Nano-crumples induced Sn-Bi bimetallic interface pattern with moderate electron bank for highly efficient CO₂ electroreduction

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CO₂ electroreduction reaction offers an attractive approach to global carbon neutrality. Industrial CO₂ electrolysis towards formate requires stepped-up current densities, which is limited by the difficulty of precisely reconciling the competing intermediates (COOH⁺ and HCOO⁺). Herein, nano-crumples induced Sn-Bi bimetallic interface-rich materials are in situ designed by tailored electrodeposition under CO₂ electrolysis conditions, significantly expediting formate production. Compared with Sn-Bi bulk alloy and pure Sn, this Sn-Bi interface pattern delivers optimum upshift of Sn p-band center, accordingly the moderate valence electron depletion, which leads to weakened Sn-C hybridization of competing COOH⁺ and suitable Sn-O hybridization of HCOO⁺. Superior partial current density up to 140 mA/cm² for formate is achieved. High Faradaic efficiency (>90%) is maintained at a wide potential window with a durability of 160 h. In this work, we elevate the interface design of highly active and stable materials for efficient CO₂ electroreduction.

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The development of carbon dioxide (CO₂) conversion strategies to produce low carbon chemicals and fuels is one of the most important solutions considered to effectively alleviate worldwide carbon emissions. CO₂ electroreduction reaction (CO₂RR) is an emerging sustainable technology that can be utilized not only to upgrade CO₂ but also to store intermittent electricity produced by renewable energy. Among the variety of possible products, formic acid or formate is of great interest owing to its wide applications in commercialized synthesis industries and formic acid fuel cells, with relatively low activation energies needed (only 2-electron transfer). The binary metallic catalysts offer an effective approach to tune the selectivity and activity of CO₂-to-formate transformation, e.g., Pd–Sn alloy, Pd–Pt bimetallic nanoparticles, Ag–Sn core–shell structures, etc. However, the industrial application of this process relies on inexpensive catalysts, stepped-up partial current density, and prolonged stability.

Our previous work reported low-cost Sn nanosheets decorated with Bi nanoparticles achieving a high Faradaic efficiency towards formate (FEformate) of 96% at −1.1 V versus reversible hydrogen electrode (RHE)14. Hitherto, it still remains challenging to delineate the structure–activity relationships of CO₂RR electrocatalytic activities through the bimetallic Sn–Bi systems. As reported, the catalytic properties are highly related to the atomic patterns, because the metal-molecule interactions occurring at the interfaces within two metals are fundamentally different from bulk alloys, e.g., bimetallic Au–Cu electrocatalyst exhibits higher synergistic activity and selectivity of CO₂, products compared to Au–Cu alloys ascribed to the stabilization of key intermediate species, *COOH towards CO formation.

Herein, in an attempt to gain a comprehensive understanding of the correlation between the catalytic activities of Sn–Bi system with their electronic structures and bimetallic patterns, we performed ab initio calculations, and identified that Sn interacting Bi at the interface is the most favorable structure for HCOOH formation. Such structure was proved to offer weakened Sn–C hybridization of competing for COOH* intermediate and optimum Sn–O hybridization of HCOOH*. Guided by the theoretical findings and with the target of exposing a more active Sn–Bi interface, nano-crumples induced Sn–Bi interface structures were experimentally designed through in situ electrodeposition under CO₂RR conditions. This design concept of exposing the specific surfaces under a capping agent has been proposed recently in the electrochemical systems.

Here, we show this interface design strategy demonstrates multiple merits to tackle the aforementioned challenges: (i) to the authors’ knowledge, a high partial current density of formate (up to 140 mA/cm²) was achieved in an H-cell; this is attributed to abundantly exposed active Sn–Bi bimetallic interface pattern originated from the nano-wrinkles/crumples under CO₂RR conditions. (ii) highest FEformate was obtained up to 96.4% at a lower potential (−0.84 V vs. RHE) through simultaneously suppressing the binding of COOH* towards CO formation, and enhancing the binding of HCOOH* towards formate formation. (iii) high Faradaic efficiency of formate (>90%) was maintained at wide potentials window (−0.74 to −1.14 V vs. RHE) with a durability of 160 h; this is ascribed to well-defined surface structures at steady crumples grown on interconnected porous carbon fabric network, which offers expedite mass transport and electronic conductivity. This manipulation of electronic structures of active sites by nano-crumples elucidates the correlations among morphology, surface structures, electronic properties, and reaction pathways, providing a rational design strategy to enhance the catalytic performance of nanostructured materials.

The atomic pattern effects were investigated and elaborated on the CO₂RR electrocatalytic activities through the bimetallic Sn–Bi interface and alloy (Fig. 1b, c, and Supplementary Fig. 2). As reported, COOH* and HCOO* are the two major competing intermediates for CO and HCOOH production, respectively. Thus, two pathways via these two intermediates are considered in this study and originated from the hydrogenation of the adsorbed bicarbonate (CO₃H*) species, which is reported as the primary carbon source for CO₂RR toward formate production with neutral KHCO₃ electrolyte. The free energy profiles obtained from DFT analysis demonstrate that the HCOOH formation via the HCOO* intermediate is the favorable pathway on both surfaces owing to the relatively lower free energy of this pathway. The free energy difference for the intermediates HCOO* and COOH* via the first proton-electron transfer reaction is higher on Sn–Bi bimetallic interface (0.73 eV) than on the Sn–Bi alloy surface (0.56 eV). This difference indicates that the formation of HCOO* intermediate is more thermodynamically facile compared to the formation of COOH* on the former structure. Moreover, for the second proton-electron transfer reaction step towards HCOOH* or CO* formation, the free energy difference between two competing products is also higher on Sn–Bi bimetallic interface (0.64 eV) than that on Sn–Bi alloy surface (0.44 eV). We also studied CO₂ reduction activity on the in-plane Sn–Bi heterostructure (Supplementary Fig. 1). The results shown in that figure confirm that the Sn–Bi interface models (i.e., the current interface model and the in-plane model) all have higher activity towards formate formation than Sn–Bi bulk alloy model.

The adsorption energies (Eₐd) of the three main intermediates on the two Sn–Bi surfaces and pure Sn(200) surface were calculated and listed in Supplementary Table 2. It was found that COOH* prefers bonding with the surface via C atom while CO₃H* and HCOO* tend to bond the surface with O atom. The adsorption of COOH is the weakest on Sn–Bi bimetallic interface (Eₐd of −1.62 eV); the adsorption of HCOO is moderate (Eₐd of −3.09 eV) while the adsorption of CO₃H is the strongest (Eₐd of −3.64 eV). To further understand these different sequences of adsorption strength for three intermediates, an electronic state analysis was conducted through the partial density of states...
As expected, fewer overlapping areas of orbitals on Sn indicate weaker adsorption strength of COOH*(or hole)-donating capacity of the hole (or electron) scavengers is proposed as the tailoring of metal adsorbate. The black dashed lines indicate the positions of the metal surfaces.

(PDATS) for these three adsorbed systems (Supplementary Figs. 3–4). Moreover, the outermost valence p orbital of Sn atom on pure Sn and two Sn–Bi surface models (without adsorbates) were analyzed along with the p band center within the overall range of orbital30, as shown in Fig. 1d. It can be seen that the addition of Bi uplifts the electron states of Sn away from the Fermi level for both Sn–Bi models, suggesting the electron donation from Sn to Bi14,31. Notably, the p-band center of Sn–Bi interface model lies among that of pure Sn and Sn–Bi alloy, delivering a moderate state or electron bank. Consequently, the PDOS of Sn–C atoms in COOH* adsorption and Sn–O atoms in HCOO* adsorption (Supplementary Fig. 3 and Fig. 1e) shows that there are more harmonic p-p and p-s overlaps between the C-2p and Sn-5s, Sn-5p states on Sn–Bi alloy model compared to those of Sn–Bi bimetallic interface in COOH adsorption, indicating weaker adsorption strength of COOH* of the latter24,32. As expected, fewer overlapping areas of p-p and p-s orbitals between O-2p and Sn-5p, Sn-5s for HCOO* adsorption were also found on the Sn–Bi interface compared with those of alloy.

The reason why moderate electron bank of Sn in bimetallic Sn–Bi interface results in the weakest COOH adsorption was proposed as the tailoring of metal–carbon hybridization. The electron donation from the COOH to the metal by σ bonding and π backdonation from the metal to the COOH describes the concerted coupling of the COOH levels to the metal sp states and the d states (Fig. 1D)33–35. Pure Sn with higher electronic density and alloy Sn in Sn–Bi with the most electronic depletion could both create stronger p–d interaction through π backbonding and σ bonding36, respectively, compared to Sn with moderate electronic density in Sn–Bi. This is because the sufficient electron (or hole)-donating capacity of the hole (or electron) scavengers is required to allow for the extraction of holes (or electrons) from the molecule complex31. Such phenomenon is also evidenced by the volume slices of calculated charge densities and corresponding optimized configurations for the three models with COOH adsorbate. The black dashed lines indicate the positions of the metal surfaces.

In brief, the enhanced reactivity of Sn–Bi bimetallic interface can be ascribed to the following aspects as unveiled by the theoretical calculations: (i) Sn exhibits electron density depletion and owns the moderate valence electron bank by interacting Bi at the interface; (ii) the binding of COOH is weakened enabling suppressed CO formation; (iii) the affinity of HCOO is tuned by the optimum moderate adsorption, boosting HCOOH production.

**Synthesis and structural characterization.** Inspired by these theoretical findings, we investigated a simplified method to expose abundant active Sn–Bi interface. As shown in Fig. 2a, in situ electrodeposition (ED) and evolution under CO2RR conditions were applied to purposefully expose Sn–Bi interfaces, which were induced by the steered crumple densities with
precisely controlled ED parameters. The three-dimensional highly porous carbon fabrics (3D CF) were adopted as the substrates to disperse the catalytic sites in luxuriant and orthometric carbon fibers. Such CF substrates were activated through carbonization, while the tortile bimetallic nanosheets were so thin that they were almost transparent to the electron beam. The Sn–Bi bimetallic interface showed that microcrumpled roughness on the surface densities of crumpled structures were higher with longer ED time and higher CO2RR conditions. The Sn–Bi interface is more active according to the DFT calculations, thus the aforementioned Sn–Bi materials induced by crumpled structures are expected to have higher activities towards CO2RR ascribed to the abundant active sites.

Crystal structures and electronic structures analysis. The crystal structures and electronic structures analysis of the Sn–Bi
bimetallic interface at the crumples and Sn–Bi alloy are shown in Fig. 3. A comparison of the X-ray diffraction (XRD) patterns of the Sn–Bi bimetallic interface and Sn–Bi alloy is displayed in Fig. 3a. The XRD pattern of the Sn–Bi bimetallic interface matches well with the peaks of Sn (tetragonal, JCPDS# 04-0673) and Bi (rhombohedral, JCPDS# 44-1246), which confirm the coexistence of Sn and Bi-metal phases with the predominant crystal planes of (200) and (110), respectively. The crystal planes distribution of aforementioned Sn–Bi bimetallic interface at the crumples was also identified by two-dimensional synchrotron X-ray diffraction (2D-XRD) with a beam size of ~3 × 6 μm, as shown in Fig. 3b. That result further confirmed that no bulk alloy peak was observed for the Sn–Bi bimetallic interface materials compared with the Sn–Bi alloy sample (Supplementary Fig. 11). These results reveal that negligible amounts of Bi atoms enter into the Sn lattice (and vice versa), thus almost no Sn–Bi bulk alloy was formed during the electrodeposition synthesis. Nevertheless, there is a distinct Sn–Bi (200) alloy peak located at 2θ of 29° for the Sn–Bi polyhedron materials fabricated by the hydrothermal method (tetragonal, JCPDS#27-0896, Supplementary Figs. 11–12), which was used as the reference of Sn–Bi bulk alloy in line with the DFT calculations. Because the Sn–Bi binary material by in situ ED under CO2RR method preferably forms the Sn–Bi interface or surface alloy structure, the hydrothermal method was adopted to fabricate the Sn–Bi bulk alloy structure to compare the aforementioned Sn–Bi bimetallic interface material. Synchrotron 2D-XRD pattern (Supplementary Fig. 11c) further confirmed the existence of Sn–Bi (200) crystal planes together with crystals of SnO2 and Bi2O3, which were more likely due to the oxidation process in hydrothermal procedure14. It was also observed that the Bragg reflections of Sn–Bi (200) alloy peak shift to lower 2θ angles, indicating the linear expansion of the tetrahedral Sn lattice due to the addition of larger Bi atoms into Sn (lattice mismatch >22%)23,43.

X-ray absorption spectroscopy (XAS) was conducted to investigate the electronic structures of Sn–Bi materials. Figure 3c±e depicted the X-ray Absorption Near-edge Fine Structure (XANES) spectra of Bi L3-edge, Sn K-edge, and Sn L3-edge respectively, which reveal the pre-edge features based on the absorption edge or the location of white lines. In general, the shapes of the Bi L3-edge for the Sn–Bi bimetallic interface and alloy are close to that of the Bi foil (Fig. 3c) whereas the white line intensity at ~13,440 eV is much weaker than the reported Bi2O3.44. The latter implies that the Bi in the materials is mainly in the metallic state. A negative shift of the absorption edge position was found for the Bi L3-edge after interacting Sn elements compared with that of Bi foil (Fig. 3c), illustrating the electron density transfer from Sn to Bi. This is also confirmed by the opposite shift of Sn K-edge with Bi elements introduced (Fig. 3d). The intensity of the white line (2p → 5d orbital transition) in the XANES at Bi L-edge of Sn–Bi alloy is slightly lower than that of the Sn–Bi bimetallic interface, which can be attributed to more filling of the Bi 5d bands due to alloying with Sn. This implies the modivative electron transfer in the Sn–Bi interface compared with pure Sn and Sn–Bi alloy, which is also consistent with previous DFT results. In addition, these findings were also observed in Fig. 3d, e with the evidence of a more positive shift and higher intensity of white line of Sn K-edge and L1-edge in Sn–Bi alloy. A slight lowering of the white line peak intensity of Sn K-edge for the Sn–Bi bimetallic interface compared to the Sn–Bi alloy (Fig. 3d), also indicates a less oxidized state of Sn in the bimetallic interface structure.

X-ray photoelectron spectroscopy (XPS) was conducted to study the surface oxidation states of Sn and Bi elements in Sn–Bi materials (Fig. 3f and Supplementary Fig. 13). The peaks located
Sn K-edge and Bi L3-edge of Sn at 495.4 eV and 487.0 eV are mainly adsorption for Sn. Spectra shift to the higher energy for the Sn–Sn bond and accumulation of Bi in Sn–Bi interface, indicating the slightly higher oxidation state of Bi atoms. These Sn K-edge and Bi L3-edge of Sn at 493.6 eV and 485.2 eV corresponds to metallic Sn 0 and Sn 2+/4+ , respectively, when exposed to the air. The XPS spectra of Sn indicate that the surface Sn was partially oxidized in a short time (Fig. 4). In the Sn K-edge EXAFS spectra (Fig. 4a), metallic Sn 0 and Sn 2+/4+ were characterized by employing Sn and SnO2 as references respectively, where the peaks located at 1.42 Å and 2.80 Å correspond to Sn–O and Sn–Sn bonds. The one prominent peak observed at around 2.87 Å can be attributed to the combined scattering path of Sn–Sn bonds and Sn–Bi bonds. Likewise, a dominant peak appearing at a similar position with the Bi–Bi bond of Bi reference was detected and identified as the combined scattering path of Bi–Bi and Sn–Bi bonds (Fig. 4b). This is owing to that the existence of Bi triggers the electron depletion of surface Sn atoms, potentially building the interaction between the electron density of these two elements, which leads to a trace amount of Sn–Bi bonds. Moreover, the Sn–Bi bond length lies between the Sn–Sn and Bi–Bi bonds. Representative fitting of the EXAFS spectra to the R space of Sn–Bi bimetallic interface and alloy materials are shown in Fig. 4c, d and Supplementary Fig. 14. Sn K-edge and Bi L3-edge EXAFS spectra fit simultaneously with constraints employed to ensure that the bond lengths and disorder factors for Sn–Bi and Bi–Sn bonds are the same. The corresponding fittings to the k space are depicted in Supplementary Fig. 15. The fitting results of in situ FT-EXAFS for Sn–Bi interface and alloy are summarized in Supplementary Table 4 and Table 5. Compared with Sn–Bi alloy, Sn–Bi bimetallic interface has higher coordination numbers applied voltages to investigate the local atomic structures and chemical environment (Fig. 4). In the Sn K-edge EXAFS spectra (Fig. 4a), metallic Sn 0 and Sn 2+/4+ were characterized by employing Sn and SnO2 as references respectively, where the peaks located at 1.42 Å and 2.80 Å correspond to Sn–O and Sn–Sn bonds. The one prominent peak observed at around 2.87 Å can be attributed to the combined scattering path of Sn–Sn and Sn–Bi bonds. Likewise, a dominant peak appearing at a similar position with the Bi–Bi bond of Bi reference was detected and identified as the combined scattering path of Bi–Bi and Sn–Bi bonds (Fig. 4b). 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**In situ extended X-ray absorption fine structure and Raman analysis.** In situ extended X-ray absorption fine structure (EXAFS) was performed under operating conditions at various applied voltages to investigate the local atomic structures and chemical environment (Fig. 4). In the Sn K-edge EXAFS spectra (Fig. 4a), metallic Sn 0 and Sn 2+/4+ were characterized by employing Sn and SnO2 as references respectively, where the peaks located at 1.42 Å and 2.80 Å correspond to Sn–O and Sn–Sn bonds. The one prominent peak observed at around 2.87 Å can be attributed to the combined scattering path of Sn–Sn and Sn–Bi bonds. Likewise, a dominant peak appearing at a similar position with the Bi–Bi bond of Bi reference was detected and identified as the combined scattering path of Bi–Bi and Sn–Bi bonds (Fig. 4b). This is owing to that the existence of Bi triggers the electron depletion of surface Sn atoms, potentially building the interaction between the electron density of these two elements, which leads to a trace amount of Sn–Bi bonds. Moreover, the Sn–Bi bond length lies between the Sn–Sn and Bi–Bi bonds. Representative fitting of the EXAFS spectra to the R space of Sn–Bi bimetallic interface and alloy materials are shown in Fig. 4c, d and Supplementary Fig. 14. Sn K-edge and Bi L3-edge EXAFS spectra fit simultaneously with constraints employed to ensure that the bond lengths and disorder factors for Sn–Bi and Bi–Sn bonds are the same. The corresponding fittings to the k space are depicted in Supplementary Fig. 15. The fitting results of in situ FT-EXAFS for Sn–Bi interface and alloy are summarized in Supplementary Table 4 and Table 5. Compared with Sn–Bi alloy, Sn–Bi bimetallic interface has higher coordination numbers applied voltages to investigate the local atomic structures and chemical environment (Fig. 4). In the Sn K-edge EXAFS spectra (Fig. 4a), metallic Sn 0 and Sn 2+/4+ were characterized by employing Sn and SnO2 as references respectively, where the peaks located at 1.42 Å and 2.80 Å correspond to Sn–O and Sn–Sn bonds. The one prominent peak observed at around 2.87 Å can be attributed to the combined scattering path of Sn–Sn and Sn–Bi bonds. Likewise, a dominant peak appearing at a similar position with the Bi–Bi bond of Bi reference was detected and identified as the combined scattering path of Bi–Bi and Sn–Bi bonds (Fig. 4b). This is owing to that the existence of Bi triggers the electron depletion of surface Sn atoms, potentially building the interaction between the electron density of these two elements, which leads to a trace amount of Sn–Bi bonds. Moreover, the Sn–Bi bond length lies between the Sn–Sn and Bi–Bi bonds. Representative fitting of the EXAFS spectra to the R space of Sn–Bi bimetallic interface and alloy materials are shown in Fig. 4c, d and Supplementary Fig. 14. Sn K-edge and Bi L3-edge EXAFS spectra fit simultaneously with constraints employed to ensure that the bond lengths and disorder factors for Sn–Bi and Bi–Sn bonds are the same. The corresponding fittings to the k space are depicted in Supplementary Fig. 15. The fitting results of in situ FT-EXAFS for Sn–Bi interface and alloy are summarized in Supplementary Table 4 and Table 5. Compared with Sn–Bi alloy, Sn–Bi bimetallic interface has higher coordination numbers.
(CN) of Sn–Sn and Bi–Bi but lower CN of Sn–Bi. This confirms the segregation nature of Sn–Bi bimetallic interface structure compared to Sn–Bi bulk alloy structure, consistent with the previous characterization. Larger Bi atoms result in lower CN with Sn (e.g., total CN of 3.4 for Sn in Sn–Bi alloy) compared to that of Sn–Sn (CN = 4) in Sn foil reference. Wavelet transform EXAFS was also performed with high resolution in both k and R space (Supplementary Fig. 16). The strong WT signal of Sn–Bi and Sn–Sn bonds were visible, compared to the SnO2 reference counterpart.

Upon application of potential from an open circuit potential (OCP) to −1.24 V (vs. RHE) during CO2RR, the Sn–Bi bimetallic interface/alloy structure can be well maintained, indicated by the little difference of in situ Fourier-transform EXAFS spectra for Sn K-edge (Fig. 4e) and Bi L3-edge (Fig. 4f). The fitting results of Sn K-edge show that the main peaks tended to slightly shift to a longer bond length when decreasing the potentials to 1.24 V (Supplementary Table 4). Considering that an increase in Sn–Sn coordination numbers is paralleled by a decrease in Sn–Bi coordination numbers, it is likely that further dealloying of Sn–Bi phase takes place (i.e., further segregation of Sn and Bi). The fitting of in situ EXAFS of Bi L3-edge also shows the increased distortion of Bi–Sn and Bi–Bi bonds with the cathodic voltages decreasing. In situ XANES spectra of Sn K-edge and Bi L3-edge of Sn–Bi interface and alloy samples at different applied potentials are presented in Supplementary Figs. 17–18. The slight lowering of the white line peak intensity and lower-energy shift of absorption edge when decreasing the potentials indicate the electron density accumulation resulted from the slight reduction of Sn and Bi under operating conditions.

The XAS data acquisition details and in situ liquid cell used for measurements (Supplementary Fig. 19) are described in the Supplementary Information. In situ Raman spectroscopy studies on the intermediate adsorption for Sn–Bi interface samples at various potentials were carried out (Fig. 4g) to show the mechanism of surface chemical environments under different potentials. The characteristic Raman bands can be assigned to the corresponding adsorbed surface intermediates: (1) symmetric C–O stretching vibration of HCOO− (ν1, 1010–1020 cm−1), (2) symmetric C–O stretching vibration of CO2− (ν1, 1600–1070 cm−1), (3) ν3 mode of HCOO−, i.e., symmetric O–C–O bending (scissor) mode (796–802 cm−1). Obviously, with different applied potentials, the distributions of adsorbed intermediate species are different. Moreover, with the increase of potential, the prominent HCOO− peak gradually disappeared while the CO2− peak became dominant starting from −0.84 V vs. RHE. This observation might be caused by: (i) a rise in local pH values; (ii) the equilibrium exchange between bicarbonate (CO32−H+) with dissolved CO2, which affects the transport of CO2 across the double layer.

**Electrochemical CO2 reduction performance.** The catalytic performance of Sn–Bi bimetallic interface and Sn–Bi alloy for CO2RR was evaluated in an H-cell with CO2-purged 0.5 M KHCO3 as the electrolyte (Fig. 5). Linear sweep voltammetry (LSV) was conducted in the CO2- and Ar-purged catholyte to initially evaluate the CO2RR performance (Supplementary Fig. 20). Accordingly, the gaseous and liquid products were quantitatively analyzed via online gas chromatograph (GC) and 1H nuclear magnetic resonance (1H NMR) spectroscopy, respectively. Sn–Bi interface material demonstrates a remarkable maximum formate Faradaic efficiency (FE) of 96.4 ± 2.5% at a low potential of −0.94 V vs. RHE (Fig. 5b). The FEformate is maintained over 90% at a wide potential window (−0.74 to −1.14 V vs. RHE), which might be attributed to the efficient mass transport of porous microchannel structures, ensuring the desired local environment near the active sites. This reveals that the crumpled Sn–Bi interface material achieves a higher selectivity of formate at a lower overpotential. For comparison, SnO2, electrodeposited Sn and Bi were also synthesized and evaluated to further manifest the synergistic effects of Sn and Bi at the electrochemical interfaces.

Comparing various catalysts toward formate formation (Fig. 5c, Supplementary Fig. 21), a notable improvement of FEformate is obtained after involving Bi at the interface of pure Sn. In addition, the overpotential of achieving the maximum FEformate decreases. It is attributed that Sn tends to transfer electrons from the p orbital to the interface Bi atoms and owns the moderate valence electron bank compared to pure Sn and Sn–Bi alloy, which best balances the adsorption of two competing HCOO and COOH intermediates (Supplementary Table 2) and delivers the best selectivity of formate. As exhibited in Fig. 5d, the highest HCOOH partial current density (PCD) is reached by the Sn–Bi interface material compared to those of pure Sn, Bi, SnO2, and Sn–Bi alloy. More importantly, to the best of our knowledge, the PCDformate outperforms most of the reported Sn-based and Bi-based catalysts at low potentials (−0.74 to −1.14 V vs. RHE) with high FEformate (>90%) (Supplementary Table 6). The PCDformate of this work at −0.94 V is also comparable with one of the highest reported performances using three-dimensional bismuthene catalysts. A superior PCDformate of 140 mA/cm2 is achieved at −1.24 V vs. RHE. This is attributed to the enriched active Sn–Bi interface sites created by the abundant crumplles.

Long-term performance is another feature introduced by catalysts developed in this work. The stability testing was evaluated at a constant potential of −0.84 V and FEformate at around 90% (Fig. 5e), Sn–Bi interface material presents a stable current density of around 40 mA/cm2 and FEformate of over 90% for around 160 h with negligible degradation (Supplementary Figs. 22–23), which far exceeds other recently reported data of Sn-based or Bi-based materials. The HAADF-STEM and EDS mapping also depicted the stable existence of Sn–Bi interface after the long-term stability test (Supplementary Fig. 24). This demonstrates that this material by in situ electrodeposition under CO2RR and ligand modification is highly stable during CO2RR. This is benefited from well-defined surface structures at steady crumpled fabricated by the controlled ED method. On the other hand, Sn–Bi alloy fabricated by the hydrothermal method holds lower stability (around 60 h) with a constant current density of 28 mA/cm2 compared with the electrodeposited Sn–Bi interface, revealing the simultaneous improvements in terms of activity and stability. After the stability test, the Sn–Bi alloy maintains the phases as confirmed by SEM images, TEM images, and EDS element mapping (Supplementary Figs. 23, 25).

We report a method of in situ electrodeposition to expose the active Sn–Bi interface and reveal the correlation between the catalytic activities of Sn–Bi system with their bimetallic patterns, as well as the evolutions of their local atomic structures and chemical environment during CO2RR, which have not been discussed in the other reported Sn–Bi alloy or oxides system to the best of our knowledge. A distinct comparison of our work with those in the literature is also illustrated in Fig. 6. The reported best FEformate during CO2RR and corresponding PCDformate are summarized for the present Sn-based and Bi-based catalysts. It is shown that the PCDformate of the synthesized materials surpasses almost all the currently reported data in the literature at all operating voltages (Fig. 6a). Figure 6b displays the comparison of FEformate. As shown in this
for various samples: Sn–Bi stability testing of Sn not only ensures a uniform distribution of active Sn porous three-dimensional carbon fabric employed in this work crumple-induced Sn density to the intrinsic activity improvements of abundant deposition under CO2RR conditions. We prove experimentally potential window (Fig. 6 CO2RR performance comparison with the reported data in the literature. a FE toward CO, formate and H2 for Sn–Bi interface and Sn–Bi alloy. c FE of formate. d Partial current density toward formate for various samples: Sn–Bi interface, Sn–Bi alloy, ED–Bi from electrodeposition, SnOx from hydrothermal method, and ED–Sn from electrodeposition. e The stability testing of Sn–Bi interface and alloy at $-0.84$ V vs. RHE.

figure, the corresponding FE maintains over 90% at a wide potential window ($-0.74$ to $-1.14$ V vs. RHE) and is at the top array among the published data.

Given the performance advance of this study compared with the literature, we attribute the >100 mA/cm$^2$ CO2RR current density to the intrinsic activity improvements of abundant crumple-induced Sn–Bi interface active sites by in situ electrodeposition under CO2RR conditions. We prove experimentally and theoretically that the fine-tuned exposing Sn–Bi interface is the most favorable structure for HCOOH formation compared to pure Sn and Sn–Bi bulk alloy. In addition, the nano-crumple-induced Sn–Bi interface material on carbon fabric substrate ensures rapid mass/charge transport hierarchically. Firstly, it has microflower morphology assembled from tortile nanosheets, growing tridimensionally and orienting to different angles, which provides multiple interconnected channels$^{25}$. Secondly, the porous three-dimensional carbon fabric employed in this work not only ensures a uniform distribution of active Sn–Bi interface material but also endows with interlaced channels for mass and charge transfer on the microscale.

The CO2RR was also tested in a homemade GDE flow cell (Supplementary Fig. 26), which shows the performance of ~320 mA/cm$^2$ at 1.20 V vs. RHE using neutral electrolyte (0.5 M KHCO3), resulting from better mass transportations. The performance comparisons of flow cells in this study with those in the literature are listed in Supplementary Table 7. To reflect the intrinsic activity of a catalyst, we evaluated the electrochemically active surface area (ECSA) measurements and normalized current density plots as well (Supplementary Figs. 27–29). The double-layer capacitance and the corresponding ECSA are summarized in Supplementary Table 8.

Discussion

In this study, we report the fine control of overpotential electrodeposition under in situ CO2RR can be used to achieve an
abundantly exposed active Sn–Bi interface pattern induced by nano-crumples morphology, which offers an attractive route to improve current densities at low potentials for formate production. As revealed by DFT calculations, XPS and in situ XAS characterizations, Sn–Bi bimetallic interface delivers the optimum upshift of the p-band center of Sn, and accordingly the moderate valence electron depletion, which leads to fragile adsorption of COOH and moderate adsorption of HCOO. Thus, with a lower thermodynamic barrier of HCOOH formation, a superior partial current density for formate is obtained (up to 140 mA/Cm2). High FE_{formate} (>90%) is maintained at a wide potential window (−0.74 to −1.14 V vs. RHE) with longer durability (160 h) than those reported in previous studies. This design concept can also be extended to the highly active and stable interface design of other bimetallic catalytic systems.

**Methods**

**Computational details.** Density functional theory (DFT) calculations were realized via Vienna Ab Initio Simulation Package (VASP)59, version 5.4.4. The projector-augmented wave (PAW) framework was employed to calculate the interactions between valence electrons and ion cores60. The effect of electron exchange-correlation was estimated through Perdew-Burke-Ernzerhof functional based on generalized gradient approximation, known as PBE-GGA61. For all the structural relaxations, the convergence criteria include $1 \times 10^{-6}$ eV for self-consistency loop of electronic structure, 0.001 Ry for energy cutoff for the plane-waves, and 0.01 eV/Å for Hellmann-Feynman force. We also adopted spin-polarization calculations, 2 $\times$ 2 $\times$ 1 Monkhorst-Pack k-points, and Gaussian smearing method ($\sigma = 0.1$ eV). The change in adsorption energy ($<0.01$ eV) is negligible when improving the calculations for accurate interaction cutoff of 450 eV or k-points of 4 $\times$ 4 $\times$ 1. In this work, van der Waals interaction was considered to incorporate the long-range dispersion effects by implementing DFT-D2 method proposed by Grimme et al.63. A vacuum layer of 15 Å was implemented to avoid periodic interactions of neighboring slabs. Three surface models were built for DFT calculations (Supplementary Fig. 1)14,16,23.

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**Crumpled Sn–Bi interface preparation.** 3D porous conductive carbon fabric (Fuel Cell Earth) was employed as the substrate to grow Sn–Bi interface structures, which was pretreated by consecutive ultrasonication in distilled deionized (DDI) water, acetonitrile, and ethanol. Then it was activated by immersing into HNO3 solution (65 wt %) overnight. The loading of catalysts on CF was about 1.0 mg/cm2 by weighing the CF before and after the deposition step. The ED-Bi and ED-Sn samples were synthesized by CC-ED with the metal precursor composed of Tin(II) acetate solution and Bismuth(III) chloride solution, respectively. The densities of crumple were controlled by different times of CC-ED and flow speed of CO2 during in situ ED and evolution.

**Sn–Bi alloy preparation.** Sn–Bi alloy structure was directly grown on the CF substrate by the hydrothermal method14,68. Specifically, 0.143 g of Tin (II) acetate (Alfa), and 0.190 g of Bismuth (III) chloride (Sigma–Aldrich), 0.073 g of urea (Sigma–Aldrich), and 0.112 g of ammonium fluoride (Sigma–Aldrich) were transferred in 60 mL DDI water by vigorous stirring. The pH values were tuned by hydrochloric acid until the solution attained transparency. The solution along with one piece of pretreated CF (2.5 $\times$ 5.0 cm2) was transferred into a 100 mL Teflon-lined autoclave and heated to 180 °C for 10 h. Sn–Bi alloy on CF obtained from the hydrothermal process was rinsed repeatedly with DDI water and ethanol, then dried overnight at 80 °C under vacuum. The loading of Sn–Bi alloy on CF was also around 1.0 mg/cm2 by weighing the CF before and after the hydrothermal procedure. SnO2 sample was also obtained by this hydrothermal method with a metal precursor composed of only Tin (II) acetate.

**Characterization.** The as-prepared materials were characterized by XRD (Rigaku Miniflex 600) to disclose crystal structures. XPS (Thermo Scientific K-Alpha XPS spectrometer) was employed to reveal elemental compositions and oxidation states. SEM (LEO FESEM 1530 and Oxford Ultima Extreme) and TEM (TEM E2010 F) were employed to observe the morphologies and microstructures. High-resolution TEM and scanning TEM were conducted using a high-brightness electron source and an aberration-correcting transmission electron microscope, the FEI Titan 80–300 (FEI Company, The Netherlands) equipped with a Gatan Quantum energy filter (Gatan Imaging Systems, Inc., Toronto, Canada). In situ XANES and EXAFS results were analyzed via Athena and Artemis software packages (http://bruceralv.github.io/demeter/).

In situ Raman Spectroscopy was conducted by an in situ Raman custom-made flow cell with a working electrode of 0.5 cm2 and a CO2-purged 0.5 M KHCO3 electrolyte. A laser confocal microspectrometer (Renishaw in Via) with a 532 nm wavelength laser was utilized to collect Raman spectrum. To obtain a clear analysis, the background of raw data within 700–1100 cm$^{-1}$ was processed via automatic intelligent fitting-mode baseline subtraction by WIRE software.

**Electrochemical measurement.** According to our previous work14, CO$_2$RR experiments were performed in an H-cell and both catholyte and anolyte were 0.3 M KHCO3 solution (30 mL). The as-prepared materials were used as the working electrode, while the reference electrode was SCE, and the counter electrode was platinum foil. The catholyte was continuously bubbled with CO2 for 30 min before the measurement to make it CO2-saturated. CO2RR tests were carried out through the chronoamperometry technique at constant potentials ranging from 0.44 to −1.24 V (vs. RHE) for 1 h at each potential using a BioLogic VSP300 potentiostat. Throughout this study, current densities were normalized to the geometric surface area. The results presented are the averaged values with error bars from three independent measurements. All the experiments were performed under ambient pressure and at room temperature (25 °C). The Chronoamperometry technique was also employed in the stability measurement, and the potential was set to −0.84 V vs. RHE. The electrolyte samples (800 µL each) were collected every 3 h in the first three days and sealed for further NMR analyses. Gas products (CO and H2) were analyzed by the online GC. Then the products were analyzed every 6 h until FE_{formate} dropped under 90%. To eliminate the effect of produced formate accumulation in the electrolyte, the electrolyte was renewed every 24 h15. The stability tests were repeated three times.

**Products analysis.** The analyses of products were the same as our lab reported28. The concentration of liquid products, especially formate in this work, in the catholyte was quantified by a 500 MHz 1H liquid NMR spectrometer (Bruker Advance) with the water suppression method14. Gas products, such as CO and H2, were quantified using online gas chromatography (GC, SRI 8610 C) with a packed Molecular Sieve column, Helium as carrier gas, a detector (FID), and the carrier gas of Helium (Praxair Gas, 99.999%).

**Faradic efficiency and partial current density.** Faradic efficiency (FE) can be calculated as the following equation:

$$FE = \frac{zFE_{\text{formate}}}{Q} \quad \text{(2)}$$

where, z is the number of electrons exchanged in the reaction (two-electron transfer for formate and CO production), n is the number of moles of product.
formed, F is the Faraday constant, and Q is the total amount of charges passed through the CO2RR process. The partial current density was then obtained by multiplying the Faradic efficiency with the average current density.

Data availability
All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials.

Code availability
VESTA (https://jp-minerals.org/vesta/en), Bader Charge Analysis code (https://theory.cm.utexas.edu/henkelman/research/bader), and Athena software (http://bruceravel.github.io/demeter) are all open-source packages.

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**Author contributions**

B.R., G.W., and Z.C. devised the concept and wrote the manuscript; B.R. conducted DFT simulations and analyses; B.R. synthesized the materials and carried out materials characterizations; D.L., Z.Z., and Q.M. contributed to the materials characterizations; B.R. and R.G. performed XAS characterizations; G.W. and W.Q. performed electrochemical experiments; L.R.-S. supervised the DFT simulations; Y.C. contributed to the XPS characterization; X.W., A.Y., and Z.C. supervised the whole project. All authors participated in the discussion and commented on the results of the manuscript.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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