Atomic layer confined vacancies for atomic-level insights into carbon dioxide electroreduction

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The role of oxygen vacancies in carbon dioxide electroreduction remains somewhat unclear. Here we construct a model of oxygen vacancies confined in atomic layer, taking the synthetic oxygen-deficient cobalt oxide single-unit-cell layers as an example. Density functional theory calculations demonstrate the main defect is the oxygen(II) vacancy, while X-ray absorption fine structure spectroscopy reveals their distinct oxygen vacancy concentrations. Proton transfer is theoretically/experimentally demonstrated to be a rate-limiting step, while energy calculations unveil that the presence of oxygen(II) vacancies lower the rate-limiting activation barrier from 0.51 to 0.40 eV via stabilizing the formate anion radical intermediate, confirmed by the lowered onset potential from 0.81 to 0.78 V and decreased Tafel slope from 48 to 37 mV/dec. Hence, vacancy-rich cobalt oxide single-unit-cell layers exhibit current densities of 2.7 mA cm\(^{-2}\) with ca. 85% formate selectivity during 40-h tests. This work establishes a clear atomic-level correlation between oxygen vacancies and carbon dioxide electroreduction.
Motivated by the increasing trepidations about CO₂-induced global warming and depletion of the finite fossil fuel resources, developing renewable energy alternatives epitomizes one of the major scientific challenges for the twenty-first century. In this current scenario, electrochemical CO₂ reduction into hydrocarbon fuels is considered as a potentially ‘clean’ approach for attaining fuels and bulk chemicals that are usually derived from oil or natural gas. Electro catalytic CO₂ reduction mainly encompasses of the following elementary steps: (1) CO₂ adsorption on active sites; (2) activation of CO₂ to form CO₃²⁻ or HCO₃⁻ or other intermediates; (3) dissociation of C=O bond comprising the participation of protons and electron transfer (one, two or multiple electron process); (4) desorption of reduced products from the active sites. In relation to these, the most critical bottleneck in developing efficient CO₂ electroreduction lies in the chemical activation of CO₂ (refs 4,9), which usually entails high overpotentials and instigates the formation of excess competitive reduction products such as H₂, thus bringing about in low energetic efficiency and poor product selectivity. Therefore, lowering the activation energy barrier of CO₂ holds the key to a major breakthrough in electrocatalytic CO₂ reduction.

Recently, oxygen vacancies in oxides have been reported to promote CO₂ activation and dissociation processes by means of tailoring their electronic structures, charge transport and surface properties. The presence of oxygen vacancies decorates the surface as electron-rich, while the excess electrons indulge CO₂ adsorption and activation. For instance, Zapot et al. demonstrate that the reduced (101) surface of anatase TiO₂ is considerably more auspicious for CO₂ adsorption accompanying charge transfer to CO₂ molecules for forming CO₂⁻ species in comparison with the oxidized surface. In addition, Li et al. report that the formed CO₂⁻ intermediate could be spontaneously dissociated into CO even in the dark on a partially oxygen-depleted Cu(1)/TiO₂₋ₓ surface. However, to date, atomic-level comprehensions on the role of oxygen vacancies during CO₂ reduction is still at infant stage. This is primarily credited to the following two reasons: (1) oxygen vacancies are usually present on the interior of catalysts rather than on the surface, and hence they may possibly not effectively embroil the catalytic reactions; and (2) the presence of abundant microstructures such as interface, and capping agents, could adversely affect or cover the effect of oxygen vacancies on CO₂ reduction activity. To gain in-depth atomic-level understanding on the correlation between oxygen vacancies and CO₂ reduction property, it would be rather vital to simplify the catalyst model and conduct it with the real catalyst containing oxygen vacancies.

Herein, we initially construct an ideal and simple model of intact oxide-based atomic layer and hence deliberately create oxygen vacancies on the surface, with efforts to disclose atom-level insights between oxygen vacancies and CO₂ reduction catalysis. The atomic thickness not only favours building clear atomic structure, but also enables the majority of oxygen vacancies distribution on the surface. In this regard, a model of Co₃O₄ atomic layer with oxygen vacancies would be a promising candidate, thanks to its wide applications in catalysis as well as its environmental friendliness, abundance of reserves and favourable thermal stability. However, for non-layered compounds, especially for cubic Co₃O₄ without anisotropy, fabrication of its atomic layer is particularly a daring task owing to the hard breakage of strong in-plane bonds and the lack of intrinsic driving force for two-dimensional anisotropic growth, let alone the designed synthesis of Co₃O₄ atomic layer with well-controlled oxygen vacancies.

**Results**

Characterizations for Co₃O₄ single-unit-cell layers. To achieve the above important goal, V-rich and V-poor Co₃O₄ single-unit-cell layers were successfully fabricated via a lamellar inorganic–organic hybrid intermediate strategy (Fig. 1a). Initially, a lamellar Co(CO₃)₀.5(OH)·0.11H₂O–CTAB hybrid was synthesized via a self-assembly process between Co(acac)₃ and CTAB, in which the ordered mesostructure was verified by the corresponding small-angle X-ray diffraction pattern obtained at 180 °C for 12 h (Supplementary Fig. 1a). With the reaction time extending to 20 h, the lamellar Co(CO₃)₀.5(OH)·0.11H₂O–CTAB hybrid gradually self-exfoliates into the ultrathin Co(CO₃)₀.5(OH)·0.11H₂O layers, confirmed by the corresponding X-ray diffraction, transmission electron microscopy (TEM) and atomic force microscopy (AFM) characterizations in Supplementary Fig. 1. Then, the following fast-heating process in distinct air and O₂ atmospheres resulted in the successful formation of Co₃O₄ single-unit-cell layers with different concentrations of oxygen vacancies. Taking the products obtained at 320 °C for 5 min in air as an example, their X-ray diffraction pattern for the accumulated powder sample could be readily indexed to cubic Co₃O₄ (JCPDS No. 78–1969), further verified by the corresponding Raman spectra (Supplementary Fig. 2a,b). In addition, their X-ray photoelectron spectra (XPS) spectra in Supplementary Fig. 2d,e demonstrated the formation of pure Co₃O₄. Further confirmed by the corresponding infrared spectrum in Supplementary Fig. 2c, indicating the absence of impurities such as CTAB on the surface of the as-obtained sample. TEM image in Fig. 1b reveals their sheet-like morphology, while the nearly transparent feature indicates their ultrathin thickness. The high-resolution TEM image in Fig. 1c illustrates their [001] orientation, while the AFM image and the corresponding height profiles in Fig. 1d,e reveal their average 0.84 nm thickness, which fairly agrees with the thickness of one unit cell along the [001] direction. More importantly, their O 1s core level spectrum in Fig. 2a clearly showed two distinct peaks: one peak at 529.8 eV was deemed as the lattice oxygen, while the other one located at 531.4 eV could be ascribed to the oxygen atoms in the vicinity of an oxygen vacancy. However, their peak area of 531.4 eV is widely different with that calculated at 320 °C for 5 min in the O₂ atmosphere (Fig. 1f–i), which indicates that the ultrathin Co₃O₄ sheets obtained in the air atmosphere possess larger concentration of oxygen vacancies than those obtained in the O₂ atmosphere. Therefore, all the above results proved the successful synthesis of Co₃O₄ single-unit-cell layers with distinct oxygen vacancy concentrations, thus providing the ideal material models to study the relationship between oxygen vacancies and CO₂ reduction activity.

Synchrotron radiation XAFS measurements. To further disclose the distinct oxygen vacancy concentrations in those fabricated Co₃O₄ samples, X-ray absorption fine structure spectroscopy (XAFS) measurements at Co K-edge were carried out at 1W1B station in BSRF (Beijing Synchrotron Radiation Facility, China). As shown by the raw Co K-edge EXAFS data in Supplementary Fig. 3, the post-edge oscillation amplitude for the V-rich Co₃O₄ single-unit-cell layers exhibited obvious differences in comparison with the V-poor Co₃O₄ single-unit-cell layers and bulk counterpart, further confirmed by their corresponding Co K-edge k²|γ(k)| oscillation curve and Fourier transformed k²|γ(k)| functions (Fig. 2b,c), qualitatively revealing their distinct local atomic arrangement. To obtain quantitative structural parameters around Co atoms confined in the Co₃O₄ single-unit-cell layers, a least-squares curve fitting was conducted and the EXAFS data fitting results were shown in Table 1 and Supplementary Fig. 4.
Figure 1 | Preparation and characterization for the V₀-rich and V₀-poor Co₃O₄ single-unit-cell layer. (a) Scheme for the formation of V₀-rich and V₀-poor Co₃O₄ single-unit-cell layer, respectively. Characterization for the V₀-rich Co₃O₄ single-unit-cell layer: (b) TEM image, (c) HRTEM image, (d) AFM image and (e) the corresponding height profiles; the numbers from 1 to 3 in d correspond to the numbers from 1 to 3 in e. Characterization for the V₀-poor Co₃O₄ single-unit-cell layer: (f) TEM image, (g) HRTEM image. (h) AFM image and (i) the corresponding height profiles; the numbers from 1 to 3 in i corresponding to the numbers from 1 to 3 in h. The scale bars in b–d and f–h are 250, 1, 500, 200, 1 and 500 nm, respectively.

Figure 2 | XPS spectra and synchrotron radiation XAFS measurements. (a) O 1s XPS spectra of V₀-rich and V₀-poor Co₃O₄ single-unit-cell layers. (b) Co K-edge extended XAFS oscillation function k²χ(k). (c) The corresponding Fourier transforms FT(k²χ(k)).

For the V₀-poor Co₃O₄ single-unit-cell layers, the coordination numbers for Co-O, Co-Co₁, Co-O₁, Co-Co₂ and Co-O₂ coordinations reduced, while their disorder degrees increased compared with bulk counterpart, which implied the presence of many dangling bonds as well as an obvious distortion on their surface. The surface distortion in turn helped to endow them with excellent structural stability. More importantly, the coordination numbers for Co-O, Co-Co₁ and Co-O₂ coordinations, confined in the V₀-rich Co₃O₄ single-unit-cell layers, further decreased as compared with the V₀-poor Co₃O₄ single-unit-cell layers, while their coordination numbers for Co-Co₂ coordinating did not show any noticeable variation (Table 1).
which indicated the former’s higher concentration of oxygen vacancies. Thus, the EXAFS results clearly demonstrated the distinct oxygen vacancy concentrations in the synthesized two samples of Co$_3$O$_4$ single-unit-cell layers, fairly agreeing with that of the O 1s XPS spectra in Fig. 2a, and the results revealed by inductively coupled plasma atomic emission spectroscopy and titration method (see details in Methods section).

### Electrocatlytic reduction of CO$_2$ into formate.

To give evidences of the correlation between oxygen vacancies and CO$_2$ reduction activity, the potentiodynamic electrochemical behaviours for the V$_o$-rich and V$_o$-poor Co$_3$O$_4$ single-unit-cell layers were investigated in CO$_2$-saturated 0.1 M KHCO$_3$ solution. As shown by the linear sweep voltammetry (LSV) in Fig. 3a, the large cathodic peaks appeared at ca. –0.87 V versus saturated calomel electrode (SCE) could be attributed to the catalytic CO$_2$ reduction, and it was reduced peaks were observed in the corresponding N$_2$-saturated 0.1 M KHCO$_3$ solution. For instance, the V$_o$-rich Co$_3$O$_4$ single-unit-cell layers exhibited a current density of 2.7 mA cm$^{-2}$ at –0.87 V versus SCE, roughly two times as large as that of the V$_o$-poor Co$_3$O$_4$ single-unit-cell layers, strongly demonstrating the significant role of oxygen vacancies in improving CO$_2$ electroreduction activity. It is noticeable that the cathodic reduction peak at ca. –0.87 V versus SCE may be closely related to the reduction of CO$_2$ into formate in the electrolyte. To further pinpoint the reduction products, stepped-potential electrolyses at each given potential for 4 h were performed to quantify the liquid and gas products by $^1$H nuclear magnetic resonance and gas chromatography analysis. The results in Fig. 3b revealed that the V$_o$-rich Co$_3$O$_4$ single-unit-cell layers possessed a maximum faradaic efficiency of 87.6% for producing formate at a moderately negative potential of –0.87 V versus SCE, while the V$_o$-poor Co$_3$O$_4$ single-unit-cell layers showed a faradaic efficiency of 67.3%, further demonstrating the former’s superior selectivity for formate production. Moreover, as shown in Supplementary Fig. 5, both the V$_o$-rich and V$_o$-poor Co$_3$O$_4$ single-unit-cell layers produced the gas products of H$_2$, CO and CH$_4$ with different selectivities at different potentials, in which the faradaic efficiencies of CO and CH$_4$ for the V$_o$-rich Co$_3$O$_4$ single-unit-cell layers were still higher than those of the V$_o$-poor Co$_3$O$_4$ single-unit-cell layers, further confirming the superior activity induced by abundant oxygen vacancies. Importantly, one can also see that at moderate applied potentials, the main CO$_2$ reduction product was the formate for both the V$_o$-rich and V$_o$-poor Co$_3$O$_4$ single-unit-cell layers. In addition, Fig. 3b also illustrates that the V$_o$-rich Co$_3$O$_4$ single-unit-cell layers attained an onset potential of –0.78 V versus SCE, which was smaller than –0.81 V versus SCE for the V$_o$-poor Co$_3$O$_4$ single-unit-cell layers, confirming the high activity of the V$_o$-rich Co$_3$O$_4$ single-unit-cell layers. Furthermore, the LSV curves in N$_2$-saturated 0.1 M KHCO$_3$ solution further indicated that the V$_o$-rich Co$_3$O$_4$ single-unit-cell layers also possessed increased H$_2$O reduction activity relative to the V$_o$-poor Co$_3$O$_4$ single-unit-cell layers, especially at very negative potentials, which in turn implied the higher catalytic activity induced by the abundant oxygen vacancies. Thus, the above results demonstrated that the V$_o$-rich Co$_3$O$_4$ single-unit-cell layers possessed relatively higher activity and selectivity towards CO$_2$ electroreduction into formate compared with the V$_o$-poor Co$_3$O$_4$ single-unit-cell layers.

Table 1 | EXAFS curve-fitting results.

| Sample                  | Path | N   | R (Å) | $\sigma^2$ (10$^{-2}$Å$^2$) | $\Delta E_p$(eV) |
|-------------------------|------|-----|-------|---------------------------|------------------|
| Co$_3$O$_4$ theory      | Co-O | 5.3 | 1.91  | 2.8 ± 0.2                 | 1.8 ± 1.0        |
|                         | Co-Co | 4.0 | 2.85  | 3.0 ± 0.2                 | 2.2 ± 1.0        |
|                         | Co-O | 5.3 | 2.82  | 3.5 ± 0.2                 | 1.8 ± 1.0        |
|                         | Co-Co | 5.3 | 2.82  | 3.5 ± 0.2                 | 1.8 ± 1.0        |
|                         | Co-O | 5.3 | 2.82  | 3.5 ± 0.2                 | 1.8 ± 1.0        |
|                         | Co-Co | 5.3 | 2.82  | 3.5 ± 0.2                 | 1.8 ± 1.0        |
| Bulk Co$_3$O$_4$        | Co-O | 4.6 | 1.91  | 3.5 ± 0.4                 | 1.7 ± 1.0        |
|                         | Co-Co | 4.6 | 1.91  | 3.5 ± 0.4                 | 1.7 ± 1.0        |
|                         | Co-O | 4.6 | 1.91  | 3.5 ± 0.4                 | 1.7 ± 1.0        |
|                         | Co-Co | 4.6 | 1.91  | 3.5 ± 0.4                 | 1.7 ± 1.0        |
| V$_o$-poor Co$_3$O$_4$ single-unit-cell layers | Co-O | 4.2 | 1.89  | 4.0 ± 0.4                 | –2.4 ± 1.0       |
|                         | Co-Co | 4.2 | 1.89  | 4.0 ± 0.4                 | –2.4 ± 1.0       |
|                         | Co-O | 4.2 | 1.89  | 4.0 ± 0.4                 | –2.4 ± 1.0       |
|                         | Co-Co | 4.2 | 1.89  | 4.0 ± 0.4                 | –2.4 ± 1.0       |
| V$_o$-rich Co$_3$O$_4$ single-unit-cell layers | Co-O | 4.2 | 1.89  | 4.0 ± 0.4                 | –2.4 ± 1.0       |
|                         | Co-Co | 4.2 | 1.89  | 4.0 ± 0.4                 | –2.4 ± 1.0       |
|                         | Co-O | 4.2 | 1.89  | 4.0 ± 0.4                 | –2.4 ± 1.0       |
|                         | Co-Co | 4.2 | 1.89  | 4.0 ± 0.4                 | –2.4 ± 1.0       |

Structural parameters around Co atoms extracted from EXAFS curve-fitting for Co$_3$O$_4$ theory, bulk Co$_3$O$_4$ fabricated according to a previous study$^{23}$, V$_o$-rich and V$_o$-poor Co$_3$O$_4$ single-unit-cell layers. During the fitting of bulk Co$_3$O$_4$, its coordination numbers were fixed as the nominal values (that is, the same as that of Co$_3$O$_4$ theory), while the internal atomic distances R, Debye-Waller factor $\sigma^2$, and the edge-energy shifts $\Delta E_p$ were allowed to run freely. The uncertainties in the fitting results for the samples were provided.

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significant criterion to evaluate a catalyst and hence to test the stability of catalyst continuous CO2 reduction at —0.87 V versus SCE was conducted for probing the durability of the above electrocatalysts. The V_0-rich Co3O4 single-unit-cell layers showed negligible decay in the steady-state current density and their Faradaic efficiency for producing formate was always ~85% during the tested period of 40 h (Fig. 3f; Supplementary Fig. 6), suggesting their very favourable stability, further confirmed by their corresponding post-reaction analysis in Supplementary Figs 7 and 8. In contrast, the V_0-poor Co3O4 single-unit-cell layers possessed relatively poor long-term stability with Faradaic efficiency down to ca. 65%.

Discussion

Notably, the promoted CO2 reduction activity and selectivity could be primarily ascribed to the oxygen vacancies confined in Co3O4 single-unit-cell layers, in which the confined oxygen vacancies could serve as the active sites for stabilizing the reduction intermediates and hence lowering the activation energy.
barrier. Here it is suggested that CO₂ molecules are initially adsorbed on the surface of catalysts and hence undergo the following reaction steps during its reduction into formate:

\[ \text{CO}_2(g) + e^- + \rightarrow \text{CO}_2^{*} \]  

(1)

\[ \text{CO}_2^{*} + \text{HCO}_3^- + e^- \rightarrow \text{HCOO}^- + \text{CO}_3^{2-} \]  

(2)

\[ \text{HCOO}^- \rightarrow \text{HCOO}^- + \ast \]  

(3)

where the asterisk denotes a catalytically active site and the whole reaction can be written as

\[ \text{CO}_2(g) + \text{HCO}_3^- + 2e^- \rightarrow \text{HCOO}^- + \text{CO}_3^{2-} \]  

(4)

In other words, the adsorption process of CO₂ molecules plays a vital role in affecting the reduction activity. In this case, the volumetric CO₂ adsorption measurement was carried out, and the results in Fig. 4a revealed that the \( V_o \)-rich Co₃O₄ single-unit-cell layers exhibited a higher CO₂ adsorption capacity than the \( V_o \)-poor Co₃O₄ single-unit-cell layers, indicating that the higher oxygen vacancy concentration allowed for increased CO₂ adsorption. Moreover, the additional electrolysis data provided some insights into the mechanisms underlying CO₂ reduction into formate for the above two samples. As shown in Fig. 4b, the \( V_o \)-rich and \( V_o \)-poor Co₃O₄ single-unit-cell layers possessed the Tafel slopes of 37 and 48 mV dec⁻¹, respectively. Note that the Tafel slopes close to 59 mV dec⁻¹ supported a possible reduction mechanism that involved a chemical rate-determining H⁺ transfer step. To disclose whether the H⁺ transfer was the rate-limiting step, we further performed the electrolyses at a constant applied potential with HCO₃⁻ concentrations ranging from 0.5 to 0.025 M, with KClO₄ added to the electrolyte to maintain ionic strength. As shown by the log([formate]) versus log([HCO₃⁻]) plots in Fig. 4c, the \( V_o \)-rich and \( V_o \)-poor Co₃O₄ single-unit-cell layers exhibited the slopes of 0.92 and 0.90, respectively, indicating approximate first-order dependence of the reaction rate on the concentration of HCO₃⁻. To verify whether the proton donation process from HCO₃⁻ was the rate-limiting step, we performed the corresponding theoretical analysis and the details were shown in Supplementary Methods. The results clearly demonstrated that the reaction rate for formate product showed the first-order dependence on the concentration of HCO₃⁻, only based on the assumption that the second step (2) was the rate-limiting step. The theoretical analysis as well as the experimental results synergistically confirmed that H⁺ donation from HCO₃⁻ was indeed the rate-limiting step for both the \( V_o \)-rich and \( V_o \)-poor Co₃O₄ single-unit-cell layers. In addition, to disclose the surface coverage of possible reaction intermediates, we further conducted the theoretical analysis based on the experimental Tafel slopes and the log([formate]) versus log([HCO₃⁻]) plots in Fig. 4b, c. The results revealed that the \( V_o \)-rich Co₃O₄ single-unit-cell layer has a surface coverage of CO₃^{2-} \( \approx \) 1, while the \( V_o \)-poor Co₃O₄ single-unit-cell layer has a surface coverage of CO₃^{2-} \( \approx \) 0.27.

To further verify the crucial rate-determining step, we performed density functional theory (DFT) method to calculate the full CO₂ catalytic reduction cycle on the two materials. Based on the above XAFS, TEM and AFM results, we first optimized configurations for the model of Co₃O₄ single-unit-cell layers and

![Figure 4](image-url)
found that Co(III) atoms rather than Co(II) atoms were exposed on the surface (Supplementary Fig. 9a,b; Supplementary Tables 1 and 2). In addition, two types of oxygen atoms were distributed on the surface of single-unit-cell layers: the one binds with three Co(III) atoms was named as O(I) and the other binds with two Co(III) atoms and one Co(II) atom was named as O(II). For the oxygen vacancies confined in Co3O4 single-unit-cell layers, the formation energy of O(II) vacancy was smaller by 0.44 eV than that of O(I) vacancy and hence it was expected that $V_{O(II)}$ was the main defect in the $V_o$-rich Co3O4 single-unit-cell layers (Supplementary Fig. 9c,d; Supplementary Table 1). Note that $V_{O(III)}$ was easily recovered by hydroxyls from the dissociation of water molecule in water solution33 and hence the O(II) vacancy model with two hydroxyls was adopted in the following calculations for the $V_o$-rich Co3O4 single-unit-cell layers (Supplementary Figs 10 and 11). As shown in Fig. 5, the free energy potential of each elementary step is calculated and corrected by the equilibrium potential of the whole reaction relative to the normal hydrogen electrode (NHE) (Supplementary Tables 3 and 4). To simulate the real electrochemical surroundings, extra 0.92 e− or 0.62 e− (Supplementary Fig. 12; Supplementary Table 5) was added in calculating the energy of CO2− and HCOO− and catalyst surfaces for $V_o$-poor and $V_o$-rich Co3O4 single-unit-cell layers, respectively. Although it is possible to decouple the proton and electron donations during DFT calculations, it is very difficult to separate the processes in modelling the present system. So, the energy of $(H^+ + e^-)$ was calculated using the computational hydrogen electrode at −0.225 V versus NHE and at this potential the energy of the extra electron is set as 0.225 eV. That is to say, at pH = 6.8 of the present system, the corrected potential is −0.67 V versus SCE, which is the equilibrium potential for the CO2/HCOO− couple6. At equilibrium potential, the produced HCOO− has the same free energy with the reactant. Of note, in Fig. 5, the free energy of reactant CO2 + $(H^+ + e^-) + e^- \rightarrow COO^-$ was set as 0.00 eV on each material, while the free energies of the CO2−, HCOO− intermediate and the product of HCOO− were shifted according to it. The free energy change of the formation of CO2− on the $V_o$-rich Co3O4 single-unit-cell layer is higher than that on the $V_o$-poor single-unit-cell layer, which suggests the former’s lower surface coverage of CO2− according to quasi-equilibrium assumption, fairly agreeing with the above theoretical analysis. Owing to the highest peak along the free energy surface, the formation of HCOO− intermediate binding with two Co(III) atoms through two oxygen atoms with a bidentate configuration on both surfaces (Supplementary Table 4) is the rate-limiting step of the whole reaction, which is further demonstrated by their corresponding Tafel slopes in Fig. 4b, the log((formate) versus log([HCOO−])) plots in Fig. 4c as well as the corresponding theoretical analysis in Supplementary Methods. The energy barrier of the rate-limiting step is reduced by 0.11 eV and the energy barrier of the whole reaction is reduced by 0.03 eV on the $V_o$-rich Co3O4 single-unit-cell layers than that on the $V_o$-poor Co3O4 single-unit-cell layers based on the assumption that the additional energy barrier on top the free energy difference is almost the same for both samples. Compared with the defect free Co3O4 single-unit-cell layers, the presence of O(II) vacancy helped to stabilize the HCOO− intermediate and hence favoured the hydrogenation process. This strongly accounted for their lowered onset potential from 0.81 to 0.78 V versus SCE and decreased Tafel slope from 48 to 37 mV dec−1 for CO2 reduction into formate (Figs 3a,b and 4b), hence accelerating their overall catalytic reduction rate. In addition, the desorption process of HCOO− was exothermic, indicating that the formed HCOO− could be reasonably desorbed from the catalyst surfaces under reductive electrochemical conditions (Supplementary Fig. 13), which would be expected to provide enough space for sustaining the following CO2 reduction reactions. Furthermore, electrochemical impedance spectra in Fig. 4d revealed that the presence of O(II) vacancy led to an improved electric conductivity, which favoured enhanced charge transport in the $V_o$-rich and $V_o$-poor single-unit-cell layers and hence helped to promote their CO2 reduction activity24. As a consequence, theoretical and experimental results both verified that the $V_{O(III)}$ confined in Co3O4 single-unit-cell layers favoured the rate-limiting H+ transfer step via stabilizing the HCOO− intermediate, hence lowering their overall activation energy and definitely accelerating the speed of CO2 reduction catalysis.

In conclusion, oxygen vacancies confined in atomic layers were put forward as an excellent platform for attaining atomic-level insights into the role of oxygen vacancies in CO2 reduction catalysis. $V_o$-rich and $V_o$-poor Co3O4 single-unit-cell layers were first controllably synthesized via a lamellar hybrid intermediate strategy and hence taken as examples to semi-quantify how oxygen vacancies matter in CO2 reduction. EXAFS and XPS results demonstrated the distinct oxygen vacancy concentration in these two samples, while DFT calculations revealed O(II) vacancy was the main defect in the Co3O4 single-unit-cell layers. CO2 adsorption isotherms revealed that the presence of O(II) vacancy facilitated CO2 adsorption, while DFT calculations suggested that it also favoured spontaneous HCOO− desorption, which prevented catalyst deactivation. More importantly, electrokinetic results and theoretical analysis demonstrated that the donation of a proton from HCOO− was a rate-determining step, while DFT calculations disclosed that $V_{O(III)}$ confined in Co3O4 single-unit-cell layers favoured the rate-limiting proton transfer step via stabilizing the HCOO− intermediate, and hence lowered the activation energy barrier from 0.51 to 0.40 eV. This probably accelerated the speed of CO2 reduction, which was further confirmed by their lowered onset potential from 0.81 to

![Figure 5](image-url)
0.78 V versus SCE and decreased Tafel slope from 48 to 0.78 V versus SCE. Briefly, this work gains atomic-level insights into the role of oxygen vacancies in CO2 reduction catalysis through semi-quantifying the relationship among model, structure and performance, holding promise for designing efficient and robust CO2 reduction catalysts.

Methods

Synthesis of ultrathin Co(CO3)2(OH)-0.01H2O layers. In a typical procedure, 600 mg Co(acac)3 (Alfa Aesar) was added into a mixed solution of 60 ml ethylene glycol and 5 ml distilled water for 1 h. The mixture was then transferred into a 100 ml Teflon-lined autoclave, sealed and heated at 180 °C for 1 h. After cooling to room temperature naturally, the mixture was centrifuged, washed with ethanol and water for many times, and then dried in vacuum overnight for further characterization.

Synthesis of V-rich Co3O4 single-unit-cell layers. In a typical procedure, the as-obtained ultrathin Co(CO3)2(OH)-0.11H2O sheets were directly heated at 320 °C for 5 min in air and then cooled to room temperature. The obtained powders were collected for further characterization.

Synthesis of V-poor Co3O4 single-unit-cell layers. In a typical procedure, the as-obtained ultrathin Co(CO3)2(OH)-0.11H2O sheets were directly heated at 320 °C for 5 min in O2 and then cooled to room temperature. The obtained powders were collected for further characterization.

Characterization. TEM images and high-resolution TEM image were performed by using a JEOL-2010 SEM with an acceleration voltage of 200 kV. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Discover diffractometer using Cu Kα radiation (λ = 1.54178 Å). TEM images and high-resolution TEM images were performed by using a JEOL JEM-2010 TEM with an acceleration voltage of 200 kV. A double-crystal monochromator crystals were used to monochromatize the X-ray beam. TEM images were acquired on a JEOL JEM-2011 microscope equipped with a high-resolution field emission gun and a Gatan GIF-TRIO energy dispersive detector. X-ray photoelectron spectroscopy (XPS) spectra and EXAFS analysis.

EXAFS experimental details. An amount of 2 mg sample was homogeneously mixed with 100 mg graphite and hence pressed into circular pellets with a diameter of 10 mm for further EXAFS measurement under ambient conditions. The EXAFS data were collected at the BSRF beamlines at the Stanford Synchrotron Radiation Lightsource (SSRL). A double-crystal monochromator crystals were used to monochromatize the X-ray beam. The K-edge was fixed at 1.54178 Å. The XPS spectra were acquired on a SIGMA Probe ESCA system equipped with a monochromatized Al Kα X-ray source (1486.7 eV). The spectra were analyzed by the CasaXPS software. EXAFS analyses were carried out using IFEFFIT software packages.

Electrochemical measurements. Electrochemical measurements were carried out in a three-electrode system at an electrochemical station (CHI760E). Typically, 15 mg sample and 40 μl Nafion solution (5 wt%) were dispersed in 1 ml water/ethanol (v:v = 1:1). The resulting mixture was sonicated for 1 h to form a homogeneous ink. Then, 40 μl of the dispersion was loaded onto a glassy carbon electrode with 12 mm diameter. For CO2 reduction experiments, LSV with a scan rate of 20 mV s⁻¹ was conducted in 60 ml CO2-saturated 0.1 M HCl solution (the HClO4 electrode was purged with CO2 for 30 min before the measurement.). For carbon dioxide reduction, the LSV with a scan rate of 20 mV s⁻¹ was also conducted in N2-saturated 0.1 M HCl solution. The glassy carbon electrode served as the working electrode. The counter and the reference electrodes were the graphite rod and the SCE reference electrode, respectively. The outlet gases were analysed by gas chromatography (6890A with TDX-01 columns) equipped with thermal conductivity detector. The liquid products were quantified by nuclear magnetic resonance (Bruker AVANCE AV III 400) spectroscopy, in which 0.5 ml electrolyte was mixed with 0.1 ml D2O and 0.03 μl dimethyl sulfoxide (Sigma, 99.99%) was added as an internal standard. The ECSA of the working electrode could be calculated according to the following equation ECSA = Ï‚ where Ï‚ is the specific surface area of the smooth oxide electrode and Rc is the roughness factor of the working electrodes. Notably, S was generally equal to the geometric area of glassy carbon electrode (in this work, S = 1.13 cm²). The roughness factor (Rc) was estimated from the double-layer capacitance of a smooth oxidized surface (60 μm² cm⁻²) using the relation R = C/60μm² cm⁻². The Co was determined by measuring the capacitive current associated with double-layer charging from the scan rate dependence of CVs. For this, the potential window of CVs was sampled from 0.3 to 0.2 V versus SCE (0.1 M Na2SO4 solution). The scan rates were 10, 20, 50, 80, 100, 120 and 150 mV s⁻¹. The Co was estimated by plotting the ΔI (I–Io) at 0.25 V versus SCE against the scan rate, in which the slope was twice that of cp, Tafel slopes for formate production (I = kCp × ln(Cp/C0)). The Faraday efficiency (ηform) was calculated as follows: ηform = 2F × XPSI/C2F × XPSI/(F × I), where F is the Faraday constant.

Element analysis results. To further quantify the CoO ratio of V-rich and V-poor Co3O4 single-unit-cell layers, we further perform the following two methods.

1. Inductively coupled plasma atomic emission spectrometry: an amount of 0.1000 ± 0.0001 g Co3O4 single-unit-cell layers were dissolved into 3 ml HCl (AR), and then 0.3 ml H2O2 (30%, AR) was added into the above solution drop by drop under stirring. After 5 min stirring, the system was heated in a sealed conical flask to totally dissolve the Co3O4, and then cooled down to room temperature naturally. Afterwards, the residual solution was transferred into 25 ml volumetric flask and then diluted with deionized water to 25 ml. Finally, the content of Co in Co3O4 single-unit-cell layers was measured by inductively coupled plasma atomic emission spectrometer. Five independent measurements were conducted for the same samples.

2. Inductively coupled plasma/atomic absorption spectrometry (ICP-AAS): an amount of 0.0001 g Co3O4 single-unit-cell layers were dissolved into 3 ml HCl (AR), and then 0.3 ml H2O2 (30%, AR) was added into the above solution drop by drop under stirring. After 5 min stirring, the system was heated in a sealed conical flask to totally dissolve the Co3O4, and then cooled down to room temperature naturally. Afterwards, the residual solution was transferred into 25 ml volumetric flask and then diluted with deionized water and HCl (AR) to calibration (CHCl = 2 M). Then, 5 ml solution was taken out and poured into a conical flask. The pH of the system was adjusted to 6 with ammonium buffer solution (pH = 10). After that, 50 mg Murexide indicator was added into the mixed system and thereafter EDTA solution (0.01 M) was added drop by drop under stirring till the colour of the mixed system turned from yellow to purple. The Co mass contents of V-rich and V-poor Co3O4 single-unit-cell layers could be obtained from the following equations: Co²⁺ + EDTA → Co[EDTA]²⁻.
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Author contributions

Y.X., Y.F.S. and G.S. conceived and designed the experiments. S.G., X.C.J., X.L.Z. and Q.T.H. performed sample synthesis, characterization and CO2 reduction measurements. Z.T.S. and W.H.Z. carried out the first-principles calculations. W.L., T.Y. and S.Q.W. analysed the XAFS data. All authors contributed to data analysis and writing of this manuscript.

Additional information

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