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ZnSn Nanocatalyst: Ultra-high Formate Selectivity from CO₂ Electrochemical Reduction and the Structure Evolution Effect

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ABSTRACT: The introduction of tin (Sn) into Zn-based catalyst can change its intrinsic properties of the electrochemically reduction of CO₂ to CO, obtaining a high formate yield. The electron transfer from Zn to Sn lowers down the *d*-band center of Sn, leading to a more reliable surface adsorption of the *OCHO intermediate and resulting high formate selectivity. The obtained ZnSn catalyst enables formate formation with a drastically boosted Faradaic efficiency (FE) up to 94%, which is 2.04 and 1.34 times of pure Zn and Sn foils, respectively, indicating a synergistic effect between Zn and Sn. During the electrochemical CO₂ reduction reaction (eCO₂RR) process, the morphology of the ZnSn catalyst evolved from nanoparticles to nanosheets, nanoneedles and collapsed structures, corresponding to the activation, stabilization and decay stages, respectively. This study provides a facile and controllable approach for the construction of novel bimetallic catalyst favoring formate selectivity based on the synergistic effect.

Keywords: Electrochemical CO₂ reduction reactions, ZnSn bimetallic catalyst, Formate selectivity, Morphology evolution, Composition evolution

1. Introduction

Electrochemical CO₂ reduction reaction (eCO₂RR) is attractive to close the carbon cycle by consuming CO₂ and providing CO, H₂, hydrocarbon and other chemical products [1-6]. Until now, many efforts have been made to promote the activity and selectivity of eCO₂RR, including size and morphology engineering [7-10], grain boundary construction [11], crystal face optimization [12, 13] and composite fabrication of relative catalysts [14-18]. However, the selectivity of eCO₂RR is still a challenge because of the similar thermodynamic potentials of the reduction products and competing hydrogen evolution reaction (HER) [19].

Formate is considered to be one of the most economically profitable products of eCO₂RR because of its vast utilization in organic chemistry industry and renewable [20, 21]. Metal-based electrocatalysts, such as Pb [22, 23], Hg [24], Cd [25], and In [26-30], have been attempted to reduce CO₂ to formate. However, the cost and environment consideration limit their industrial applications in CO₂ electroreduction industry. In this work, an environment friendly and low-cost Zn-Sn catalyst material with high formate selectivity was reported.

As a non-toxic and accessible material with weak *CO adsorption, Zn was regarded as a representative catalyst to produce CO by eCO₂RR. In the past a few years, many progress have been achieved in improving the activity and selectivity of CO over Zn-based catalysts by engineering their morphology [31], sizes [32] and crystal planes [13], *etc.* An encouraging formate selectivity was also observed in Zn electrode catalyst,

however, a high overpotential was required for the eCO₂RR catalysis, which was far from adequate for industrial applications [33]. Recently, bimetallic catalysts have demonstrated impressive performance in eCO₂RR since the binding energy of reaction intermediates can be controlled by modifying the electronic structure and composition of the catalyst [30, 34-38]. A 94% Faradaic efficiency (FE) of formate (94%) was achieved at moderate potential using a bimetallic Zn-Bi catalyst, which was caused by the bifunctional interfaces and grain boundaries between the two metals [39]. Due to a lower *d*-band center of Pd in the Pd-Zn alloy compared to pure Pd an enhanced formate selectivity was also observed in Pd-Zn catalyst [40].

Tin (Sn) is a typical catalyst for selective formation formate from eCO₂RR due to its moderate binding energy to *OCHO [10, 41, 42], as well as its lower cost and abundant supply [43]. A high formic acid selectivity of 97.9% at -1.34 V vs. reversible hydrogen electrode (RHE) was achieved using a SnO₂/ZnO composite catalyst [44]. However, problems such as poor activity and ambiguous catalytic active sites of Sn catalysts hinged their practical application.

Herein, a ZnSn catalyst supported on bulk Zn foil *via* a combination of dry process (calcination of pre-treated Zn foil) and wet process (etching and a facile galvanic replacement reaction [45]). The results showed that the catalytic activity of ZnSn catalyst reached a near unity formate FE (FE_{formate}) of 94% at -1.06 V vs. RHE which was approximate 1.25 times higher than those of the previously reported Sn-based catalysts [46-48]. In the Zn-Sn bimetallic catalyst, the electron transfer from Zn to Sn lowers down the *d*-band center of Sn, which leads to a stable surface absorption of the

intermediate *OCHO and result in high formate selectivity. The morphology evolution of ZnSn catalysts during the eCO₂RR process was further studied by scanning electron microscopy (SEM). The morphology evolution of nanoparticles, nanoflowers nanoneedles correspond to the of activation, stabilization and decay processes of the ZnSn catalyst during the electrolysis process.

2. Experiments

2.1. Material synthesis

Zn foil (99.99%, 0.5 cm × 1 cm × 0.0005 cm) was used as the substrate, which was ultrasonically cleaned in acetone and deionized water before use. After pretreatment, this Zn foil was heated to 300 °C with a heating rate of 2 °C min⁻¹ in air and kept for 4 h to obtain ZnO nanofilm. ZnSn catalyst was prepared by soaking the as-fabricated ZnO foil in SnCl₂ solution with different concentrations (5, 10, 20, 30, 40 mM) for 1.5 min. For comparison, the commercial Zn foil, Sn foil and the ZnO precursor mentioned above were cleaned with the same procedure and subjected to electrochemical tests under the same conditions.

2.2. Electrochemical testing

CO₂ electrochemical reduction tests were conducted with a CHI760E electrochemical workstation in a home-made gas-tight H-type cell separated by a Nafion 117 membrane. The prepared ZnSn acted as a working electrode, a commercial graphite rod as counter electrode, and Ag/AgCl (in saturated KCl electrolyte) electrode

acted as a reference electrode. CO₂-saturated 0.5 M KHCO₃ was used as electrolyte and the flow rate of CO₂ was 20 standard cubic centimeters per minute (sccm) before and during the electrochemical tests. All the applied potentials are converted to RHE using the following equation:

$$E \text{ (vs. RHE)} = E \text{ (vs. Ag/AgCl)} + 0.197 \text{ V} + 0.0591 \text{ V} \times \text{pH}.$$

2.3. Product analysis

Gaseous products were analyzed by a gas chromatograph (Shanghai Ruimin GC-2060) with Ar as the carrier gas every 15 min. Hydrogen concentration was measured by a thermal conductivity detector, and carbon monoxide concentration by a flame ionization detector. The FE of CO (or H₂) generation is calculated as follows:

$$FE_{CO} (\%) = \frac{Q_{CO}}{Q_{total}} \times 100\% = \frac{\frac{v}{60s/min} \times \frac{c}{24000 \text{ cm}^3/mol} \times zF}{i} \times 100\%$$

Here, Q is the electric quantity during the eCO₂RR process; v (= 20 sccm) is the flow rate of the CO₂; c is the concentration of CO (or H₂) in the 1 mL sampling-loop in gas chromatography; z (= 2) is the number of transferred electrons for 1 mol CO (or H₂) generation; F (= 96485 C mol⁻¹) is the faradaic constant; and i (A) is the recorded current during electrolysis.

The main liquid product formate was analyzed by the ion chromatography (Soptop IC1820). The mobile phase was 5 mM KOH aqueous solution. The FE for formate generation was calculated as follows:

$$FE_{\text{formate}}(\%) = \frac{Q_{\text{formate}}}{Q_{\text{total}}} \times 100\% = \frac{n_{\text{formate}}zF}{it} \times 100\%$$

Here, n_{formate} is obtained from the standard curve with respect to the relationship between the conductivity and corresponding concentration of HCOONa; z ($=2$) is the number of transferred electrons for 1 mol formate formation; F ($= 96485 \text{ C mol}^{-1}$) is the faradaic constant; i (A) is the recorded current during electrolysis; and t (s) is the electrolysis time.

2.5. Structural characterizations

X-ray diffraction (XRD) patterns of the electrocatalysts were identified on a Bruker D8 Advance X-ray diffractometer. X-ray photoelectron spectroscopy (XPS, Escalab 250XI) was used to analyze the surface chemical composition and valence states of the catalyst. The Binding energies (B.E.) was calibrated by C 1s core level at 284.6 eV. The microstructure and chemical composition of the samples were observed and determined by scanning electron microscopy (SEM, Sigma-300) equipped with energy dispersion spectroscopy (EDS).

3. Results and discussion

ZnSn catalyst was synthesized by a combination of dry and wet process, as shown in Fig. 1a. First, the pre-treated Zn foil was calcined to obtain a rough and dense ZnO nanofilm on its surface (ZnO/Zn foil), which was the dry process. The formation of rough and dense ZnO nanofilm was beneficial to the following replacement reaction in acid solution. In the subsequent wet process, the as-prepared ZnO/Zn foil (referred to

as ZnO hereinafter) was immersed in acid solutions containing SnCl_2 with different concentrations to partially etch the ZnO nanofilm. Then, a galvanic replacement reaction occurred between Zn and Sn due to their different redox potentials. The formation of dense ZnO nanofilm may be conducive to the formation of ZnSn catalyst, which is beneficial to formate formation to a certain extent.

Fig. 1 (a) The schematic illustration of ZnSn catalysts growth on Zn foil. (b) $\text{FE}_{\text{formate}}$ from the eCO_2RR test on ZnSn catalysts in SnCl_2 solution with different concentrations. The eCO_2RR tests were carried out in CO_2 -saturated 0.5 M KHCO_3 at $-1.06 \text{ V}_{\text{RHE}}$ for 1.5 h. (c) FEs of H_2 , CO, and formate on Sn foil, Zn foil, ZnO and ZnSn catalyst in CO_2 -saturated 0.5 M KHCO_3 at $-1.06 \text{ V}_{\text{RHE}}$ for 1.5 h.

To investigate the influence of SnCl_2 concentration on the formate selectivity of the obtained ZnSn catalyst, eCO₂RR tests were carried out in CO₂-saturated 0.5 M KHCO₃ at $-1.06 \text{ V}_{\text{RHE}}$ for 1.5 h. The results showed that the formate selectivity could be easily tuned by just changing the concentration of SnCl_2 solution. As seen in Fig. 1b, as the SnCl_2 concentration increased to 20 mM, the $\text{FE}_{\text{formate}}$ increased and reached a peak value of 94%. However, as the concentration of SnCl_2 continued to increase, the $\text{FE}_{\text{formate}}$ began to decrease, indicating 20 mM was the optimal SnCl_2 concentration. The eCO₂RR performance was then compared with pure Zn foil, Sn foil and ZnO materials at -1.06 V vs. RHE (Fig. 1c). The results exhibited that the pure Zn foil predominantly yielded formate (46%) and CO (43%). The formate selectivity of the catalyst increased to 68% after coating ZnO nanofilm (ZnO catalyst). Meanwhile, the main product of Sn foil catalyst in the process of CO₂RR was formate (70%); as well as some H₂ and CO, which was basically consistent with the literature [49]. It is worth noting that when Sn was introduced, the $\text{FE}_{\text{formate}}$ of the ZnSn catalyst significantly increased to 94%, which was 2.04 and 1.34 times of pure Zn and Sn foils, respectively, indicating the synergy effect between Zn and Sn. The results demonstrated that the introduction of Sn can regulate the electrocatalytic activity of Zn and promote the formate selectivity from eCO₂RR.

The XRD patterns in Fig. 2 show the crystal structures of Zn foil, ZnO, ZnSn and Sn foil catalysts. All the diffraction peaks of Zn foil at 36.30° , 39.00° , 43.23° , 54.33° , 70.06° , 77.02° , 82.10° and 86.56° can be assigned to the metallic Zn phase (PDF: 04-0831). In the XRD pattern of ZnO, a small number of peaks can be observed, typically

at 34.42° , 36.25° and 69.09° , which indicates the existence of ZnO phase (PDF: 36-1451). Note that the (101) peak at 36.25° of ZnO and the (002) peak at 36.29° of Zn are close to each other and merge into one peak. For ZnSn catalyst, diffraction peaks of standard Sn (PDF: 04-0673) and standard pattern Zn (PDF: 04-0831) can be observed, indicating that Sn^{2+} was reduced to metallic Sn through the replacement reaction with Zn. Besides, it was found that the characteristic peak intensity belonged to Sn is significantly greater than those of Zn, which to some extent indicates that Sn is the main component of ZnSn catalyst before the electrochemical reduction process. In addition, all diffraction peaks in Sn foil match well with the metallic Sn phase (PDF: 04-0673). Then, the morphologies of Zn foil, Sn foil, ZnO, and ZnSn catalysts before eCO_2RR tests were characterized (Fig. S1). As seen, the surfaces of Sn and Zn foil are both smooth before reaction or treatment (Fig. S1 a-b). After calcinated in air, the surface of the Zn foil became rough due to the formation of ZnO nanoparticles with an average size of 20 nm on the surface, with the average size of 20 nm (Fig. S1 c). When the ZnO foil was immersed in SnCl_2 solution, the substitution between Sn^{2+} and Zn occurred. Meanwhile, the surface of the ZnO foil became rougher because the resulting Sn nanosheets grew evenly on the surface of the Zn foil, as shown in the red circle of Fig. S1 d.

Fig. 2 XRD patterns of Sn foil, ZnSn, ZnO and Zn foil.

To investigate the eCO₂RR properties of the electrodes with the product distribution, a series of electrochemical tests were carried out. Fig. 3a shows the LSV curves of Sn foil, Zn foil, ZnO and ZnSn in Ar or CO₂-saturated 0.5 M KHCO₃ in the potential range of -0.50 V to -1.25 V_{RHE} and the inset showed the corresponding enlarged part from -1.10 V to -1.25 V_{RHE}. As seen, no catalysts have CO₂ reduction activity in Ar atmosphere, and this current density is derived from the hydrogen evolution reaction (HER). In contrast, all catalysts in CO₂ atmosphere show higher current density and lower initial potential compared with those in Ar atmosphere. This indicates that all the catalyst surfaces are more prone to eCO₂RR. Moreover, the difference in current density of ZnSn catalyst under CO₂ atmosphere and Ar atmosphere is significantly higher than that of other reference catalysts under -1.06 V potential, implying the better eCO₂RR activity for ZnSn catalyst. Fig. 3b displays the FE_{formate} of

Zn foil, ZnO, Sn foil and ZnSn electrodes at different potentials. Unexpectedly, the FE_{formate} of ZnSn catalyst in the entire potential range is at all applied potentials are remarkably higher than those of Sn foil, Zn foil and ZnO. It is worth mentioning that with a more negative potential, the FE_{formate} of ZnSn catalyst gradually increases and reaches a maximum value of 94% at -1.06 V vs. RHE, exceeding most of the reported Sn-based catalysts [50-52]. As the potential continues to become more negative, the yield of hydrogen spiked and formate formation was suppressed, possibly due to HER being more favorable in a more negative potential region. The partial formate densities (j_{formate}) of the catalysts were then analyzed and presented in Fig. 3c. As seen, the j_{formate} of ZnSn catalyst in the potential ranges from -0.86 V to -1.25 V_{RHE} is higher than that of Zn foil, Sn foil and ZnO electrode. The j_{formate} of ZnSn catalyst is 9.95 mA cm⁻² at -1.06 V vs. RHE and it reaches the maximum value of 12.86 mA cm⁻² at -1.16 V vs. RHE, which was 1.68, 1.29 and 1.41 times of those of Zn foil (7.65 mA cm⁻²), Sn foil (9.98 mA cm⁻²) and ZnO (9.09 mA cm⁻²) electrode, respectively, at the same potential. This indicates that the introduction of Sn can improve the performance of the Zn-based catalyst, which roots from the possible synergistic effect between Sn and Zn. In addition, we also provide electrochemical double layer capacitance measurements for (a) electropolished Zn, (b) Sn and (c) ZnSn electrodes in Fig. S2 to compare the electrochemically active area (ECSA). By defining the ECSA of electropolished Zn to be 1, the normalized ECSA of Sn and ZnSn electrodes are determined as 1.05 and 1.56 respectively. The ECSA-calibrated current densities are presented in Fig. S2d. In addition, the ECSA of ZnO is not provided because zinc oxide and other oxides are

easily reduced under cathodic current, making it difficult for ZnO electrodes to obtain stable electrochemical bilayer and ECSA.

Fig. 3 (a) LSV results of Zn foil, ZnO, Sn foil and ZnSn electrode in Ar-saturated (dashed line), or CO₂-saturated (solid line) 0.5 M aqueous KHCO₃ solution with a scanning rate of 10 mV s⁻¹ and insert is the enlarged LSV curves within the potential range of -1.10 to -1.25 V_{RHE}. (b) FEs of Zn foil, ZnO, Sn foil and ZnSn electrode at different potentials. (c) Formate current density of Zn foil, ZnO, Sn foil and ZnSn electrode at different potentials. (d) Tafel plots at different overpotentials (η) as a function with the j_{formate} , on Zn foil, ZnO, Sn foil and ZnSn electrode.

To further gain the kinetic mechanism of formate formation from eCO₂RR on the catalysts, Tafel plots in Fig. 3d show the relationship between overpotentials (η) and

$\log(j_{\text{formate}})$. The Tafel slope of ZnSn electrode (147 mV dec^{-1}) is much smaller than those of Zn foil ($241.7 \text{ mV dec}^{-1}$), Sn foil ($218.3 \text{ mV dec}^{-1}$) and ZnO ($291.6 \text{ mV dec}^{-1}$), suggesting the enhanced kinetic performance of ZnSn electrode to reduce CO_2 to formate. Besides, the Tafel slope of ZnSn catalyst was between the theoretical value of 118 mV dec^{-1} and 200 mV dec^{-1} , demonstrating that the rate determining step of formate generation from e CO_2 RR was the initial one-electron transfer step and CO_2 adsorption [53]. The possible reaction pathway of the e CO_2 RR to formate is *via* the $\ast\text{OCHO}$ pathway rather than the $\ast\text{COOH}$ pathway. The former pathway leads to the production of formic acid and the latter to CO, as follows:

For CO pathway:

For formate pathway:

To identify the real active centers of catalysts during e CO_2 RR with more confidence, XRD and XPS analyses were immediately performed to study the structures of catalysts after completing the e CO_2 RR process. XRD patterns of the ZnO catalyst at 36.30° , 39.00° , 43.23° , 54.33° , 70.06° and 82.10° in Fig. 4a completely correspond to the characteristic diffraction peak of the metal Zn (PDF:04-0831),

proving the ZnO in the catalyst is reduced to the metal Zn. The Zn foil and Sn foil catalysts still retain the form of metallic Zn (PDF:04-0831) and metallic Sn (PDF: 04-0673), respectively, after the eCO₂RR process. The phase compositions of ZnSn catalyst are mainly metallic Zn (PDF:04-0831) and metallic Sn (PDF: 04-0673) after the eCO₂RR process, and they are probably the real catalytic active centers. Moreover, compared with XRD patterns of ZnSn catalyst before electrocatalysis (Fig. 2), the characteristic peak intensity of Sn decreases significantly, while that of Zn increase expressively, indicating that both the composition and structure of ZnSn catalyst have undergone great changes after the electrochemical reduction process. Furthermore, the chemical valence states on the surface of ZnSn catalyst after eCO₂RR were further determined by XPS measurements. As seen in Zn 2p XPS spectra (Fig. 4b), the binding energies at 1044.9 and 1021.9 eV match well with Zn 2p_{1/2} and 2p_{3/2}, respectively, indicating the Zn sites on the ZnSn surface are in Zn⁰ state. The binding energies of Sn 3d at 493.4 and 484.4 eV demonstrate that Sn sites on the surface are in Sn⁰ state, which is consistent with the previously reported values (Fig. 4c) [54]. In addition, peaks at 494.7eV and 487.5 eV correspond to Sn^{x+} [55], which is likely caused by partial oxidation of Sn in air. Furthermore, in contrast to the standard Zn and Sn, Zn 2p XPS peaks shift to higher binding energy, while and Sn 3d XPS peaks shift to lower binding energy. This binding shifts indicate that electrons in ZnSn catalyst transfer from Zn to Sn, due to the lower work function of Zn than Sn (3.63 eV vs. 4.42 eV) [56]. Based on these results, we propose Sn as the active center, which can be regulated by Zn. Because the electron transfer from Zn, the increase of 3d electron density in Sn will lower the d-

band center. According to the d-band center theory, the lowered d-band centers in the ZnSn catalyst will increase the bonding states and reduce the antibonding states, weakening the interaction between catalyst and adsorbents. Therefore, we believe that the lowered d-band center in ZnSn catalyst tend to weaken the adsorption of $^*\text{COOH}$, thus promoting its high selectivity to formate through the $^*\text{OCHO}$ adsorption pathway.

Fig. 4 (a) XRD patterns of Sn foil, ZnSn, ZnO and Zn foil after eCO₂RR process, (b) Zn 2p and (c) Sn 3d XPS spectra of ZnSn electrode after eCO₂RR process.

The morphology of Zn foil, Sn foil, ZnO and ZnSn catalyst after CO₂ electroreduction were characterized by SEM, as shown in Fig. S3, which were totally different from those before eCO₂RR tests (Fig. 2). After electroreduction process, obvious nanoflowers can be observed on the surface of Zn foil (Fig. S3a), while Sn nanoparticles clearly appear on the surface of Sn foil (Fig. S3b). Nanoparticles on the surface of ZnO become more aggregated (Fig. S3c). In particular, two different morphologies, nanoparticles and nanoflowers, appear on the surface of ZnSn electrode at the same time. These results indicate that the ZnSn nano-catalysts undergo surface reconstruction during the entire electrochemical CO₂ reduction process, promoting the synergistic interaction between Zn and Sn.

To assess the stability of the as-synthesized catalyst, the ZnSn catalyst was electrolyzed at -1.06 V vs. RHE for 12 h (Fig. 5a). The results show that the catalytic current density firstly increases gradually and then tends to be stable within a prolonged electrolysis time. Impressively, the FE_{formate} increases rapidly from 60% to 94% in the initial 3.0 h, indicating that the catalyst is gradually activated and stabilized at the initial stage of electrolysis. When the electrolysis time is extended to 3~6 h, the FE_{formate} remains almost stable. Until 12 h, the FE_{formate} slightly decreases. Furthermore, we compared our ZnSn catalyst with other reported electrodes in terms of the maximum FE_{formate} at certain potentials (Fig. 5b and Table S2). The selectivity of formate of the

ZnSn electrode in this work is at the leading level, even surpassing those of Sb [50], sulfur derived Bi [51] and Sn [52], *etc.*

Fig. 5 (a) Long-term stability of the ZnSn electrode at -1.06 V vs. RHE for 12 h and the corresponding FE_{formate} . (b) Comparison of ZnSn electrode with other reported electrodes in terms of the highest FE_{formate} at certain potentials. The formate selectivities of the involved electrocatalysts are summarized in Table S2.

We propose that the variation trend of the formate selectivity is originated from the morphology evolution of ZnSn catalyst during eCO₂RR process investigated by SEM, as shown in Fig. 6 a-f, including the evolution of the morphology and the distribution of Zn and Sn on the surface of ZnSn electrode after electrocatalysis for different time. According to SEM results, eCO₂RR process can be divided into three stages, namely initial activation stage, stabilization stage and decay stage. The atomic proportions of Zn and Sn in the ZnSn catalyst at different electrolysis stage are also measured by EDS and shown in Table S1. At the beginning, ZnSn electrode shows a uniform coating of Sn on the surface (Fig. S4) with a Zn/Sn ratio of 15.13 : 84.87 (Table S1), suggesting a higher Sn ratio before the electrolysis process. This result is also

consistent with the XRD result before the electrolysis process (Fig. 2). After 0.5 h of electrolysis, a small amount of Zn nanoparticles deposited on the surface of ZnSn electrode (with a Zn/Sn ratio of 28.17 : 71.83), which resulted from surface reconstruction induced by the continuous dissolution of Zn from the electrode surface and their re-deposition at a negative reduction potential (Fig. 6a) [31]. After 1.0 h of electrolysis, the surface of ZnSn was partially activated and the surface roughness further increased with an increased Zn/Sn ratio of 39.91 : 60.09, owing to the enhanced interaction between Sn and Zn with the extension of electrolysis time (Fig. 6b). At this stage, the FE_{formate} achieved an increase trend with 64%, 80% and 90% after 0.5h, 1.0 h and 1.5 h of electrolysis, corresponding to the activation stage, as shown in Fig. 5a. After 1.5~3.0 h of electrolysis, the ZnSn catalyst was further activated and entered into a stabilization stage. At this stage, Zn/Sn ratio reached about 65: 35 and Zn nanoflowers began to appear on the surface of Sn in addition to Zn nanoparticles, (Fig. 6c and d). Moreover, the enhanced FE_{formate} remained above 90% at this stage, suggesting that the nanoflowers significantly improved the formate selectivity of the catalyst. After electrolysis for 6.0 hours (Fig. 6e), the Zn nanoflowers further grew into needle-like structures to obtain increased surface area and continuously enhanced formate selectivity. Although the Zn/Sn ratio increased to about 80: 20, the formation of needle structures still improved the formate selectivity, so that a balanced and stable FE_{formate} could still be achieved. This result indicates that this stage (3.0~6.0 h) resembles the stabilization stage, indicating that the service life of ZnSn catalyst is relatively long. This could explain the formate selectivity of ZnSn catalyst increased gradually at the

initial stage and stabilized at 1.5~6.0 h of electrolysis (Fig. 5a). After electrolysis for 12 h (Fig. 6f), the nanostructure of ZnSn catalyst tends to partially collapse together with a decrease of Sn content in the electrode, which corresponds to the decay stage of the eCO₂RR process with a slight decrease in formate selectivity. From above results, the atomic ratio of Zn to Sn shows an increasing trend (activation stage) at the first 1.5 hours of electrolysis, accompanied by the appearance of nanoparticles with unsmooth surface and the greatly improved formate selectivity. Then, the Zn/Sn atomic ratio continue to increase in the stabilization stage (after 1.5-6.0 hours of electrolysis) and the appearance of nanoflowers and nanoneedles increases the surface area, which are profitable to the interaction between Zn and Sn and significantly promoting the formate selectivity from CO₂ electroreduction. Furthermore, the relative long stabilization stage in the evolution progress is beneficial to maintaining high selectivity of formate from CO₂ electroreduction. Then, the structure of ZnSn catalyst begin to collapse after electrolysis for 12 hours (decay stage) with an increased Zn/Sn atomic ratio and slight decline of the formate selectivity. In addition, the fundamental reason of morphology evolution of the electrocatalyst is also related to the electrochemical reduction potential of Zn and Sn. Compared with Sn, the redox potential of Zn²⁺/Zn (−0.76 V vs. normal hydrogen electrode, NHE) is much lower than that of Sn²⁺/Sn (−0.137 V vs. NHE), which should be the reason why the Zn content increases with increasing electrolysis time. These results demonstrate that the evolution of morphology of ZnSn catalyst and the Zn/Sn atomic proportion during the eCO₂RR process results in the FE variation of formate from increasing to plateau to slight attenuation in the end.

Fig. 6 SEM images and the corresponding mapping images of ZnSn electrode after the eCO₂RR testing for (a) 0.5 h, (b) 1 h, (c) 1.5 h, (d) 3 h, (e) 6 h and (f) 12 h.

To elucidate the origin of the unprecedented improvement in formate selectivity over ZnSn catalyst, we propose a possible pathway for eCO₂RR in this system. The Zn active centers on Zn foil and ZnO electrodes are probably electro-reducing CO₂ *via* a

COOH* intermediate pathway, thus further producing CO. However, with the introduction of Sn active sites, the ZnSn catalyst exhibits a similar formate-selective property to that of monometallic Sn. Therefore, Sn is regarded as the active site for the selective reduction of CO₂ to formate on ZnSn catalyst. Consequently, the oxyphilic surface of Sn tends to absorb *O atoms in CO₂ molecules to stabilize the *OCHO intermediates, as shown in Fig. 7a. This indicates that the ZnSn electrode will adopt a *OCHO pathway, which will further yield formate. Meanwhile, the pathway of CO production will shut down due to the decrease of the number of Zn active sites and the deactivation of Zn sites. The formation of nanoflower structure of ZnSn can promote the production of formate. In addition, XPS results and the work function values of Zn and Sn both prove that the interaction between Zn and Sn leads to the electron transfer from Zn to Sn on the surface of ZnSn. Besides, according to the *d*-band center theory, the *d*-band center of Sn would be lowered due to the increase of electron filling of *d*-band [57-59], as shown in Fig. 7b. The lowered *d*-band center of Sn is beneficial to decreasing the adsorption energy of oxygen species intermediate on the ZnSn catalyst, and further effectively enhancing the formate selectivity from eCO₂RR [40]. Furthermore, the morphology and composition evolution of ZnSn catalyst in the eCO₂RR process leads to the variation trend of FE_{formate} from increasing to stable to slight attenuation.

Fig. 7 (a) Possible reaction pathways for the electrochemical reduction of CO_2 to C_1 products on the surface of ZnSn catalyst. (b) The possible relationship between the position of d -band center and the formate selectivity from eCO_2RR on ZnSn catalyst.

3. Conclusions

In summary, it is of great significance to study the structure-activity relationship of bimetallic eCO_2RR catalysts, especially the influence of morphology and composition on the activity. In this study, a novel bimetallic eCO_2RR catalyst with ultra-high formate selectivity was developed and the influence of structure evolution of

the catalyst on the performance of eCO₂RR was also demonstrated. The selectivity of formate can be regulated by changing the concentration of SnCl₂ solution. The ZnSn catalyst can obtain the highest formate selectivity of 94% at moderate overpotential, which is among the best catalysts towards formate formation. Impressively, the formate selectivity is related to the electron transformation from Zn to Sn and the synergistic effect between Zn and Sn, which decreased the *d*-band center of Sn and stabilize the surface adsorption of the *OCHO intermediate to shut down the CO pathway. In addition, the structure evolution of morphology and Zn/Sn atomic ratio indicates an eCO₂RR performance stage from activation to stabilization and decay. Meanwhile, the nanoflower structure in the stabilization stage is favorable for the interaction between Zn and Sn and thus promotes the selectivity of formate for CO₂ electroreduction.

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(a) The schematic illustration of ZnSn catalysts growth on Zn foil and (b) the possible

reaction pathways for the electrochemical reduction of CO₂ to C₁ products on the surface of ZnSn catalyst.

CRediT Author Statement

This statement is to certify the contribution of all the authors for the manuscript [JCIS-21-5916] titled “ZnSn Nanocatalyst: Ultra-high Formate Selectivity from CO₂ Electrochemical Reduction and the Structure Evolution Effect” which were submitted on **Journal of Colloid and Interface Science**.

Wenjuan Li: Experimentalizing, data analysis, writing original draft preparation, **Zhengrong Zhang**: Part of data analysis, Software, **Wenhui Liu**: Part of data analysis, **Quan Gan**: improving the English writing, **Minmin Liu**: Reviewing, modifying and Editing, **Shengjuan Huo**: Supervision, Experiment design, Writing, Reviewing and Editing, **Wei Chen**: Reviewing and Editing.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: