β-PdBi2 Monolayer: Two-Dimensional Topological Metal with Superior Catalytic Activity for Carbon Dioxide Electroreduction to Formic Acid

Xiaorong Zhu,† Yu Wang, † Yu Jing, ‡ Thomas Heine,*§ Yafei Li*†

ABSTRACT: The lack of efficient electrocatalysts has been a main obstacle for the large-scale commercialization of CO2 electroreduction. In this work, we demonstrate that two-dimensional (2D) β-PdBi2 monolayer is a promising solution for this issue. β-PdBi2 monolayer is a stable 2D crystal and the three-dimensional (3D) bulk interlayer energy is similar as for other layered materials that can be exfoliated into 2D crystals. Interestingly, β-PdBi2 monolayer has rather intriguing electronic properties: while being metallic, it also has a nontrivial topological point. Remarkably, the extra electronic states at the Fermi level induced by the intrinsinc spin–orbit coupling (SOC) effect significantly enhance the adsorption of OCHO* intermediate on β-PdBi2 monolayer, resulting in a rather small onset potential of −0.26 V vs. RHE for CO2 electroreduction to HCOOH. These results not only suggest a promising candidate for CO2 electrolysis but also deepen our understanding of the factors dominating the catalytic activity of 2D materials.

Formic acid (HCOOH) is an important chemical intermediate and a promising liquid fuel for driving direct formic acid fuel cells. At present, methanol carbonylation remains the most common industrial strategy for the production of HCOOH. However, this method is energy intensive and can cause environmental pollution. In contrast, the utilization of electricity generated from renewable energy sources such as wind and solar energy to produce HCOOH through CO2 electroreduction represents a more efficient and green strategy, which also helps to reduce the amount of CO2 in the atmosphere. CO2 is a stable linear molecule with robust chemical inertness. Therefore, the CO2 electroreduction requires an electrocatalyst to activate the C=O bonds and accelerate the reaction kinetics. In the 1980s, Hori et al. reported that some metals (Pb, Cd, Hg, TI) have good activity for the electroreduction of CO2 to HCOOH. However, these metals are highly toxic and therefore cannot be used in industrial production. The noble metal Pd catalyzes CO2 reduction to HCOOH at a very low overpotential, but it suffers gradual activity decay induced by the formation of a poisoning CO adlayer. Although the preparation of HCOOH from Sn-based electrocatalysts has received much attention recently, it is often accompanied by a large amount of H2 and CO products due to its limited catalytic selectivity.

In recent years, the application of two-dimensional (2D) metals in the field of CO2 electroreduction has received widespread attention. The large specific surface area of 2D materials facilitates the diffusion of reactants, and its more exposed active sites are conducive to rapid charge transfer. Xie et al. reported that atomically thin Co layers show significantly improved catalytic activity for CO2 reduction to HCOOH compared to bulk Co. However, the ultrathin transition metal layers are prone to oxidation, causing a rapid decay in cyclability. Recently, group-15 metal elements, including Sb and Bi,3 were revealed to be highly active and selective for CO2 electroreduction to HCOOH when thinned into 2D few-layer structures. However, the reported current density of 2D Sb and Bi electrocatalysts is generally lower than 30 mA cm−2, which is far below the technical requirements for large-scale industrial applications (~200 mA cm−2).10 At present, stable and efficient 2D electrocatalysts for CO2 reduction to HCOOH are highly sought.

In this communication, by means of density functional theory (DFT) calculations (using the PBE functional, see supporting information for the computational details), we identified a novel 2D material, namely, β-PdBi2 monolayer, as a promising candidate. Bulk β-PdBi2 has been known since 1985,11 while its layered structure was discovered in 1953.12 According to our results, β-PdBi2 monolayer is experimentally viable and shows rather good catalytic performance towards CO2 electroreduction to HCOOH. In particular, the intrinsic spin–orbit coupling (SOC) effect plays an important role in governing the catalytic activity of the β-PdBi2 monolayer.

![Figure 1](image)

**Figure 1.** (a) Side view of the bulk β-PdBi2. (b) Top view of the single-layer β-PdBi2 structure.
between PdBi layers. Nevertheless, isolating a β-PdBi layer from the bulk phase still results in a slight lattice shrinkage ($a = b = 3.34$ Å). In β-PdBi monolayer, every four Bi atoms are face-shared with the neighbouring PdBi motifs to a 2D network (Figure 1b). By intruding a fracture in a five-layer model of β-PdBi, the cleavage energy of β-PdBi monolayer was estimated to be 0.88 J m$^{-2}$ (Figure S1), which is comparable to calculations at the same computational level for well-known 2D crystals that have been realized experimentally via various exfoliation techniques, such as MoS$_2$ (0.42 J m$^{-2}$) and Ca$_2$N (1.09 J m$^{-2}$).  

High mechanical and chemical stability are prerequisites for any catalyst. The calculated phonon dispersion of β-PdBi monolayer is shown in Figure S2. No imaginary phonon modes are present, which is indicative for good kinetic stability. Moreover, ab initio molecular dynamics simulations in a 6×6×1 super cell confirm the thermodynamic stability. According to our results (Figure S3), β-PdBi monolayer remains crystalline throughout a 10 ps simulation at 500 K, suggesting that β-PdBi monolayer has appreciable thermodynamic stability as its structure is separated from other local minima by an adequate barrier on the potential energy surface.

Figure 2. Band structure and DOS of β-PdBi$_2$ monolayer. The activity of an electrocatalyst is fundamentally governed by its electronic structure. Therefore, we have calculated the band structure of β-PdBi$_2$ monolayer to obtain a preliminary understanding of its catalytic activity. As shown in Figure 2, β-PdBi$_2$ monolayer is metallic with several energy levels crossing the Fermi level, which is the same as in bulk β-PdBi (Figure S4). Interestingly, there is a Dirac-like cone at the M (0.5, 0.5, 0) point below the Fermi level. Since Bi and Pd are both heavy elements that give raise to considerable SOC, we also calculated the SOC-corrected band structure of β-PdBi$_2$ monolayer (Figure 2). Remarkably, although the metallic character of β-PdBi$_2$ monolayer is still preserved, SOC opens a large gap at the Dirac-like cone at the M point and a flat band emerges at the Fermi level. According to the calculated orbital-resolved band structures (Figure S5), the flat band is mainly contributed by the 6$p_a$ and 6$p_b$ orbitals of Bi and partially by the 4$d_{xy}$ and 4$d_{xy}$ orbitals of Pd. Especially, due to the existence of the flat band, the DOS at the Fermi level is very high (an effect that is not reflected without consideration of SOC) (Figure 2). A higher DOS at the Fermi level is likely to promote electron transfer and thus enhances the affinity to adsorbed species, which is beneficial for electrocatalytic activity. To substantiate our results, we also calculated the band structure and DOS of β-PdBi$_2$ monolayer using the hybrid HSE06 functional. Both functionals (PBE and HSE06) produce very similar results (Figure S6). The SOC-induced deformation of the Dirac-like point is a strong hint for the existence of topologically nontrivial phase, which we have confirmed by calculation of the $Z_2$ topological invariant (ν) of β-PdBi$_2$ monolayer. Due to the existence of structural inversion symmetry, the ν of β-PdBi$_2$ monolayer can be directly calculated on the basis of the parity of the Bloch wave function for all the filled bands at the four time-reversal-invariant momenta (TRIM) points in the Brillouin zone (Γ, X, M and Y). Especially, the parities at X and Y points are identical for β-PdBi$_2$ monolayer owing to the square symmetry, and thus have no effect on the band topology. Therefore, we calculated the parity eigenvalues of the Bloch wave function for the occupied single degenerate bands of β-PdBi$_2$ monolayer at the Γ and M points. As listed in Table S1, the product of the parity eigenvalues at the Γ point is +1, whereas it is −1 at the M point, resulting in ν = 1 and confirming the topological states for β-PdBi$_2$ monolayer. To confirm the non-trivial topological character, we identified the topological edge states of a ~10 nm wide β-PdBi$_2$ nanoribbon (Figure S7). The calculated edge band structure show the topological edge states, which conclusively confirms the nontrivial band topology for 2D β-PdBi$_2$ monolayer. Thus, β-PdBi$_2$ monolayer can be interpreted as a 2D nontrivial topological metal.

Figure 3. (a) Geometric structures of various states and (b) free energy diagrams of CO$_2$ electroreduction to HCOOH on β-PdBi$_2$ monolayer. Next, we investigated the catalytic activity of β-PdBi$_2$ monolayer for CO$_2$ electroreduction to HCOOH. The water-solid interface was simulated by explicitly placing one water layer above the surface of β-PdBi$_2$ monolayer (Figure S8). As SOC is strongly affecting the electronic properties close to the Fermi level, it has been included in reaction free energy (ΔG) calculations in the manner of single-point correction. Generally, the electroreduction of CO$_2$ to HCOOH initiates with the hydrogenation of C atom through a proton-coupled electron transfer process, resulting in the formation of an OCHO* species (Figure 3a). According to our calculations, this step is endothermic with a ΔG of 0.20 eV for β-PdBi$_2$ monolayer (Figure 3b). The formed OCHO* species is stabilized on the top of Bi atom with a Bi-O length of 2.68 Å. Upon the second proton-coupled electron transfer that is also endothermic by 0.11 eV, the OCHO* species transforms to a physisorbed HCOOH* species that can be spontaneously released from β-PdBi$_2$ monolayer. Therefore, the potential-limiting step for CO$_2$ electroreduction to HCOOH on β-PdBi$_2$ monolayer is the formation of OCHO* species. In particular, when the SOC correction is canceled, the ΔG of this step is pronouncedly increased to be 0.37 eV (Figure 3b), indicative of the essential role of SOC, with the consequence of high DOS formation, in boosting the catalytic activity. Since the ΔG for the OCHO formation is equal
to the adsorption free energy of OCHO* (ΔGOCO2*), the SOC effect actually significantly enhances the adsorption of OCHO* species on β-PdBi2 monolayer, which is consistent with the above DOS analysis. Here, we should note that recently several studies also demonstrated that the topological surface states can enhance the adsorption of hydrogen on catalysts.\(^\text{18}\)

In addition to HCOOH, carbon monoxide (CO) is also a possible product of two-electron (2e) CO\(_2\) electroreduction if the first hydrogenation of CO occurs on the O atom. However, according to our calculations (Figure S9), the formation of COOH* intermediate on β-PdBi2 monolayer through the hydrogenation of O atom is significantly endothermic by \(1.04\) eV, which is much higher than the formation of OCHO* species (0.20 eV). Therefore, the formation of CO on β-PdBi2 monolayer could be effectively overwhelmed, contributing to the high selectivity for the formation of HCOOH. Remarkably, the surface of β-PdBi2 monolayer only slightly attracts CO by physisorption (adsorption energy of \(-0.26\) eV) and the chemisorbed species is repulsive. This implies that β-PdBi2 monolayer presents a high resistance to CO poisoning, which is a large advantage over Pd catalysts.\(^1\) Moreover, the competing HER can be effectively suppressed due to the rather positive adsorption free energy of H* species (0.81 eV) on β-PdBi2 monolayer. Therefore, HCOOH will be the major product for CO\(_2\) electroreduction on β-PdBi2 monolayer.

**Figure 4.** Simulated polarization curves of CO\(_2\) electroreduction to HCOOH on β-PdBi2 monolayer.

Finally, on the basis of above obtained SOC-corrected data, we further constructed a microkinetics model for the CO\(_2\) conversion to HCOOH to give an intuitive demonstration of the catalytic performance of β-PdBi2 monolayer. As presented in Figure 4, the simulated polarization curve of β-PdBi2 monolayer shows a current onset at approximately \(-0.26\) V, which is much less than the experimentally measured onset potentials of other Bi-based catalysts.\(^3\) Remarkably, with increasing electrode potential, the current density of β-PdBi2 monolayer rapidly increases and reaches 200 mA cm\(^{-2}\) at a potential of \(-0.63\) V vs. RHE, which meets the commercialization requirement of an efficient catalyst for CO\(_2\) electroreduction. The above results vividly demonstrate that β-PdBi2 monolayer is a promising electrocatalyst for CO\(_2\) reduction to HCOOH.

To summarize, the structural, electronic and catalytic properties of a proposed 2D material, namely, β-PdBi2 monolayer, have been systematically studied on the basis of DFT. β-PdBi2 monolayer is a nontrivial 2D topological metal with high experimental feasibility and good stability. The intrinsic SOC effect enhances the adsorption of the OCHO* intermediate on β-PdBi2 monolayer, leading to superior catalytic activity for CO\(_2\) electroreduction to HCOOH. In particular, the high current density at low operating potentials provided by β-PdBi2 monolayers would make the production of HCOOH via CO\(_2\) electroreduction commercially viable. Our work highlights the role of SOC effects in boosting the catalytic activity, which would promote more experimental and theoretical efforts on developing topological materials for catalysis application.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

Computational methods, structure of bulk β-PdBi2, phonon spectrum of β-PdBi2 monolayer, MD simulations results, band structure of bulk β-PdBi2, orbital-resolved band structures of β-PdBi2 monolayer, HSE band structure and DOS of β-PdBi2 monolayer, parity eigenvalues of the Bloch wave function for the occupied spin-degenerate bands of β-PdBi2 monolayer, geometric structure and electronic band structure of β-PdBi2 nanoribbon, views of solvent model of water on β-PdBi2 monolayer, free energy diagrams of CO\(_2\) electroreduction to CO on β-PdBi2 monolayer.

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**Notes**

The authors declare no competing financial interests.

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CO₂, HCOOH, •OCHO
Supporting Information

β-PdBi$_2$ Monolayer: Two-Dimensional Topological Metal with Superior Catalytic Activity for Carbon Dioxide Electroreduction to Formic Acid

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**Computational Details**

**DFT Calculations.** Density functional theory (DFT) calculations were performed using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional\(^1\) and the projector-augmented wave (PAW) approach,\(^2,3\) as implemented in the VASP software.\(^4,5\) A 460 eV cutoff energy for the kinetic energy was adopted after thorough testing. \(k\)-space samplings of 12 × 12 × 12 for the unit cell of bulk \(\beta\)-PdBi\(_2\) and 12 × 12 × 1 for the unit cell of \(\beta\)-PdBi\(_2\) monolayer have been employed. The energy convergence threshold was set as 1×10\(^{-5}\) eV, and all geometric structures were fully optimized until the force on each ion was less than 0.01 eV/Å. For monolayer calculations, the distance of vacuum space was set to be 20 Å to avoid the interaction between periodic images. For thermodynamics calculations of electrochemical reactions, van der Waals interactions were included utilizing Grimme’s D3 method.\(^6\)

The phonon spectrum was computed using Phonopy code\(^7\) with density functional perturbation theory (DFPT).\(^8\) Molecular dynamics simulations were performed using a 6 × 6 × 1 supercell of \(\beta\)-PdBi\(_2\) monolayer within the NVT ensemble, and were lasted for 10 ps with a time step of 1.0 fs. The Nosé-Hoover thermostat has been employed.\(^9\)

**Free Energy Calculations.** We used a 3×3×1 supercell to explore the catalytic activity of the \(\beta\)-PdBi\(_2\) monolayer with the computational hydrogen electrode (CHE) model.\(^10\) The free energy \((G)\) of each species was calculated as

\[
G = E_{\text{tot}} + E_{\text{ZPE}} - TS \quad (S1)
\]

where \(E_{\text{tot}}\) is the total (internuclear repulsion and electronic energy of the PBE optimized structure with single-point spin-orbit coupling (SOC) corrections included) energy from the DFT calculations, \(T\) is system temperature (298.15 K), and \(E_{\text{ZPE}}\) and \(S\) are zero-point energy and entropy, respectively. The \(E_{\text{ZPE}}\) and \(S\) corrections to reaction intermediates were calculated by a harmonic analysis, where contributions from the basic \(\beta\)-PdBi\(_2\) slab were neglected, while these of small molecules are taken from the NIST database. The \(E_{\text{ZPE}}\) and \(S\) corrections of HCOOH* and CO\(_2\) are taken as the corresponding molecular values, as HCOOH* and CO\(_2\) are physisorbed on the surface of the \(\beta\)-PdBi\(_2\) monolayer. The solvent effect on the intermediates has been taken into account by using an explicit water layer as shown in Figure S7. As revealed by previous works, the effect of one layer of water on adsorbate is essentially equivalent to more water layers.\(^11\)

After calculating the \(G\) of each species (Table S2), we obtained the free energy changes \((\Delta G_{n}, n=1, 2, 3)\) of the elementary reaction steps. Following the computational hydrogen electrode (CHE) model, the effects of electrode potential \((U)\) and pH on CO\(_2\) reduction reaction can be treated as the energy shifts to free energy change in the electrochemical steps: \(\Delta G_{U} = -eU\) and \(\Delta G_{pH} = -k_b T \ln 10 \times pH\). In this work the value of pH was assumed to be zero for acidic medium.

**Microkinetics Simulations.** Following previous study,\(^12\) we further constructed a micro-kinetics model for the conversion of CO\(_2\) to HCOOH on the \(\beta\)-PdBi\(_2\) , of which the reaction process is summarized as:

\[
\text{CO}_2^{\text{aq}} + * \xrightleftharpoons[k_{-1}]{k_1} \text{CO}_2^* \quad (S2)
\]
\[
\begin{align*}
\text{CO}_2^* + \text{H}^+ + \text{e}^- & \xrightleftharpoons[k_2]{k_1} \text{OCHO}^* \quad (S3) \\
\text{OCHO}^* + \text{H}^+ + \text{e}^- & \xrightleftharpoons[k_3]{k_2} \text{HCOOH}^* \quad (S4) \\
\text{HCOOH}^* & \xrightleftharpoons[k_4]{k_5} \text{HCOOH(aq)} + \text{*} \quad (S5)
\end{align*}
\]

where \( k_i \) (\( i = 1-4 \)) is rate constant, and \( k_i \) is rate constant of the reverse reaction. Based on steady-state approximation, the dynamical coverage rate of * (active site), \( \text{CO}_2^* \), \( \text{OCHO}^* \) and \( \text{HCOOH}^* \) can be written as:

\[
\frac{\partial \theta_\text{*}}{\partial t} = -k_1 x_{\text{CO}_2(aq)} \theta_\text{*} + k_{-1} \theta_{\text{CO}_2^*} + k_4 \theta_{\text{HCOOH}^*} - k_{-4} x_{\text{HCOOH(aq)}} \theta_\text{*} \quad (S6)
\]

\[
\frac{\partial \theta_{\text{CO}_2^*}}{\partial t} = k_1 x_{\text{CO}_2(aq)} \theta_\text{*} - k_{-1} \theta_{\text{CO}_2^*} - k_2 \theta_{\text{CO}_2^*} + k_{-2} \theta_{\text{OCHO}^*} \quad (S7)
\]

\[
\frac{\partial \theta_{\text{OCHO}^*}}{\partial t} = k_2 \theta_{\text{CO}_2^*} - k_{-2} \theta_{\text{OCHO}^*} - k_3 \theta_{\text{OCHO}^*} + k_{-3} \theta_{\text{HCOOH}^*} \quad (S8)
\]

\[
\frac{\partial \theta_{\text{HCOOH}^*}}{\partial t} = k_3 \theta_{\text{OCHO}^*} - k_{-3} \theta_{\text{HCOOH}^*} - k_4 \theta_{\text{HCOOH}^*} + k_{-4} x_{\text{HCOOH(aq)}} \theta_\text{*} \quad (S9)
\]

where \( \theta \) is the coverage of the reaction intermediate, \( t \) is the time, and \( x_{\text{CO}_2(aq)} \) and \( x_{\text{HCOOH(aq)}} \) are the mole fraction of \( \text{CO}_2(aq) \) and \( \text{HCOOH(aq)} \), respectively. \( x_{\text{CO}_2(aq)} \) is taken as \( 5.79 \times 10^{-4} \), corresponding to 1 atm \( \text{CO}_2(g) \) in equilibrium with \( \text{CO}_2(aq) \). Since \( x_{\text{HCOOH}} \) should be relatively lower than \( x_{\text{CO}_2(aq)} \) during catalysis, we assume that \( x_{\text{HCOOH}} \) is \( 1 \times 10^{-5} \). Besides, these coverages on the \( \beta \)-PdBi \(_2\) monolayer satisfy the following condition:

\[
\theta_\text{*} + \theta_{\text{CO}_2^*} + \theta_{\text{OCHO}^*} + \theta_{\text{HCOOH}^*} = 1 \quad (S10)
\]

According to the transition state theory, for \( \text{CO}_2 \) adsorption and \( \text{HCOOH} \) removal steps, their rate constant \( k_i \) is calculated by,

\[
k_i = A' \exp \left( \frac{-G_{a,i}}{k_B T} \right) \quad (S11)
\]

where \( G_{a,i} \) is activation free energy and \( A' \) is an effective pre-exponential factor deduced by \((xk_B T)/h \), \( x \) is the effective coefficient, \( k_B \) is the Boltzmann constant, and \( h \) is Planck constant. As the adsorption-desorption step on the slab surface typically involves an energy barrier of 0.22-0.28 eV due to the solvent reorganization,\(^{13, 14}\) the \( A' \) for \( \text{HCOOH} \) desorption can be estimated as \( 1.20 \times 10^8 \text{ s}^{-1} \). In addition, the equilibrium constant \( (K) \) of \( \text{CO}_2 \) adsorption and \( \text{HCOOH} \) desorption are expressed as:

\[
K_i = \exp \left( \frac{-\Delta G_i}{k_B T} \right) \quad (S12)
\]

where \( \Delta G \) is the free energy change of \( \text{CO}_2 \) adsorption and \( \text{HCOOH} \) desorption.
The $k_i$ of electrochemical step, which depends on the electrode potential ($U$), is calculated by,

$$k_i = A_i \exp \left( -\frac{E_{a,i}}{k_B T} \right) \exp \left( -\frac{e\beta_i (U_i - U_i)}{k_B T} \right) \quad (S13)$$

where $U_i$ is the reversible potential of step $i$ deduced by $U_i = -\Delta G_i / e$, $E_{a,i}$ is the activation energy at the reversible potential $U_i$ of step $i$, and $\beta_i$ is the symmetric factor taken as 0.5. We assume that $A_i$ is $1.23 \times 10^9 \text{ s}^{-1}$, as solvent reorganization may also bring an energy barrier for direct proton-electron transfer. The $E_{a,i}$ of the direct proton-electron transfer is generally small, and thereby we adopted $E_{a,i} = 0.3 \text{ eV}$ for OCHO* and HCOOH* formation steps. In addition, the $K_i$ of nonelectrochemical step also depends on the $U$, and is given as:

$$K_i = \exp \left( -\frac{eU + \Delta G_i}{k_B T} \right) \quad (S14)$$

For all reaction steps, the $k_i$ can be calculated from the its rate constant and equilibrium constant; that is:

$$k_i = \frac{k_i}{K_i} \quad (S15)$$

These rate equations are solved at steady state, and then we can get the turn over frequency (TOF). Finally, the current density ($j$) can be calculated by:

$$j = e\rho \text{TOF} \quad (S16)$$

where $\rho$ is the surface density of active sites.
Figure S1. Cleavage energy as a function of the separation distance for a fracture in bulk β-PdBi2. Inset is a schematic of monolayer separation from its neighboring four-layer configuration.

Figure S2. Phonon spectrum of the β-PdBi2 monolayer.
Figure S3. The evolution of the total energy of ab initio molecular dynamics (FPMD) simulations for the $\beta$-PdBi$_2$ monolayer at 500 K. The inset is the snapshot structures of the $\beta$-PdBi$_2$ monolayer at 10 ps.
Figure S4. Band structures of bulk $\beta$-PdBi$_2$ computed with (bottom) and without (upper) the consideration of the SOC effect.

Figure S5. Orbital-resolved band structures for (a) Bi and (b) Pd atoms of the $\beta$-PdBi$_2$ monolayer. Red, orange, green, dark yellow, olive, cyan, purple and pink dots indicate the contributions of Bi-$p_x$, Bi-$p_y$, Bi-$p_z$, Pd-$d_{z^2}$, Pd-$d_{x^2-y^2}$, Pd-$d_{xy}$, Pd-$d_{x^2-y^2}$, respectively. Larger dot means higher contribution while smaller one indicates lower contribution. The smooth lines represent zero contribution.
Figure S6. Band structure and total DOS of the $\beta$-PdBi$_2$ monolayer calculated using HSE+SOC. The pure HSE results without the consideration of SOC correction are also given for comparison.

Figure S7. (a) Optimized structure of $\beta$-PdBi$_2$ nanoribbon in a $1 \times 4 \times 1$ supercell. (b) Electronic band structure of $\beta$-PdBi$_2$ nanoribbon calculated with PBE+SOC level of theory.
**Figure S8.** Side and top views of solvent model of water molecules on the surface of the \( \beta \)-PdBi\(_2\) monolayer.

**Figure S9.** Free energy diagrams of CO\(_2\) electroreduction to CO on the \( \beta \)-PdBi\(_2\) monolayer. Inset is the optimized configuration of COOH\(^*\) adsorption on the Bi atom of the \( \beta \)-PdBi\(_2\) monolayer.
Table S1. Parities of 20 occupied spin-degenerate bands at the TRIM points (Γ and M) for the β-PdBi₂ monolayer

|     | +   | +   | -   | +   | +   | -   | +   | -   | +   | +   | +   | +   | +   | +   | -   | -   | (+) |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| M   | +   | -   | +   | +   | -   | -   | +   | -   | -   | -   | +   | -   | -   | -   | +   | -   | -   | (−) |

The topological indexes ν is established by

$$\delta(K_i) = \prod_{m=1}^{N} \xi_{2m}^i, (-1)^\nu = \prod_{i=1}^{2} \delta(K_i) = \delta(G)\delta(M) \quad (S17)$$

Where δ is the product of parity eigenvalues at the TRIM points (Γ and M points), ξ = ±1 are the parity eigenvalues and N is the number of the occupied bands. For the β-PdBi₂ monolayer, there are 40 electrons in one unit cell, corresponding to 20 spin-degenerate bands. Thus we calculated the parity eigenvalues of the Bloch wave function for the 20 occupied sin-degenerate bands at Γ and M points in the Brillouin zone.

Table S2. Zero-point energy correction (E_{ZPE}), entropy contribution (TS), and the total free energy correction (G-E_{elec}) of the various states for CO₂ electroreduction.

| Species | $E_{ZPE}$ (eV) | TS (eV) | G-E_{elec} (eV) |
|---------|----------------|---------|-----------------|
| H₂      | 0.28           | -0.42   | -0.14           |
| H₂O     | 0.56           | -0.68   | -0.12           |
| CO₂     | 0.31           | -0.66   | -0.35           |
| HCOO    | 0.89           | -0.89   | 0.00            |
| H       | 0.13           | -0.61   | -0.48           |
| CO      | 0.59           | -0.23   | 0.36            |
| *COOH   | 0.59           | -0.25   | 0.34            |
| *OCHO   | 0.59           | -0.25   | 0.34            |
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