Ultrathin Bismuth Nanosheets as a Highly Efficient CO₂ Reduction Electrocatalyst

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Electrochemical reduction of CO₂ to value-added products is an important and challenging reaction for sustainable energy study. Herein, bismuth nanosheets with thickness of around 10 nm were prepared through the electrochemical reduction of Bi³⁺. Ultrathin Bi nanosheets with numerous low-coordination sites can efficiently reduce CO₂ to formate in aqueous solution. Within the potential range of −0.9 to −1.2 V vs. reversible hydrogen electrode (RHE), the faradaic efficiency of formate is over 90%, outperforming many Bi catalysts. At −0.7 V, the Bi nanosheets exhibit much higher current for formate generation than that of bulk Bi, attributed to a high surface area and also modified intrinsic electronic properties brought about by the ultrathin structure. DFT calculations demonstrate that Bi nanosheets have much higher density of states at the Fermi level compared to bulk Bi, favoring improved CO₂ reduction on Bi nanosheets. At −1.0 V, Bi nanosheets exhibit high selectivity for formate and excellent stability during 5 h of electrolysis.

With accelerated depletion of fossil fuels and global warming, the capture and utilization of CO₂ becomes an imperative task.[1] Electrochemical CO₂ reduction (CO₂RR) is a promising alternative to produce useful fuels.[2] However, electrochemical CO₂ reduction reactions still present challenges, such as high overpotential and low faradaic efficiency, because the kinetically favored hydrogen evolution reaction (HER) competes in aqueous electrolytes, giving poor product selectivity.[3] To improve electrochemical CO₂ reduction selectivity, a wide variety of novel metallic electrodes (such as Au, Ag, and Pd) have been explored for the electrochemical reduction of CO₂.[4] Combining experimental and theoretical models verified that the structures (including size, geometry, and morphology) of the metal greatly affect the corresponding catalytic activity, and low-dimensional structures revealed robust propensity for CO₂ reduction. Au nanowires, triangular Ag nanoplates, and AgIn dendrites can effectively catalyze the reduction of CO₂ to CO owing to the high ratio of edges to corner sites and optimal exposed crystal facets.[5] Further, oxide-derived nanostructured metals with rough surfaces can suppress proton reduction and improve CO₂ reduction selectivity.[6] Delicate structures of noble metals have recently been designed for CO₂RR,[6, 7] and the selectivity for CO₂ reduction in aqueous solutions can approach 95%,[6] however the high prices of noble metals hinders practical applications.

Bi catalysts present features of low toxicity, cost-effectiveness, and excellent stability, are good candidates for CO₂ electrocatalytic reduction. In aqueous electrolytes, the main reduction product on Bi catalysts is formic acid. Similar to other electrocatalysts, the CO₂RR activity is dependent on the morphology of Bi.[9] Recently, dendritic Bi prepared by electrodeposition methods in combination with halide ions, shows very high current density and formate selectivity for CO₂ reduction.[10] Besides dendrite morphology, nanosheet structures with numerous coordinatively unsaturated sites favor the stabilization of intermediate species generated during the reaction, showing great advantages toward CO₂ reduction. Xie reported that ultrathin Co₃O₄ can effectively catalyze CO₂ reduction and exhibits much higher formate selectivity than for bulk materials.[11] Sn quantum sheets with lowered Sn–Sn coordination numbers facilitate electron transfer from CO₂ to CO₂⁻ intermediates, accompanying a decrease in overpotential for formate generation.[12] Therefore, designing ultrathin-structured Bi should promote CO₂ electrocatalytic reduction.

Herein, layered Bi was fabricated through electrochemical reduction of bismuth oxide sulfates and bismuth sulfides grown on carbon paper (Scheme 1). During reduction, Bi atoms transformed from Bi³⁺ in dendritic precursors and lead to the formation of nanosheet structures. It is interesting to find that the nanosheet morphology of prepared Bi is independent of the precursor anions. 10 nm Bi layers show much higher selectivity for formate than bulk Bi (see below), with a faradaic efficiency for formate over 90% across a wide potential range. The excellent CO₂ reduction activity may result from low-coordinate Bi species, which favors the stabilization of generated intermediates during formate generation. DFT calculation show that layer structures have a higher density of states compared to bulk Bi.

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Bi$_2$S$_3$ was prepared by the hydrothermal reaction of bismuth nitrate and thiourea in aqueous solution. X-ray diffraction (XRD) demonstrates the formation of Bi$_2$S$_3$ phases with branch-like morphology as detected by scanning electron microscopy (SEM; Figure S1 in the Supporting Information). After calcination at 500 °C in air atmosphere, Bi$_2$S$_3$ was transformed into bismuth oxide sulfate [Bi$_2$O$_3$(SO$_4$)$_{10}$] phase, retaining the branched morphology (Figure S2). The electrochemical reduction of bismuth oxide sulfate was performed in CO$_2$-saturated NaHCO$_3$ (0.5 m) aqueous solution at /V vs. reversible hydrogen electrode (RHE) for 2 h. This was accompanied by a color change of bismuth species on carbon paper from white to dark-brown. The obtained Bi catalyst was assigned to rhombohedral metallic Bi phase using XRD, corresponding to JCPDS card No. 85-1329 (Figure 1d). The morphology observed by SEM and high-resolution transmission electron microscopy (HRTEM) shows that the synthesized Bi has ultrathin layer structures of approximately 10 nm (Figure 1a–c and Figure S3). The inset in Figure 1c shows that the lattice-fringe distance of 2.3 Å corresponds to the (110) interplanar spacing of rhombohedral Bi, corroborating the XRD result. Note that bismuth sulfides can also be transformed into layer-structured Bi through electroreduction (Figure S4).

To investigate the electrochemical activity of Bi catalysts, cyclic voltammograms (CVs) of fabricated Bi nanosheets were carried out in CO$_2$-bubbled NaHCO$_3$ solutions (pH 7.2) and N$_2$-bubbled NaH$_2$PO$_4$/Na$_2$HPO$_4$ solutions (pH 7.2). As shown in Figure 2a, the reduction current greatly increased under CO$_2$ atmosphere compared to a N$_2$, and the onset potential for clear reduction current in CO$_2$-bubbled KHCO$_3$ was −0.58 V vs. RHE. Under the same conditions, CVs for commercial bulk Bi as the control sample were evaluated. The current density in the presence of CO$_2$ was also enhanced (Figure 2b), which indicated that both synthesized Bi nanosheets and bulk Bi exhibit effective catalytic activity for CO$_2$ reduction. The onset potential for bulk Bi is about −0.71 V vs. RHE. The positive onset-potential shift of 130 mV for Bi nanosheets compared with commercial bulk Bi particles means that CO$_2$ reduction on Bi nanosheets is more favorable than on the bulk Bi catalyst.

The CO$_2$ reduction products in the gas phase and liquid phase were quantitatively analyzed during electrolysis by online-gas chromatography (GC) and ion chromatography (IC; details shown in experimental section). Formate was detected in solution; the corresponding faradaic efficiencies (FEs) at different potentials are shown in Figure 2c. At −0.6 V, FE of formate
mate approaches about 60%, which is much higher than that of bulk Bi (ca. 10%) and dendrite-shaped Bi previously reported by our group or other nanostructured Bi catalysts. Within the potential range of $-0.9$ to $-1.2$ V vs. RHE, the FEs of formate are over 90%, whereas FEs on bulk Bi are below 80% for all the measured potential ranges. Gas products $\text{H}_2$ and CO were observed, and the corresponding FEs are displayed in Figure 2d. Side-product $\text{H}_2$ generated through proton reduction is greatly suppressed on the Bi nanosheets compared to that of bulk Bi, especially in the low-overpotential region. Only trace amounts of CO are generated on these two types of Bi catalyst, with FEs below 5%. Combining the low onset potential for formate generation and high formate selectivity, Bi nanosheets are more effective than bulk Bi toward electrochemical CO$_2$ reduction. Moreover, the substrate of carbon paper was used as a working electrode for CO$_2$ reduction. $\text{H}_2$ was detected as the main product and FEs were over 90% within all the applied potential ranges (Figure S5). FEs of both CO and formate were below 5%. The high formate selectivity of Bi nanosheets comes from Bi species and not the carbon paper substrate. As mentioned, the activity is proposed to originate from low-coordinate Bi, which enhances the adsorption of CO$_2$ and favors the stabilization of intermediate species.

The partial current densities of formate on two types of Bi catalysts are shown in Figure 3a, where ultrathin Bi displays much higher cathodic current for formate generation than bulk Bi. At $-0.7$ V, the formate partial current on Bi nanosheets reached 1.53 mA cm$^{-2}$, 19 times higher than that of bulk Bi (0.08 mA cm$^{-2}$, Figure 3a). The greatly enhanced CO$_2$ reduction activity of Bi nanosheets may be related to the increased number of active surface sites. To estimate the intrinsic activity of Bi catalysts per active site, the electrochemical surface area (ECSA) was determined using the redox reaction of surface active sites, where the redox peak area represents the amount of active Bi species (Figure S6). ECSA analysis of Bi nanosheets

Figure 2. Cyclic voltammogram curves of ultrathin Bi nanosheets (a) and commercial bulk Bi (b) in N$_2$-bubbled NaH$_2$PO$_4$/Na$_2$HPO$_4$ solution (0.5 M, pH 7.2) and CO$_2$-bubbled NaHCO$_3$ (0.5 M) aqueous solution with scanning rate of 10 mV s$^{-1}$. Faradaic efficiencies (FEs) for formate (c), and CO/$\text{H}_2$ (d) catalyzed by Bi nanosheets and bulk Bi.

Figure 3. Formate partial-current densities (a) and Tafel plots for formate production (b) on Bi nanosheets and bulk Bi.
shows 8.3 times greater peak area than that of bulk Bi. The above results mean that the enhanced CO₂ reduction activity of Bi nanosheets is not only a result of increased ECSA, but also an intrinsic property of the morphology of ultrathin layers (see DFT results below). At high overpotential (−1.0 V vs. RHE), the difference in formate production rate on these two type of Bi catalysts decreases to 2 times faster for the nanosheets, which is much less than the observed difference of ECSA. A possible reason is that the Bi nanosheets are not fully accessible by CO₂ owing limited mass transfer diffusion and low CO₂ concentration, yet accompanying a high CO₂ consumption rate at high overpotential. Therefore, the surface area effect on the CO₂ reduction rate is overestimated at high overpotential.

Kinetic insights for CO₂ reduction to formate are indicated in Tafel plots fitted in the low-overpotential region (Figure 3 b). The slope values for Bi nanosheets and bulk Bi are 96 and 155 mV dec⁻¹, respectively, similar to theoretical value of 118 mV dec⁻¹. This indicates that the process of one electron being transferred to adsorbed CO₂ forming *CO₂⁻ intermediate species is the rate-limiting step for CO₂ reduction.[14] The lower Tafel slope (96 mV dec⁻¹) of Bi nanosheets than that of bulk Bi (155 mV dec⁻¹) clearly demonstrates the remarkable improvement for formate generation on ultrathin Bi nanosheets.

The effect of electrolyte concentration for CO₂ reduction on Bi nanosheet electrodes was explored. When the concentration of NaHCO₃ was decreased from 0.5 to 0.3 or 0.1 M, the main product was still formate. Partial current density and FEs of formate are shown in Figure 4 and Figure S7, respectively. As electrolyte concentration decreases, both the current density and formate FE decrease. At −0.8 V vs. RHE, the partial current density of 0.5, 0.3, and 0.1 M NaHCO₃ is 3.95, 1.92, and 0.30 mA cm⁻², corresponding to formate FEs of 88.7 %, 59.8 %, and 20.6 %, respectively. This is consistent with a high NaHCO₃ favoring the reduction of CO₂ to formate.[15]

To understand the enhancement of intrinsic catalytic activity of Bi nanosheets relative to bulk Bi, DFT was performed to calculate the density of states (DOS) of Bi. Based on the result of total and partial density of states (PDOS) of p and d bands (Figure 5 and Figure S8), the occupancy for the d band is negligible, and most electron density resides in the p band. Compared with bulk Bi, Bi nanosheets show a higher PDOS of the p band around the Fermi level, which usually facilitates orbital hybridization of catalyst with adsorbed reactant. High DOS around the Fermi level optimizes the adsorption of intermediate species and facilitates CO₂ reduction.[16]

Finally the stability of Bi nanosheets was evaluated at −1.0 V vs. RHE. As shown in Figure 6, over 5 h operation, changes in the cathodic current and faradaic efficiency for formate generation is negligible. After 5 h CO₂ reduction, the crystal phase of the used Bi catalyst was intact as shown by XRD analysis (Figure S9). Bi nanosheets exhibiting high activity and robust stability are highly promising electrocatalysts for CO₂ electrochemical reduction.

In conclusion, Bi nanosheet structures were fabricated as effective CO₂ reduction catalysts, producing formate in aqueous solution. Compared to bulk Bi, Bi nanosheets show a much higher cathodic current for formate generation per active site, attributed to numerous low-coordinated Bi atoms on the nanosheet surface and a high density of states around the Fermi level as verified by DFT. Bi nanosheets exhibit high selectivity and excellent stability during 5 h electrolysis at −1.0 V vs.
RHE. This work provides a new route to nanosheet structures and demonstrates the advantage of nanostructured Bi electrocatalysts.

**Experimental Section**

**Chemicals**

Bi(NO$_3$)$_3$·5H$_2$O (Sinopharm, 99%), thiourea (Tianjin Damao, 99.0%), NaHCO$_3$ (Sigma–Aldrich, 99.7%), and HCl aqueous solution (Tianjin Damao, 36%) were used as received. Commercial bulk Bi was bought from Sigma Aldrich. CO$_2$ gas (99.9995 %) was purchased from the Dalian DATE gas company. Ultrapure water was obtained by a ELGA Lab Water system. Carbon paper (T060, Toray) was calcined in muffle oven at 500 °C for 6 h under air atmosphere to remove organic impurities remaining on the surface.

**Preparation of Bi-based electrodes**

Bi electrodes were prepared in four steps using carbon paper as substrate. Firstly, Bi crystals were introduced on the substrate through chronoamperometry in a three-electrode system. The treated carbon paper was used as the working electrode, Pt wire as the counter electrode and an Hg$_2$Cl$_2$/Hg/saturated KCl electrode (SCE) as the reference electrode. 20 mM Bi(NO$_3$)$_3$ aqueous solutions containing 0.6 M hydrochloric acid were used as the electrolyte. The electrochemical deposition experiment was carried out at a constant potential of $-0.35$ V vs. SCE for 200 s. Then, carbon paper deposited with Bi crystals was immersed into a 50 mL Teflon-lined stainless-steel autoclave containing water (40 mL), Bi(NO$_3$)$_3$ (0.49 g), and thiourea (0.2 g). The autoclave was heated at 180 °C for 20 h and then cooled down naturally. The carbon paper was taken out from the autoclave, rinsed several times with ultrapure water and dried at 80 °C overnight. Thirdly, the carbon paper with black bismuth sulfide was calcined at 500 °C for 2 h in air atmosphere to transform bismuth sulfide to bismuth oxide sulfate. Finally, the bismuth oxide sulfate electrode was electrochemically reduced in CO$_2$-bubbled aqueous NaHCO$_3$ (0.5 M) at $-1.0$ V (vs. RHE) for 2 h to obtain metallic Bi electrodes.

As control sample, commercial bulk Bi was ground into particles with a mortar. Bulk Bi-based electrodes were casted as follows. 1 g Bulk Bi catalyst and 300 μL Nafion (5 wt%, Du Pont, Corp.) were mixed with 3 mL ethanol and ultrasonically dispersed into a uniform ink. The obtained ink was spray-coated onto carbon paper (4 cm$^2$), and then dried with compressed air to yield a catalyst layer with a loading weight of 0.25 g cm$^{-2}$.

**Materials characterization**

Powder X-ray diffraction (XRD) spectra were measured on a Rigaku D/Max2500PC diffractometer with CuK$\alpha$ radiation ($\lambda = 1.5418$ Å) operating at 40 kV and 40 mA over the 2θ range of 5–90° with a scan speed of 5° min$^{-1}$. Scanning electron microscopy (SEM) was recorded on JEOL JSM-6360 operating at an acceleration voltage of 20 kV. High-resolution transmission electron microscopy (HRTEM) was collected on a JEOL JEM-2000EX (120 kV) microscope.

**Electrochemical measurements for CO$_2$ reduction**

Electrochemical measurements were performed on a Princeton Applied Research VersaSTAT 3 potentiostat (EG&G Instrument) in a two-compartment electrochemical cell (separated by Nafion mem-

branes) with three electrode system. Pt wire and an Hg$_2$Cl$_2$/Hg/saturated KCl electrode (SCE) were used as the counter electrode and the reference electrode, respectively. The prepared Bi catalyst electrodes was used as the working electrode. CO$_2$-saturated NaHCO$_3$ (0.5 M) aqueous solution was used as electrolyte, and the cathodic electrolyte was bubbled with CO$_2$ gas and stirred at 500 rpm during CO$_2$ electrolysis. The generated gas products were analyzed online by a gas chromatography (GC, Shimadzu GC-2014). The hydrogen and CO were quantified by a thermal conductivity detector (TCD) and flame ionization detector (FID), respectively. Calibrations were performed using CO and H$_2$ samples with different concentrations. The aqueous product was quantified by ion chromatography (ICS-1100, Dionex Corporation). Faradaic efficiencies (FEs) were calculated using Equation (1):

$$FE = \frac{C \times V \times n}{I \times t / F} \times 100\%$$

where C is the concentration of product (mol L$^{-1}$); V is the volume of reduction product (L); n is the number of electrons transferred, (equal to 2 for formate, CO and H$_2$); I is the reaction current (A); t is reaction time (s); and F is the Faraday constant (96485 C mol$^{-1}$).

**Calculation of electrochemical surface area**

Cyclic voltammetry of ultrathin Bi nanosheets and bulk Bi electrodes was measured in 50 mM aqueous KOH at a scan rate of 10 mV s$^{-1}$. During the cathodic scanning period, the reduction peak appears, which corresponds to the reduction of the oxide monolayer formed during the anodic scan period (Figure S5). ECSA was estimated based on the area of the reduction peak.

**Computational details**

To interpret the higher electrochemical CO$_2$ reduction activity observed over layer slab structures compared with bulk slabs, the total density of states (TDOS) and the local density of states (LDOS) have been calculated based on density functional theory (DFT). All of the electronic structure calculations were performed using the gradient-corrected Perdew–Burke–Ernzerhof (GGA-PBE) functional as implemented in the VASP code.$^{[18]}$ The electron–ion interactions were described by the projector-augmented wave (PAW)$^{[19]}$ method with a kinetic energy cutoff of 400 eV. We used a 3×3×6 slab size to simulate the 1.5 nm thick layer slab under vacuum in the direction perpendicular to the surface of 15 Å. Structures of 8×8×8 and 11×11×1 K points were employed for bulk and layered structure, respectively, with 0.1 eV smearing of the Fermi level. The force convergence was set to be smaller than 0.02 eV Å$^{-1}$. Spin polarization effects and dipole corrections for the (100) surface were taken into account.

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**Conflict of interest**

The authors declare no conflict of interest.
Keywords: bismuth · CO2 reduction · electrocatalysis · nanosheets · non-precious metals


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It's bismuth time: Bismuth nanosheets with thickness of approximately 10 nm were fabricated through the electrochemical reduction of Bi^{3+}. As a CO₂ reduction electrocatalyst, ultrathin Bi nanosheets exhibit high selectivity for formate generation owing to a high density of states near the Fermi level, as verified by DFT calculations.