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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. CO₂ 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 CO₂^{•-} from CO₂, -1.90 V *versus* the standard hydrogen electrode, imposes a high overpotential

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 self-reconstruction, 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

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Bi-based metal-organic framework (Bi-MOF) into $\text{Bi}_2\text{O}_2\text{CO}_3$, and the applied cathodic potential further helped to reduce the $\text{Bi}_2\text{O}_2\text{CO}_3$ 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 BiVO_4 under working conditions, which significantly enhanced the CO_2 reduction performance.²⁷ We anticipate that designing new precatalysts with specific structures will play a significant role in developing highly efficient Bi-based catalysts.

Bi_2O_3 , 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, Bi_2O_3 possesses CO_2RR advantages like other Bi-based materials. For example, the Bi-O structure of Bi_2O_3 has been reported to be conducive to CO_2RR *via* enhancing the CO_2 adsorption capacity and improving the stability of the CO_2^{*} intermediate.^{28,29} Many Bi-based catalysts with the Bi-O structure, such as Bi_2O_3 nanosheet/nitrogen-doped graphene quantum dots ($\text{Bi}_2\text{O}_3\text{-NGQDs}$),³⁰ $\beta\text{-Bi}_2\text{O}_3$ fractals³¹ and Bi_2O_3 nanosheets grown on a conductive multi-channel carbon matrix ($\text{Bi}_2\text{O}_3\text{NS@MCCM}$),³² exhibit a high CO_2RR performance. Our aim is to prepare a highly active Bi_2O_3 material and study its *in situ* reconstruction process in electrolytic CO_2 reduction.

Herein, a porous vegetable sponge-like bismuth oxide (VS- Bi_2O_3) was synthesized using a microwave ultrasonic synthesis method and exhibited an excellent performance for catalyzing CO_2 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- Bi_2O_3 took place under CO_2RR conditions, with a fine nanosheet structure containing metallic Bi and $\text{Bi}_2\text{O}_2\text{CO}_3$ formed. The porous structure of VS- Bi_2O_3 might be favorable for reconstruction during the CO_2RR , and the generated $\text{Bi}_2\text{O}_2\text{CO}_3$ 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- Bi_2O_3 was fabricated using a featured microwave ultrasonic synthesis method based on a previous report with modifications.³³ Firstly, 489.8 mg $\text{Bi}(\text{NO}_3)_3\cdot5\text{H}_2\text{O}$ 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 constant-temperature heating mode was chosen to synthesize the VS- Bi_2O_3 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- Bi_2O_3 was obtained after drying at 60 °C for 12 h using a vacuum oven.

The produced VS- Bi_2O_3 was then calcined using a muffle furnace to fabricate the contrast bulk Bi_2O_3 (B- Bi_2O_3). 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 $\text{K}\alpha$ 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 CO_2 gas chambers, respectively. The anion exchange membrane (Fumasep FAB-PK-130, Fuel Cell Store) was placed between the anolyte and catholyte chambers for separation of the electrolyte and the exchange of anions. Nickel foam of size $3 \times 3\text{ cm}^2$ 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- Bi_2O_3 was mixed with 25 μL Sustainion™ XA-9 solution and 1 mL dispersion liquid (isopropanol : H_2O = 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 CO_2 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 $E_{\text{RHE}} = E_{\text{Ag}/\text{AgCl}} + 0.205 + 0.059 \times \text{pH} + i \times R_{\text{cell}}$. Gas products were analyzed *via* gas chromatography (RAMIN, GC2060), using a thermal conductivity detector (TCD) for detecting H_2 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 D_2O (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- Bi_2O_3 matches with cubic Bi_2O_3 (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- Bi_2O_3 . 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 \AA that corresponds to the (111) plane of Bi_2O_3 (PDF#27-0052), confirming the weak crystallinity of VS- Bi_2O_3 . The B- Bi_2O_3 obtained from the VS- Bi_2O_3 *via* annealing in air has a high crystallinity, with the XRD pattern aligning well with monoclinic Bi_2O_3 (PDF#41-1449) (Fig. S4, ESI[†]).

The CO_2RR processes for VS- Bi_2O_3 and B- Bi_2O_3 were carried out in 1 M KOH electrolyte ($\text{pH} = 14$) using a flow cell system (Fig. S5, ESI[†]). During the CO_2RR , VS- Bi_2O_3 underwent *in situ*

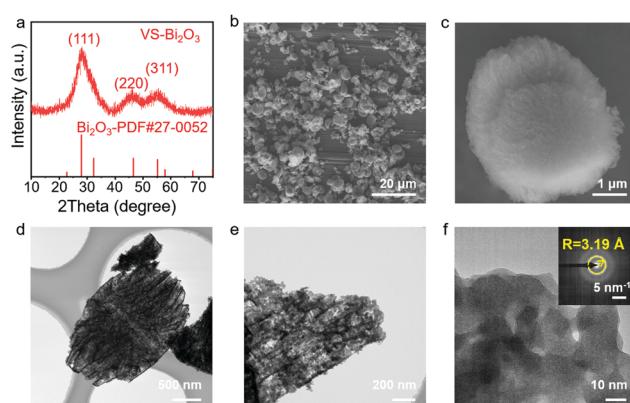


Fig. 1 (a) XRD pattern of VS- Bi_2O_3 in which the wide peaks indicate the weak crystallinity of VS- Bi_2O_3 , (b and c) SEM images of VS- Bi_2O_3 showing the vegetable sponge-like morphology. (d and e) TEM images of VS- Bi_2O_3 showing lots of open pores. (f) HR-TEM image of VS- Bi_2O_3 displaying no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

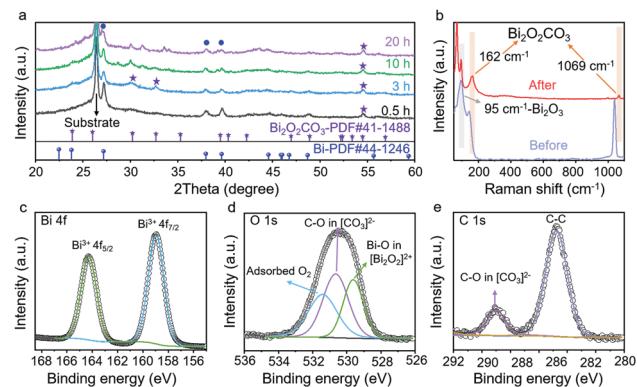


Fig. 2 (a) XRD patterns of VS- Bi_2O_3 electrolyzing the CO_2RR at 100 mA cm^{-2} after 0.5, 3, 10 and 20 h, respectively. $\text{Bi}_2\text{O}_2\text{CO}_3$ and Bi were formed and maintained during the CO_2RR . (b) Raman spectra of VS- Bi_2O_3 before (blue line) and after (red line) the CO_2RR for 3 h. $\text{Bi}_2\text{O}_2\text{CO}_3$ (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- Bi_2O_3 (at 100 mA cm^{-2} for 24 h), demonstrating the existence of $\text{Bi}_2\text{O}_2\text{CO}_3$.

reconstruction according to the XRD measurements for different electrolysis times. As shown in Fig. 2a, tetragonal $\text{Bi}_2\text{O}_2\text{CO}_3$ (PDF#41-1488) appeared after 0.5 h of electrolysis at 100 mA cm^{-2} . As the catalysis process proceeds, the featured peaks of $\text{Bi}_2\text{O}_2\text{CO}_3$ (marked with purple stars) become noticeable for the XRD patterns after 3, 10, and 20 h. Furthermore, the Raman spectrum of the VS- Bi_2O_3 sample after electrolysis also demonstrates the formed $\text{Bi}_2\text{O}_2\text{CO}_3$ *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 Bi_2O_3 (in light grey shadow) (Fig. 2b).³⁵ As for B- Bi_2O_3 , scarce $\text{Bi}_2\text{O}_2\text{CO}_3$ was detected after electrolysis (Fig. S6, ESI[†]).

To further analyse the surface valence states, X-ray photo-electron spectroscopy (XPS) was conducted. Post-electrolysis XPS inspections of VS- Bi_2O_3 (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 Bi^{3+} , demonstrating a single oxidation state of Bi^{3+} .^{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 $[\text{Bi}_2\text{O}_2]^{2+}$ layers, the O atoms in C–O in the $[\text{CO}_3]^{2-}$ 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 $[\text{CO}_3]^{2-}$ layers.³⁶ XPS spectroscopy verifies the existence of $\text{Bi}_2\text{O}_2\text{CO}_3$ 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- Bi_2O_3 were carried out. As shown in Fig. 3a and b, vegetable sponge-like frames of VS- Bi_2O_3 evolve into a nanosheet morphology after CO_2RR 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- Bi_2O_3 underwent several transformation steps under different cathodic potentials. The shape first transformed from the vegetable sponge-like to thick nanosheet-assembled plates, and

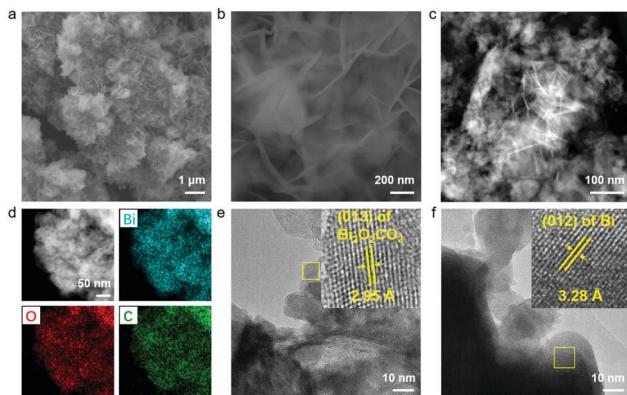


Fig. 3 (a and b) SEM, (c) TEM and (d) STEM-EDS elemental maps of VS- Bi_2O_3 after the CO_2RR for 10 h. (e and f) HR-TEM images of VS- Bi_2O_3 after the CO_2RR for 10 h in which $\text{Bi}_2\text{O}_2\text{CO}_3$ and metallic Bi are detected via their characteristic facets.

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- Bi_2O_3 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 $\text{Bi}_2\text{O}_2\text{CO}_3$. The high-resolution TEM image in Fig. 3e proves this point as well, with the lattice spacing of 2.95 \AA aligning well with the (013) facet of $\text{Bi}_2\text{O}_2\text{CO}_3$. Fig. 3f shows a 3.28 \AA lattice space in accordance with the (012) plane of metallic bismuth, which was derived from the *in situ* reduction of VS- Bi_2O_3 .

The above measurements illustrate that the prepared VS- Bi_2O_3 is prone to undergo reconstruction under the working conditions. The sample was changed into metallic bismuth and $\text{Bi}_2\text{O}_2\text{CO}_3$ after electrolysis, among which the $\text{Bi}_2\text{O}_2\text{CO}_3$ did not appear in the B- Bi_2O_3 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- Bi_2O_3 to Bi and $\text{Bi}_2\text{O}_2\text{CO}_3$ during the CO_2RR process. $\text{Bi}_2\text{O}_2\text{CO}_3$ is a layered structure consisting of CO_3^{2-} and $[\text{Bi}_2\text{O}_2]^{2+}$, which has been reported to exhibit a lower overpotential compared with metallic bismuth.³⁷

To figure out the phase transformation from Bi_2O_3 to $\text{Bi}_2\text{O}_2\text{CO}_3$ and Bi, three XRD samples obtained under different conditions were prepared (Table S1 and Fig. S11, ESI†). The results indicate that VS- Bi_2O_3 did not react directly with the KOH electrolyte in the absence of CO_2 under ambient conditions. However, when VS- Bi_2O_3 was introduced into the CO_2 atmosphere, $\text{Bi}_2\text{O}_2\text{CO}_3$ was generated with no metallic Bi formed. Furthermore, the VS- Bi_2O_3 changed into metallic Bi and $\text{Bi}_2\text{O}_2\text{CO}_3$ with the current density applied. Based on the above results, we speculated that the $\text{Bi}_2\text{O}_2\text{CO}_3$ might be formed via the intercalation of CO_3^{2-} into the layered structure of the bismuth oxide compound. Previous reports have revealed that the presence of CO_2 during the CO_2RR process plays a

significant role in maintaining the stable existence of $\text{Bi}_2\text{O}_2\text{CO}_3$ 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 $\text{Bi}_2\text{O}_2\text{CO}_3$, and the 1 M KOH electrolyte in this work can provide a large amount of OH^- , which might promote the generation of $\text{Bi}_2\text{O}_2\text{CO}_3$.⁷

We then carried out the CO_2RR to assess the electrocatalytic performance and identify the role of $\text{Bi}_2\text{O}_2\text{CO}_3$. As shown in Fig. 4a and Fig. S12 (ESI†), VS- Bi_2O_3 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 $\text{FE}(\text{HCOO}^-)$ of around 93.6%. The $\text{FE}(\text{HCOO}^-)$ 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 $\text{FE}(\text{HCOO}^-)$ 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 $\text{FE}(\text{HCOO}^-)$ of around 93.7%. As for the contrast sample, B- Bi_2O_3 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- Bi_2O_3 needs an applied potential of -1.11 V to reach that goal, which is 380 mV more negative than VS- Bi_2O_3 with a low $\text{FE}(\text{HCOO}^-)$ 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- Bi_2O_3 . The CO_2RR performance measurements unveil the superb activity and exclusive selectivity of VS- Bi_2O_3 for the electrochemical conversion of CO_2 into formate, indicating the significance of $\text{Bi}_2\text{O}_2\text{CO}_3$ derived from VS- Bi_2O_3 .

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- Bi_2O_3 and B- Bi_2O_3 under open-circuit potential at a steady state, from which a smaller arc can be observed in VS- Bi_2O_3 (red) compared with B- Bi_2O_3 (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- Bi_2O_3 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 $\text{Bi}_2\text{O}_2\text{CO}_3$ derived from VS- Bi_2O_3 . 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 CO_2 to formate (Fig. 4d). The performance comparison of VS- Bi_2O_3 with previous Bi-based materials is listed in Table S2 (ESI†).

$\text{Bi}_2\text{O}_2\text{CO}_3$ is a layered structure consisting of CO_3^{2-} and $[\text{Bi}_2\text{O}_2]^{2+}$.³⁷ The presence of metastable oxides has previously been reported to be able to stabilize the reduced CO_2 intermediate, which plays a vital role in lowering the overpotential

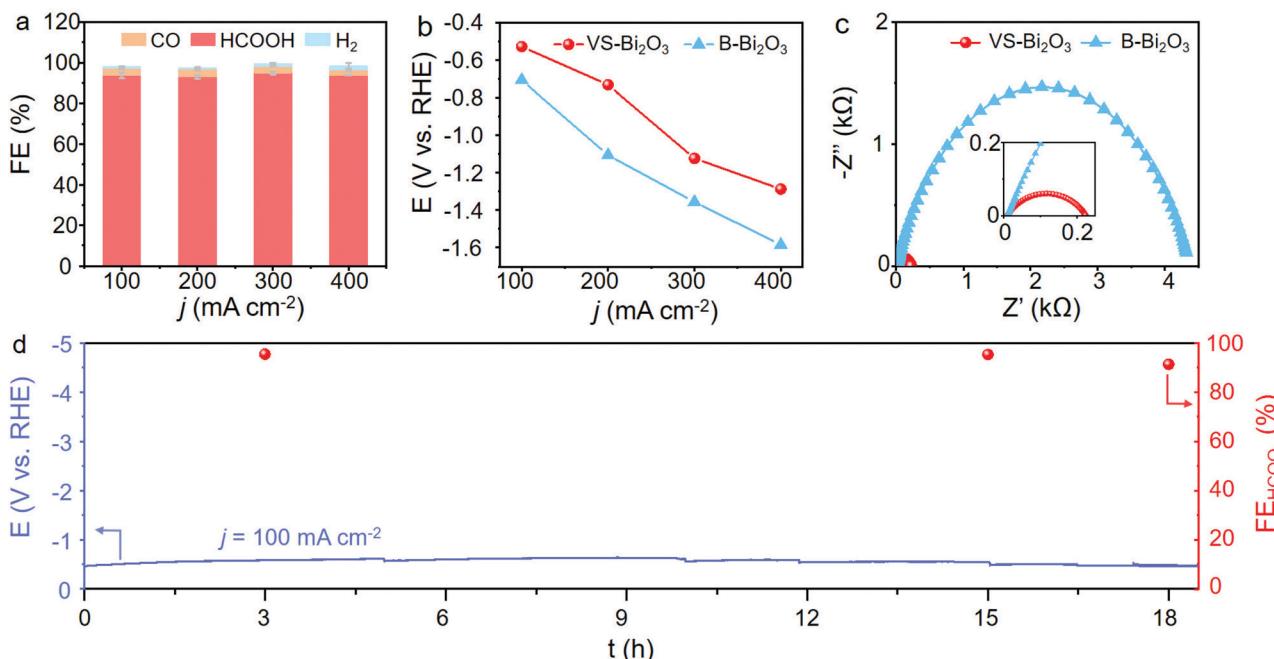


Fig. 4 (a) Faradaic efficiencies plot (with error bars) of VS-Bi₂O₃ in 1 M KOH electrolyte using a flow cell system. (b) Current density dependence of potential values for VS-Bi₂O₃ and B-Bi₂O₃. (c) Fitting results of Nyquist plots for VS-Bi₂O₃ and B-Bi₂O₃ under open-circuit potential at a steady state, 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.

Acknowledgements

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