

The Cu foil was mechanically polished with sandpaper, and subsequently rinsed in 0.5 M sulfuric acid, acetone, and deionized water with sonication, respectively, and finally dried in an N₂ atmosphere (ESI, Fig. S1†). The Cu nanocone electrode was prepared using a modified method.27 Typically, the cleaned Cu foil was immersed into an electrochemical bath containing 0.03 M CuSO₄, 0.0024 M NiSO₄, 0.24 M NaH₂PO₂, 0.05 M Na₃C₆H₅O₇·2H₂O, 0.5 M H₃BO₃, and 6 g L⁻¹ polyethylene glycol, in which the pH was adjusted to 8 using NaOH (denoted as standard bath A). All electrolysis experiments in this work were controlled using a CHI660E potentiostat (CH Instruments). Electrodeposition was carried out at a potential of 1.08 V (aqueous KCl-saturated Ag/AgCl) at 75 °C for 20 min with Pt mesh as the counter electrode, during which the bath was continuously stirred at a speed of 110 rpm. Then, the prepared Cu-Ni nanocone electrode was washed with copious deionized water and dried under vacuum overnight. Finally, the Cu nanocone catalyst was obtained by immersing Cu-Ni nanocones into 0.1 M H₂SO₄ for 1 hour to dealloy the Ni.

Fabrication of Cu@Sn nanocones on Cu foil (Cu@Sn nanocones)

The Cu nanocones on Cu foil was covered by chemically resistant epoxy with a surface area of approximately 0.6 cm² exposed to the Sn electroplating bath, which consisted of 2 M NaOH, 0.1 M Na₃C₆H₅O₇, and 0.05 M SnSO₄ (denoted as standard bath B). The electrodeposition of Sn on the Cu nanocone surface was conducted at a constant current density of 3.3 mA cm⁻² with a time of 200, 700, 800, 900, and 1400 s, respectively,28 during which the solution was vigorously stirred. The resulting Cu@Sn nanocones were rinsed with deionized water and dried under vacuum overnight.

Fabrication of bulk Sn on Cu foil (bulk Sn)

The bulk Sn electrode was prepared by electrodepositing nanostructured Sn on the cleaned Cu foil (0.6 cm² geometrical area) in standard bath B with vigorous stirring. The current density was kept constant at 3.3 mA cm⁻², and the deposition time was set to 800 s.

Fabrication of Cu@Sn nanocones on Cu foam (Cu@Sn nanocones/Cu foam)

Electrodeposition of Cu–Ni bimetallic nanocones over Cu foam was performed in a standard bath A at −1.12 V (aqueous KCl-saturated Ag/AgCl) and 75 °C for 20 min, similar to the procedure for growing Cu–Ni nanocones on Cu foil, followed by removal of Ni in 0.1 M H₂SO₄. Then, the Sn electroplating was applied in a standard bath B with a current density of 3.3 mA cm⁻² to obtain Cu@Sn nanocone/Cu foam, while the plating time was prolonged to 2100 s because of the increased deposition current density of the Cu–Ni nanocones on the Cu foam (ESI, Fig. S2 and S3†).

Physical characterization

X-ray diffraction (XRD) data were obtained with a Bruker D8 ADVANCE diffractometer using Cu-Kα radiation (λ = 0.15406 nm). X-ray photoelectron spectroscopy (XPS) was measured on an AXIS UltraDLD instrument with Al Kα radiation (450 W). Field emission scanning electron microscopy (FESEM, JEM-7800F Prime) and energy dispersive spectra (EDS, Scientific NORANTM System 7) were used to observe the morphology and identify the elemental distribution of the samples. Scanning transmission electron microscopy (STEM) elemental mapping was recorded on FEI TALOS F200X apparatus. Inductively coupled plasma (ICP) measurements were performed on an Agilent 725 ICP Optical Emission Spectrometer.
Electrochemical measurements

An airtight two-compartment and three-electrode H-cell was used for CO₂ electrolysis under ambient conditions (ESI, Fig. S4†). The electrolytes were filled into both cathodic and anodic compartments, separated by a Nafion 117 membrane (Dupont). An SCE and platinum gauze served as the reference electrode and counter electrode, respectively. The SCE electrode was stored in fresh KCl-saturated solution after electrolysis, and periodically checked against the pristine one to record the minute potential drift. All reported potentials were corrected for ohmic loss (\(iR_u\)). The \(R_u\) values were measured using the \(R_u\) test function built into the potentiostat, and automatically compensated for by the workstation with a level of 80% during electrolysis, while the remaining 20% was corrected manually using following the equation:²⁹,³²,³³

\[
E_{100\% \text{ iR-corrected}} = E_{80\% \text{ iR-corrected}} - 20\% \times R_u \times \text{average } i
\]

where \(E_{100\% \text{ iR-corrected}}\) is the final potential; \(E_{80\% \text{ iR-corrected}}\) is the applied potential in the electrolysis; average \(i\) is the average current obtained by dividing the total electric charge by the electrolysis time. In this work, the reported current density was normalized by the geometric surface area, and all potentials applied for CO₂ electrolysis were converted to the RHE scale using:

\[
E_{\text{RHE}} = E_{\text{SCE}} + 0.242 \text{ V} + 0.0591 \times \text{pH}_{\text{electrolyte}}
\]

Prior to each run, the oxide on the catalyst surface was reduced at \(-1.2 \text{ V (vs. SCE)}\) in the N₂-saturated electrolyte for 10 min, followed by bubbling CO₂ into electrolyte for 30 min at 60.0 sccm. During the electrolysis, the cathodic electrolyte was continuously purged with CO₂ at 20.0 sccm, and magnetically stirred at a fixed speed.

Product quantification

The quantification of gas products was performed with an online gas chromatograph (Synpec M3000), H₂, CO, CH₄, and CO₂ multi-carbon compounds were automatically separated using two different columns (a plot Q column and a plot U column), and subsequently quantified using thermal conductivity detectors (TCD). An external standard method was used and calibrated with a standard gas mixture consisting of H₂, CO, CH₄, C₂H₄, and CO₂. The partial current densities of CO and H₂ production were calculated from the gas chromatography (GC) peak areas as follows:³⁴

\[
j_{\text{CO}} = \frac{\text{peak area}}{\alpha} \times \text{flowrate} \times \frac{2Fp_0}{RT} \times (\text{electrode area})^{-1}
\]

\[
j_{\text{H}_2} = \frac{\text{peak area}}{\beta} \times \text{flowrate} \times \frac{2Fp_0}{RT} \times (\text{electrode area})^{-1}
\]

where \(\alpha\) and \(\beta\) are conversion factors for CO and H₂, respectively, based on calibration of the gas chromatograph with standard samples, \(p_0 = 1.013\ \text{bar}\) and \(T_0 = 273.15\ \text{K}\).

Formate concentration was analyzed on a Bruker 600 MHz nuclear magnetic resonance (NMR) spectrometer. The standard curve was made using sodium formate (99.99%, Sigma-Aldrich), D₂O (99.9%, Sigma-Aldrich), and internal standard (tris(trimethylsilyl) phosphate [TMSP], 0.05 wt% in D₂O, Sigma-Aldrich), as shown in Fig. S5. A 0.3 mL catholyte after electrolysis was added to a mixture of 0.02 mL internal standard (0.05 wt% TMSP) and 0.18 mL D₂O. The one-dimensional ¹H spectrum was measured with water suppression using a presaturation method. The area ratio of the formate peak to the TMSP peak was compared to the standard curve to quantify the formate concentration, and the faradaic efficiency was calculated as follows:

\[
\text{Faradaic efficiency} = \frac{2F \times n_{\text{formate}}}{Q}
\]

where \(F\) is the Faraday constant, \(n_{\text{formate}}\) is the total amount of formate, and \(Q\) is the total electric charge.

Numerical simulation

The free electron density on different electrodes was simulated using Electric Currents modules of COMSOL Multiphysics under a specific electrode bias potential, according to previous work.²⁵ The radius of the high-curvature sharp tip was set to 10 nm and the bulk Sn particle was assumed to be spherical with a diameter of 500 nm. All 3D catalysts were represented by two-dimensional axisymmetric models on the simulation, while the conductivity of the Sn-based electrode was set to be 8.8 × 10⁶ S m⁻¹. The electric field was the opposite gradient of the electric potential:

\[
\vec{E} = -\nabla V.
\]

In this work, we used the Gouy–Chapman–Stern model which is composed of a Helmholtz layer and a diffusion layer to describe the electric double layer. The surface-adsorbed potassium ions in the Helmholtz layer was assumed to be a monolayer. The diffusion layer was established based on the equilibrium between the electrostatic force and diffusion. To calculate the cation density in the electrical double layer, the “Electrostatics” and the “Transport of diluted species” modules were combined and solved in the steady state:

\[
\nabla^2 V = 0, \quad d < d_H
\]

\[
\nabla^2 V = (C_k - C_{\text{HCO}_3})F, \quad d > d_H
\]

\[
\nabla \left( D \nabla C_i + \frac{DZ_i}{k_BT} C_i \nabla V \right) = 0
\]

where the \(d\) is the distance from the electrode surface to the electrolyte, and the \(C_i\) is the concentration of potassium or bicarbonate, respectively. The thickness of the Helmholtz layer \(d_H\), the valencies \(Z_i\), the temperature \(T\), and the diffusion coefficient \(D\) were taken from prior work.²²
Results and discussion

Characterization of the as-synthesized catalysts

As illustrated in Fig. 1a, the fabrication process of Cu@Sn nanocones started with the synthesis of Cu–Ni nanocones on the Cu foil. With the utilization of the Ni mediator and H$_3$BO$_3$ crystal modifier in the electroplating bath, the vertical growth of the Cu–Ni nanocrystals can be accelerated by the deposited Ni atoms on the tip, which was reduced by the hypophosphite and instantly displaced by the copper ions owing to their difference in redox potentials, while the lateral growth was simultaneously inhibited by a modifier, which eventually led to the formation of a highly dense bimetallic conical structure (ESI, Fig. S2 and S6†). Subsequently, the surface Ni (ESI, Fig. S7†) of the nanocones was removed from immersion in dilute sulfuric acid, followed by the electrodeposition of Sn at a constant current density (ESI, Fig. S9†), and the final nanoconic form of the catalyst was generated.

The crystal structure of the Cu nanoconic precursor after removing Ni was investigated with XRD measurements (Fig. 1b), which showed a face-centered cubic (fcc) structure with (111), (200), (220) crystal facets (JCPDS 04-0836). XPS analysis revealed that Ni peaks were absent after the dealloying process, indicating the complete removal of Ni atoms from the Cu nanoconic surface (ESI, Fig. S10†). After electroplating of Sn, four additional peaks located at 30.6°, 32.0°, 44.9°, and 55.3° were observed in the XRD pattern of the Cu@Sn nanocones (Fig. 1b), which are indexed to the (200), (101), (211), and (301) planes of metallic Sn (JCPDS 86-2265), respectively. However, the detailed Sn 3d$_{5/2}$ XPS spectrum shows the co-existence of Sn$^{4+}$ (486.5 eV) and Sn$^0$ (484.6 eV) on the catalyst surface (Fig. 1c), due to the strong oxygen affinity to Sn which makes it easy for the surface to be partially oxidized in the air.$^{19,35}$

The morphology and structure of the as-prepared samples were investigated by scanning electron microscopy (SEM), Fig. S11† reveals a layer of uniform and densely packed Cu nanocones with a radius as small as 10 nm lying on the Cu foil substrate, which have slightly rough surface. The Cu@Sn nanocones inherit the conical structure of the Cu nanoconic precursors and become smoother (Fig. 2a and b). In addition, scanning transmission electron microscopy equipped with energy dispersive X-ray spectroscopy (STEM-EDS) mapping images clearly showed the uniform and conformal coating of Sn on the Cu nanoconic surface (Fig. 2c). A further morphology examination of Cu@Sn nanocones using STEM confirmed that the catalyst has a high-curvature conical structure, consistent with the SEM results (Fig. 2d). A high-resolution TEM (HRTEM) image of a nanocone tip shows an ordered crystalline structure in the interior, and an approximate 3 nm thick mixture on the surface was identified (Fig. 2e). The inner lattice spacing was 0.213 nm, belonging to the (111) plane of fcc Cu.$^{27}$ The outside layer verified by HRTEM tests was most likely composed of tetragonal Sn that showed the lattice fringes of (101) planes$^{17,39}$ and partially oxidized SnO$_x$,$^{6}$ which would be reduced to metallic Sn under cathodic potentials during CO$_2$ reduction.$^{20}$ Based on the above structural characterizations, we believe that the dense Cu@Sn nanocone electrode consists of sharp tips with the surface fully covered by a thin Sn/Sn oxide hybrid layer. Unexpectedly, a small amount of bulk Sn was also observed lying above the Cu@Sn nanocone layer after Sn deposition (ESI, Fig. S12†). To highlight the catalytic performance of Cu@Sn nanocones for CO$_2$ reduction, bulk Sn deposited on Cu foil was prepared (Fig. 2f and g).

Electrocatalytic performance of CO$_2$ reduction

The CO$_2$ reduction ability of as-synthesized catalysts was first tested by performing cyclic voltammogram (CV) measurements...
in N₂ or CO₂-saturated 0.1 M KHCO₃ (ESI, Fig. S13†). The cathodic current densities in an N₂ atmosphere are due to hydrogen evolution, of which the Cu nanocones had the most positive onset potential at around −0.5 V. In addition, a lower current density was observed in a CO₂ atmosphere for Cu nanocones relative to an N₂ atmosphere, which may originate from the slight inhibition of adsorbed CO against the H₂ evolution. In contrast, Cu@Sn nanocones with an Sn deposition time of 800 s and bulk Sn both displayed increased catalytic activities with CO₂ purge, while a faster reduction kinetic was achieved on the former over the entire potential window. The cathode peaks around −0.2 V were attributed to the reduction of tin oxide on the catalyst surface, and did not appear on the Cu nanocone electrode.

To investigate the catalytic performance of Cu nanocones, Cu@Sn nanocones (after optimizing the Sn deposition time, all Cu@Sn nanocones were referred to the Cu@Sn nanocones with Sn deposition time of 800 s hereafter; Fig. S14 and S15†) and bulk Sn electrodes for CO₂ reduction, electrolysis at various potentials was conducted in 0.1 M CO₂-saturated KHCO₃ electrolyte. The gaseous product and liquid product were determined using GC and a NMR spectrometer, respectively. As expected, the total current densities of all samples gradually increased when applied potentials became more negative (Fig. 3a and S16†). Notably, the formate faradaic efficiency of Cu@Sn nanocones increased rapidly at first as a potential negatively shifted and also significantly exceeded that of bulk Sn over the entire potential range, achieving a maximum level of 88.4% at −1.1 V (vs. RHE) (Fig. 3b). The H₂ and CO accounted for the remaining products, and no other hydrocarbon was observed (Fig. 3c and d). After CO₂ electrolysis, the conical structure of Cu@Sn nanocones was well preserved (ESI, Fig. S17†). For the bulk Sn deposited on Cu foil, the formate selectivity only had a moderate value of 64% at −1.1 V (Fig. 3b), close to the value of prior work. Although Cu nanocones delivered the highest current densities from −0.6 V to −1.2 V, it primarily produced H₂ and displayed low formate faradaic efficiencies below 31% (Fig. S18†). Meanwhile, a small amount of CH₄ and C₂H₄ was also detected in the gas products (ESI, Fig. S18†). For the prior Cu–Sn alloy catalysts, the bimetallic Cu–

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**Fig. 2** SEM images of (a and b) Cu@Sn nanocones on Cu foil, (c) STEM elemental mapping of Cu@Sn nanocones, (d) STEM image of Cu@Sn nanocones, (e) TEM image of Cu@Sn nano-tips, SEM images of (f and g) bulk Sn on Cu foil.
Sn interface (formed by depositing Sn on Cu surface) was directly exposed to the electrolytes and reagents. The presence of an optimized amount of Sn on the Cu surface could alter the adsorption of H and disfavor the hydrogenation process to reduce the selectivity toward H2 and HCOOH, while keeping the adsorption of CO relatively unperturbed on the Cu sites, resulting in the improved CO selectivity above 80%.35,40,41 On the basis of CO2 reduction results and TEM characterization, it can be concluded that the sharp nanostructured Sn fully coated on the Cu nanoconic surface are the active sites responsible for the improved formate selectivity in CO2 reduction rather than the Cu nanocones support or the bimetallic Cu–Sn interface. Moreover, the Cu@Sn nanocones displayed the highest formate partial current density (jHCOO⁻) at potentials more negative than −0.8 V, and obtained a jHCOO⁻ of 18 mA cm⁻² at −1.1 V, which was approximately 2.1- and 2.9-times higher than that of bulk Sn and Cu nanocones, respectively (ESI, Fig. S19†). According to the measured double-layer capacitance in Fig. S20,† the electrochemical active surface area (ECSA) for Cu@Sn nanocones was 1.8-times higher than that of bulk Sn. Therefore, the 2.1-times increase in formate partial current density of Cu@Sn nanocones relative to bulk Sn would indicate a faster electron transfer and higher intrinsic activity. The onset formation2,29 of formate on sharp Cu@Sn nanocones can be clearly observed at −0.55 V, implying an overpotential of 540 mV (the equilibrium potential is −0.01 V vs. RHE), which is reduced by 100 mV compared with that of bulk Sn (Fig. 3b). This result further verifies the enhanced performance.

To explore the electrokinetic mechanism of CO2 reduction on the Cu@Sn nanocones and bulk Sn, Tafel plots were
constructed, and are presented in Fig. 3e. It is widely considered that the electroreduction of CO$_2$ to formate involves two electrons [eqn (1)-(5)], which is initiated by the first electron transfer to a CO$_2$ molecule to form a surface-adsorbed CO$_2$$^-$ intermediate, and followed by the reaction of CO$_2$$^-$ intermediate with one proton and another electron to generate the final product:$$\text{CO}_2(\text{solution}) \rightarrow \text{CO}_2(\text{ads})$$
$$\text{CO}_2(\text{ads}) + e^- \rightarrow \text{CO}_2^- (\text{ads})$$
$$\text{CO}_2^- (\text{ads}) + \text{HCO}_3^- \rightarrow \text{HCOO}^-(\text{ads}) + \text{CO}_3^{2-} \quad (3)$$
$$\text{HCOO}^-(\text{ads}) + e^- \rightarrow \text{HCOO}^-(\text{ads}) \quad (4)$$
$$\text{HCOO}^- (\text{ads}) \rightarrow \text{HCOO}^- (\text{solution}) \quad (5)$$

The Tafel slope of bulk Sn is 118.5 mV dec$^{-1}$, corresponding to a mechanism whereby the reaction rate is controlled by the initial electron transfer to the adsorbed CO$_2$ [eqn (2)], while a Tafel slope of 59 mV dec$^{-1}$ implies the rate-determining chemical step [eqn (3)].$^{42}$ Interestingly, Cu@Sn nanocones showed an intermediate slope of 80.1 mV dec$^{-1}$. To further
toward formate on Cu@Sn nanocones, an electric-field-induced-reagent-concentration (FIRC) effect, the local K⁺ concentration on the nanotip was high, so the effect of the increased potassium concentration in the bulk electrolyte on formate selectivity was relatively weak. The trend of the increment in formate selectivity with increasing K⁺ concentration was more obvious on the bulk Sn. Nevertheless, enriching local K⁺ ions on the catalyst surface by sharpening the structure with Cu@Sn nanocones is more effective than increasing the salinity in the bulk electrolyte for catalyzing CO₂ conversion to formate.

Practically, loading of a catalyst onto a 3D porous substrate such as Cu foam (ESI, Fig. S23†) could increase the active sites and facilitate the mass transfer of reactants to improve the catalytic activity for CO₂ conversion. Therefore, we cultivated

![Fig. 5 (a and b) SEM images of Cu@Sn nanocones/Cu foam, (c) current density and formate faradaic efficiency, (d) stability test for catalysing CO₂ reduction at −1.1 V of Cu@Sn nanocones/Cu foam.](image-url)
Cu@Sn nanocones over a Cu foam substrate via a facile electrodeposition process similar to the process used on Cu foil (ESI, Fig. S24†). SEM images reveal the densely packed Cu@Sn nanocones on the Cu foam framework (Fig. 5a), and the radius of the spiky tip is about 10 nm (Fig. 5b). SEM-EDS mapping confirms the uniform and conformal coating of Sn on Cu nanocones (ESI, Fig. S25†). Electrolysis at Cu@Sn nanocones/Cu foam was measured around the optimal potential (−1.0 V to −1.2 V) in CO₂-saturated solution consisting of 0.1 M KHCO₃ and 0.3 M KCl. Interestingly, Cu@Sn nanocones/Cu foam reached a maximum formate faradaic efficiency of 90.4%, and delivered a high current density of 57.7 mA cm⁻² at −1.1 V (Fig. 5c), indicating a superior performance to most noble-metal-free Sn-based catalysts (Table S2†). In addition to the high activity and selectivity, stability is another critical factor in evaluating the efficiency of a catalyst. The stability of the Cu@Sn nanocones/Cu foam catalyst was investigated at −1.1 V for 10 h in the optimal electrolyte with electrolyte being replaced every hour.₆,2₆ As shown in Fig. 5d, we observed almost no decline of current density, and the slight fluctuation during electrolysis was ascribed to bubble formation and desorption on the catalyst surface. Meanwhile, the faradaic efficiency of formate was slightly decreased after a long-term test, but always remained above 82%. After electrolysis for 10 h, the conical structure of Cu@Sn nanocones/Cu foam was maintained, but its surface became rougher (ESI, Fig. S26†). This slight surface restructuring and sintering of nanostructured Sn may expose Cu active sites during the electrolysis, which are more favorable to H₂ generation and may be responsible for the decreased selectivity in formate production.₃₅,₄₈

Conclusions

In summary, densely packed and spiky Cu@Sn nanocone electrodes were fabricated by a facile and cheap electrodeposition approach. As the high-curvature nanotip would generate a strong electric field to concentrate local K⁺, the as-prepared Cu@Sn nanocones on Cu foil was able to selectively reduce CO₂ to formate at a faradaic efficiency of 88.4%. Further combined with the large surface area and efficient mass transfer, the loading of sharp Cu@Sn nanocones on 3D Cu foam gives an excellent catalytic performance with a faradaic efficiency of 90% and a high current density of 57.7 mA cm⁻². The remarkable performance of highly dense and cost-effective Cu@Sn nanocones/Cu foam demonstrated here may open up new avenues to design efficient electrocatalysts for commercial formate production.

Conflicts of interest

There are no conflicts to declare.

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Notes and references
