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Enhanced Electrocatalytic CO₂ Reduction of Bismuth Nanosheets with Introducing Surface Bismuth Subcarbonate

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Abstract: The electrocatalytic CO₂ reduction reaction (CO₂RR) into hydrocarbon products is one of the most promising approaches for CO₂ utilization in modern society. However, the application of CO₂RR requires optimizing state-of-the-art catalysts as well as elucidating the catalytic interface formation mechanism. In this study, a flower-like nano-structured Bi catalyst is prepared by a facile pulse current electrodeposition method wherein the morphologies could be accurately controlled. Interestingly, nano-structured Bi is inclined to generate Bi₂O₂CO₃ in the air and form a stable Bi₂O₂CO₃@Bi interface, which could enhance the CO₂ adsorption and conversion. In-situ Raman spectroscopy analysis also proves the existence of Bi₂O₂CO₃ on the electrode surface. In a practical CO₂ reduction test by a flow-cell reactor, the Bi₂O₂CO₃@Bi electrode delivers a high faradaic efficiency of the CO₂ to formate/formic acid (~90%) at −1.07 V vs. reversible hydrogen electrode (RHE) with no obvious decay during more than a 10 h continuous test. The introducing surface Bi₂O₂CO₃ in nano-structured Bi supports a promising strategy as well as facile access to prepare improved CO₂RR electrocatalysts.

Keywords: CO₂ reduction; bismuth; Bi₂O₂CO₃; interface; formic acid

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1. Introduction

Carbon dioxide (CO₂) conversion through a physicochemical process has been considered as a promising means to halt greenhouse gas emissions and global warming [1,2]. Moreover, extraterrestrial CO₂ utilization is the only effective method for human beings to survive in outer space for a long-term [3]. The electrochemical CO₂ reduction reaction (CO₂RR) has advantages, including facile operation, controllable product, and scalable application, as well as when it is coupled with renewable resources such as solar and potential energy [4,5]. A variety of CO₂RR products, such as methane (CH₄), ethylene (C₂H₄), formate/formic acid (HCOOH), and methanol (CH₃OH) could be achieved and used as fuels or chemical raw materials [6,7]. Among the above hydrocarbons, HCOOH is a desired product with high economic value and broad applications, and could be produced with high Faradaic efficiency (FE) at low over-potential due to its relatively simple two-electron transfer reductive procedure [8,9].

However, the electrochemical CO₂RR to HCOOH still has some issues to be solved, including the inert nature of CO₂, complicated electron transfers and sluggish reaction kinetics, the parasitic chemical reaction of hydrogen evolution, and poor long-term stability [7–11]. Metal-based catalysts for HCOOH have been widely studied, e.g., Sn, Pb, Hg, Cd, In, Bi, and so on [12,13]. Nevertheless, most of the metal catalysts (Pb, Hg, Cd, and In) are toxic and lead to severe environmental pollution [14]. Among the other non-toxic candidates, Bi-based catalysts possess lower over-potential and higher FE than Sn and the others [15–18]. Bulk-structured Bi catalysts, i.e., dendritic-revealed low electrocatalytic

CO₂RR activity, have a high hydrogen evolution reaction (HER) with the increase of applied potential, leading to unsatisfied FE_{HCOOH} [12,19,20]. Recently, nano-structured Bi catalysts, such as nanoparticles [21,22], nanosheet [23], nanorod [24], nano-dendrites [25], and nanotube [26,27], have been synthesized and have exhibited higher FE_{HCOOH} than the bulk catalysts [28,29]. In addition, metal Bi⁰ is assumed to be the active site in the Bi and Bi-based electrochemical CO₂RR catalysts in previous studies [14–16,25,28,30,31].

Although Bi-based catalysts show remarkable FE_{HCOOH} selectivity on electrochemical CO₂RR, the current density is still low in the CO₂ concentration aqueous reaction and inapplicable for large-scale industrial production. It is noteworthy that previous studies of Bi metal electrocatalysts did not take notice of the generated Bi-based compound during CO₂RR and its influence on electrochemical performance, especially in the nanoscale electrodes with a high CO₂ chemisorption activity [32–34]. Therefore, it is necessary to investigate the catalytic active site governing the CO₂RR in Bi metal catalyst and elucidate the formation mechanism of Bi-based compounds from Bi metal. Recent research indicated that the Bi–O and [Bi₂O₂]²⁺ bonds played a key role in adsorbing CO₂ as well as forming the *OOCH intermediate, thus improving the FE_{HCOOH} product and inhibiting HER [35–40]. As a result, Bi-based compounds that contained Bi–O bonds, such as bismuth oxides (Bi₂O₃, BiO_x) [27,36,37,40–43] and bismuth subcarbonate (Bi₂O₂CO₃) [17,35,38,44–47], have been prepared and disclosed with improved CO₂RR performance. For instance, Zhou et al. reported the induced crystal distortion in the two-dimensional [Bi₂O₂]²⁺ layer in the BiOCl nanoplate, which increased the CO₂RR active sites [39]. Zhang et al. synthesized pure layered Bi₂O₂CO₃ by a solvothermal method, An et al. received a petal-shaped Bi₂O₂CO₃ composite by a morphological transformation of Bi metal [32], and Wang et al. prepared a Bi₂O₂CO₃ nanosheet by reduction of the BiOI precursor [38]. These complexes showed improved Faradaic formate selectivity and a wide operating potential range. It could be concluded that the existence of Bi³⁺–O^{2–} pairs, rather than Bi⁰ in a Bi-based catalyst, enhanced the CO₂ adsorption and activation as well as stabilized the *OOCH intermediate [48–50].

In this study, a facile route to synthesize a flower-like Bi catalyst by electrodeposition on carbon paper was carried out. By employing a pulse current electrodeposit (PC) method in ethylene glycol (EG), the morphologies of the Bi electrode could be accurately controlled. Compared with bulk-structured Bi metal, the nano-structured Bi catalyst was inclined to generate Bi₂O₂CO₃ on its surface and the in-situ Bi³⁺–O^{2–} pairs formation could enhance the CO₂ adsorption and formate conversion. In situ Raman spectroscopy was employed to observe the formation of Bi₂O₂CO₃ on the Bi metal surface and the achieved bismuth subcarbonate covered Bi metal (Bi₂O₂CO₃@Bi) has been carefully characterized. The introduction of Bi₂O₂CO₃ to a Bi metal catalyst significantly improved the CO₂RR performance, which delivered a high FE_{HCOOH} of ~90% at –0.95 V vs. RHE in a three-electrode flow-cell reactor with no obvious decay during more than a 10 h continuous test. On the other hand, the bulk-structured Bi metal catalyst showed a low FE_{HCOOH} and HER side reaction in a range of applied potential.

2. Experimental Section

2.1. Sample Preparation

Flower-like Bi was directly prepared on a selected substrate by the PC method with a two-electrode system. Carbon paper (CP, TGP-H-060, Toray, Japan) was used as the substrate for product deposition and washed several times by deionized water and ethanol to remove the impurities and then dried under 50 °C for 12 h before use. In brief, 0.5 mmol Bi(NO₃)₃·5H₂O (Tianjin Yongda Chemical Reagent Company Limited, Tianjin, China) was slowly dissolved into 50 ml EG (Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China), then 5 ml of anhydrous dimethyl sulfoxide (DMSO, Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China) was added and stirred for 1 h at 40 °C to form a homogeneous solution. Subsequently, the pretreated carbon paper was immersed into the solution and the synthetic process was carried out at room temperature, which was

controlled by the PC method at 2 s duty time and 4 s pause time (total cycles = 600, duty cycle = 0.33). The potential range between the anode and cathode was applied from 1.6 to 2.5 V and the corresponding current was ~0.4, 0.8, 1.2, and 1.6 mA, respectively. A Pt mesh (1.00 cm × 2.00 cm) was employed as the auxiliary electrode. The achieved bismuth nanosheets were dried at room temperature for 60 h to introduce the bismuth subcarbonate composite on the surface of the Bi/CP electrode.

2.2. Sample Characterizations

The surface morphologies of the samples were observed by a Helios G4 CX Field emission scanning electron microscope (FESEM, Thermo Fisher, Waltham, MS, USA) at an accelerating voltage of 5 kV. X-ray diffraction (XRD) patterns were recorded on a X'pert Pro MPD diffractometer with Cu K α radiation (Philips, Amsterdam, Netherlands). Transmission electron microscopy (TEM) images and high-resolution TEM (HR-TEM) images were obtained on a JEM-2011 electron microscope operated at 200 kV (JEOL, Tokyo, Japan). The binding energies of Bi, O, and C were carried out on an Axis Ultra X-ray photoelectron spectrometer (XPS, Shimadzu, Kyoto, Japan) with an Mg K α = 1253.6 eV excitation source. All the binding energies were corrected with C1s level at 284.8 eV as an internal standard. In situ Raman spectra were studied using a laser confocal Raman spectrometer (LabRAM-010, Horiba, Loos, France) with a 633 nm laser source.

2.3. Electrochemical Measurements

All the electrochemical measurements were performed by using a Biologic VMP3 electrochemical workstation with a three-electrode electrochemical cell. The prepared Bi₂O₂CO₃@Bi/CP (2.00 cm²), Ag/AgCl electrode filled with 3 M KCl solution, and an IrO₂/CP (2.00 cm²) were used as the working, reference, and counter electrode, respectively. The electrochemical properties were evaluated using a linear sweep voltammetry (LSV) range from −0.3 to −1.2 V vs. the RHE and cyclic voltammetry (CV) range from 0.4 to −1.2 V vs. the RHE at a scan rate of 20 mV s^{−1} under N₂– or CO₂– saturated 0.5 M KHCO₃. The pH of the CO₂– and N₂– saturated electrolytes are 7.2 and 8.8, respectively. The durability test was carried out by chronoamperometry in a commercialized flow cell reactor with CO₂ saturated by a 0.5 M KHCO₃ electrolyte. More details can be seen in the supporting information. The conversion equation for the Ag/AgCl reference electrode to RHE is described as follows:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.0591 \text{ pH}$$

3. Results and Discussion

Scheme 1 reveals the electrodeposition reaction and surface conversion of flower-like bismuth into Bi₂O₂CO₃. During the electrodeposition process, Bi³⁺ ions were reduced into Bi⁰ and underwent nucleation and continuous growth on the carbon fiber substrate to form a multilayer flower-like bismuth film after 60 min. The Bi₂O₂CO₃ composite was generated slowly on the surface of the obtained Bi/CP sample after exposing it to air. Indeed, O₂, H₂O, or CO₂ molecules adsorbed and interacted with the exposed Bi, and the oxide or hydroxide intermediate would be produced in the form of a thin layer [32,38]. As shown in Scheme 1, Bi₂O₂CO₃ was eventually generated on the surface of the electrode after a series of physicochemical reactions. The in-situ conversion processes from Bi to Bi₂O₂CO₃ are inferred as follows:

Scheme 1. Schematic reaction mechanism of Bi^{3+} reduction and formation of flower-like $\text{Bi}_2\text{O}_2\text{CO}_3$ @Bi/CP.

First, the Bi nanosheet reacted with the absorbed O_2 and formed a surface oxide layer as depicted in Equation (2). At the same time, the absorbed CO_2 and H_2O involved reactions that produced buffers on the Bi surface (Equations (3) and (4)). Finally, the oxidized Bi^{3+} layers combined with the buffer ions CO_3^{2-} as shown in Equation (5). The total reaction could be described in Equation (6). CO_2 and O_2 absorbed onto the surface of the Bi nanosheets and then converted into $\text{Bi}_2\text{O}_2\text{CO}_3$. Moreover, the unstable $\text{Bi}(\text{OH})_3$ intermediate would form and react with CO_2 to transform into $\text{Bi}_2\text{O}_2\text{CO}_3$ [32,51]. It is worth noting that the conversion of the nano Bi into $\text{Bi}_2\text{O}_2\text{CO}_3$ was faster than the bulk Bi [33]. The nano size Bi is a very efficient material for capturing CO_2 [33]. For the in-situ conversion, a large number of Bi–O bonds and grain boundaries formed and were exposed on the surface. Figure S1 shows the color of Bi/CP changed from black to silver, revealing the formation of $\text{Bi}_2\text{O}_2\text{CO}_3$ after the drying treatment. In addition, the nano-structured Bi could transform into $\text{Bi}_2\text{O}_2\text{CO}_3$ more easily than the dendrite bulk due to its reactive surface characteristics, which indicates the morphologies of Bi played a key role in the subsequent $\text{Bi}_2\text{O}_2\text{CO}_3$ conversion processes.

Figure 1a,b displays the original carbon fiber with graining and the clusters of bismuth, which both appeared after electrodeposition, respectively. A multilayer flower-like bismuth with a diameter of about 1000 nm could be observed in Figure 1c. It can be explored that a longer deposition time led to the formation of a thicker Bi layer (Figure 1c,d) and a high current was inclined to form a Bi dendrite cluster with a large size, and thus covered the surface of the CP substrate (Figure S2). It should be noted that the electrodeposition time also has an impact on the morphology of the catalysts. Figure S3 showed the micrographs of an electrode under ~90 min deposition. A longer time of deposition led the nanosheets growing continuously, which further formed the multilayered Bi catalysts with obvious particle aggregation and damaged the flower-like structure. More details are shown in Figure S4, in which the flower-like Bi formed a thin layer on the surface of the carbon fiber uniformly. Compared to the nano-structured Bi generated at a low electrodeposition current density, the scree-structured Bi with a micro scale was obtained at a current density greater

than 1.2 mA cm^{-2} . The desired flower-like bismuth could be achieved at an appropriate current density range of 0.8 to 1 A cm^{-2} .

Figure 1. SEM images (a–d) of Bi/CP at different electrodeposition times: (a) rough carbon fiber; (b) Bi/CP 20 min; (c) Bi/CP 40 min; (d) Bismuth flower features of Bi/CP 60 min.

The morphology of $\text{Bi}_2\text{O}_2\text{CO}_3@\text{Bi}/\text{CP}$ was similar to the multilayer flower-like Bi. As shown in Figure S3 and S5, some fuzzy streaks can clearly be seen on the SEM images of $\text{Bi}_2\text{O}_2\text{CO}_3@\text{Bi}/\text{CP}$, which is attributed to the decrease in conductivity. The reduction in electrical conductivity could be ascribed to introducing $\text{Bi}_2\text{O}_2\text{CO}_3$ into Bi/CP. X-ray diffraction (XRD) patterns are provided in Figure 2a to reveal the crystal types and changes of the samples. The (002) and (024) planes corresponding to graphite (JCPDS No. 01-0640) in all the samples are assigned to the CP. Furthermore, the crystalline structures of the as-prepared Bi/CP and $\text{Bi}_2\text{O}_2\text{CO}_3@\text{Bi}/\text{CP}$ achieved by exposing them to air are distinctly different. The peaks at 26.83° , 37.65° , 39.34° , and 48.45° can be indexed to the (012), (104), (110), and (202) planes of the rhombohedral Bi (JCPDS No. 85-1329), respectively, and no other impurity peaks are observed. The intensive peak $\sim 26.83^\circ$, which is attributed to the preferred orientation of the (012) plane, manifests the growth of flower-like Bi upon deposition. The spectrum of the sample exposed to the air presents the peaks at 23.83° , 29.93° , 32.40° and 45.22° , which corresponds to the (021), (023), (110) and (024) planes of $\text{Bi}_2\text{O}_2\text{CO}_3$ (JCPDS No. 411488). In addition, Figure 2a shows that a wide weak peak appears in the XRD patterns of the $\text{Bi}_2\text{O}_2\text{CO}_3@\text{Bi}/\text{CP}$, implying the composite has converted to an amorphous phase. It could be demonstrated that a partial flower-like Bi was converted into $\text{Bi}_2\text{O}_2\text{CO}_3$ after exposing it to the air. According to previous studies, O_2 and CO_2 were freely chemi-absorbed on the bismuth surface in the air and led to the conversion reaction of $\text{Bi}_2\text{O}_2\text{CO}_3$ [33]. To obtain further details on the delicate structure of the $\text{Bi}_2\text{O}_2\text{CO}_3@\text{Bi}/\text{CP}$, a high-resolution TEM image (Figure 2b) is shown and proves that there is a fragment of the lattice and the interface of Bi and $\text{Bi}_2\text{O}_2\text{CO}_3$. The apparent lattice fringes in Figure 2b are measured at ~ 0.295 and ~ 0.328 nm, corresponding to the (012) plane of $\text{Bi}_2\text{O}_2\text{CO}_3$ and the (013) plane of Bi, respectively. Combined with the aforementioned SEM and XRD results, the existence of the transformed $\text{Bi}_2\text{O}_2\text{CO}_3$ and primal Bi could be verified in the $\text{Bi}_2\text{O}_2\text{CO}_3@\text{Bi}/\text{CP}$, implying the conversion process of the Bi nanosheets to $\text{Bi}_2\text{O}_2\text{CO}_3$ on the interfaces.

Figure 2. Characterizations of Bi₂O₂CO₃@Bi/CP samples. (a) XRD pattern of the synthesized Bi/CP in EG solution. Curve A: sample A electrodeposited at 1.2 mA by PC method, Curve B: sample B electrodeposited at 0.8 mA by PC method and put in an argon atmosphere, Curve C: sample C and D electrodeposited at 0.8 mA and exposed in air for three days and more than seven days, individually. (b) High resolution TEM images of Bi₂O₂CO₃@Bi/CP. (c–e) X-ray photoelectron spectroscopy (XPS) spectra: (c) C1s, (d) O1s and (e) Bi 4f.

The surface chemical states of the Bi₂O₂CO₃@Bi/CP were further investigated by XPS measurement. Figure 2c–e displays the high-resolution C 1s, O 1s, and Bi 4f spectrum, respectively, thereby confirming the formation of Bi₂O₂CO₃. As shown in Figure 2c, three peaks at 284.79, 285.68, and 288.29 eV, which were attributed to the C–C, C–O, and O–C=O groups, respectively, are found in C1s spectrum, indicating the existence of CO₃²⁻. The O1s peak (Figure 2d) could be subdivided into two peaks of 530.17 and 531.46 eV, and were assigned to the Bi–O bond and CO₃²⁻ species in Bi₂O₂CO₃, respectively. Figure 2e shows two intensive symmetrical peaks located at 159.33 and 164.64 eV, implying the characteristic spin orbit splitting of the Bi³⁺ 4f peaks and corresponding to Bi³⁺ 4f_{7/2} and Bi³⁺ 4f_{5/2}, respectively. Otherwise, two subordinate peaks at 157.24 and 162.59 eV are ascribed to the presence of Bi⁰. The XPS results are consistent with the above characterizations and further validate the surface transformation from nano-structured Bi to Bi₂O₂CO₃ in air.

An in-situ Raman spectroscopy study was performed to explore the surface transformation mechanism of the Bi₂O₂CO₃@Bi/CP electrode. The measurement was carried out through an electrochemical reduction procedure at −0.9 V vs. RHE in the CO₂ saturated 0.5 M KHCO₃ electrolyte. The Raman spectra (Figure 3) indicate the peaks at 92 cm^{−1} are related to the Bi–Bi bond that appeared at the beginning. The intensity of the peak at 154 cm^{−1} (belonged to the Bi–O bond) decreased and almost disappeared after a six min reduction, which is attributed to the reduction of surface Bi₂O₂CO₃ into Bi. The broad external vibration peak at 264.05 cm^{−1} [26,40], as well as a weak peak around 502.94 cm^{−1} attributed to the Bi=O bond, are assigned to Bi₂O₂CO₃ [52], which did not vanish even after a continuous reduction process (Figure S6). In this study, flower-like Bi nanosheets

could provide plenty of reaction sites to regenerate $\text{Bi}_2\text{O}_2\text{CO}_3$ on its surface in a CO_2 rich environment and the composite would not reduce, even in a relative negative potential (~ -0.90 V vs. RHE) during the heterogeneous electrocatalysis process.

Figure 3. In-situ Raman spectra of $\text{Bi}_2\text{O}_2\text{CO}_3$ @Bi/CP during the electrochemical reduction of CO_2 at -0.90 V vs. RHE in the CO_2 saturated 0.50 M KHCO_3 electrolyte.

To study the electrochemical CO_2 RR performance of the obtained catalysts, linear sweep voltammetry (LSV) measurements were conducted from -0.3 to -1.2 V vs. RHE in the CO_2 saturated 0.50 M KHCO_3 electrolyte. As shown in Figure 4a, the CO_2 RR Faradaic onset potential is observed at -0.56 and -0.76 V vs. RHE for the $\text{Bi}_2\text{O}_2\text{CO}_3$ @Bi/CP and the Bi/CP electrode in the CO_2 saturated 0.50 M KHCO_3 electrolyte, respectively. In addition, the onset potential of HER on carbon paper is -0.84 V vs. RHE. The lower onset potential of $\text{Bi}_2\text{O}_2\text{CO}_3$ @Bi/CP manifests a higher CO_2 reduction activity, indicating that introducing $\text{Bi}_2\text{O}_2\text{CO}_3$ into Bi-based catalysts is favorable to CO_2 RR. The total current density (J_{tot}) of the $\text{Bi}_2\text{O}_2\text{CO}_3$ @Bi/CP electrode is ~ 20 mA cm^{-2} at -1.07 V vs. RHE, which is much higher than those in the N_2 -saturated condition and sufficiently demonstrates the CO_2 RR activity (Figure S7). The cyclic voltammetry curves in Figure 4b and S8 exhibit an oxidation peak at ~ 0.31 V and a reduction peak at ~ 0.12 V, which can be attributed to the $\text{Bi}^{3+}/\text{Bi}^0$ redox process in the $\text{Bi}_2\text{O}_2\text{CO}_3$ @Bi/CP electrode, and another reduction peak at a more negative potential (-0.90 V) is assigned to the electrochemical CO_2 reduction or competitive H_2 evolution. The as-prepared $\text{Bi}_2\text{O}_2\text{CO}_3$ @Bi/CP electrode revealed a high interface resistance, leading to a relatively low current density during the initial CV cycles. After several redox cycles, the adsorbed impurities, such as inert gas on the surface of the electrode, have been removed and the catalytic interface became dynamically stable, and thus the CV current density reached the maximum. After that, the $\text{Bi}_2\text{O}_2\text{CO}_3$ composite in the electrode gradually reduced during the negative potential and the current density decreased. The redox peaks still remained after 50 cycles, which indicates the stability of the $\text{Bi}_2\text{O}_2\text{CO}_3$ @Bi interfaces and is in accordance with the previous reports [53,54]. Meanwhile, an observable positive shift in the reduction peak was recorded on the CVs curves, which was attributed to the conversion of Bi–O or Bi=O to Bi–Bi bonds [47].

Figure 4. (a) LSV curves of Carbon paper, Bi electrodeposited at 1.6 mA (0.8 mA cm^{-2}) and $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}/\text{CP}$; (b) CV curves of $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}/\text{CP}$ in CO_2 -saturated 0.50 M KHCO_3 electrolyte; (c) Charging current density differences plotted against scan rates; (d) FE of CO_2RR products at various potentials on $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}/\text{CP}$ in CO_2 -saturated 0.50 M KHCO_3 electrolyte.

The electrochemical surface area (ECSA) of the electrodes was evaluated by CV measurements at a potential range from 0 to -0.2 V vs. RHE with a variety of scanning rates (Figure S9). As shown in Figure 4c, the current densities of the electrodes are proportional to the scanning rates and the $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}/\text{CP}$ ($1890 \mu\text{F cm}^{-2}$) delivers a four times greater double layer capacitance than the Bi/CP ($423 \mu\text{F cm}^{-2}$). The higher ECSA of the $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}/\text{CP}$ confirms the electrode could provide more catalytic active sites, which could benefit the CO_2RR performance.

To practically evaluate the catalytic performance of the $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}/\text{CP}$ electrode, we performed CO_2RR tests in a three-electrode flow-cell reactor (Figure S10). The $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}/\text{CP}$ and IrO_2/CP were employed as the work and counter electrode, respectively. More details can be found in the Supplementary Data. Figure 4d shows the product distribution ratio results obtained at a wide potential ranging (-0.67 to -1.17 V). The highest FE of HCOOH ($\sim 82\%$) was reached on the Bi/CP electrode at -0.89 V vs. RHE as shown in Figure S11, and the $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}/\text{CP}$ electrode conveyed a maximum FE_{HCOOH} of 89%, which was achieved at -1.07 V vs. RHE . The enhancement of the CO_2RR performance by introducing $\text{Bi}_2\text{O}_2\text{CO}_3$ into the Bi/CP electrode could be attributed to the large amounts of Bi–O bonds and grain boundaries, which lowers the energy barrier for the formation of the CO_2^- intermediate and promotes the production of formate [39,40]. The residual $\text{Bi}_2\text{O}_2\text{CO}_3$ in the catalyst was expected to form a surface environment to improve the CO_2 adsorption process and is of great benefit to CO_2 reduction activation.

In addition, to evaluate the long-term durability of the $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}/\text{CP}$ electrode, the CO_2RR tests were performed at -1.07 V vs. RHE in the same flow-cell reactor. As shown in Figure 5a,b, a constant current density is achieved at $\sim 18.6 \text{ mA cm}^{-2}$ with no

remarkable decline, and the FE_{HCOOH} value is found to be basically consistent with the former result and within the range of 84–89% during a 10 h continuous test. As a result, the $Bi_2O_2CO_3@Bi/CP$ electrode exhibits outstanding stability and high selectivity in a practical CO_2 catalytic measurement.

Figure 5. Stability test of the $Bi_2O_2CO_3@Bi/CP$ electrode evaluated at -1.07 V vs. RHE in a CO_2 saturated 0.5 M $KHCO_3$ electrolyte by a flow-cell reactor. (a) partial current densities of $HCOOH$ (J_{HCOOH}) and FE during the test; (b) the real-time current density of the test.

4. Conclusions

In summary, a flower-like Bi nanosheet was fabricated by pulse current electrodeposition, and the morphologies could be accurately and facily controlled by the current density. The achieved flower-like Bi nanosheets could form stable $Bi_2O_2CO_3@Bi$ interfaces after being exposed to air, which was also confirmed by the in-situ Raman spectroscopy. The $Bi_2O_2CO_3@Bi$ interfaces exhibited an improved CO_2 reduction activity than the bulk Bi electrode. The electrochemical test demonstrated that the $Bi_2O_2CO_3@Bi/CP$ electrode conveyed an excellent FE_{HCOOH} of 89% at -1.07 V vs. RHE with a current density of ~ 16 mA cm⁻² in a flow-cell reactor. In addition, the catalyst showed an outstanding stability and no obvious degradation after a continuous test of over 10 h. This composite catalyst supports a rational strategy for designing Bi-based CO_2RR catalysts and can also be applied to various electrochemical energy conversion and storage fields.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/coatings12020233/s1>, Figure S1. The sample photo of original carbon paper, dendrite Bi/CP, and $Bi_2O_2CO_3@Bi/CP$. Figure S2. SEM images of samples on different pulse current: (a) 0.4 mA cm⁻², (b) 0.8 mA cm⁻², (c) 1.2 mA cm⁻², and (d) 1.6 mA cm⁻². Figure S3. SEM image of electrode at 90 min electrodeposition with a current density of 0.8 mA cm⁻². Figure S4. SEM photographs at different magnifications. Figure S5. SEM characterizations of a flower-like Bi sample exposed in air for a long time (>60 h). Figure S6. The particular Raman spectra of $Bi_2O_2CO_3@Bi/CP$: (a) the Bi–Bi bond peak and Bi–O bond peak; (b) the broad external vibration peaks on $Bi_2O_2CO_3$; and (c) the Bi=O bond peak. Figure S7. LSV curves of Carbon paper, Bi/CP, and $Bi_2O_2CO_3@Bi/CP$ in the N_2 saturated 0.5 M $KHCO_3$. Figure S8. The typical CV curve of a pristine $Bi_2O_2CO_3@Bi/CP$ at scanning rate of 20 mV s⁻¹ from -1.2 to 0.4 V vs. RHE. Figure S9. CV curves of different samples: (a) the CV curves result of original carbon paper; (b) the CV curves test of Bi/CP; (c) the CV curves of $Bi_2O_2CO_3@Bi/CP$. Figure S10. A flow cell reactor for CO_2RR with auxiliary equipment, including peristaltic pump, mass flow meter, resource gas, and electrochemical station. Figure S11. FE of CO_2RR products at various potentials in CO_2 -saturated 0.5 M $KHCO_3$ electrolytes on Bi/CP.

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