Controllable CO$_2$ electrocatalytic reduction via ferroelectric switching on single atom anchored In$_2$Se$_3$ monolayer

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Efficient and selective CO$_2$ electroreduction into chemical fuels promises to alleviate environmental pollution and energy crisis, but it relies on catalysts with controllable product selectivity and reaction path. Here, by means of first-principles calculations, we identify six ferroelectric catalysts comprising transition-metal atoms anchored on In$_2$Se$_3$ monolayer, whose catalytic performance can be controlled by ferroelectric switching based on adjusted d-band center and occupation of supported metal atoms. The polarization dependent activation allows effective control of the limiting potential of CO$_2$ reduction on TM@In$_2$Se$_3$ (TM = Ni, Pd, Rh, Nb, and Re) as well as the reaction paths and final products on Nb@In$_2$Se$_3$ and Re@In$_2$Se$_3$. Interestingly, the ferroelectric switching can even reanimate the stuck catalytic CO$_2$ reduction on Zr@In$_2$Se$_3$. The fairly low limiting potential and the unique ferroelectric controllable CO$_2$ catalytic performance on atomically dispersed transition-metals on In$_2$Se$_3$ clearly distinguish them from traditional single atom catalysts, and open an avenue toward improving catalytic activity and selectivity for efficient and controllable electrochemical CO$_2$ reduction reaction.

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The ever-rising global energy consumption and its negative impact on the environment are major challenges in front of human beings in the 21st century. Public health is severely threatened by the greenhouse effect due to the excessive fossil fuel usage. It is highly desirable to develop technologies that can convert the greenhouse gas (i.e., CO₂) into sustainable and clean energy sources. Among various possibilities, catalytic reduction of CO₂ into hydrocarbon fuels, which features environmental friendliness, high efficiency, and low cost, has been recognized as one of the most promising approaches. Single atom catalysts (SACs), first proposed for CO oxidation in 2011, offer us excellent candidates to activate and convert CO₂ efficiently when transition metal (TM) atoms are used, because the coexistence of empty and occupied TM d-orbitals can accept lone-pair electrons, and then back-donate these electrons to the antibonding orbitals to weaken the C=O bonds. Notably, two-dimensional (2D) materials serve as promising substrates for atomically dispersed transition metal atoms for CO₂ reduction due to their large surface-to-volume ratios, short carrier diffusion distances, unique electronic properties, and abundant active sites. The catalytic performance of these 2D SACs stems from versatile advantageous characteristics. For example, catalysts with singly dispersed Ni, Co, Cu, Pt, and Pd atoms on graphene, Pt or Pd atom anchored on C₆H₅, V-β₁₂ boron monolayer, and Co decorated metal–organic frameworks all have shown great potential for CO₂ reduction.

Despite latest advances, there is still plenty of room to improve the catalytic activity and selectivity of CO₂ reduction in order to satisfy large-scale industrial applications. Recent studies have shown that electric polarization plays an important role in determining catalytic activities and selectivities, and can greatly improve the catalytic performance compared with the unpolarized counterparts. For instance, Janus TM dichalcogenides possess better catalytic abilities for water splitting and N₂ fixation, since the catalysis-related properties, including surface stoichiometry, electronic structure, adsorption strengths, and reaction activation energies, can be tuned by the polarization. Moreover, by utilizing the polarization from the substrate, the overpotential of oxygen evolution reaction on TiO₂ surface can be strongly reduced.

Inspired by these recent achievements, we expect that ferroelectrics, viz., materials with switchable ferroelectric polarization, hold promise as efficient catalysts since their unique reversible polarization provides an additional mechanism to adjust empty and occupied d-orbitals of adsorbed metal atoms. The activation of reactants can thus be controlled, while the catalytic properties of the supported metal, such as activity and selectivity, can be tuned. These expectations have been partially confirmed in ABO₃ perovskite ferroelectrics. For instance, reversing the polarization of ferroelectric PbTiO₃ substrate makes CrO₂ monolayer overcome the limiting factor stemming from the Sabatier principle, and thus display excellent catalytic behaviours for both NOx decomposition and CO oxidation. Reorienting the polarization direction of the ferroelectric PbTiO₃ substrate can dramatically change the chemisorption energies of CO, O, C, and N on the PbTiO₃-supported Pt films, and alter the reaction paths of the dissociations. The oxygen evolution reaction activity of TiO₂ film on a ferroelectric SrTiO₃ substrate can be strongly enhanced relative to unsupported TiO₂ due to the presence of dynamic dipoles in response to the charge on the adsorbed species, while the reaction path can be modulated via ferroelectric switching. However, these predictions have not been experimentally realized so far, mainly due to the instability and depolarization in traditional ABO₃ perovskite ferroelectrics when the thickness is smaller than a critical value. Encouragingly, the emergence of 2D ferroelectric materials, exemplified by In₄Se₅, CuInP₂S₆, and SnTe, provides an excellent opportunity to verify controllable catalysis in ferroelectrics. The realization of ferroelectricity at room temperature makes it feasible for 2D ferroelectrics to be used for controllable catalytic CO₂ reduction.

In this work, based on the experimentally available 2D ferroelectrics, we theoretically investigate the potential of using transition metal decorated α-In₄Se₅ monolayers as the ferroelectric SACs toward electrochemical CO₂ reduction. Our efforts identify six catalysts with singly dispersed TM atoms anchored on the 2D ferroelectric substrate, namely α-In₄Se₅ monolayer, with polarization downwards or upwards (denoted as TM@P↓-In₄Se₅ or TM@P↑-In₄Se₅). The switchable polarization can not only alter the reaction barrier and paths of CO₂ reduction, but also lead to different final products. It can even reconvert the stuck CO₂ reduction. These performance improvements stem from the synergistic effects of adjusted empty and occupied d-orbitals (d orbital center) of adsorbed metal atom, polarization dependent electron transfer, and CO₂ adsorption energies under ferroelectric switching. These ferroelectric SACs, catalytic mechanism, and the polarization dependent catalytic CO₂ reduction open an avenue for controllable CO₂ reduction reaction (CO₂RR), and introduce a feasible approach to significantly improve the efficiency of such reactions.

**Results**

**Screening ferroelectric catalysts.** The ferroelectric α-In₄Se₅ monolayer was chosen as the substrate of potential catalysts due to the following reasons: (1) it is the ground-state phase among possible phases (see Supplementary Fig. 1), even in the presence of adatoms and in electrochemical environment (see Supplementary Fig. 2 and Supplementary Tables 1–2), which is consistent with the recent theoretical finding by Ding et al. Note that two α-In₄Se₅ (α and α') phases have been predicted to share similar atomic structures and are almost energetically degenerate, and they have the same CO₂RR performance (Supplementary Fig. 3). We thus mainly focus on α-In₄Se₅ in this study. (2) it is stable at room temperature and has been experimentally synthesized and its ferroelectricity with switchable polarization under room temperature has been explicitly demonstrated. With the polarization locking from the asymmetric arrangement of its quintuple layers (see Fig. 1a, b), their orientations can be reversed by the shift of the middle Se layer. However, as a ferroelectric semiconductor with a sizable band gap (1.46 eV), α-In₄Se₅ monolayer does not have enough electrons to be injected into the antibonding 2π orbital of CO₂ so that the strong sp-hybridization symmetry of the carbon atom can not be disrupted. Thus, the material itself is not suitable as a catalyst for CO₂ reduction, which is corroborated by our theoretical study: upon adsorption on In₄Se₅, the inherent linear O=≡C=O structure of CO₂ molecule is well maintained (see Supplementary Fig. 4 and Supplementary Table 3).

To activate electrochemical CO₂ reduction, we introduced transition metal atoms to decorate α-In₄Se₅ monolayer, which provide extra electrons to break the strong sp hybridization, thus activating the CO₂ molecule. Compared with conventional metal catalysts, SACs normally exhibit higher catalytic performances because of the high ratio of low-coordinated configurations. However, the transition metals have to be screened since only the SACs with well balanced empty/occupied d orbitals can exhibit optimal catalytic performance. To find suitable SACs, 29 transition metal atoms were chosen and chemically adsorbed (see Supplementary Fig. 5) on both surfaces of the In₄Se₅ monolayer, and the energetically most favorable configurations were identified. The possible metal substitutions into the In₄Se₅ monolayer were excluded due to the large formation energy of In vacancy, high diffusion barriers of In
atoms (see Supplementary Fig. 6), and low CO$_2$RR activities (see Supplementary Fig. 7). Then we evaluated all the composites based on two key criteria. First, to ensure the stability of the active site, the single transition metal atom should be steadily adsorbed on the In$_2$Se$_3$ monolayer surface without breaking the underlying structure, and the favourable adsorption site should not change significantly after the polarization switching; second, the single transition metal atom should be able to activate CO$_2$, in other words, the linear structure of O=C=O should be broken after adsorption, at least in one polarization state.

After a comprehensive investigation of the energetically most favorable adsorption configurations (Fig. 1a, b) and their stabilities, we screened out six TM atoms (TM = Ni, Pd, Rh, Zr, Nb and Re) as promising catalysts toward CO$_2$ reduction for further examinations. Other 23 candidates are either unstable or cannot effectively activate CO$_2$ molecules (see details in the Supplementary Information).

**Stability of SACs and polarization dependent d band center.** Although the screened TM@In$_2$Se$_3$ are stable (without structural breaking) and able to activate CO$_2$ molecules, transition metal atoms need to uniformly disperse on the substrate to prevent any aggregation of the deposited atoms and maximize the catalytic efficiency.

To achieve this goal, strong binding strength, high diffusion energy barrier, and negative clustering energy are essential. At the energetically most favorable site, all the six TM atoms have rather strong binding energies (Table 1) that are comparable to previously predicted SACs, indicating sufficiently strong interactions between the metal atoms and the substrate, as evidenced by the strong TM–Se bonds, in other words, the linear structure of O=C=O should be broken after adsorption, at least in one polarization state.

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Table 1 Parameters for the pure TM@In$_2$Se$_3$ and CO$_2$ adsorbed TM@In$_2$Se$_3$: adsorption site ($S_{ad}$), binding energies of TM atom ($E_{b,TM}$ in eV/atom) and CO$_2$ molecule ($E_{b,CO}_2$ in eV/molecule), charge lost from the adsorbed TM atoms ($Q_{TM}$ in e/atom), average TM-Se bond length ($l_{TM-Se}$ in Å), migration barrier ($E_{m,TM}$ in eV), charge gained by the adsorbed CO$_2$ molecule ($Q_{CO}_2$ in e/molecule), and bond angle ($\angle$OCO in $^\circ$).

| Catalysts       | $S_{ad}$ | $E_{b,TM}$ | $E_{b,CO}_2$ | $Q_{TM}$ | $l_{TM-Se}$ | $E_{m,TM}$ | $Q_{CO}_2$ | $\angle$OCO |
|-----------------|---------|------------|-------------|----------|------------|------------|------------|------------|
| Ni@P $\downarrow$ In$_2$Se$_3$ | C       | -2.72      | 1.78        | 0.40     | 2.31       | -1.39      | 0.45       | 146.4      |
| Ni@P $\downarrow$ In$_2$Se$_3$ | C       | -1.97      | 1.41        | 0.37     | 2.37       | -1.08      | 0.40       | 146.5      |
| Pd@P $\downarrow$ In$_2$Se$_3$ | C       | -1.69      | 1.19        | 0.14     | 2.50       | -0.84      | 0.33       | 149.2      |
| Pd@P $\downarrow$ In$_2$Se$_3$ | C       | -1.14      | 0.84        | 0.12     | 2.58       | -0.79      | 0.28       | 151.2      |
| Rh@P $\downarrow$ In$_2$Se$_3$ | I       | -4.09      | 4.19        | 0.12     | 2.38       | -1.05      | 0.40       | 146.5      |
| Rh@P $\downarrow$ In$_2$Se$_3$ | I       | -2.36      | 2.49        | 0.08     | 2.49       | -0.76      | 0.26       | 153.9      |
| Zr@P $\downarrow$ In$_2$Se$_3$ | I       | -6.26      | 6.13        | 2.10     | 2.58       | -0.01      | 0.02       | 179.2      |
| Zr@P $\uparrow$ In$_2$Se$_3$ | I       | -5.01      | 5.06        | 2.03     | 2.61       | -3.39      | 1.13       | 126.2      |
| Nb@P $\downarrow$ In$_2$Se$_3$ | I       | -7.08      | 4.63        | 1.70     | 2.46       | -2.54      | 0.92       | 131.1      |
| Nb@P $\uparrow$ In$_2$Se$_3$ | I       | -4.73      | 4.21        | 1.61     | 2.59       | -2.47      | 0.85       | 134.7      |
| Re@P $\downarrow$ In$_2$Se$_3$ | C       | -2.36      | 5.18        | 0.90     | 2.34       | -2.11      | 0.69       | 134.8      |
| Re@P $\uparrow$ In$_2$Se$_3$ | C       | -1.07      | 3.25        | 0.71     | 2.36       | -2.02      | 0.61       | 136.8      |

and $-0.04$ eV for Pd@P $\downarrow$ In$_2$Se$_3$ and Pd@P $\uparrow$ In$_2$Se$_3$, respectively; see details in SI) indicate that it is not energetically favorable to form clusters on the catalyst surface. In the AIMD simulations, the out-of-plane polarization of ferroelectric In$_2$Se$_3$ monolayer can be well retained, and the metal atom stays anchored at the energetically favorable site even at room-temperature (300 K) for at least 15 ps (see Supplementary Fig. 11a). Besides, AIMD simulations at 300 K are also performed to investigate two dispersely adsorbed Pd atoms on P $\downarrow$ In$_2$Se$_3$ (2 Pd@P $\downarrow$ In$_2$Se$_3$). The two Pd atoms can maintain dispersely adsorbed features without metal clustering and structural phase transition for 15 ps (see Supplementary Fig. 11b). The distance between the two Pd atoms stays almost unchanged (as shown in the inset of Supplementary Fig. 11). The possible metal (e.g. Pd and Nb) agglomerations are excluded by the further kinetic Monte Carlo (kMC) simulations, the clusters will not form at the surface for 100 seconds at the room-temperature (see Supplementary Figs. 12–14). Overall, the strong adsorption energies, high diffusion barriers, negative clustering energies, molecular dynamics simulation, and KMC results all indicate strong stability of the 2D ferroelectric SACs.

Good stabilities of the ferroelectric substrate and the catalysts themselves are key prerequisites to achieve the goal of controllable catalysis. The stability of ferroelectric α-In$_2$Se$_3$ monolayer has been unambiguously demonstrated by our simulations (Supplementary Fig. 1) and also by the recent theoretical and experimental studies,$^{35,36,39,40}$ but stabilities under harsh environments for CO$_2$RR still need to be addressed. To this end, based on the dissolution potential$^{57–59}$ we have evaluated and confirmed the electrochemical stability of our proposed system under acidic conditions (see Supplementary Table 2).

Different from traditional SACs like Pd@C$_3$N$_4$, the switchable polarization in ferroelectric catalysts proposed herein provides an extra degree of freedom to modulate and control catalytic reactivities. The average TM-Se bond length, binding energy, and electron transfer are highly polarization dependent (Table 1). Compared with the corresponding catalysts with upwards polarization, TM@P $\downarrow$ In$_2$Se$_3$ generally have shorter average TM-Se bond length, larger absolute value of binding energy, and more electron transfer, due to the large electrostatic potential difference on In$_2$Se$_3$ as in metal porphyrin molecules.$^{40}$ The balance between empty and occupied d orbitals, caused by the polarization dependent electron transfer, significantly affect the catalytic activity of TM@In$_2$Se$_3$. Taking Pd@In$_2$Se$_3$ as an example, the charge is redistributed between the Pd and Se atoms (see Fig. 11), and the d orbitals of Pd atom is depleted. Compared with Pd@P $\downarrow$ In$_2$Se$_3$, more electron transfer occurs in Pd@P $\downarrow$ In$_2$Se$_3$, shifting the Pd-d orbitals to higher energy closer to the Fermi level. As illustrated in Fig. 1c, the d band center of Pd@P $\downarrow$ In$_2$Se$_3$ (−1.45 eV) is higher than that of Pd@P $\downarrow$ In$_2$Se$_3$ (−4.13 eV), indicating that Pd@P $\downarrow$ In$_2$Se$_3$ possesses better catalytic ability.$^{40}$ Similar phenomena occur in the other five TM@In$_2$Se$_3$ catalysts (see Fig. 1c) under the same mechanism: the d band center of the TM atom is closer to the Fermi level when it is placed on P $\downarrow$ In$_2$Se$_3$. Note that the position differences of the d band center under opposite polarizations for TM@In$_2$Se$_3$ (TM = Nb, Re) are rather pronounced, while such differences for TM@In$_2$Se$_3$ (TM = Ni, Pd and Rh) are only moderate. These contrasting results imply that both reaction paths and barriers are affected by the polarization (see a detailed catalytic classification below). Considering that the localized electronic states near the Fermi level lead to high N$_2$ catalytic activity in the catalyst Co$_2$@GDY (cobalt dimer-anchored graphdiyne)$^{39}$, we expect that the modulation of the electronic structure of TM@In$_2$Se$_3$ caused by the polarization switching has a major influence on the subsequent CO$_2$ hydrogenation process.

Since the catalytic activity of the TM@In$_2$Se$_3$ systems is polarization dependent, the effective ferroelectric switching of TM@In$_2$Se$_3$ is essential to achieve controllable catalytic reduction. We reverse the polarization orientation of Pd@In$_2$Se$_3$ (as a typical example, see Supplementary Figs. 15 and 16) via a three-step concerted mechanism on the most effective kinetic path.$^{38}$ We find that the energy barrier of the polarization switching after Pd decoration is 0.29 eV/UC (0.15 eV/UC) for P $\downarrow$ to P $\uparrow$ (P $\downarrow$ to P $\uparrow$), which is slightly larger than the value for the bare ferroelectric layer (0.13 eV/UC), but it is still accessible to experimental manipulation.$^{38}$ It is noted that the ferroelectric switching behaviors are not significantly affected by the metal adsorption. Although the local area of metal anchoring site is metallized due to the hybridization between the metal and surrounding Se atoms, the semiconducting feature of the whole substrate and the associated ferroelectricity can be well preserved (see Supplementary Fig. 17). Considering that the out-of-plane ferroelectric switching of thin In$_2$Se$_3$ flakes has been experimentally achieved,$^{50}$ it should be feasible to achieve similar polarization orientation reversal in TM@In$_2$Se$_3$ systems.

**Tunable activation of CO$_2$ by polarization switching.** Effective activation of CO$_2$ molecule is the key for the subsequent reduction. Based on the structural analysis, almost all the TM@In$_2$Se$_3$ catalysts could effectively activate CO$_2$ molecule (see Fig. 2 and
Supplementary Fig. 18) by forming the bidentate C-TM-O species. The only exception is Zr@P ↓-In2Se3, where the linear O= C=O structure is well preserved (only bent by 0.8°) because of the monodentate TM-O configuration. Moreover, the binding energies of the catalysts with the activated CO2 molecule (−3.39 to −0.76 eV; see Table 1) are comparable to the reported catalysts.61,62 The strong hybridization of O π and TM d orbitals and the significant charge transfer between TM@In2Se3 and CO2 ensure the inert molecule chemically captured (see Fig. 2b, d, and Supplementary Fig. 19). Note that the degree of CO2 activation on two opposite surfaces are obviously different as seen from the angles of ∠OCO (see Table 1), which are generally smaller when the molecule is adsorbed on the surface with polarization downwars. Meanwhile, the activation degree of CO2 on TM@In2Se3 (TM = Nb, Re) is significantly higher than that on TM@In2Se3 (TM = Ni, Pd, Rh), as indicated by the larger binding energies (−3.39 to −2.02 eV vs −1.39 to −0.76 eV), more electron transfer (0.61 to 0.92 e vs 0.26 to 0.45 e), and smaller angles of ∠OCO (131.1° to 136.8° vs 146.4° to 151.2°).

The distinct behaviours on different ferroelectric surfaces are attributed to the mechanism of CO2 catalytic activation, namely coexistence of charge depletion and accumulation between the TM atoms and CO2 molecules. The empty TM d orbital could accept electrons from the highest occupied molecular orbitals (∑σ↓ orbital) of the CO2 molecule, while the occupied TM d orbital could back-donate electrons to the lowest unoccupied molecular orbitals (∑π↑ orbital) of the CO2 molecule (Fig. 2e). As indicated in Fig. 2b and d, the d orbital occupations of TM atoms on the ferroelectric In2Se3 layer can be effectively modulated by the switchable polarization. The synergy of electron acceptance, back donation, and polarization dependent d orbital occupation ensures that CO2 can be efficiently activated, while the activation degree is ferroelectric controllable in TM@In2Se3 catalysts.61 For example, while isolated Pd atom has fully occupied d orbitals (4a10), upon adsorption on the In2Se3 substrate, the Pd atom loses partial d electrons to form the Pd-Se bond, and the resulting empty Pd d orbitals provide channels for electron acceptance and back donations to activate CO2 molecules. Compared with other TM@In2Se3 catalysts, where the TM atoms have intrinsic partially occupied d orbitals, Pd@In2Se3 catalyst has a lower degree of CO2 activation as indicated by the relatively larger ∠OCO and smaller charge transfer (see Table 1). Furthermore, for TM@In2Se3 under polarization switching, the density of states (DOS) variations are more evident than the CO2 binding energy and electron transfer. This is due to the fact that the DOS variation is directly related with the orbital shift under the polarization flip, such as the d band center, as seen in Fig. 1c, while the charge transfer and the CO2 binding energy are mainly related to the itinerant electrons induced by the polarization.

**Selectivity for CO2RR vs HER.** As an important competing side reaction, hydrogen evolution reaction (HER) may significantly restrain the Faradaic efficiency of CO2RR by consuming proton–electron pairs from the electrolyte solution.63 To check if CO2RR is more favourable, we first calculated Gibbs free energy changes (ΔG) at the first hydrogenation step of CO2RR (*+CO2 + H+ +e− → OCHO*) and HER (* + H+ + e− → H2*). According to the Brønsted–Evans–Polanyi relation, reactions with lower ΔG have smaller reaction barriers and hence are kinetically more favoured. As shown in Supplementary Fig. 20, for the first hydrogenation step of CO2RR, Rh@In2Se3, Pd@In2Se3, and Re@P ↑-In2Se3 prefer to form carboxyl (OCHO*), while Ni@In2Se3, Nb@In2Se3, and Re@P ↑-In2Se3 tend to produce formate (*OCHO*). Since CO2 molecule cannot be activated on Zr@P ↓-In2Se3, it is not considered here. The Gibbs free energy changes

![Fig. 2 Tunable activation of CO2 by polarization switching.](https://doi.org/10.1038/s41467-021-25426-5) The differential charge density plots and partial density of states of CO2 adsorbed on Pd@In2Se3 (a, b) for Pd@P ↓-In2Se3, and c, d for Pd@P ↑-In2Se3). e Simplified schematic diagrams of CO2 bonding to transition metals.

![Fig. 3 Selectivity for CO2RR vs HER.](https://doi.org/10.1038/s41467-021-25426-5) Gibbs free energy changes (ΔG) of initial protonation of CO2RR vs. HER on TM@In2Se3 (TM = Ni, Pd, Rh, Zr, Nb and Re). Data points in the purple region denote higher selectivity toward CO2RR, while those in the blue region toward HER. Black and red symbols stand for ΔG(OCHO*) vs ΔG(H*) and ΔG(OCHO*) vs ΔG(H+), respectively.
(Fig. 3) indicate that all the screened TM@In$_2$Se$_3$ catalysts have a higher selectivity toward CO$_2$RR. These results demonstrate the feasibility of using TM@In$_2$Se$_3$ catalysts as cathodes for CO$_2$RR with a high Faradaic efficiency.

**Tunable CO$_2$RR by polarization switching.** As a result of polarization dependent $d$ band center (see Fig. 1c), CO$_2$ molecules are activated to different degrees depending on the ferroelectric surfaces. It is thus expected that the reaction barrier, reaction path, and even the intermediate/final product of CO$_2$ reduction will be polarization dependent and controllable via ferroelectric switching.

Considering the complexity of CO$_2$ reaction, we comprehensively searched the minimum energy reaction paths of CO$_2$RR on each TM@In$_2$Se$_3$ (TM = Ni, Pd, Rh, Zr, Nb and Re) catalyst (Supplementary Fig. 20). Table 2 summarizes the effects of the polarization switching on the CO$_2$RR, from the aspects of potential determining steps, limiting potential ($U_l$), and final product.

Tunable limiting potential of CO$_2$RR (on TM@In$_2$Se$_3$, TM = Ni, Pd, Rh). Since the activation degree of CO$_2$ on the ferroelectric surface depends on polarization direction due to the adjusted empty and occupied $d$-orbitals (shifted $d$ band center), the reaction barrier of the CO$_2$ hydrogenation process is also affected. Taking the Rh@In$_2$Se$_3$ catalyst as an example (see Fig. 4a), though the configurations of activated CO$_2$ (with C atom connecting with Rh atom) under different polarization directions are the same, the energy barriers are obviously different: the reaction of CO$_2^* \rightarrow$ OCOH$^*$ is downhill on Rh@P ↑ -In$_2$Se$_3$, but uphill on Rh@P ↓ -In$_2$Se$_3$. In the subsequent hydrogenation steps, the polarization reversal does not change the most favourable path of CO$_2$RR, both following the paths of CO$_2^* \rightarrow$ OCOH$^* \rightarrow$ CO$^* \rightarrow$ CHO$^* \rightarrow$ CH$_2$O$^* \rightarrow$ CH$_2$OH$^* \rightarrow$ CH$_3$OH$^* \rightarrow$ OH$^* \rightarrow$ H$_2$O$^*$, with the final product of CH$_4$. However, the reaction barrier for each step, the potential-determining step

### Table 2 Potential determining steps (PDS), limiting potentials ($U_l$ V vs RHE), and final product of CO$_2$RR with TM@In$_2$Se$_3$ catalysts.

| Catalyst | PDS | $U_l$ | Product |
|----------|-----|-------|---------|
| Ni@P ↓ -In$_2$Se$_3$ | HOCHO$^*$→CHO$^*$ | -0.36 | CH$_4$ |
| Ni@P ↑ -In$_2$Se$_3$ | HOCHO$^*$→CHO$^*$ | -0.47 | CH$_4$ |
| Pd@P ↓ -In$_2$Se$_3$ | CO$^*$→CHO$^*$ | -0.77 | CH$_4$ |
| Pd@P ↑ -In$_2$Se$_3$ | CO$^*$→CHO$^*$ | -0.87 | CH$_4$ |
| Rh@P ↓ -In$_2$Se$_3$ | CHO$^*$→CH$_2$O$^*$ | -0.26 | CH$_4$ |
| Rh@P ↑ -In$_2$Se$_3$ | CHO$^*$→CH$_2$O$^*$ | -0.43 | CH$_4$ |
| Zr@P ↓ -In$_2$Se$_3$ | HOCHO$^*$→CHO$^*$ | -2.33 | CH$_4$ |
| Re@P ↓ -In$_2$Se$_3$ | OH$^*$→H$_2$O$^*$ | -0.60 | CH$_3$OH |
| Re@P ↑ -In$_2$Se$_3$ | COH$^*$→C$^*$ | -0.85 | CH$_4$ |
| Nb@P ↓ -In$_2$Se$_3$ | OH$^*$→H$_2$O$^*$ | -0.64 | CH$_3$OH |
| Nb@P ↑ -In$_2$Se$_3$ | OCHO$^*$→HOCHO$^*$ | -0.58 | HOCHO |

![Fig. 4 CO$_2$RR paths on Rh@In$_2$Se$_3$ and Zr@In$_2$Se$_3$.](image-url) The free-energy profile for the CO$_2$ electrochemical reduction reactions along the minimum energy path at 0 V (vs. RHE) on a Rh@In$_2$Se$_3$ and b Zr@In$_2$Se$_3$. The insets show the optimized configurations of the intermediates. The pink (light blue) shaded area indicates the catalytic reaction when the polarization is pointing upwards (downwards). This color scheme is also used in Fig. 5.
Reactivating stuck catalytic reaction of CO2RR (on Zr@In2Se3).

Zr@P ↓ -In2Se3 cannot activate CO2 molecules, it is thus unsuitable for CO2 reduction. In contrast, CO2 can be activated on Zr@P ↑ -In2Se3 with two oxygen atoms bridging over Zr atom (Supplementary Fig. 18i, j). With more protons, it follows the subsequent hydrogenation steps, the hydrogenation step is spontaneously, in contrast to the 0.36 eV energy barrier for the dehydration process on Zr@P ↓ -In2Se3.

Since polarization can modulate interaction strength as indicated above, it is expected that the binding strength of the intermediate HOCHO* can be weakened when the polarization direction of In2Se3 is reversed, so that the catalytic reduction can proceed. Indeed, we found that when polarization direction is reversed from up to down at this step, the barrier decreases ($\Delta G = 0.61$ eV for the reduction of HOCHO* to CHO* on Zr@P ↓ -In2Se3). More importantly, HOCHO* on the Zr@P ↓ -In2Se3 is merely 40 meV higher than that on Zr@P ↑ -In2Se3, which indicates that the polarization switching is relatively easy to achieve. The conclusion holds true under dilute Zr concentration, while the local ferroelectric switching around HOCHO* is prohibited due to the higher energy barrier (see Supplementary Fig. 22). Additionally, according to the subsequent hydrogenation steps, the $U_f$ for Zr@P ↓ -In2Se3 is $-0.77$ V vs. RHE, which is significantly lower than that for Zr@P ↑ -In2Se3 ($-2.33$ V vs. RHE). Moreover, the H2O* at Zr@P ↓ -In2Se3 could be removed spontaneously, in contrast to the 0.36 eV energy barrier for the dehydration process on Zr@P ↓ -In2Se3.

Therefore, though CO2 molecule cannot be activated on Zr@P ↓ -In2Se3 for reduction, the polarization reversal can reactivate the catalytic reduction on Zr@P ↓ -In2Se3 with a reasonable limiting potential. During the hydrogenation process, appropriate polarization switching could either reinitiate the CO2 reduction or accelerate the reaction rate by reducing the reaction barriers.

Tuning CO2RR path and final product (on Nb@In2Se3 and Re@In2Se3). In contrast to the aforementioned TM@In2Se3 (TM = Ni, Pd, Rh), the activations of CO2 molecule are much deeper on Nb@In2Se3 and Re@In2Se3, as evidenced by the smaller bond angle $\angle OCO$ (Table 1), much larger $E_b$-CO2 values (2.02-2.54 eV), and more pronounced charge transfer between CO2 and the catalyst ($Q$-CO2, 0.61-0.92e). The huge differences of $d$ band center ($-2.52$ to $-2.52$ eV at P ↓; $-7.03$ → $-6.72$ eV at P ↑, see Fig. 1c) render the catalytic reaction more sensitive to the
polarization switching, leading to different reaction paths and even different final products according to the Sebastian principles. Indeed, the polarization switching in the catalysts of Nb@In2Se3 and Re@In2Se3 could partially or even totally alter the CO2RR path, thus leading to the different final products. As illustrated in Fig. 5a, for CO2RR on Re@P ↑-In2Se3 catalyst, the minimum energy path is $\text{CO}_2^{*} \rightarrow \text{OCHO}^{*} \rightarrow \text{OCHOH}^{*} \rightarrow \text{HOCOO}^{*} \rightarrow \text{OOH}^{*} \rightarrow \text{H}_2\text{O}^{*}$, the final product is methane, and the PDS is $\text{OH}^{*} \rightarrow \text{H}_2\text{O}^{*}$ with $U_l$ of 0.65 eV; In sharp contrast, the reaction paths on Re@P ↑-In2Se3 is $\text{CO}_2^{*} \rightarrow \text{COOH}^{*} \rightarrow \text{CO}^{*} \rightarrow \text{CO}^{*} \rightarrow \text{CH}^{2*} \rightarrow \text{CH}_3^{*}$ with $U_l$ of 0.85 eV. Similar CO2RR phenomena were also observed on Nb@In2Se3 catalyst. The most favourable path on Nb@P ↑-In2Se3 surface is $\text{CO}_2^{*} \rightarrow \text{OCHO}^{*} \rightarrow \text{OCHOH}^{*} \rightarrow \text{HOCOO}^{*} \rightarrow \text{OOH}^{*} \rightarrow \text{H}_2\text{O}^{*}$, producing methanol with $U_l$ of 0.64 eV; in comparison, the $\text{CO}_2^{*} \rightarrow \text{OCHO}^{*} \rightarrow \text{HOCHO}^{*}$ path on Nb@P ↑-In2Se3 produces methanoic acid with $U_l$ of 0.58 eV (Fig. 5b).

Note that selective generation of desired chemical fuel products has been pursued in the development of electrochemical CO2RR catalyst over decades5, our strategies via feasible ferroelectric switching can achieve the goal without complex and high-cost steps that use different catalysts or electrolytes to produce desired fuels67–70. As shown in Fig. 6, our proposed ferroelectric SACs base on experimentally available In2Se3 and unique polarization dependent catalytic performance thus open an avenue for controllable CO2 reduction.

Figure 6 Schematic diagram of ferroelectric controllable CO2RR. Here, metal anchored α-In2Se3 monolayer is placed between the electrodes to achieve ferroelectric switching and controllable catalysis, tuned by the reversal of the bias direction.

Discussion

In conclusion, by comprehensive DFT computations, we have screened out six TM@In2Se3 (TM = Ni, Nb, Pd, Re, Rh and Zr) as effective ferroelectric catalysts for electrochemical CO2RR. We reexamined the chemical reactions by using larger supercells (TM@4 × 4 or 6 × 6 In2Se3, Supplementary Fig. 24) or different exchange functions (PBE + U or RPBE; Supplementary Figs. 25 and 26). All these approaches lead to the same conclusion about the ferroelectric controlled CO2 reduction, with the key numerical results only slightly different, indicating the robustness of our conclusion. More details of the simulations can be found in the Supplementary Information.

Data availability

Source data are provided with this paper. The data used in this study are presented in the text and Supplementary Information. Additional data and information are available from the corresponding author upon reasonable request. Source data are provided with this paper.

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Author contributions

L.K. proposed, designed the project and organized the paper. L.J. and X.T. conducted the simulations, data analyses and wrote the manuscript. L.J. and X.T. made equal contributions to the work. X.M., Y.G., S.S., A.D., Z.C. and C.C. contributed to the discussion of results and manuscript revision.

Competing interests

The authors declare no competing interests.

Additional information

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