Heterophase engineering of SnO₂/Sn₃O₄ drives enhanced carbon dioxide electrocatalytic reduction to formic acid

Jun Wu¹, Ying Xie², Shichao Du², Zhiyu Ren^{2*}, Peng Yu², Xiuwen Wang¹, Guiling Wang^{1*} and Honggang Fu^{2*}

ABSTRACT Sn-based electrocatalysts have been gaining increasing attention due to their potential contribution in the conversion of CO₂ into HCOOH driven by sustainable energy sources; however, their actual capability to catalyze CO₂ reduction reaction (CO₂RR) still cannot meet the requirements of commercial-scale applications. Therefore developing Sn-based catalyst is of vital importance. Herein, the sheet-like heterophase SnO₂/Sn₃O₄ with a high density of phase interfaces has been first engineered by a facile hydrothermal process, with Sn₃O₄ as the dominant phase. The evidences from experiments and theoretical simulation indicate that the charge redistribution and built-in electric field at heterophase interfaces boost CO₂ adsorption and HCOO* formation, accelerate the charge transfer between the catalysts and reactants, and ultimately greatly elevate the intrinsic activity of the heterophase SnO₂/Sn₃O₄ towards CO₂RR. Meanwhile, the *in-situ* generated porous structure and metal Sn during CO₂ RR improve the mass transmission within the interlayer volume and the conductivity of SnO₂/Sn₃O₄. The heterophase SnO₂/Sn₃O₄ displays high activity and selectivity for CO₂RR, achieving an improvement in CO₂ reduction current density, 88.3% Faradaic efficiency of HCOOH conversion at −0.9 V_{RHE}, along with a long-term tolerance in CO₂RR. This study demonstrates that heterophase interface engineering is an efficient strategy to regulate advanced catalysts for different applications.

Keywords: heterophase engineering, SnO₂/Sn₃O₄, electrocatalytic CO₂ reduction reaction, formic acid, density functional theory calculation

INTRODUCTION

The total amount of CO₂ emission derived from industrial production processes in the world is more than 24 billion tons per year, of which 15 billion tons can be absorbed by plants, while the remaining 9 billion tons become the main waste gas leading to the greenhouse effect, global warming, glaciers melting, rise of sea level and a series of other serious problems. It is very urgent to develop technologies capable of efficiently alleviating atmospheric pollution and expediting global scalability of carbon-neutral resource cycle [1–5]. Electrochemical CO₂ reduction is a powerful strategy for converting CO₂ into the value-added chemical or fuel mainly due to its feasible operating conditions and high density storage capacity of the intermittent renewable energy synchronously [6,7]. However, owing to the complicated and sluggish kinetic pathways of electrocatalytic CO₂ reduction reaction (CO₂RR) that involves the simultaneous (or successive) transfer of multiple-electron/proton coupling accompanied with various possible intermediates and products [8,9], CO₂RR usually suffers from low current density, large applied potential, and even poor selectivity [10–12]. Therefore, engineering high-efficiency electrocatalysts, and further giving insight into the catalytic essence are of significance to achieve CO₂ conversion at a reasonable efficiency and cost, but remain a major challenge [13–15].

Up to now, although C₂ products have higher energy densities and wider prospect in the chemical industry, the high catalytic efficiencies and production rates for C₁ products (e.g., CO, CH₄, HCOOH, and/or formate) offer

¹ Key Laboratory of Superlight Materials and Surface Technology of Ministry of Education, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China

² Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education of China, School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, China

* Corresponding authors (emails: wanguiling@hrbeu.edu.cn (Wang G); fuhg@vip.sina.com (Fu H); zyren@hlju.edu.cn (Ren Z))

more immediate opportunities for the commercial-scale applications of CO₂RR [16–20]. Sn-based material is one kind of attractive electrocatalyst for CO₂RR due to its low toxicity, abundant reserve, and especially it can selectively form HCOOH (or formate) [21–23]. Nevertheless, its high cathodic potential, low faradaic efficiency, weak conversion capacity and poor prolonged durability for CO₂RR are inevitable issues. To boost the catalytic performance of Sn-based catalysts, tremendous researches have been focused on modulating the catalysts' morphology [24], size [25], oxidation state [26], crystallization degree [27], component [28], and even surface defect [29]. Luc *et al.* [30] revealed that the oxygen vacancies in an AgSn/SnO_x core-shell structure can contribute to CO₂ activation. Bai *et al.* [31] and Zheng *et al.* [32] demonstrated the incorporation of Pd and Cu into metal Sn can effectively suppress H₂ evolution, resulting in remarkable enhancement in selective HCOOH or formate generation. It is noteworthy that, although the transformation of SnO_x into metal Sn at low cathodic potential is unavoidable, the low oxidized Sn^{δ+} is always the catalytic active site that can effectively facilitate the adsorption of CO₂, the formation of intermediate HCOO*, and the generation of HCOOH [26,33,34]. Apparently, it is particularly significant in engineering high-efficiency CO₂ catalysts to reveal the intrinsic characteristics of Sn-based catalysts. Unfortunately, the relationship between the structure characteristics, especially phase and heterophase characteristics, and the catalytic activity of SnO_x is so far rarely explored. The heterophase interface engineering has been regarded as an effective strategy to fine regulate the local electronic configuration of active sites on the heterophase interface, and then to modulate the adsorption and conversion of reactants and key intermediates, thus achieving the intriguing photocatalysis and electrocatalysis [35–41]. SnO_x heterophase could effectively trigger CO₂RR.

In this study, a series of SnO_x catalysts have been successfully adjusted from SnO₂ to SnO₂/Sn₃O₄, then to Sn₃O₄, by simply changing the starting ratio of SnCl₂·2H₂O and NaOH in a facile hydrothermal reaction. As a proof-of-concept study, the phase-dependent catalytic activity towards CO₂RR and the change in structure characteristics of the synthesized SnO_x catalysts have been systematically investigated. Compared with Sn₃O₄ and SnO₂, the resultant SnO₂/Sn₃O₄ heterophase displays excellent activity, selectivity and stability in the conversion of CO₂ to HCOOH, achieving a remarkable CO₂ current density (19.03 mA cm⁻²) and 88.3% Faradaic efficiency of HCOOH (FE_{HCOOH}) at -0.9 V_{RHE}. Further evidences from

experiments and density functional theory (DFT) calculations reveal the priority of SnO₂/Sn₃O₄ heterophase interface in the selective reduction of CO₂ to HCOOH.

EXPERIMENTAL SECTION

Material synthesis

SnCl₂·2H₂O (2 mmol) and 7.5 mmol of NaOH powder were dissolved in 35 mL and 5 mL of distilled water with stirring, respectively. Subsequently, the NaOH solution was poured into the SnCl₂·2H₂O solution under vigorous stirring. After continuous stirring for 5 min, the mixed solution was transferred into a 50-mL hydrothermal kettle. Afterwards, a piece of carbon cloth (CC, 3 cm × 4 cm) was placed in the hydrothermal kettle, which was then kept in an oven at 160°C for 12 h. When the temperature dropped to room temperature, the CC was taken out and washed with distilled water and ethanol for several times, and dried under vacuum at 60°C. As a comparison, we just added different amounts (1 and 3 mmol) of SnCl₂·2H₂O for SnO₂ and Sn₃O₄ respectively, and the other processes were the same as that of SnO₂/Sn₃O₄, with the CC washed by water and acetone thoroughly prior to use.

Characterization

X-ray diffraction (XRD) patterns were taken on a Rigaku D/max-III B diffractometer (2θ = 1°–80°, Cu Kα radiation, λ = 0.15406 nm). Scanning electron microscopy (SEM) images were acquired by using Hitachi S-4800 SEM with an acceleration voltage at 15 kV. Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-3010 TEM. X-ray photoelectron spectroscopy (XPS) was measured at AXIS ULTRA DLD. X-ray absorption spectroscopy (XAS) was carried out with a Si (111) double crystal monochromator at 3.5 GeV, 150–210 mA, including X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses. CO₂-temperature programmed deposition (TPD) measurements were conducted in a U-type quartz reactor with a Micromeritics AutoChem-II instrument equipped with a thermal conductivity detector (TCD). The gas phase products were performed with a Kechuang 2002 Gas chromatography (GC), composed of flame ionization detector (FID) and a thermal conductivity detector (TCD) systems. The Bruker AVIIHD 400 MHz was used to measure the liquid phase products.

Electrochemical measurements

Performance measurements were characterized with a

type H cell separated by a Nafion 117 proton exchange membrane in the middle. Each compartment contained 10 mL headspace and 20 mL of $0.5 \text{ mol L}^{-1} \text{ KHCO}_3$ electrolyte. Electrochemical measurements were carried out by Princeton Applied Research (VersaSTAT 3, USA) at room temperature ($25 \pm 2^\circ\text{C}$). The counter electrode and reference electrode were a Pt mesh and the saturated Ag/AgCl, respectively, and a piece of $\text{SnO}_2/\text{Sn}_3\text{O}_4$ (or SnO_2 and Sn_3O_4)/CC ($1 \text{ cm} \times 1 \text{ cm}$) was used as working electrode. CO_2 (or Ar) gas was injected into the electrolyte before electrolysis at least 30 min to ensure the electrolyte to reach CO_2 -saturation (pH 7.78) (or Ar-saturation, pH 8.82). The linear scan voltammetry (LSV) measurements were conducted from 0 to $-1.1 \text{ V}_{\text{RHE}}$ at a scan rate of 5 mV s^{-1} . The chronoamperometry were conducted at $-0.9 \text{ V}_{\text{RHE}}$ for 12 h. During the electrolysis, the gas phase products were quantitatively analyzed by GC on-line detection. The gas phase composition was analyzed by GC every 30 min with different potentials applied. The electrolyte after electrolysis was collected and analyzed with ^1H -nuclear magnetic resonance (^1H -NMR) to monitor the concentration of liquid phase products (add 0.1 mL D_2O and 0.5 μL dimethyl sulfoxide to 0.5 mL electrolyte). Electrochemical impedance spectra (EIS) were performed with an AUTOLAB electrochemical workstation in $0.5 \text{ mol L}^{-1} \text{ KHCO}_3$ at room temperature. The potential (E) was converted to the value versus reversible hydrogen electrode (RHE) in this study by the equation:

$$E(\text{vs. RHE}) = E(\text{vs. Ag/AgCl}) + 0.1980 \text{ V} + 0.059 \times \text{pH}.$$

The Faradaic efficiency (FE) of gas phase and liquid phase products can be calculated (details in Supplementary information). The specific electrochemical active surface area (ECSA) of the electrodes was calculated from C_{dl} according to $\text{ECSA} = C_{\text{dl}}/C_s$, where C_{dl} is the double-layer capacitance and C_s is the specific capacitance.

Theoretical calculation

DFT calculations were performed by using the plane-wave technique implemented in the Cambridge Sequential Total Energy Package (CASTEP) (details in Supplementary information).

RESULTS AND DISCUSSION

Structure and morphology of $\text{SnO}_2/\text{Sn}_3\text{O}_4$

According to the design, various SnO_x catalysts have vertically grown on the surface of CC by a facile hydrothermal process (Fig. 1a), in which the proportion of

$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and NaOH in the reaction system is of importance for the formation of different crystal phases. The phases and crystal structures of the SnO_x catalysts were analyzed by XRD. As shown in Fig. 1b, the obtained catalysts evolve from SnO_2 into Sn_3O_4 accompanied by increasing mole ratio of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and NaOH. When the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}/\text{NaOH}$ mole ratio is 2:7.5, the identified XRD peaks can be perfectly assigned to the rutile tetragonal phase SnO_2 (PDF#41-1445) and triclinic phase Sn_3O_4 (PDF#16-0737), indicating that the resulting product is a composite. The change in the crystalline phase also produces a drastic change in the morphology of the SnO_x catalysts.

As evidenced by the SEM images, the pure SnO_2 reveals clusters of nanoflowers, assembled with two-dimension nanosheets sharp at the tip (Fig. S1a, b), while, the pure Sn_3O_4 grows to thick square nanoplates interlaced on the surface of CC (Fig. S2a, b). The characteristic SEM images clearly show that the $\text{SnO}_2/\text{Sn}_3\text{O}_4$ presents uniform thin-sheet structure in micron scale (Fig. 1c). The detail microstructure of the heterophase $\text{SnO}_2/\text{Sn}_3\text{O}_4$ nanosheets was further characterized by TEM (Fig. 1d). In the high resolution TEM (HRTEM) image (Fig. 1e), the lattice spacings of 0.335 and 0.325 nm assigned to SnO_2 (110) facet and Sn_3O_4 (111), respectively, confirm that the high-density $\text{SnO}_2/\text{Sn}_3\text{O}_4$ heterophase interfaces have formed in the nanosheets. Such intrinsic lattice spacings can also be recognized in SnO_2 and Sn_3O_4 , which coincides with the XRD results (Figs S1c–e, S2c–e, and Fig. 1b). The selected area electron diffraction (SAED) collected at the interface with the diffraction rings centered at (110) and (211) for SnO_2 , and (210) for Sn_3O_4 (the inset of Fig. 1e) further reveals the coexistence of SnO_2 and Sn_3O_4 in the nanosheets. All above characterization results demonstrate that the catalysts of SnO_2 , Sn_3O_4 , and heterophase $\text{SnO}_2/\text{Sn}_3\text{O}_4$ have been successfully synthesized as expected. The obtained $\text{SnO}_2/\text{Sn}_3\text{O}_4$ heterophase interface structure will promote charge transfer, and enhance the adsorption and conversion of reactants, which can contribute to the improvement of CO_2 reduction performance.

The chemical composition and valence-state information of the SnO_x catalysts were identified by XPS. The clear Sn, O, and C peaks emerge in the XPS survey spectra of all SnO_x catalysts (Fig. S3). In the high-resolution Sn 3d XPS spectra (Fig. 2a), different from pure SnO_2 (the binding energies of 487.55 and 495.95 eV for Sn^{IV}), the Sn 3d_{5/2} and Sn 3d_{3/2} peaks of pure Sn_3O_4 can be deconvoluted into two peak groups at 487.00 and 495.40 eV for Sn^{II} , and 487.55 and 495.95 eV for Sn^{IV} [42,43]. It is

Figure 1 (a) Schematic illustration of the synthetic process for the heterophase $\text{SnO}_2/\text{Sn}_3\text{O}_4$ nanosheets on CC. (b) XRD patterns of $\text{SnO}_2/\text{Sn}_3\text{O}_4$, SnO_2 , and Sn_3O_4 . (c–e) SEM, TEM and HRTEM images of $\text{SnO}_2/\text{Sn}_3\text{O}_4$ on CC, respectively. The inset of (e) is the corresponding SAED pattern.

worth noting that the Sn 3d binding energies of the heterophase $\text{SnO}_2/\text{Sn}_3\text{O}_4$ nanosheets are situated between SnO_2 and Sn_3O_4 , and the Sn $3d_{5/2}$ and Sn $3d_{3/2}$ peaks can also be fitted to two peak groups at binding energies of 487.05 and 495.45 eV for Sn^{II} , the 487.60 and 496.05 eV for Sn^{IV} . Moreover, the content of Sn^{II} in the heterophase $\text{SnO}_2/\text{Sn}_3\text{O}_4$ is higher than that of Sn^{IV} , demonstrating that Sn_3O_4 is the dominant phase (Table S1). Accordingly, the binding energy of 531.2, 532.5 and 533.45 eV laid at the O– Sn^{II} , O– Sn^{IV} and O–CS (oxygen groups on the surface of CC) can be observed in the O 1s XPS spectra of

$\text{SnO}_2/\text{Sn}_3\text{O}_4$ and Sn_3O_4 , while only the O– Sn^{IV} and O–CS peaks exist in that of SnO_2 (Fig. 2b and Table S2) [44].

Furthermore, the more detailed phase structure was explored by the X-ray absorption fine structure (XAFS) selectively measured at Sn L_3 -edge. In the normalized XANES (Fig. 2c), the absorption edge energy of Sn L_3 -edge in $\text{SnO}_2/\text{Sn}_3\text{O}_4$ is located between pure SnO_2 and pure Sn_3O_4 , inclined to Sn_3O_4 , indicating that low-valent Sn^{II} is the main component in the $\text{SnO}_2/\text{Sn}_3\text{O}_4$ heterophase, which is consistent with the analyses of Sn 3d XPS and O 1s XPS (Tables S1, S2). The more low-valent Sn^{II}

species would contribute to the adsorption/activation of CO_2 [34], implying better catalytic activity of $\text{SnO}_2/\text{Sn}_3\text{O}_4$ towards CO_2RR . In the Fourier-transformed k^2 -weighted EXAFS of $\text{SnO}_2/\text{Sn}_3\text{O}_4$, the main peak at $1.5 \text{ \AA}$ is attributed to the first shell (Sn-O) scattering, and its intensity is between those of SnO_2 and Sn_3O_4 (Fig. 2d). The additional peak approximately at $2.75 \text{ \AA}$ belongs to the Sn-Sn interaction for Sn foil, absent in the EXAFS of $\text{SnO}_2/\text{Sn}_3\text{O}_4$, SnO_2 and Sn_3O_4 .

Electrocatalytic performance of the catalysts

The electrocatalytic CO_2 reduction activities of the three SnO_x catalysts were evaluated by LSV in a sealed two-compartment flow cell filled with a CO_2 -saturated $0.5 \text{ mol L}^{-1} \text{ KHCO}_3$ aqueous solution as the electrolyte (Fig. 3a). Apparently, the onset potential at each SnO_x electrocatalyst in CO_2 -saturated solution appears at about $-0.5 \text{ V}_{\text{RHE}}$, more positive than that in Ar-saturated solution, illustrating that all SnO_x catalysts can indeed motivate CO_2RR in the presence of CO_2 . Moreover, in the

potential range from -0.5 to $-1.1 \text{ V}_{\text{RHE}}$, a notable increase in the geometric current densities at SnO_x electrocatalysts, especially $\text{SnO}_2/\text{Sn}_3\text{O}_4$, can also be observed in the polarization curves measured in CO_2 -saturated solution, implying the higher capacity of the heterophase $\text{SnO}_2/\text{Sn}_3\text{O}_4$ for electrocatalytic CO_2RR . Furthermore, the liquid and gas phase products obtained at different applied potentials were determined by $^1\text{H-NMR}$ and online GC, respectively.

The potential-dependent FEs of the major electrocatalytic products (HCOOH , CO and H_2) are compared in Fig. 3b. The total FE of all products at each applied potential is almost as high as 90%, and the FE of selectively produced HCOOH (FE_{HCOOH}) gradually increases firstly and then decreases with the change of the investigated potential from -0.6 to $-1.1 \text{ V}_{\text{RHE}}$. Remarkably, $\text{SnO}_2/\text{Sn}_3\text{O}_4$ shows the highest selectivity for HCOOH conversion at each applied potential compared with SnO_2 and Sn_3O_4 , which can be well verified based on the product analyses (Fig. 3c). Particularly, the FE_{HCOOH} for

Figure 2 (a, b) The high-resolution Sn 3d and O 1s XPS spectra of $\text{SnO}_2/\text{Sn}_3\text{O}_4$, SnO_2 , and Sn_3O_4 , respectively. (c) Sn L₃-edge XANES spectra of $\text{SnO}_2/\text{Sn}_3\text{O}_4$, SnO_2 , Sn_3O_4 and Sn foil. The inset is the pre-edge features of all samples. (d) Fourier transforms of k^2 -weighted EXAFS data for the Sn L₃-edge of $\text{SnO}_2/\text{Sn}_3\text{O}_4$, SnO_2 , Sn_3O_4 and Sn foil (without phase shift).

Figure 3 (a) The LSV of SnO₂/Sn₃O₄, SnO₂ and Sn₃O₄ in Ar-saturated (dashed line) or CO₂-saturated (solid line) 0.5 mol L⁻¹ KHCO₃ solution. (b) Potential-dependent FEs of HCOOH, CO, and H₂ for SnO₂/Sn₃O₄, SnO₂ and Sn₃O₄ under different applied potentials. (c) Partial current densities of HCOOH for three SnO_x catalysts recorded under different applied potentials. (d) The chronoamperometry response and time-dependent FE_{HCOOH} for SnO₂/Sn₃O₄, SnO₂ and Sn₃O₄ at -0.9 V_{RHE}.

SnO₂/Sn₃O₄ reaches the maximum of 88.3% at -0.9 V_{RHE} (the maximum FE_{HCOOH} of 38.6% for SnO₂ and 50.2% for Sn₃O₄ at -0.9 V_{RHE}); at the same time, the generation of H₂ and CO is almost completely suppressed by SnO₂/Sn₃O₄. The excellent CO₂RR activity possibly benefits from the SnO₂/Sn₃O₄ heterophase interface, which could generate a built-in electric field to reform the local electronic structure for CO₂ adsorption and intermediate HCOO* formation, and to promote the electron transport for improving the catalytic reaction kinetics [45]. As a strong evidence, the calculated Tafel slope of SnO₂/Sn₃O₄ is 246.5 mV dec⁻¹, obviously lower than those of SnO₂ (321.9 mV dec⁻¹) and Sn₃O₄ (254.2 mV dec⁻¹) (Fig. S4). Moreover, the results from ¹H-NMR spectra (Fig. S5) clearly indicate that HCOOH is indeed derived from CO₂ gas. Such activities surpass that of overwhelming majority of previously reported Sn-based CO₂RR electrocatalysts (see the details in Table S3).

The stability of a catalyst is a significant factor for its practical application in CO₂RR as well. Thus, CO₂RR on various SnO_x catalysts has been conducted using chron-

oamperometry at -0.9 V_{RHE} in 0.5 mol L⁻¹ KHCO₃ aqueous solution with the bubbled CO₂. During 12 h-CO₂RR, SnO₂/Sn₃O₄ exhibits a virtually indistinguishable decay (less than 5%) in the HCOOH current density as well as an essentially constant FE_{HCOOH} at about 86.4% (Fig. 3d), illustrating that SnO₂/Sn₃O₄ has a good tolerance in the electrocatalytic CO₂RR. Similarly, Sn₃O₄ also achieves stable current densities and FE_{HCOOH} during a long-term operation. However, it is worth mentioning that the long-term stability of SnO₂ is inferior to those of SnO₂/Sn₃O₄ and Sn₃O₄. The composition and morphology of SnO_x catalysts after CO₂RR were further characterized. As shown in Fig. S6a, after a continuous 12 h-CO₂RR, besides some faint diffraction peaks assigned to the residual SnO₂, a large number of distinct diffraction peaks belonging to metal Sn appear in the XRD pattern of SnO₂; whereas, hardly any diffraction peaks of metal Sn can be observed in that of Sn₃O₄. The above results suggest that, compared with SnO₂ easier to be reduced into metal Sn, Sn₃O₄ is more stable during CO₂RR. Accordingly, metal Sn emerging in SnO₂/Sn₃O₄ after a continuous CO₂RR is

mainly converted from SnO_2 , and most of Sn_3O_4 still retain, indicating the active catalyst under catalytic turnover condition is Sn/SnO_x as reported by previous studies [46–48]. Similar results can also be evidenced by XPS measurement. The primary active component of the three catalysts shows negligible variation, and oxide species still contain $\text{O}-\text{Sn}^{\text{II}}$, $\text{O}-\text{Sn}^{\text{IV}}$ and $\text{O}-\text{CS}$. However, after the 12 h- CO_2RR , the content of $\text{O}-\text{Sn}^{\text{IV}}$ in SnO_2 and $\text{SnO}_2/\text{Sn}_3\text{O}_4$ decreases significantly relative to $\text{O}-\text{Sn}^{\text{II}}$, indicating that SnO_2 is easy to reduce to a low-valence-state Sn in the catalysts (Fig. S6b, c and Table S2). Somewhat differently, in the high-resolution Sn 3d XPS spectra of SnO_2 and $\text{SnO}_2/\text{Sn}_3\text{O}_4$ after 12 h- CO_2RR , two weak peaks centered at 485.05 and 493.35 eV can be identified as metal Sn; whereas, there are only Sn^{II} and Sn^{IV} peaks in the high-resolution Sn 3d XPS spectra of Sn_3O_4 after CO_2RR (Fig. S6d–f). Only a small amount of metallic Sn detected may be attributed to the re-oxidation of metal Sn exposed to the air. Further evidences from the SEM images reveal that, different from no significant change in the morphologies of Sn_3O_4 and $\text{SnO}_2/\text{Sn}_3\text{O}_4$, almost all SnO_2 nanoflowers have been destroyed after performance testing (Fig. S7a–c). Significantly, there are many holes with different sizes in the heterophase $\text{SnO}_2/\text{Sn}_3\text{O}_4$ (Fig. S7d, e). The formation of porous structure is mainly attributed to the reduction or dissolution of SnO_2 at the negative applied potentials, as evidenced by the decrease in Sn^{IV} content in $\text{SnO}_2/\text{Sn}_3\text{O}_4$ (Tables S1, S2). Meanwhile, the HRTEM image of $\text{SnO}_2/\text{Sn}_3\text{O}_4$ still shows three lattice fringes of 0.335, 0.329 and 0.291 nm corresponding to SnO_2 (110), Sn_3O_4 (111) and Sn (200), respectively (Fig. S7f). Such porous structure is advantageous for the stable CO_2RR over $\text{SnO}_2/\text{Sn}_3\text{O}_4$ to a certain degree, not only by exposing more accessible catalytic sites for the CO_2RR , but also by offering channels for the reactant/electrolyte transport.

Electrocatalytic mechanism of the catalysts

The $\text{SnO}_2/\text{Sn}_3\text{O}_4$ heterophase interface is responsible for the enhanced CO_2RR performance. To elucidate it, we compared the specific activities of SnO_2 , Sn_3O_4 and $\text{SnO}_2/\text{Sn}_3\text{O}_4$, because the normalization of the geometric surface area of the catalyst does not account for their intrinsic activity. Hereby, the ECSAs have been estimated by the double layer capacitance (C_{dl}) (Fig. S8) [6,49], and the calculated ECSA of $\text{SnO}_2/\text{Sn}_3\text{O}_4$ is about 26.90 cm^2 , which is almost the same as that of Sn_3O_4 (25.86 cm^2), but much smaller than that of SnO_2 (71.03 cm^2). As expected, the trends of ECSA-normalized partial current density for HCOOH production generally coincide with those for

geometric current densities, with $\text{SnO}_2/\text{Sn}_3\text{O}_4$ still being the most active for CO_2RR (Fig. 4a), illustrating that $\text{SnO}_2/\text{Sn}_3\text{O}_4$ has the highest intrinsic capacity derived from the local regulated electronic configuration towards catalyzing CO_2 into HCOOH. Particularly, when the applied potential is negative to $-0.9 \text{ V}_{\text{RHE}}$, the ECSA-normalized partial current density of $\text{SnO}_2/\text{Sn}_3\text{O}_4$ for HCOOH is about 0.62 mA cm^{-2} , seven times larger than that of SnO_2 . Secondly, $\text{SnO}_2/\text{Sn}_3\text{O}_4$ has a faster CO_2RR kinetics relative to SnO_2 and Sn_3O_4 , which is further corroborated by EIS (Fig. 4b). The charge transfer resistance (R_{ct}) of $\text{SnO}_2/\text{Sn}_3\text{O}_4$ is distinctly lower than those of SnO_2 and Sn_3O_4 , signifying that the electron transfer from $\text{SnO}_2/\text{Sn}_3\text{O}_4$ to the adsorbed CO_2 is faster (Table S4) [50]. It is ascribed to the porous sheet-like heterophase structure, in which the built-in electric field between $\text{SnO}_2/\text{Sn}_3\text{O}_4$ heterophase interface can accelerate the charge transmission [45]. Besides, the porous structure is conducive to the intimate contact between the catalysts and reactant/electrolyte within the interlayer volume [51–53], and meanwhile, the generated metal Sn also improves the conductivity of $\text{SnO}_2/\text{Sn}_3\text{O}_4$.

More importantly, $\text{SnO}_2/\text{Sn}_3\text{O}_4$ also displays a strong binding thermodynamics of reactant CO_2 , as evidenced by CO_2 -TPD measurements (Fig. 4c). Different from the similar CO_2 adsorption energy/capacity of the three SnO_x catalysts at low-temperature ($270\text{--}290^\circ\text{C}$), the CO_2 desorption temperature (840°C) of $\text{SnO}_2/\text{Sn}_3\text{O}_4$ is higher than those of SnO_2 (788°C) and Sn_3O_4 (825°C) in the case of high-temperature CO_2 -TPD process. The above results indicate $\text{SnO}_2/\text{Sn}_3\text{O}_4$ has the strong CO_2 binding capacity, which is conducive to the adsorption/activation of CO_2 [54]. To clarify the strong capability of $\text{SnO}_2/\text{Sn}_3\text{O}_4$ for stabilizing $\text{CO}_2^{\cdot-}$ intermediate, the typical LSVs measurements in Ar-saturated solution were carried out, in which OH^- as a substitute was used to evaluate the binding affinity of $\text{CO}_2^{\cdot-}$ on SnO_x catalysts [46,55–57]. As indicated by the anodic LSVs (Fig. 4d), the potential for the oxidative adsorption of OH^- on $\text{SnO}_2/\text{Sn}_3\text{O}_4$ is more negative than those of SnO_2 and Sn_3O_4 , revealing a stronger binding to OH^- group. These results indicate that $\text{SnO}_2/\text{Sn}_3\text{O}_4$ is capable of binding and further converting $\text{CO}_2^{\cdot-}$ intermediate.

To gain insight into the contribution of the $\text{SnO}_2/\text{Sn}_3\text{O}_4$ heterophase interface to the enhanced performance in CO_2RR , the density of state (DOS) per catalyst has been calculated with DFT calculation. The DOS of SnO_x is dominated by p-orbital electronic states, which are considered to be active in catalytic CO_2RR . As illustrated in Fig. 5a and Fig. S9, the $\text{SnO}_2/\text{Sn}_3\text{O}_4$ exhibits a remarkably

Figure 4 (a) Surface-area-normalized current densities of SnO₂/Sn₃O₄, SnO₂ and Sn₃O₄ for HCOOH production, respectively. (b) Nyquist plots of SnO₂/Sn₃O₄, SnO₂ and Sn₃O₄ with the potential of -0.9 V_{RHE}. The inset image is the equivalent circuit diagram. R_s and R_{ct} represent the electrolyte and charge transfer resistance, respectively. (c) CO₂-TPD profiles for SnO₂/Sn₃O₄, SnO₂ and Sn₃O₄. (d) Single oxidative LSV scans in Ar-saturated 0.5 mol L⁻¹ KOH for SnO₂/Sn₃O₄, SnO₂ and Sn₃O₄.

higher electron density at Fermi level (E_f) than SnO₂ and Sn₃O₄, which is vital for endowing SnO₂/Sn₃O₄ with faster electron transport capability and facilitating the conversion from CO₂^{*} to intermediate HCOO* at the catalytic sites [58]. And, the high DOS around E_f conduces to optimizing and reinforcing the affinity between SnO₂/Sn₃O₄ and the reactant/intermediate by forming the orbit hybridization during CO₂RR [59].

Furthermore, a theoretical thermodynamic analysis of the key HCOO* intermediates on SnO_x catalysts was performed by DFT calculations. During CO₂RR, the most probable adsorption configuration on the SnO₂(110) surface, Sn₃O₄(111) surface and SnO₂/Sn₃O₄ interface and the most favorable free energy pathways of CO₂ reduction toward HCOOH are illustrated in Fig. 5b, c. It is apparent that, except for SnO₂, both SnO₂/Sn₃O₄ and Sn₃O₄ are more favorable for adsorbing and stabilizing HCOO* intermediate in thermodynamics. The SnO₂/Sn₃O₄ surface is more susceptible to the adsorption of HCOO*

intermediates than the Sn₃O₄ surface. Consequently, SnO₂/Sn₃O₄ exhibits the lowest overpotential and highest FE_{HCOOH} essentially in agreement with the experimental results. In addition, in view of metallic Sn generated *in-situ* during CO₂RR (Fig. S6a), the effect of metallic Sn on CO₂RR was also investigated by comparing the adsorption of the key HCOO* intermediates on the new Sn/SnO₂ and Sn/Sn₃O₄ interfaces (Fig. S10 and Table S5). Obviously, the SnO₂/Sn₃O₄ heterophase interface is still the optimal active site for CO₂ reduction to HCOOH. For SnO₂/Sn₃O₄, the advantage in HCOOH production lies in the strong charge redistribution occurred at the SnO₂/Sn₃O₄ heterophase interface region (Fig. S11), which could regulate the valence electron state of active sites and improve the electronic conductivity [11].

CONCLUSIONS

In summary, the phases of SnO_x catalysts were adjusted to SnO₂, SnO₂/Sn₃O₄, and Sn₃O₄ through simply changing

Figure 5 (a) DOS of the p- and sum-orbital of the SnO_x catalysts. (b) Optimized adsorption configurations of CO₂ on SnO_x catalysts: (I) SnO₂ (110) surface, (II) Sn₃O₄ (111) surface, and (III) SnO₂ (110)/Sn₃O₄ (111) surface; Sn: dark grey; O: red; C: light grey; H: white. (c) The calculated free energy diagrams of the electrocatalytic CO₂RR into HCOOH without considering the effect of electrode potential ($U=0$ V).

the ratio of SnCl₂·2H₂O and NaOH during the hydrothermal process, and the correlation between SnO_x phase and CO₂RR activity has been elucidated by combining experimental verification and theoretical simulation. The distinct SnO₂/Sn₃O₄ heterophase effect contributes to high-efficiency catalytic sites for CO₂RR with a 2.3-fold and 1.8-fold enhanced capacity of HCOOH production than SnO₂ and Sn₃O₄. The significant improvements in the activity and selectivity of CO₂RR can be interpreted in terms of the enhanced adsorption of CO₂/intermediate, the accelerated charge transfer, the faster mass transmission and better conductivity, which is mainly attributed to the synergistic effect of the charge redistribution at the SnO₂/Sn₃O₄ heterophase interface, the abundant and stable low-valent Sn^{II} species, as well as the *in-situ* derived porous structure and metal Sn during CO₂RR. Our work opens up new opportunities for creating high-activity materials *via* engineering heterophase for versatile energy conversion technologies in the future.

Received 17 March 2020; accepted 17 April 2020;
published online 29 June 2020

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Acknowledgements We acknowledge the support from the National Natural Science Foundation of China (21573062, 21631004 and 21901065), the Natural Science Foundation of Heilongjiang Province (B2018008), the Youth Science and Technology Innovation Team Project of Heilongjiang Province (2018-KYYWF-1593), and the University Nursing Program for Young Scholars with Creative Talents in Heilongjiang Province (UNPYSCT-2018009).

Author contributions Wu J performed the experiments with help from Fu H, Ren Z and Wang G. Ren Z, Wu J and Fu H wrote this paper. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

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

Jun Wu received her BSc and MSc degrees from Heilongjiang University in 2013 and 2016, respectively. She is currently a PhD candidate in material science and engineering under the supervision of Prof. Guiling Wang and Prof. Honggang Fu at Harbin Engineering University. Her current research focuses on the design and synthesis of nanomaterials for energy conversion.

Zhiyu Ren received her BSc degree in 2001 and MSc degree in 2004 from Heilongjiang University. Then, she joined Heilongjiang University as an assistant professor. In 2008, she received her PhD degree from Jilin University. She became a full professor in 2014. Her interest focuses on the surface crystal engineering and defect regulation of advanced transition metal-based compounds and carbon-based nanocomposites for electrocatalysis (e.g., water splitting, carbon dioxide reduction, and organic small molecule oxidation).

Guiling Wang received his PhD in 2006 from the Institute of Chemical Engineering, Harbin Engineering University. He became a full professor at the College of Material Science and Chemical Engineering, Harbin Engineering University in 2007. His research interests focus on the design and controlled synthesis of electrode materials of NaBH₄ fuel cells, H₂O₂ fuel cell, supercapacitors and lithium ion batteries.

Honggang Fu received his BSc degree in 1984 and MSc degree in 1987 from Jilin University. Then, he joined Heilongjiang University as an assistant professor. In 1999, he received his PhD degree from Harbin Institute of Technology. He became a full professor in 2000. Currently, he is a Cheung Kong Scholar. His interest focuses on the oxide-based semiconductor nanomaterials for solar energy conversion and photocatalysis, carbon-based nanomaterials for energy conversion and storage, and W(Mo,V)-based catalysts for

HER and OER. Up to now, he has published over 300 peer-reviewed papers as corresponding author with more than 13,000 citations and H-index of 60.

SnO₂/Sn₃O₄异相工程促进二氧化碳电催化还原生成甲酸

吴君¹, 谢颖², 杜世超², 任志宇^{2*}, 于鹏², 王秀文¹, 王贵领^{1*}, 付宏刚^{2*}

摘要 锡(Sn)基电催化剂可以以可持续能源为动力将二氧化碳转化为甲酸, 因而获得越来越多的关注, 但其催化二氧化碳还原反应(CO₂RR)的能力仍然达不到商业应用要求, 因此开发高效Sn基催化剂极为重要. 本文利用简单的水热过程, 首次设计合成得到以Sn₃O₄为主的具有高密度相界面的片状SnO₂/Sn₃O₄异相催化剂. 实验和理论模拟结果表明, 异相界面的电荷再分布和内建电场促进了CO₂的吸附和HCOO*的形成, 加速了催化剂和反应物之间的电荷转移, 最终大大提高了SnO₂/Sn₃O₄异相催化剂对CO₂RR的内在活性. 同时, 在CO₂RR过程中原位生成的多孔结构和金属Sn改善了反应物和电子在SnO₂/Sn₃O₄片内的传质和传荷. SnO₂/Sn₃O₄异相催化剂对CO₂RR表现出较高的活性和选择性, 提高了CO₂还原电流密度. 在−0.9 V_{RHE}时甲酸的法拉第效率为88.3%, 且对CO₂RR具有长期的耐受性. 该研究结果表明, 异相界面工程是调节先进催化性能的一种有效策略.