Enhanced Electrocatalytic CO\textsubscript{2} Reduction of Bismuth Nanosheets with Introducing Surface Bismuth Subcarbonate

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Abstract: The electrocatalytic CO\textsubscript{2} reduction reaction (CO\textsubscript{2}RR) into hydrocarbon products is one of the most promising approaches for CO\textsubscript{2} utilization in modern society. However, the application of CO\textsubscript{2}RR 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 Bi\textsubscript{2}O\textsubscript{3}CO\textsubscript{2} in the air and form a stable Bi\textsubscript{2}O\textsubscript{3}CO\textsubscript{3}@Bi interface, which could enhance the CO\textsubscript{2} adsorption and conversion. In-situ Raman spectroscopy analysis also proves the existence of Bi\textsubscript{2}O\textsubscript{3}CO\textsubscript{3} on the electrode surface. In a practical CO\textsubscript{2} reduction test by a flow-cell reactor, the Bi\textsubscript{2}O\textsubscript{3}CO\textsubscript{3}@Bi electrode delivers a high faradaic efficiency of the CO\textsubscript{2} 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 Bi\textsubscript{2}O\textsubscript{3}CO\textsubscript{3} in nano-structured Bi supports a promising strategy as well as facile access to prepare improved CO\textsubscript{2}RR electrocatalysts.

Keywords: CO\textsubscript{2} reduction; bismuth; Bi\textsubscript{2}O\textsubscript{3}CO\textsubscript{3}; interface; formic acid

1. Introduction

Carbon dioxide (CO\textsubscript{2}) conversion through a physicochemical process has been considered as a promising means to halt greenhouse gas emissions and global warming [1,2]. Moreover, extraterrestrial CO\textsubscript{2} utilization is the only effective method for human beings to survive in outer space for a long-term [3]. The electrochemical CO\textsubscript{2} reduction reaction (CO\textsubscript{2}RR) 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 CO\textsubscript{2}RR products, such as methane (CH\textsubscript{4}), ethylene (C\textsubscript{2}H\textsubscript{4}), formate/formic acid (HCOOH), and methanol (CH\textsubscript{3}OH) 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 CO\textsubscript{2}RR to HCOOH still has some issues to be solved, including the inert nature of CO\textsubscript{2}, 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...
CO₂-RR activity, have a high hydrogen evolution reaction (HER) with the increase of applied potential, leading to unsatisfied FE₃HCOOH [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 FE₃HCOOH than the bulk catalysts [28,29]. In addition, metal Bi⁰ is assumed to be the active site in the Bi and Bi-based electrochemical CO₂-RR catalysts in previous studies [14–16,25,28,30,31].

Although Bi-based catalysts show remarkable FE₃HCOOH selectivity on electrochemical CO₂-RR, 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 CO₂-RR 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 CO₂-RR 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 FE₃HCOOH product and inhibiting HER [35–40].

As a result, Bi-based compounds that contained Bi–O bonds, such as bismuth oxides (Bi₂O₃, BiOₓ) [27,36,37,40–43] and bismuth subcarbonate (Bi₂O₂CO₃) [17,35,38,44–47], have been prepared and disclosed with improved CO₂-RR 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⁺–O²⁻ 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⁺–O²⁻ 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 CO₂-RR performance, which delivered a high FE₃HCOOH 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 FE₃HCOOH 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 immerged 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 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 Kα 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, Kioto, Japan) with an Mg Kα = 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 Bi$_2$O$_2$CO$_3$@Bi/CP (2.00 cm$^2$), Ag/AgCl electrode filled with 3 M KCl solution, and an IrO$_2$/CP (2.00 cm$^2$) 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 N$_2$ or CO$_2$ saturated 0.5 M KHCO$_3$. The pH of the CO$_2$ and N$_2$ saturated electrolytes are 7.2 and 8.8, respectively. The durability test was carried out by chronoamperometry in a commercialized flow cell reactor with CO$_2$ saturated by a 0.5 M KHCO$_3$ 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 Bi$_2$O$_2$CO$_3$. During the electrodeposition process, Bi$^{3+}$ ions were reduced into Bi$^0$ and underwent nucleation and continuous growth on the carbon fiber substrate to form a multilayer flower-like bismuth film after 60 min. The Bi$_2$O$_2$CO$_3$ composite was generated slowly on the surface of the obtained Bi/CP sample after exposing it to air. Indeed, O$_2$, H$_2$O, or CO$_2$ 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, Bi$_2$O$_2$CO$_3$ was eventually generated on the surface of the electrode after a series of physicochemical reactions. The in-situ conversion processes from Bi to Bi$_2$O$_2$CO$_3$ are inferred as follows:

$$4\text{Bi(s)} + 3\text{O}_2(g) + 2\text{H}_2\text{O(l)} \rightleftharpoons 4\text{BiO}^- (s) + 4\text{OH}^- (\text{aq}) \quad (2)$$

$$\text{CO}_2(g) + 2\text{H}_2\text{O(l)} \rightleftharpoons \text{HCO}_3^- (\text{aq}) + \text{H}_3\text{O}^+ (\text{aq}) \quad (3)$$

$$\text{HCO}_3^- (\text{aq}) + 2\text{OH}^- (\text{aq}) + 2\text{H}_3\text{O}^+ (\text{aq}) \rightleftharpoons \text{CO}_3^{2-} (\text{aq}) + 3\text{H}_2\text{O(l)} \quad (4)$$

$$2\text{BiO}^- (s) + \text{CO}_3^{2-} (\text{aq}) = \text{Bi}_2\text{O}_2\text{CO}_3 (s) \quad (5)$$
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 substrate (Figure S4). It can be noted that the conversion of the nano Bi into Bi$_2$O$_2$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 Bi$_2$O$_2$CO$_3$ after the drying treatment. In addition, the nano-structured Bi could transform into Bi$_2$O$_2$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 Bi$_2$O$_2$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 0.5 A cm$^{-2}$.
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.](image)

The morphology of Bi\(_2\)O\(_2\)CO\(_3\)@Bi/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 Bi\(_2\)O\(_2\)CO\(_3\)@Bi/CP, which is attributed to the decrease in conductivity. The reduction in electrical conductivity could be ascribed to introducing Bi\(_2\)O\(_2\)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 Bi\(_2\)O\(_2\)CO\(_3\)@Bi/CP achieved by exposing them to air are distinctly different. The peaks at 26.83, 37.65, 39.34, and 48.45\(^{\circ}\) 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 ~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\(^{\circ}\), which corresponds to the (021), (023), (110) and (024) planes of Bi\(_2\)O\(_2\)CO\(_3\) (JCPDS No. 411488). In addition, Figure 2a shows that a wide weak peak appears in the XRD patterns of the Bi\(_2\)O\(_2\)CO\(_3\)@Bi/CP, implying the composite has converted to an amorphous phase. It could be demonstrated that a partial flower-like Bi was converted into Bi\(_2\)O\(_2\)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 Bi\(_2\)O\(_2\)CO\(_3\) [33]. To obtain further details on the delicate structure of the Bi\(_2\)O\(_2\)CO\(_3\)@Bi/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 Bi\(_2\)O\(_2\)CO\(_3\). The apparent lattice fringes in Figure 2b are measured at ~0.295 and ~0.328 nm, corresponding to the (012) plane of Bi\(_2\)O\(_2\)CO\(_3\) and the (013) plane of Bi, respectively. Combined with the aforementioned SEM and XRD results, the existence of the transformed Bi\(_2\)O\(_2\)CO\(_3\) and primal Bi could be verified in the Bi\(_2\)O\(_2\)CO\(_3\)@Bi/CP, implying the conversion process of the Bi nanosheets to Bi\(_2\)O\(_2\)CO\(_3\) on the interfaces.
Figure 2. Characterizations of Bi$_2$O$_2$CO$_3$@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 then 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 Bi$_2$O$_2$CO$_3$@Bi/CP. (c–e) X-ray photoelectron spectroscopy (XPS) spectra: (c) C 1s, (d) O 1s and (e) Bi 4f.

The surface chemical states of the Bi$_2$O$_2$CO$_3$@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 Bi$_2$O$_2$CO$_3$. 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 C 1s spectrum, indicating the existence of CO$_3^{2−}$. The O 1s 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 CO$_3^{2–}$ species in Bi$_2$O$_2$CO$_3$, respectively. Figure 2e shows two intensive symmetrical peaks located at 159.33 and 164.64 eV, implying the characteristic spin orbit splitting of the Bi$^{3+}$ 4f peaks and corresponding to Bi$^{3+}$ 4f$_{7/2}$ and Bi$^{3+}$ 4f$_{5/2}$, respectively. Otherwise, two subordinate peaks at 157.24 and 162.59 eV are ascribed to the presence of Bi$^0$. The XPS results are consistent with the above characterizations and further validate the surface transformation from nano-structured Bi to Bi$_2$O$_2$CO$_3$ in air.

An in-situ Raman spectroscopy study was performed to explore the surface transformation mechanism of the Bi$_2$O$_2$CO$_3$@Bi/CP electrode. The measurement was carried out through an electrochemical reduction procedure at −0.9 V vs. RHE in the CO$_2$ saturated 0.5 M KHCO$_3$ 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 Bi$_2$O$_2$CO$_3$ 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 Bi$_2$O$_2$CO$_3$ [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 Bi$_2$O$_2$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.

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 Bi$_2$O$_2$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 Bi$_2$O$_2$CO$_3$@Bi/CP manifests a higher CO$_2$ reduction activity, indicating that introducing Bi$_2$O$_2$CO$_3$ into Bi-based catalysts is favorable to CO$_2$RR. The total current density ($J_{\text{tot}}$) of the Bi$_2$O$_2$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 Bi$^{3+}$/Bi$^0$ redox process in the Bi$_2$O$_2$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 Bi$_2$O$_2$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 Bi$_2$O$_2$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 Bi$_2$O$_2$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].
which was achieved at
we performed CO
[@Bi/CP and IrO
(Figure S9). As shown in Figure 4c, the current densities of the electrodes are propor-
tional to the scanning rates and the Bi$_2$O$_2$CO$_3$@Bi/CP (1890 $\mu$F/cm$^2$) delivers a four times
greater double layer capacitance than the Bi/CP (423 $\mu$F cm$^{-2}$). The higher ECSA of the
Bi$_2$O$_2$CO$_3$@Bi/CP confirms the electrode could provide more catalytic active sites, which
could benefit the CO$_2$RR performance.

To practically evaluate the catalytic performance of the Bi$_2$O$_2$CO$_3$@Bi/CP electrode, we performed CO$_2$RR tests in a three-electrode flow-cell reactor (Figure S10). The Bi$_2$O$_2$CO$_3$ @Bi/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 ($\sim82\%$) was reached on the Bi/CP electrode at $-0.89$ V vs. RHE as shown in
Figure S11, and the Bi$_2$O$_2$CO$_3$@Bi/CP electrode conveyed a maximum FE$_{HCOOH}$ of 89%,
which was achieved at $-1.07$ V vs. RHE. The enhancement of the CO$_2$RR performance by
introducing Bi$_2$O$_2$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
Bi$_2$O$_2$CO$_3$ in the catalyst was expected to form a surface environment to improve the CO$_2$
ad sorption process and is of great benefit to CO$_2$ reduction activation.

In addition, to evaluate the long-term durability of the Bi$_2$O$_2$CO$_3$@Bi/CP electrode, the
CO$_2$RR 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 $\sim18.6$ mA cm$^{-2}$ with no

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**Figure 4.** (a) LSV curves of Carbon paper, Bi electrodeposited at 1.6 mA (0.8 mA cm$^{-2}$) and
Bi$_2$O$_2$CO$_3$@Bi/CP; (b) CV curves of Bi$_2$O$_2$CO$_3$@Bi/CP in CO$_2$-saturated 0.50 M KHCO$_3$ electrolyte;
(c) Charging current density differences plotted against scan rates; (d) FE of CO$_2$RR products at
various potentials on Bi$_2$O$_2$CO$_3$@Bi/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 Bi$_2$O$_2$CO$_3$@Bi/CP (1890 $\mu$F cm$^{-2}$) delivers a four times
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CO$_2$RR 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 $\sim18.6$ 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_{2}O_{2}CO_{3}@Bi/CP electrode exhibits outstanding stability and high selectivity in a practical CO_{2} catalytic measurement.

Figure 5. Stability test of the Bi_{2}O_{2}CO_{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 facilely controlled by the current density. The achieved flower-like Bi nanosheets could form stable Bi_{2}O_{2}CO_{3}@Bi interfaces after being exposed to air, which was also confirmed by the in-situ Raman spectroscopy. The Bi_{2}O_{2}CO_{3}@Bi interfaces exhibited an improved CO_{2} reduction activity than the bulk Bi electrode. The electrochemical test demonstrated that the Bi_{2}O_{2}CO_{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_{2}RR 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_{2}O_{2}CO_{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 characterization of a flower-like Bi sample exposed in air for a long time (>60 h). Figure S6. The particular Raman spectra of Bi_{2}O_{2}CO_{3}@Bi/CP: (a) the Bi–Bi bond peak and Bi–O bond peak; (b) the broad external vibration peaks on Bi_{2}O_{2}CO_{3}; and (c) the Bi=O bond peak. Figure S7. LSV curves of Carbon paper, Bi/CP, and Bi_{2}O_{2}CO_{3}@Bi/CP in the N_{2} saturated 0.5 M KHCO_{3}. Figure S8. The typical CV curve of a pristine Bi_{2}O_{2}CO_{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_{2}O_{2}CO_{3}@Bi/CP. Figure S10. A flow cell reactor for CO_{2}RR with auxiliary equipment, including peristaltic pump, mass flow meter, resource gas, and electrochemical station. Figure S11. FE of CO_{2}RR products at various potentials in CO_{2}-saturated 0.5 M KHCO_{3} electrolytes on Bi/CP.

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