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In situ reconstruction of vegetable sponge-like Bi₂O₃ for efficient CO₂ electroreduction to formate†

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The electrochemical reduction reaction of CO₂ provides a renewable method to close the carbon cycle and alleviate the global energy issue. Bi-based electrocatalysts present huge prospects for catalyzing formate-selective CO₂ reduction. Herein, we fabricated a porous vegetable sponge-like bismuth oxide (VS-Bi₂O₃) for the selective electroreduction of CO₂ to formate, which underwent in situ reconstruction to form 2D nanosheets containing metallic Bi and Bi₂O₂CO₃. We propose that the unique porous morphology and low crystallinity of VS-Bi₂O₃ are beneficial for the in situ generation of Bi₂O₂CO₃, which might play a significant role in enhancing the CO2 electrocatalysis performance. The catalyst delivers a 93.7% faradaic efficiency of formate at 400 mA cm⁻² and shows stability for over 18 h at 100 mA cm⁻².

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Introduction

The electrochemical CO₂ reduction reaction (CO₂RR) using renewable electricity sources is considered to be an ideal strategy for storing energy and relieving the global environment crisis caused by carbon emissions. 1-3 Through an electrocatalytic reaction, CO2 could be converted into valuable chemicals and fuels such as formic acid, CO, methanol, ethanol, ethylene, and acetate.4,5 Formic acid or formate, with a high energy density and versatile chemical features, can be applied in plenty of areas including pharmaceuticals, the leather industry, hydrogen storage, fuel cells, and metallurgy.^{6,7} Its critical potential has been presented in industrial applications for reducing CO₂ to formate via electrocatalysis.^{8,9} However, some obstacles, such as the sluggish reaction kinetics and high electricity consumption, need to be overcome before large-scale application. CO_2 is a linear molecule with the highest oxidation state, which means that it has a high thermodynamic stability (i.e., 806 kJ mol⁻¹ energy is needed to break the C=O bond).^{4,10-14} A large reorganization energy in the first electron transfer step to form $CO_2^{\bullet-}$ from CO_2 , -1.90 V versus the standard hydrogen electrode, imposes a high overpotential

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and a slow reaction rate. 15 Furthermore, the hydrogen evolution reaction (HER) competes with the desired CO2RR, leading to a selectivity loss for the generation of formate.3,11 Therefore, developing efficient electrocatalysts with low overpotentials and high selectivity becomes a key challenge for exclusively reducing CO2 to formate.

Bismuth-based (Bi-based) materials, as efficient electrocatalysts, have aroused great interest in producing formic acid or formate from CO2, due to their low cost, low toxicity and environmentally benign traits.16-18 Due to the low carbon monoxide adsorption energy and strong stabilization of intermediates, Bi-based materials are thermodynamically favorable for yielding formate instead of competitive CO or H₂. 19,20 To implement the reaction, a high overpotential of over 300 mV must generally be applied along with a low current density (usually less than 100 mA cm⁻², especially in H cell system). 21,22 Structural engineering methods, such as morphology, component and defect engineering, have been reported to promote the catalytic activities of catalytic materials. 23,24 Earlier studies regarding Bi-based catalysts with different morphologies, including dendrites, nanowires, nanoflakes, bismuthene nanosheets as well as nanoparticles, have been reported to deliver a high formate selectivity of over 90%. 7,25 However, once they interact with the surrounding reactants or products under the reduction conditions, most of the catalysts are inclined to undergo structural selfreconstruction, which can change their morphology and structure, which thus further alters the activity and selectivity of the catalysts. 22,26 For instance, Yao et al. proposed that the KHCO₃ electrolyte could moderate the dissociation and conversion of the

Bi-based metal-organic framework (Bi-MOF) into Bi₂O₂CO₃, and the applied cathodic potential further helped to reduce the Bi₂O₂CO₃ to metallic Bi, of which the unsaturated surface Bi atoms served as active sites.22 The work of Ma et al. reported bismuthene (Bi-ene) nanosheets derived from monoclinic scheelite BiVO₄ under working conditions, which significantly enhanced the CO₂ reduction performance.²⁷ We anticipate that designing new precatalysts with specific structures will play a significant role in developing highly efficient Bi-based catalysts.

Bi₂O₃, which has both high physical and chemical stability, is convenient for synthesis reactions without being much affected by the surrounding environment. This can help to rule out unnecessary influences and focus on the research priorities. Besides, Bi₂O₃ possesses CO₂RR advantages like other Bi-based materials. For example, the Bi-O structure of Bi₂O₃ has been reported to be conducive to CO₂RR via enhancing the CO2 adsorption capacity and improving the stability of the CO₂• intermediate. ^{28,29} Many Bi-based catalysts with the Bi-O structure, such as Bi₂O₃ nanosheet/nitrogen-doped graphene quantum dots (Bi₂O₃-NGQDs),³⁰ β-Bi₂O₃ fractals³¹ and Bi₂O₃ nanosheets grown on a conductive multi-channel carbon matrix (Bi₂O₃NS@MCCM), 32 exhibit a high CO₂RR performance. Our aim is to prepare a highly active Bi2O3 material and study its in situ reconstruction process in electrolytic CO2 reduction.

Herein, a porous vegetable sponge-like bismuth oxide (VS-Bi₂O₃) was synthesized using a microwave ultrasonic synthesis method and exhibited an excellent performance for catalyzing CO₂ to formate with a faradaic efficiency (FE) of around 93% under a potential ranging from -0.53 to -1.29 V (versus the reversible hydrogen electrode (RHE)), where all potentials are referenced to RHE unless mentioned otherwise) and a current density up to 400 mA cm⁻² in the flow cell system. In situ reconstruction of VS-Bi₂O₃ took place under CO₂RR conditions, with a fine nanosheet structure containing metallic Bi and Bi₂O₂CO₃ formed. The porous structure of VS-Bi₂O₃ might be favorable for reconstruction during the CO₂RR, and the generated Bi₂O₂CO₃ could maintain the superior catalytic performance of formate generation, with scarce attenuation occurring under a current density of 100 mA cm⁻² over 18 hours.

Experimental section

Synthesis of materials

The VS-Bi₂O₃ was fabricated using a featured microwave ultrasonic synthesis method based on a previous report with modifications.³³ Firstly, 489.8 mg Bi(NO₃)₃·5H₂O and 505.0 mg dicyandiamide were ultrasonically dissolved in 50 mL ethylene glycol (EG) in sequence to form a clear solution using a special three-neck flask. Then the flask was assembled with the corresponding condensation glassware using a microwave/ultrasonic/ UV combined catalytic synthesizer (XH-300UL-2+, Beijing Xianghu Science and Technology Development Co., Ltd). A constanttemperature heating mode was chosen to synthesize the VS-Bi₂O₃ sample. Typically, the microwave heating power was limited to the maximum of 300 W and the assisting ultrasonication was applied using a constant power of 500 W. The temperature was increased to 150 °C within 10 min and held there for another 10 min by the automatic program. The obtained white precipitate was then centrifugated and washed thoroughly using deionized water as well as ethanol in sequence. The white VS-Bi₂O₃ was obtained after drying at 60 °C for 12 h using a vacuum oven.

The produced VS-Bi₂O₃ was then calcined using a muffle furnace to fabricate the contrast bulk Bi₂O₃ (B-Bi₂O₃). The temperature was set as 500 °C and the furnace was supposed to reach that temperature in 100 minutes after which it remained at the same temperature for 1 h.

Characterization

X-Ray diffraction (XRD, D/max2550V) was carried out in order to interpret the crystal structure of the products. Scanning electron microscopy (SEM; Hitachi S4800) and transmission electron microscopy (TEM) were employed for the morphology change. Scanning transmission electron microscopy (STEM) and TEM characterization were performed using a Thermo Fisher Talos F200X instrument. Energy dispersive X-ray spectroscopy (EDS) was carried out using 4 in-column Super-X detectors. X-ray photoelectron spectroscopy (XPS; Thermo Escalab 250Xi) was carried out using an Al Kα X-ray beam (1486.6 eV) and was used to obtain more detailed information on the chemical compositions. In the meantime, the C 1s peak centered at 284.8 eV was set as the reference for calibration of all of the binding energies. Raman analysis was performed using a Leica DMLM microscope (Renishaw). The excitation wavelength and laser power were set as 532 nm and 3 mW, respectively.

Electrochemical measurements

The experiments were carried out using a home-made flow cell system with three poly(methyl methacrylate) (PMMA) plates to divide the anolyte, catholyte and CO2 gas chambers, respectively. The anion exchange membrane (Fumasep FAB-PK-130, Fuel Cell Store) was placed between the analyte and catholyte chambers for separation of the electrolyte and the exchange of anions. Nickel foam of size 3×3 cm² was used as the anode, counter electrode. The Ag/AgCl (3.5 M KCl) reference electrode was put in the cathode compartment. A total of 11.5 mg VS-Bi₂O₃ was mixed with 25 μL Sustainion[™] XA-9 solution and 1 mL dispersion liquid (isopropanol: H₂O = 3:1, v/v), followed by ultrasonication for 30 min to form an ink, which was then sprayed onto a piece of commercial Sigracet gas diffusion layer (GDS 28BC, Fuel Cell store), whose area was set as $3 \times 3 \text{ cm}^2$. After drying, a piece of $1.5 \times 1.5 \text{ cm}^2$ gas diffusion electrode (GDE) was tested using a flow cell reactor as the working electrode. The CO₂ gas feed rate was set as 20 standard cubic centimeters per minute (sccm). The electrolyte was 1 M KOH, which flows at a rate of 10 mL per min. All potentials were calibrated to the reversible hydrogen electrode (RHE) with iR_{cell} compensation (i serves as the applied current and R_{cell} denotes the cell resistance) according to the

equation $E_{\rm RHE} = E_{\rm Ag/AgCl} + 0.205 + 0.059 \times \rm pH + i \times R_{\rm cell}$. Gas products were analyzed via gas chromatography (RAMIN, GC2060), using a thermal conductivity detector (TCD) for detecting H2 and a flame ionization detector (FID) for the detection of CO and other gaseous hydrocarbons. The liquid product of HCOO was quantified using ¹H nuclear magnetic resonance (NMR). For analysis, 500 µL electrolyte with the liquid product in it was taken out to mix with 100 µL D₂O (with TMSP as the internal standard) to form the mixture quantified later using NMR.

Results and discussion

XRD measurements were performed in order to figure out the phase of the product. In Fig. 1a, the XRD pattern of the obtained VS-Bi₂O₃ matches with cubic Bi₂O₃ (PDF#27-0052), revealing its cubic phase. Besides, the wide peaks indicate its weak crystallinity with peaks at 27.9°, 46.4° and 55.1° corresponding to the (111), (220) and (311) facets, respectively.

The scanning electron microscopy (SEM) images (Fig. 1b and c, and Fig. S1 and S2, ESI†) show a vegetable sponge-like morphology, assembling multiple pieces of nanosheets into a hierarchical micron structure. Transmission electron microscopy (TEM) results (Fig. 1d and e and Fig. S3, ESI†) show lots of open pores in the VS-Bi₂O₃. Moreover, the high-resolution TEM (HR-TEM; Fig. 1f) image displays no obvious lattice fringe. The selected area electron diffraction (SAED; inset in Fig. 1f) image exhibits a diffraction ring with a radius of 3.19 Å that corresponds to the (111) plane of Bi₂O₃ (PDF#27-0052), confirming the weak crystallinity of VS-Bi₂O₃. The B-Bi₂O₃ obtained from the VS-Bi₂O₃ via annealing in air has a high crystallinity, with the XRD pattern aligning well with monoclinic Bi₂O₃ (PDF#41-1449) (Fig. S4, ESI†).

The CO₂RR processes for VS-Bi₂O₃ and B-Bi₂O₃ were carried out in 1 M KOH electrolyte (pH = 14) using a flow cell system (Fig. S5, ESI†). During the CO₂RR, VS-Bi₂O₃ underwent in situ

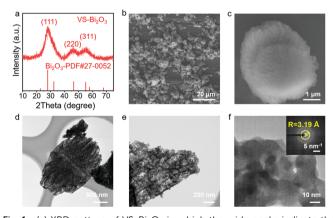


Fig. 1 (a) XRD pattern of $VS-Bi_2O_3$ in which the wide peaks indicate the weak crystallinity of VS-Bi₂O₃. (b and c) SEM images of VS-Bi₂O₃ showing the vegetable sponge-like morphology. (d and e) TEM images of $VS-Bi_2O_3$ showing lots of open pores. (f) HR-TEM image of VS-Bi₂O₃ displaying no obvious lattice fringe, and (inset) SAED image exhibiting a classic diffraction ring of Bi₂O₃ (PDF#27-0052)

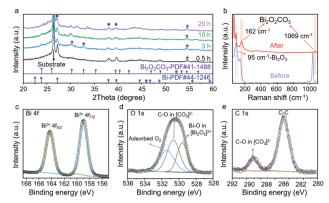


Fig. 2 (a) XRD patterns of VS-Bi $_2$ O $_3$ electrolyzing the CO $_2$ RR at 100 mA cm⁻² after 0.5, 3, 10 and 20 h, respectively. Bi₂O₂CO₃ and Bi were formed and maintained during the CO₂RR. (b) Raman spectra of VS-Bi₂O₃ before (blue line) and after (red line) the CO₂RR for 3 h. Bi₂O₂CO₃ (orange shadow) is formed in the electrolytic process. (c-e) Bi 4f, O 1s and C 1s XPS spectra, respectively, of the post-electrolysis VS-Bi₂O₃ (at 100 mA cm⁻² for 24 h), demonstrating the existence of Bi₂O₂CO₃.

reconstruction according to the XRD measurements for different electrolysis times. As shown in Fig. 2a, tetragonal Bi₂O₂CO₃ (PDF#41-1488) appeared after 0.5 h of electrolysis at 100 mA cm⁻². As the catalysis process proceeds, the featured peaks of Bi₂O₂CO₃ (marked with purple stars) become noticeable for the XRD patterns after 3, 10, and 20 h. Furthermore, the Raman spectrum of the VS-Bi₂O₃ sample after electrolysis also demonstrates the formed Bi₂O₂CO₃ via the featured peaks appearing at 162 and 1069 cm⁻¹ (in light orange shadow), ^{22,34} while the peak at 95 cm⁻¹ is attributed to Bi₂O₃ (in light grey shadow) (Fig. 2b).³⁵ As for B-Bi₂O₃, scarce Bi₂O₂CO₃ was detected after electrolysis (Fig. S6, ESI†).

To further analyse the surface valence states, X-ray photoelectron spectroscopy (XPS) was conducted. Post-electrolysis XPS inspections of VS-Bi₂O₃ (at 100 mA cm⁻² for 24 h) are shown in Fig. 2c-e. The peaks at 159 and 164.3 eV in the Bi 4f spectrum (Fig. 2c) are assigned to Bi³⁺, demonstrating a single oxidation state of Bi3+.28,30 Three obvious fitted peaks can be clearly identified in the O 1s spectrum (Fig. 2d). The peaks at 529.6, 530.7 and 531.5 eV correspond to the O atoms in the Bi-O bonds in the $[Bi_2O_2]^{2+}$ layers, the O atoms in C-O in the $[CO_3]^{2-}$ layers, and the oxygen of adsorbed O_2 , respectively.^{7,28,34} As for the C 1s XPS spectrum (Fig. 2e), the peak at 289.0 eV is indexed to the carbon atoms in the [CO₃]²⁻ layers.³⁶ XPS spectroscopy verifies the existence of Bi₂O₂CO₃ after electroreduction, in line with the XRD and Raman results.

To gain further insight into the morphology changes, SEM, TEM and HR-TEM characterizations of the post-electrolysis sample of VS-Bi₂O₃ were carried out. As shown in Fig. 3a and b, vegetable sponge-like frames of VS-Bi₂O₃ evolve into a nanosheet morphology after CO₂RR for 10 h. Combined with more post-electrolysis SEM images for different timescales in Fig. S7 and S8 (ESI†), we speculate that the morphology of VS-Bi₂O₃ underwent several transformation steps under different cathodic potentials. The shape first transformed from the vegetable sponge-like to thick nanosheet-assembled plates, and

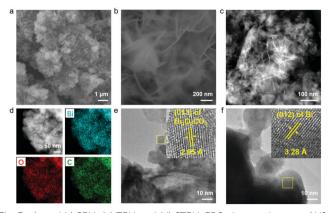


Fig. 3 (a and b) SEM, (c) TEM and (d) STEM-EDS elemental maps of VS- $\rm Bi_2O_3$ after the $\rm CO_2RR$ for 10 h. (e and f) HR-TEM images of VS-Bi₂O₃ after the CO₂RR for 10 h in which Bi₂O₂CO₃ and metallic Bi are detected via their characteristic facets

then gradually changed into thin nanosheets. The TEM image (Fig. 3c) confirms the nanosheet morphology in accordance with the SEM images. The SEM images after electrolysis of B-Bi₂O₃ are also displayed in Fig. S9 and S10 (ESI†). Scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS; Fig. 3d) shows the uniformly distributed Bi, O and C elements. It is worth noting that the presence of the carbon element to some extent reveals the existence of Bi₂O₂CO₃. The high-resolution TEM image in Fig. 3e proves this point as well, with the lattice spacing of 2.95 Å aligning well with the (013) facet of Bi₂O₂CO₃. Fig. 3f shows a 3.28 Å lattice space in accordance with the (012) plane of metallic bismuth, which was derived from the in situ reduction of VS-Bi₂O₃.

The above measurements illustrate that the prepared VS-Bi₂O₃ is prone to undergo reconstruction under the working conditions. The sample was changed into metallic bismuth and Bi₂O₂CO₃ after electrolysis, among which the Bi₂O₂CO₃ did not appear in the B-Bi₂O₃ sample (Fig. S6, ESI†). Besides, the porous vegetable sponge-like morphology is inclined to be exposed to the operating environment since its open pores can be filled with electrolytes and reactants. This may lead to the reconstruction from VS-Bi₂O₃ to Bi and Bi₂O₂CO₃ during the CO₂RR process. Bi₂O₂CO₃ is a layered structure consisting of ${\rm CO_3}^{2-}$ and ${\rm [Bi_2O_2]^{2^+}}$, which has been reported to exhibit a lower overpotential compared with metallic bismuth.³⁷

To figure out the phase transformation from Bi₂O₃ to Bi₂O₂CO₃ and Bi, three XRD samples obtained under different conditions were prepared (Table S1 and Fig. S11, ESI†). The results indicate that VS-Bi₂O₃ did not react directly with the KOH electrolyte in the absence of CO2 under ambient conditions. However, when VS-Bi₂O₃ was introduced into the CO₂ atmosphere, Bi₂O₂CO₃ was generated with no metallic Bi formed. Furthermore, the VS-Bi₂O₃ changed into metallic Bi and Bi₂O₂CO₃ with the current density applied. Based on the above results, we speculated that the Bi₂O₂CO₃ might be formed *via* the intercalation of CO₃²⁻ into the layered structure of the bismuth oxide compound. Previous reports have revealed that the presence of CO2 during the CO2RR process plays a

significant role in maintaining the stable existence of Bi2O2CO3 thanks to the consumption of most cathodic electrons. 37,38 Besides, a high local pH was also reported to be beneficial for the formation of Bi₂O₂CO₃, and the 1 M KOH electrolyte in this work can provide a large amount of OH-, which might promote the generation of Bi₂O₂CO₃.

We then carried out the CO₂RR to assess the electrocatalytic performance and identify the role of Bi₂O₂CO₃. As shown in Fig. 4a and Fig. S12 (ESI†), VS-Bi₂O₃ achieves a high current density of up to 100 mA cm⁻² at a small applied potential of only -0.53 V, with an accompanying high FE(HCOO⁻) of around 93.6%. The FE(HCOO-) remains at a high level of >93.0% over a wide potential range from -0.53 V to -1.29 V, with a potential window of 760 mV. The maximum FE(HCOO⁻) of 94.9% appears at -1.12 V delivering a current density of 300 mA cm⁻². The overall current density of 400 mA cm⁻² is achieved at a potential of -1.29 V, in the meantime sustaining a high FE(HCOO⁻) of around 93.7%. As for the contrast sample, B-Bi₂O₃ attains the same current density with a much more negative potential and a much lower selectivity for formate. Taking the current density of 200 mA cm⁻², for example, B-Bi₂O₃ needs an applied potential of -1.11 V to reach that goal, which is 380 mV more negative than VS-Bi₂O₃ with a low FE(HCOO⁻) of 85.3% under the operational conditions (Fig. 4b, and Fig. S13, ESI†). Furthermore, the potential grows markedly for the larger current densities, and a potential of -1.58 V is needed for 400 mA cm⁻², negatively shifted by 300 mV compared with VS-Bi₂O₃. The CO₂RR performance measurements unveil the superb activity and exclusive selectivity of VS-Bi₂O₃ for the electrochemical conversion of CO₂ into formate, indicating the significance of Bi₂O₂CO₃ derived from VS-Bi₂O₃.

Since efficient charge transfer at the catalyst/electrolyte interface is beneficial to the catalytic process, we carried out electrochemical impedance spectroscopy (EIS) in order to measure the kinetics of charge transfer.35 Fig. 4c shows the Nyquist plots of VS-Bi₂O₃ and B-Bi₂O₃ under open-circuit potential at a steady state, from which a smaller arc can be observed in VS-Bi₂O₃ (red) compared with B-Bi₂O₃ (blue). In the Nyquist plots, the charge transfer resistance (R_{ct}) of the electrochemical reaction can be represented by the radius of the arc, and a smaller arc usually means a smaller resistance. Thus, VS-Bi₂O₃ possesses a highly accelerated charge-transfer process thanks to its much shorter radius than the contrast bulk sample. We attributed this remarkable improvement to the appearance of Bi₂O₂CO₃ derived from VS-Bi₂O₃. Hence durability testing was carried out at the current density of 100 mA cm⁻², and the potential remained steady without any significant degradation for an electrolysis process of over 18 h, demonstrating its superior stability for converting CO₂ to formate (Fig. 4d). The performance comparison of VS-Bi₂O₃ with previous Bi-based materials is listed in Table S2 (ESI†).

Bi₂O₂CO₃ is a layered structure consisting of CO₃²⁻ and [Bi₂O₂]²⁺.³⁷ The presence of metastable oxides has previously been reported to be able to stabilize the reduced CO2 intermediate, which plays a vital role in lowering the overpotential

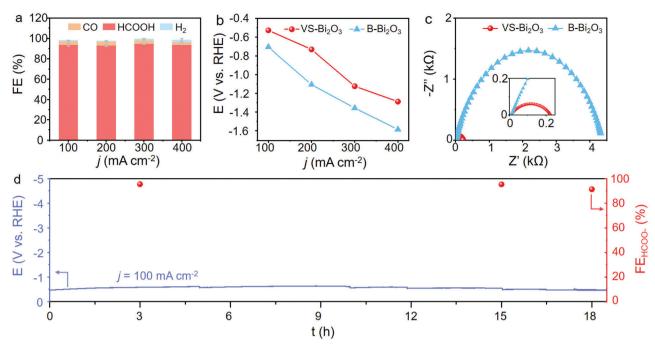


Fig. 4 (a) Faradaic efficiencies plot (with error bars) of VS-Bi₂O₃ in 1 M KOH electrolyte using a flow cell system. (b) Current density dependence of potential values for VS-Bi₂O₃ and B-Bi₂O₃. (c) Fitting results of Nyquist plots for VS-Bi₂O₃ and B-Bi₂O₃ under open-circuit potential at a steady state, where the inset shows an expanded version of the area near the origin. (d) Stability testing of VS-Bi₂O₃ at 100 mA cm⁻².

and accelerating the charge transfer required to reduce CO2 into the target formate product. 7,37-39 The Bi₂O₂CO₃ was generated in situ from VS-Bi₂O₃ during the CO₂RR process, whose existence after electrolysis at 100 mA cm⁻² for 20 h revealed that the formed Bi₂O₂CO₃ was robust enough to survive under an applied cathodic bias. However, the contrast sample B-Bi₂O₃ was reduced in situ to metallic Bi without Bi₂O₂CO₃ and was accompanied by an unsatisfactory performance. Therefore, the presence of Bi₂O₂CO₃ might play a significant role in enhancement of the CO₂RR performance.

Conclusions

In summary, through the adoption of a facile microwave/ ultrasonic synthesis method, we fabricated the porous vegetable sponge-like bismuth oxide (VS-Bi₂O₃), which underwent in situ reconstruction to form metallic Bi and Bi₂O₂CO₃ nanosheets, exhibiting excellent CO₂RR activity with near-unity formate selectivity under a high current density of 400 mA cm⁻². Besides, the durability at 100 mA cm⁻² could reach over 18 h, suggesting its remarkable long-term stability. A series of characterization measurements, such as post-electrolysis XRD, Raman, and TEM, indicate the existence of Bi₂O₂CO₃, revealing its robust stability. We further demonstrate that the porous vegetable sponge-like configuration may play a critical role in the in situ reconstruction to form Bi₂O₂CO₃, and that the appearance of Bi₂O₂CO₃ could enhance the CO₂RR performance. This study emphasizes the significance of the precatalyst structure on its in situ reconstruction and CO2RR performance optimization.

Author contributions

Hua Gui Yang, Fangxin Mao and Peng Fei Liu designed and guided the study; Yingli Shi and Chun Fang Wen performed the experiments and analyzed the experimental data; Xuefeng Wu carried out the TEM experiments; Jia Yue Zhao helped in the analysis. All the authors discussed and commented on the data and contributed to the manuscript.

Conflicts of interest

There are no conflicts to declare.

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