CO₂ Electroreduction to Formate at a Partial Current Density up to 590 mA mg⁻¹ via Micrometer-Scale Lateral Structuring of Bismuth Nanosheets

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1. Introduction

Electrocatalytic CO₂ reduction reaction (CO₂RR) using renewable electricity to transform CO₂ into valuable fuels and chemicals offers a promising strategy to achieve carbon recycling processes.¹–⁴ Formate is an important liquid product of CO₂RR with a high product value per electron and has been widely applied in various energy and industrial fields, such as hydrogen storage and fuel cells.⁵,⁶ Bi, Sn, and Pb have been demonstrated as formate-producing metals with high formate selectivity.⁷–¹¹ Among these catalysts, Bi is a potentially superior catalyst for industrial application since it is virtually nontoxic and relatively inexpensive. However, the activity of bulk Bi crystal towards CO₂RR is usually unsatisfactory: an overpotential of at least −0.8 V versus RHE (all potentials hereafter are given with respect to RHE unless otherwise stated) is required to reach a current density of 10 mA cm⁻² and 90% selectivity can only be achieved within a narrow potential window of about 300 mV, which limits its practical application.¹²–¹⁴ Reducing the thickness of bulk crystals to monolayer or few-layer materials can promote the catalytic activity, which is attributed to the dramatic increase of active sites to enhance the contact between the surface of the catalyst and CO₂RR reactants and intermediates.¹⁵ Even though theoretical works have predicted the existence of monolayer and few-layer bismuthene, only few experimental methods have been approved to obtain it directly under mild conditions since it is prone to be oxidized to Bi₂O₃ or [Bi₂O₂]²⁺ during the synthetic processes.¹⁶,¹⁷

Pumera and co-workers reported a mechanical method that Bi nanosheets with size of tenth of nanometers can be obtained by shear exfoliation in aqueous surfactant sodium dodecyl sulfate undergoing predominantly a downsizing process.¹⁸ However, nanosheets obtained by this method is usually not uniform in terms of thickness, resulting in an unoptimized catalytic performance. Jin and co-workers proposed a liquid-exfoliation strategy to prepare Bi nanosheets in the isopropanol solvent in a glovebox for 30 h,¹⁴ which needs strict isolation of air and does not provide well-controlled lateral size. Electrochemical exfoliation method is superior in controlling the layer thickness

2D bismuth nanosheets are a promising layered material for formate-producing via electrocatalytic CO₂ conversion. However, the commercial interest of bismuth nanosheets in CO₂ electroreduction is still rare due to the undesirable current density for formate at moderate operation potentials (about 200 mA mg⁻¹) and harsh synthesis conditions (high temperature and/or high pressure). This work reports the preparation of Bi nanosheets with a lateral size in micrometer-scale via electrochemical cathodic exfoliation in aqueous solution at normal pressure and temperature. As-prepared Bi LNSs (L indicates large lateral size) possess high Faradaic efficiencies over 90% within a broad potential window from −0.44 to −1.10 V versus RHE and a superior partial current density about 590 mA mg⁻¹ for formate in comparison with state-of-the-art results. Structure analysis, electrochemical results, and density functional theory calculations demonstrate that the increasing tensile lattice strain observed in Bi LNSs leads to less overlap of d orbitals and a narrower d-band width, which tuning the intermediate binding energies, and therefore promotes the intrinsic activity.
and lateral size. For example, Luo and co-workers reported electrochemical exfoliation from an industrial ingot to prepare Bi nanosheets with the tetrapropylammonium (TPA⁺) bromide solution in acetonitrile as the electrolyte with an average thickness of 2–4 nm. However, the lateral size is usually within a nanometer scale. The difficulty in synthesizing Bi nanosheets with both micrometer lateral size and nanometer thickness limits the application and performance of layered Bi nanomaterials since they tend to be stacked when fabricating to electrodes. This leads to an undesirable mass activity. To overcome the above-mentioned issues and to provide an easier approach to directly obtain uniform Bi nanosheets with micrometer lateral size and nanometer thickness, we report a facile electrochemical exfoliation method to prepare Bi nanosheets using NaI aqueous solution as the electrolyte at normal pressure and temperature in this work. The obtained micrometer-lateral sized Bi LNSs (Bi LNSs, L indicates large lateral size) are able to maintain high purity at ambient conditions. This obtained Bi LNSs show a 94.3% faradaic efficiency (FE) for formate at −0.76 V in an H-type cell and the highest current density in excess of 590 mA mg⁻¹ with a FE of 92.2% in a flow cell for converting CO₂ to formate. The enhanced performances are attributed to the lattice expansion of Bi LNSs due to the intercalation of Na⁺ cations into the layer of Bi crystals during the electrochemical cathodic exfoliation process which are understood by structure analysis together with density functional theory (DFT) calculation. This kind of crystal distortion, which acts as active sites, manipulates the adsorption and the initial activation of stable CO₂ molecules and the binding strength of reaction intermediates of CO₂RR on the catalyst surface which change the activity and selectivity of formate/formic acid from electrochemical reduction of CO₂.

2. Results and Discussion

2.1. Controllable Synthesis and Characterization of Bi LNSs

Micrometer-lateral sized few-layer Bi LNSs were synthesized via an electrochemical exfoliation process (Figure 1; Figure S1, Supporting Information). The bulk Bi crystal with layered structure is shown in Figure S1a (Supporting Information) acting as the precursor for the synthesis of Bi nanosheets and the exfoliation device is shown in Figure S1b in the Supporting Information. As schematically illustrated in Figure 1, the electrochemical exfoliation of a small (0.5 × 0.2 cm²) piece of bulk Bi crystal was carried out in a two-electrode system using a NaI aqueous solution under a N₂ atmosphere. A direct current potential was applied to allow the intercalation of Na⁺ cations into negatively charged Bi layers, which leads to the expansion and eventual exfoliation of bulk Bi crystal to Bi LNSs. At the same time, the hydrogen molecules produced at the cathode can also intercalate into the layers of Bi crystal to accelerate the exfoliation of Bi nanosheets. In order to avoid the oxidation of Bi during the synthetic process, Bi LNSs were prepared under a N₂ atmosphere in NaI electrolyte aqueous solution and an H-type cell was used to avoid oxidation of the exfoliated Bi LNSs in the anode. The reducibility of I⁻ is important to keep the exfoliated Bi LNSs stable during the synthesis. When NaCl instead of NaI was used as the electrolyte, BiOCl NSs instead of pure Bi LNSs were formed, because the oxidation of Bi happened quickly without I⁻. Detailed discussion about the role of electrolyte in the synthetic process is shown in Figure S2 in the Supporting Information.

X-ray diffraction (XRD) patterns of the as-prepared Bi LNSs before and after CO₂RR are shown in Figure 2a, which are in accordance with the rhombohedral Bi (JCPDS card No. 44–1246), confirming both high crystallinity and purity. When comparing the enlarged XRD patterns of the as-exfoliated Bi LNSs and bulk Bi crystal (Figure S1d–f, Supporting Information), all the diffraction peaks of Bi LNSs shift to a lower angle. The interplanar distances of Bi LNSs and bulk Bi calculated by Bragg’s equation affirming that d₀₀₃ and d₀₁₂ interlayer spacings of the as-exfoliated Bi LNSs augment from 3.86 and 3.22 Å of bulk Bi to 3.92 and 3.26 Å. Above results suggest the enlargement of the interlayer spacing of as-exfoliated Bi LNSs, which is caused by the lattice expansion of Bi crystal planes from the intercalation of Na⁺ cations into negatively charged Bi layers during the exfoliation process. The transmission electron microscopy (TEM) image in Figure 2b reveals the successful synthesis of Bi nanosheets. As shown in the high-resolution TEM (HRTEM) image (Figure 2c), the lattice spacing was measured to be 0.237 nm, corresponding to the (104) plane of rhombohedral Bi. The corresponding selected area electron diffraction...
(SAED) pattern in Figure 2d reveals a single set of diffraction spots with fourfold symmetry consistent with rhombohedral Bi LNSs. The interplanar spacings of 0.237 and 0.187 nm can be observed in Figure 2d, corresponding to the (104) and (202) plane of Bi LNSs, indicating the exposed (003) plane in the vertical direction. Moreover, the relative intensity ratio of (003)/(012) of the as-exfoliated Bi LNSs is about 4.5 times to that of the bulk Bi (Figure S1d–f, Supporting Information), suggesting more (003) planes are exposed due to the exfoliation of bulk Bi crystal to nanosheets. The thickness of few layers Bi LNSs is measured from typical atomic force microscopy (AFM) image in Figure 2e,f and Figure S3b (Supporting Information). The average thickness of Bi LNSs is about 4.28 nm. Based on the above analysis, the Bi atomic layers of the as-exfoliated Bi LNSs with the average thickness about 4.28 nm was calculated to be ≈11 layers.

2.2. Enhanced CO2RR Performance on Bi LNSs: High Selectivity and Mass Activity

Linear-sweep voltametric curves (LSVs) were collected in N2- and CO2-saturated 1.0 m KHCO3 aqueous solutions using Bi LNSs modified carbon paper electrode as the working electrode to assess the possibility of using the Bi LNSs as a catalyst for CO2RR. As shown in Figure 3a, an initial potential of 0 V was chosen to avoid oxidation of Bi LNSs. The Bi LNSs electrode exhibits a larger current and a less negative onset potential under a CO2 atmosphere than that under a N2 atmosphere, which indicates the CO2 reduction catalytic activity. The CV curves of Bi LNSs collected in a CO2-saturated 1.0 m KHCO3 aqueous solution in Figure S4 (Supporting Information) also shows a rapid increasement of reduction current when the potential is more negative than −0.7 V. The oxidation and reduction peaks of Bi exhibit on CV curves and the characteristics of both the oxidation and reduction processes remain unchanged upon repetitive cycling of the potential. Bulk electrolysis was conducted in an H-type cell and a flow cell configuration, respectively, to provide more detailed evidence related to the direct involvement of CO2 in the reduction process. The FEs and total current density (J) data for Bi LNSs over applied potential are presented in Figure 3b,c. Formate was the only liquid product detected in the liquid phase using 1H nuclear magnetic resonance (NMR). Gaseous products including CO and H2 were detected using gas chromatography (GC). Moreover, these three products are confirmed to be the major reduction products since the combined FE values are close to 100% at all applied potential. Figure 3b shows that the selectivity towards formate and H2 is dependent on the applied potential while the selectivity of CO is less dependent on the applied potential since only a small amount of CO was detected. The current density is gradually increased with the applied potential ranging from −0.36 to −0.86 V. The FE for formate reaches a maximum value of 94.3% at −0.76 V with a partial current density of 61.7 mA mg−1 for formate in an H-type cell.

The low solubility of CO2 in aqueous electrolyte limits the CO2 mass transport and influences to the current density and practical CO2 electrolysis in an H-type cell. The flow cell configuration could separate CO2 and electrolyte to improve CO2 mass transport. As shown in Figure 3c, Bi LNSs electrode...
shows significant increment in current density in a flow cell configuration using 1.0 M KOH as the electrolyte, in comparison with that in an H-type cell. The electrolysis results suggest that the FEs for formate of Bi LNSs in a flow cell configuration reach over 90% in a broad potential window ranging from −0.44 to −1.10 V, with the total current densities increasing from 240 to 640 mA mg\(^{-1}\) (Figure 3c). The FE for formate reaches a maximum value of 97.6% at −0.80 V with a partial current density for formate about 6.2 times compared to that in an H-type cell. In addition, the as-prepared Bi LNSs demonstrate higher current density at the potential of −1.10 V using an optimized loading amount of 0.25 mg cm\(^{-2}\) in a flow cell configuration. The details regarding optimizing loading amount are shown in Figure S5 in the Supporting Information.

The structural stability of Bi LNSs was assessed by bulk electrolysis at different applied potentials. As shown in Figure 3d, a stable FE for formate over 92.2% and a high partial current density for formate about 590 mA mg\(^{-1}\) were sustained over 3600 s at a applied potential of −1.10 V. The morphology of Bi LNSs also remains unchanged after electrolysis (Figure S6, Supporting Information). Additionally, a long-term stability test was conducted at a applied potential of −0.80 V. The FEs and partial current density for formate do not change obviously over 7.5 h (Figures S7 and S8, Supporting Information). In situ Raman spectrum of Bi LNSs during the CO\(_2\)RR electrolysis process in 1.0 M KHCO\(_3\) aqueous solution at −0.76 V for 0–10 min were shown in Figure S9 in the Supporting Information. Two characteristic peaks at ≈71 and 98 cm\(^{-1}\) are attributed to metallic Bi(0), which means the valence state of Bi remains unchanged during CO\(_2\)RR.[26] The structural stability of Bi LNSs after CO\(_2\)RR was further tested by X-ray photoelectron spectroscopy (XPS). The high-resolution XPS spectrum of Bi 4f and O 1s (Figure 5c) demonstrates that Bi LNSs is mainly compose of Bi(0) (binding energy of 156.9 and 162.2 eV) instead of Bi\(^{3+}\) (binding energy of 158.9 and 164.0 eV).[24,27]

The structure and CO\(_2\)RR performance of micrometer-lateral sized Bi LNSs, nanolateral sized Bi nanosheets (Bi SNSs, S indicates small lateral size) and Bi nanoparticles (Bi NPs) were investigated to better understand the reason of superior current density of Bi LNSs. XRD patterns demonstrate that all the prepared Bi catalysts corresponding to the rhombohedral Bi crystalline structure (ICPD Structure card No. 44–1246) in Figure 4a. Compared with the standard Bi diffraction peaks, all the diffraction peaks, in particular the (003) and (012) peaks, of the prepared Bi LNSs shift to a small angle, indicating the lattice expansion of the Bi crystal faces[25] (Figure 4b). The lattice tensile strain calculated and the simulation of CO\(_2\) reduction to formate was performed on the (003) plane of Bi crystal
(Figures S10 and S15, Supporting Information) since it was the predominantly exposed crystal plane on Bi LNSs, which can be seen from the SAED pattern of Bi LNSs in Figure 2d. Compared with the standard Bi, the lattice tensile strain percentage on (003) crystal planes of Bi LNSs, Bi SNSs and Bi NPs is 1.56%, 1.37%, and 1.35%, respectively. Moreover, the current density for formate of Bi LNSs is about 1.51 and 1.63 times of Bi SNSs and Bi NPs at the tested potential (Figure 4c), indicating that the higher tensile lattice strain (1.56%) breaks the linear scaling relationships of intermediate binding energies and thus promotes the intrinsic activity to the adsorption of CO2 for enhancing the CO2 reduction rate.

A commercial gas diffusion layers with Bi catalysts modified as working electrodes were characterized to learn the microstructure of Bi catalysts during the CO2RR process. SEM images and the cross-section SEM images of Bi catalysts on the gas diffusion layers are shown in Figure 4d–f and Figure S11 (Supporting Information). Bi LNSs exhibit nanosheet morphology with micrometer-lateral size shown in Figure 4d. Bi SNSs exhibit 3D morphology with nanosized nanosheets (Figure 4e) and Figure 4f show uniform nano particles. Unlike Bi LNSs which are able to lay flat on the working electrode (Figure S11a, Supporting Information), Bi SNSs and Bi NPs stacked on the working electrode and formed a compact catalyst layer (Figure S11b,c, Supporting Information). In this case, many active sites on Bi SNSs and Bi NPs are not available to reactants within the compact layer, therefore limit the current density for HCOO− formation (Figure S12, Supporting Information). In contrast, micrometer-lateral sized Bi LNSs with an average thickness about 4.28 nm can lay flat on the gas diffusion layer electrode, which is benefit to efficiently expose the surface atoms and is favorable for electron conduction. The optimized loading amount of Bi LNSs is only 0.25 mg cm−2 for CO2RR in this work. The larger lateral size of Bi LNSs enables an optimal catalytical performance with the use of only small amount of catalysts. Normally, geometric area normalized current density (mA cm−2) is used for comparing the activity of CO2RR catalysts. However, it cannot reveal the usage amount of catalysts which is of great importance to practical application of CO2RR catalysts. Therefore, the mass activity that normalize the current density to the loading amount of catalysts (mA mgcatalyst−1) is used in this work to evaluate the superior activity of Bi LNSs. The catalytic activity of recently reported Bi based catalytic materials for CO2RR has been recalculated to mass activity and Bi LNSs is a competitive catalyst for formate production (Table S1, Supporting Information).

The electrochemically active surface areas (ECSAs) of the prepared Bi catalysts were analyzed by measuring the double layer capacitance (Cdl) to understand the current density superiority of Bi LNSs (Figure S13, Supporting Information). Bi LNSs exhibit an obviously enhanced ECSA than Bi SNSs and Bi NPs (Figure 5a) and the current density normalized by ECSAs of Bi LNSs is 22.2% larger than that of Bi NPs (Figure S13d, Supporting Information), indicating that 1.56% lattice tensile strain promotes the intrinsic activity of Bi LNSs. Tafel analysis is often used to provide mechanistic information on the catalytic reduction of CO2. To get a better understanding of the electrochemical activity and kinetics of CO2RR on Bi LNSs, Tafel plots are examined by using the logarithm of formate partial current density versus applied potential (Figure 5b). The value...
of Bi LNSs Tafel slope (121 mV dec$^{-1}$) is approximate to the theoretical values of 119 mV dec$^{-1}$, which predicts for the processes that $^\ast$CO$_2$/CO$^\ast$ is the rate-determining step.[29] Moreover, the Tafel slope of Bi LNSs is smaller than the values obtained from Bi SNSs (133 mV dec$^{-1}$), indicating a faster electron transfer rate on Bi LNSs.[30,31]

2.3. The Relationship of Strain, Intermediate Adsorption, and CO$_2$RR Performance

To understand the reaction mechanism of CO$_2$ towards formate in this work, the possible reactions on Bi LNSs (003) and (012) crystal planes with tensile and compressive strain are investigated by using density functional theory. As we know, Bi presents excellent energy efficiency and selectivity for HCOOH against CO and HER, owing to the OCHO$^\ast$ is a main favor intermediate and the first hydrogenation via concerted proton-electron transfer (CPET) is the rate-determined step (RDS). Figure 5d,e and Figure S14 (Supporting Information) displays the energy of first, second hydrogenation, and HER steps at strains ranging from $-2\%$ to $2\%$ for the (003) and (012) planes. Initially, the (012) plane is excluded because the reaction energies of OCHO$^\ast$ shows no obvious change at strains ranging (Figure S14, Supporting Information). For the (003) plane, the tensile strain decreases adsorption energies of OCHO$^\ast$, expecting to increase overall intermediate coverage, while the second hydrogenation barrier is increased. In other words, the RDS will be changed into second CPET step if we continue increase the tensile strain. And the $2\%$ strain offers the great promise candidate ($\Delta G_{\text{max}} = 0.34 \text{ eV}$) for CO$_2$RR, even consider the HER activity (0.69 eV) under the same conditions (Figure 5e,f). From above results, it can be confirmed that strain play an important role in tuning of reaction energetics. The main reason is that the interatomic spacing of the surface atoms increases under strain, leading to less overlap of the d orbitals and a narrower d-band width. Combined with XRD analysis (Figure 4b) and DFT calculations to conclude that Bi LNSs in the presence of moderate strain is benefit for CO$_2$ toward to HCOOH under ambient conditions.

3. Conclusion

In conclusion, few layered Bi LNSs were successfully synthesized by an electrochemical cathodic exfoliation method in aqueous solution system for the first time. A significantly higher current density of formate reaches 590 mA mg$^{-1}$ with formate FE of 92.2% at $-1.10 \text{ V}$ was achieved in a flow cell configuration for CO$_2$RR. This work provides a facile synthesis for Bi nanosheets with micrometer-lateral size and proves that this material exhibits economic and efficient CO$_2$RR for formate with superior current density on an optimized low loading amount of 0.25 mg cm$^{-2}$. The micrometer-lateral size of Bi LNSs is favorable to high electronic conductivity. The lattice strain of Bi LNSs is conducive to CO$_2$ adsorption and reduce the Gibbs free energy for the formation of OCHO$^\ast$. With structural distortion such as lattice strain in layers catalysts provides an effective way for promoting the intrinsic activity of electrocatalysts, which offers insight in promoting practical CO$_2$ conversion technology.
Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Data available on request from the authors.

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