



Oxygen evolution reaction over catalytic single-site Co in a well-defined brookite TiO₂ nanorod surface

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Efficient electrocatalysts for the oxygen evolution reaction (OER) are paramount to the development of electrochemical devices for clean energy and fuel conversion. However, the structural complexity of heterogeneous electrocatalysts makes it a great challenge to elucidate the surface catalytic sites and OER mechanisms. Here, we report that catalytic single-site Co in a well-defined brookite TiO₂ nanorod (210) surface (Co-TiO₂) presents turnover frequencies that are among the highest for Co-based heterogeneous catalysts reported to date, reaching 6.6 ± 1.2 and $181.4 \pm 28 \text{ s}^{-1}$ at 300 and 400 mV overpotentials, respectively. Based on grand canonical quantum mechanics calculations and the single-site Co atomic structure validated by in situ and ex situ spectroscopic probes, we have established a full description of the catalytic reaction kinetics for Co-TiO₂ as a function of applied potential, revealing an adsorbate evolution mechanism for the OER. The computationally predicted Tafel slope and turnover frequencies exhibit exceedingly good agreement with experiment.

The oxygen evolution reaction (OER) is an important reaction and often a limiting step in many electrochemical devices that hold great potential for clean energy conversion and fuel transformation, such as water electrolyzers^{1–3}, rechargeable metal–air batteries^{4,5} and electrochemical synthesizers^{6,7}. There has been extensive effort over the past decade in the search for new OER catalysts that exhibit the required activity, durability and selectivity^{8–10}. Many catalytic materials with impressive catalytic performances in alkaline electrolytes have been studied, including layered double hydroxides^{8,11,12}, perovskites^{9,13,14}, spinel metal oxides^{15,16} and carbon materials^{17,18}. However, most heterogeneous catalysts studied thus far have non-uniform physical dimensions (morphology, structure and composition) and surface arrangements (facets), making it difficult to refine the structures of the most active surface catalytic sites to serve as synthetic targets^{12,17,19}. This same issue has obstructed accurate mechanistic studies that might provide a greater understanding of OER catalysis to enable new strategies for the development of improved catalysts. Therefore, the two unanswered questions critical to heterogeneous OER catalysis are how to identify and construct well-defined catalytic centres for efficient OER catalysis, and how to delineate unambiguously the atomistic mechanism and kinetics of the OER and competing reactions at this centre.

Recent advances in full solvent quantum mechanics (QM) and metadynamics^{20,21} methods have made it possible to simulate and determine the atomistic reaction mechanisms and free-energy reaction barriers ($\Delta G^\ddagger$) for electrocatalytic reactions. For example, our QM metadynamics calculations of the oxygen reduction reaction

on the Pt (111) surface led to a predicted $\Delta G^\ddagger$ within 0.05 eV of experiment²². For the CO reduction reaction over Cu (100)^{23,24}, our calculations predicted that the difference in the barrier for ethanol production compared with that for ethene is 0.06 eV, which is in agreement with the subsequent experimental validation of 0.066 eV. These calculations established that this level of QM calculations (density functional theory with PBE-D3) can achieve an accuracy of 0.05 eV or better in reaction free-energy barriers not only in gas/solid interfacial systems^{25–27}, but also in liquid/solid conditions^{23,28–30}.

However, to correlate directly with experiment, we must describe all reaction steps at the same applied potential, including reactants, transition states and products. To achieve this, we recently developed the grand canonical QM (GCQM) method in which the applied potential is kept constant rather than the number of electrons as in usual QM calculations³¹. This GCQM method has been applied to the OER over IrO₂ (110)²⁹ and Fe-doped γ -NiOOH (ref. ³⁰) systems, predicting a potential for 10 mA cm^{−2} within 0.05–0.10 V of experiment. It has also been used for in silico prediction of new OER catalysts³². Despite this progress, the uncertainty surrounding the use of these theoretical OER results stems from the fact that we do not have direct experimental evidence of the surface structure of the catalyst.

Here, we report the seamless integration of the controlled synthesis of nanocrystals with well-defined catalytic single sites and GCQM calculations demonstrating a detailed validation of the theory against experiment for the kinetics of the OER. The model catalyst chosen was Co-doped TiO₂ brookite-phase nanorods (Co-TiO₂) with primarily (210) surface facets. In this catalyst,

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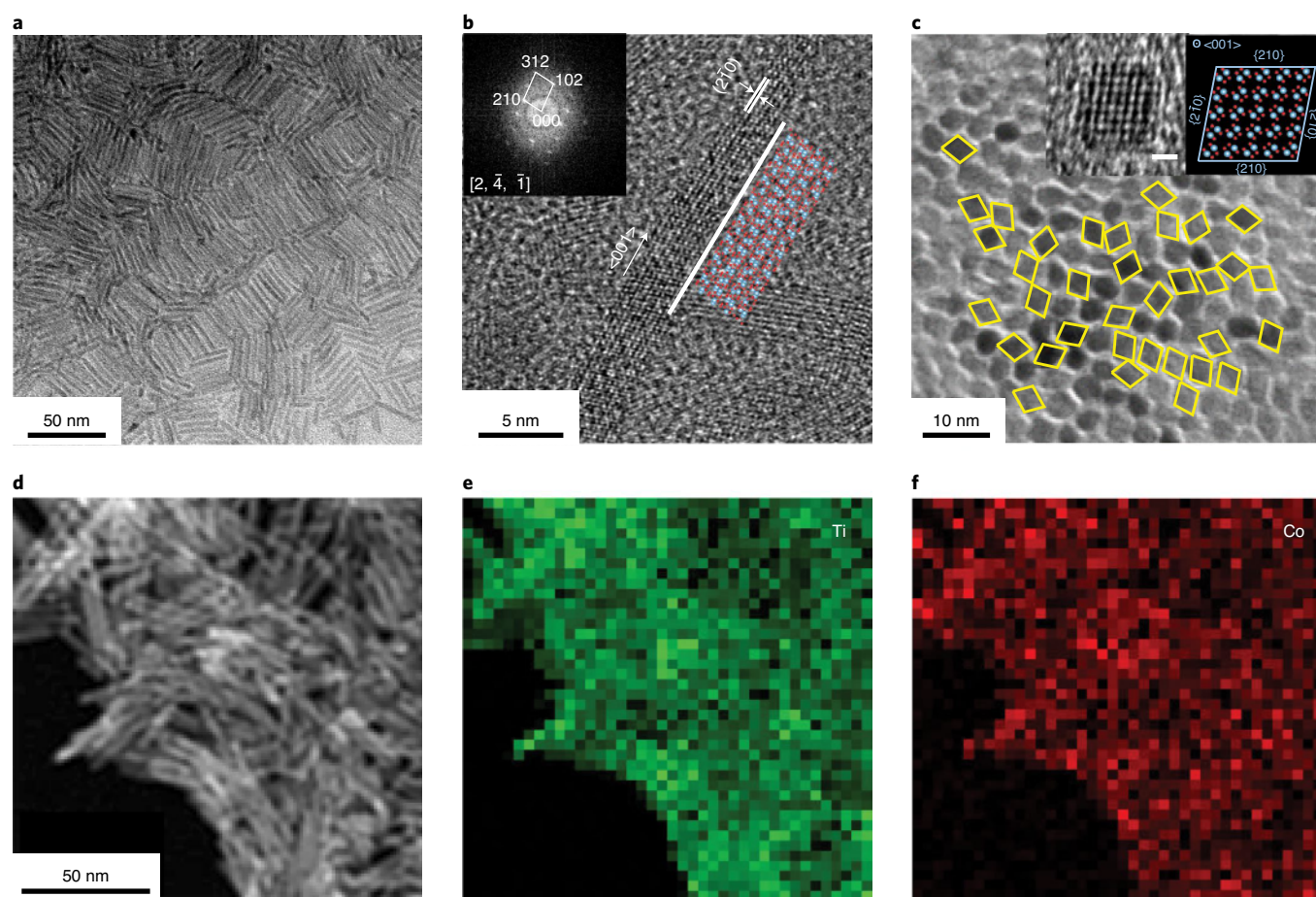


Fig. 1 | Morphology and structure characterization of Co-TiO₂ nanorods. **a**, TEM image of as-synthesized Co-TiO₂ nanorods (12% Co). **b**, Representative HRTEM image of Co-TiO₂ nanorods. The inset presents the FFT image. **c**, TEM image of the vertically aligned Co-TiO₂ nanorod assembly viewed along the longitudinal direction. The insets show a representative HRTEM image of a vertically aligned nanorod (left; scale bar, 2 nm) and the atomic model of TiO₂, viewed along the <001> direction (right). **d**, HAADF-STEM image of Co-TiO₂. **e, f**, Ti (**e**) and Co (**f**) EELS elemental mapping images of the area shown in **d**. The atomic model illustrations in **b** and **c** show brookite-phase TiO₂ with the blue and red circles representing Ti and O, respectively. The scale bar in **d** also applies to **e** and **f**.

the Co is uniformly doped in the nanorods by single-site substitution and is stable under OER conditions, as indicated by in situ extended X-ray absorption fine structure (EXAFS) spectroscopy and in situ synchrotron radiation X-ray diffraction (SRXRD). These Co-TiO₂ nanorods with Co single sites in the TiO₂ surface deliver OER turnover frequencies (TOFs) of 6.6 ± 1.2 and 181.4 ± 28 s⁻¹ per site at 300 and 400 mV overpotentials, respectively, which are very close to those determined by GCQM calculations (13.7 and 307.4 s⁻¹). Moreover, the experimental Tafel slope of 72 mV dec⁻¹ agrees with the GCQM prediction (74 mV dec⁻¹), revealing that the most favourable mechanism for the OER over the Co single sites is the adsorbate evolution mechanism (AEM). This work highlights the benefits of synthesizing well-defined catalytic single sites over monodisperse nanocrystal surfaces together with GCQM calculations for understanding and verifying the OER kinetics, providing a methodological basis for further fine-tuning electrocatalysts for improved efficiency.

Results

Synthesis and characterization of as-synthesized Co-TiO₂ nanorods. The Co-TiO₂ nanorods were synthesized by the thermal decomposition of titanium chloride (TiCl₄) and cobalt oleate precursors in a solution of 1-octadecene (ODE) with the surfactants oleic acid (OAc) and oleylamine (OAm), according to our previously

reported method³³. During the synthesis at elevated temperatures, as we demonstrated previously, OAc reacts with OAm to release a small amount of water, triggering the controlled hydrolysis of TiCl₄, while OAm guides the anisotropic growth of TiO₂ to nanorods³³. The Co doping level was tuned by the ratio of TiCl₄ and cobalt oleate, and measured by energy-dispersive X-ray spectroscopy (EDS; Supplementary Fig. 1). The formation of brookite-phase TiO₂ was evidenced from the X-ray diffraction (XRD) pattern through the characteristic brookite (121) peak at $2\theta = 30.81^\circ$ (Supplementary Fig. 2, JCPDS No. 29-1360, orthorhombic). Our present synthetic method can yield up to 12% Co dopant level (atomic Co as a percentage of all metals) without changing the brookite phase of TiO₂. The transmission electron microscopy (TEM) and scanning TEM (STEM) images (Fig. 1a and Supplementary Figs. 3 and 4) show that as-obtained Co-TiO₂ with different Co doping levels exhibit a consistent and uniform nanorod morphology with an average width of 4 ± 0.5 nm and a length of 40 ± 8 nm, similar to the undoped TiO₂ nanorods. The high-resolution TEM (HRTEM) image of Co-TiO₂ and fast Fourier transformation (FFT; Fig. 1b) suggest that these nanorods are single crystals and grow along the <001> direction with (210) surfaces on the side planes of the nanorods. Due to the uniform size and shape, the Co-TiO₂ nanorods can be readily assembled into a nanorod array at the liquid/air interface and viewed along the longitudinal direction. We found that the nanorods have

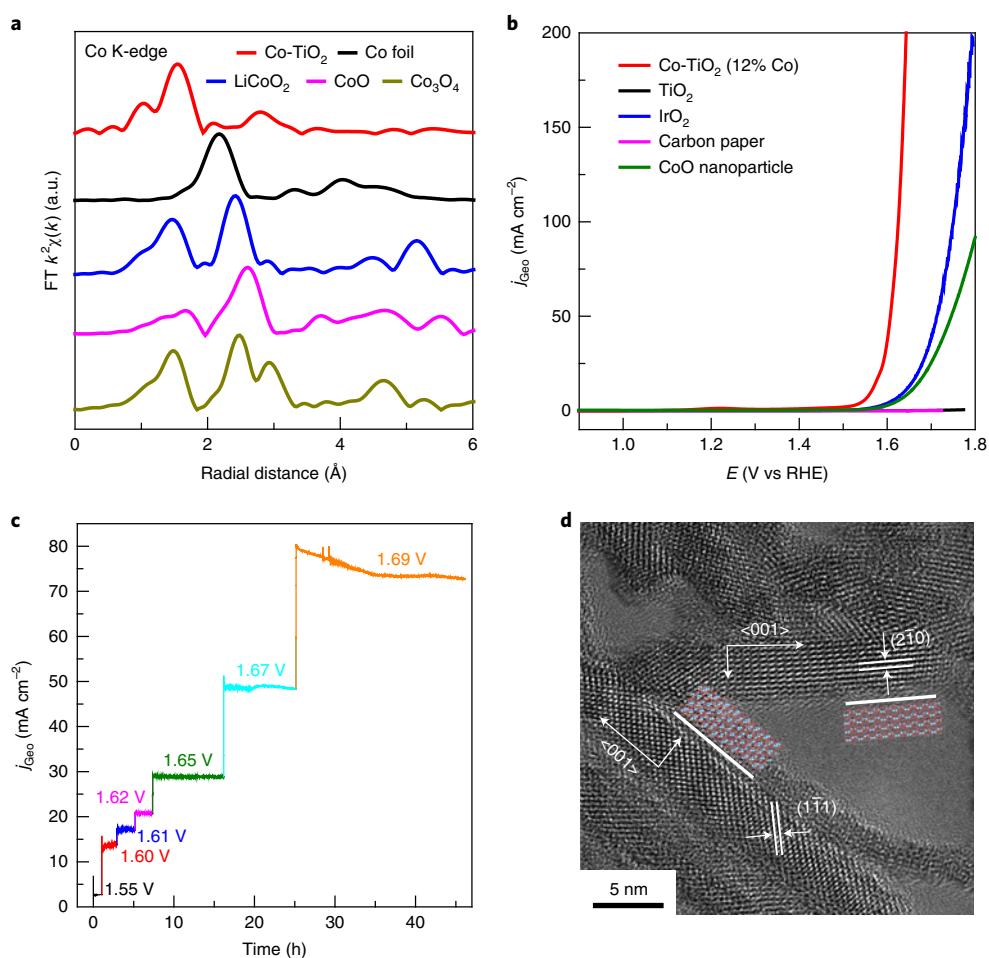


Fig. 2 | EXAFS and OER catalytic performance of Co-TiO₂ nanorods. **a**, Co K-edge FT-EXAFS spectra of Co-TiO₂ (12% Co) and other reference materials. FT, Fourier transform. **b**, LSV plots of different catalysts used for the OER. **c**, Stability test of Co-TiO₂ (12% Co) in the OER by chronoamperometry under various potentials (the segment colour matches the colour of the applied potential value). **d**, HRTEM image of Co-TiO₂ nanorods after the OER stability test. The atomic model illustrations in **d** show brookite-phase TiO₂ with the pale-blue and red circles representing Ti and O, respectively.

a rhombic shape cross-section with angles of $\sim 80/100^\circ$, confirming that the nanorods expose four (210) planes on the side facets (Fig. 1c). Such a well-defined surface structure has also been observed in pure TiO₂ and Fe-doped TiO₂ brookite-phase nanorods³³.

The uniform distribution of Co dopant in the nanorods was confirmed by high-angle annular dark-field (HAADF) STEM imaging coupled with electron energy loss spectroscopy (EELS) elemental mapping (Fig. 1d–f). The coordination environment of Co dopant was further revealed by Co K-edge EXAFS analysis. The Fourier-transformed (FT) EXAFS spectra acquired from Co-TiO₂ and reference samples are presented in Fig. 2a. We found that Co-TiO₂ does not show a peak at 2.17 Å, which is related to the Co–Co bond and can be observed in metallic Co foil. Instead, a peak at 1.56 Å, corresponding to the Co–O bond, is clearly observed in the Co-TiO₂ spectrum. This first coordination shell peak is located at a position slightly different from that of CoO, Co₃O₄ and LiCoO₂, implying a Co coordination environment different from these cobalt oxides. This peak may correspond to Co dopant in TiO₂ showing Co–O bonding in the TiO₂ matrix. More obviously, no peak similar to the Co–Co pathway in CoO, Co₃O₄ and LiCoO₂, typically in the range 2.1–2.4 Å, is observed in the Co-TiO₂ sample. This excludes the possible presence of Co metal and Co oxide secondary phases in the samples, which indicates that Co is distributed in TiO₂ as single-site substitution (more details are provided in the in situ EXAFS section).

Electrocatalysis over Co-TiO₂. The Co-TiO₂ dispersion was air-sprayed onto commercial carbon paper (Toray paper) and then annealed at 200 °C in air overnight to remove organic ligands before electrochemical study. The OER analysis was carried out in an O₂-saturated 1 M potassium hydroxide (KOH) aqueous solution. Linear scan voltammetry (LSV) curves are shown in Fig. 2b, and indicate a much lower onset potential of Co-TiO₂ compared with the other catalytic materials studied (the curves of 200 continuous LSV cycles are also provided in Supplementary Fig. 5). The overpotentials at geometric current densities (j_{Geo} , current density normalized over the electrode geometric area) of 10 and 100 mA cm⁻² for Co-TiO₂ were determined to be 332 and 396 mV, respectively, superior to those of CoO nanoparticles and IrO₂ nanoparticle catalysts with the same loading of active metal. Compared with Co-TiO₂, undoped TiO₂ and carbon paper barely generated any current, suggesting that the activity of Co-TiO₂ arises exclusively from the Co in the nanorod surface. Among the Co-TiO₂ nanorods with different Co dopant levels, the one with 12% Co exhibited the lowest overpotential (Supplementary Fig. 6), possibly due to the highest Co single-site density in the nanorod surface. Therefore, this material is discussed specifically in subsequent sections.

Online gas chromatography (GC) analysis showed that the Faradaic efficiency for O₂ formation was >95% on carbon paper-supported Co-TiO₂ at a geometric current density of 50 mA cm⁻². Even at 100 mA cm⁻², the Faradaic efficiency for O₂ formation

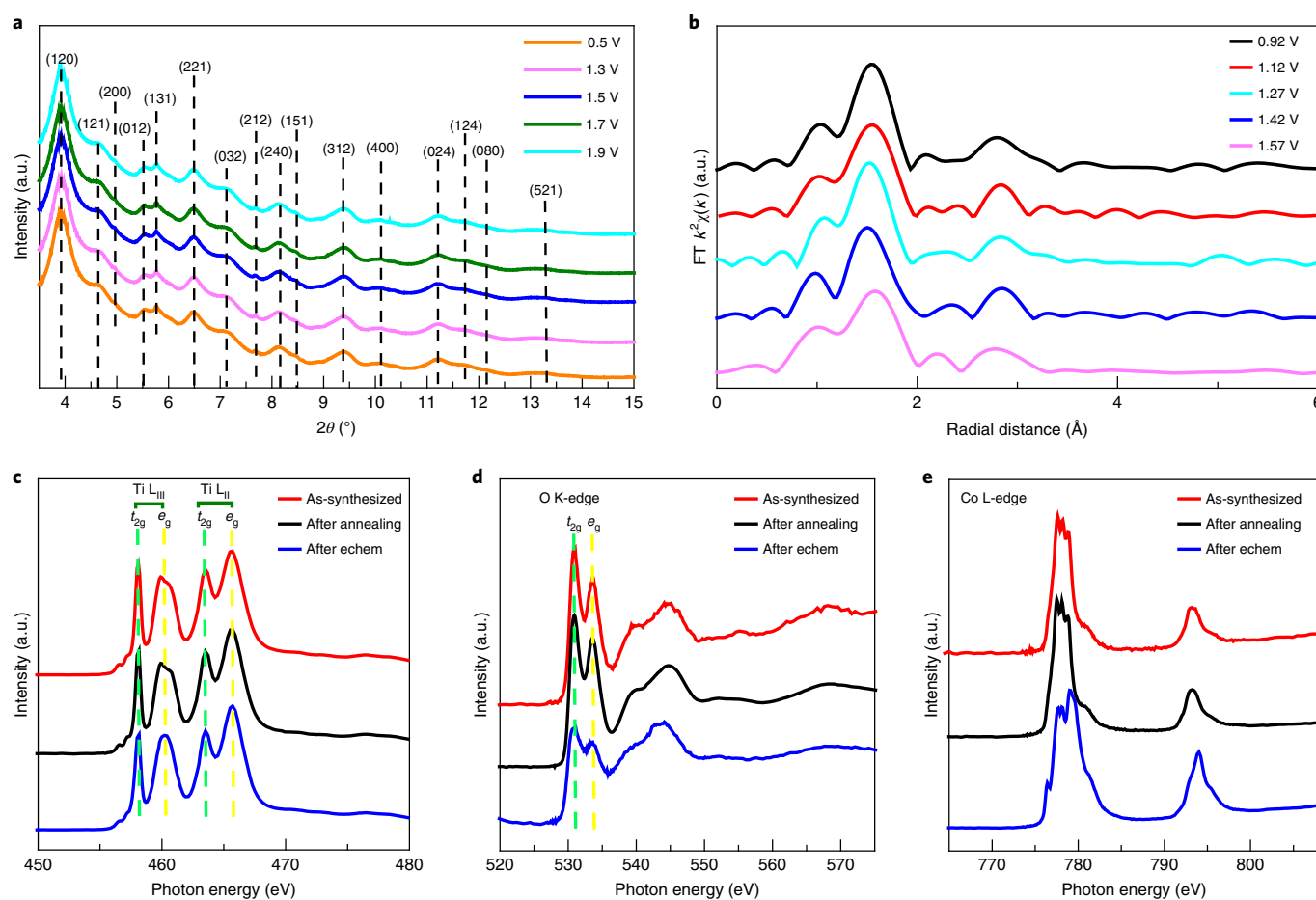


Fig. 3 | In situ and ex situ analyses of Co-TiO₂. **a**, In situ SRXRD patterns of Co-TiO₂ nanorod catalysts under the OER conditions (1M KOH aqueous electrolyte). **b**, In situ Co K-edge FT-EXAFS spectra of Co-TiO₂ nanorods under the OER conditions (1M KOH aqueous electrolyte). **c–e**, Ti L-edge (**c**), O K-edge (**d**) and Co L-edge (**e**) XAS spectra (acquired with soft X-ray excitation) of Co-TiO₂ nanorod catalysts before and after annealing and after electrochemical (echem) testing.

was still >90% (Supplementary Fig. 7). Chronoamperometry measurements taken at various potentials for 42 hours demonstrated the high stability of Co-TiO₂, with a slight current density decay observed only at high potential (Fig. 2c and Supplementary Fig. 8). In another chronoamperometry experiment performed at 1.62 V versus the reversible hydrogen electrode (RHE) for 10 hours, Co-TiO₂ preserved 99% of its original current density, whereas using CoO or IrO₂ nanoparticles as catalyst, the current density decreased to ~65 and 90% of the original, respectively (Supplementary Figs. 9–11). In addition, no obvious change in nanorod morphology was observed after the OER stability test, as shown by the HRTEM image in Fig. 2d, indicating the excellent stability of the Co-TiO₂ catalyst.

Co single-site structure during catalysis and intrinsic activity. We employed a suite of spectroscopic probes to confirm the structural stability of the Co-TiO₂ catalyst under the OER conditions. In situ SRXRD analysis showed that the brookite phase of TiO₂ remains intact under high potentials, without Co phase segregation or TiO₂ phase transition to anatase/rutile (Fig. 3a). More importantly, the in situ Co K-edge EXAFS spectra, acquired with hard X-ray excitation under the OER conditions, demonstrated that the Co single-site dopant structure is also maintained in Co-TiO₂ (Fig. 3b and Supplementary Figs. 12–17). The structural details that we obtained from high-quality EXAFS spectra of Co-TiO₂ under catalytic potentials as well as of pristine TiO₂ are summarized in Supplementary Table 1. The Ti coordination environment (atomic

distances and coordination numbers in the first and second coordination shells) is consistent in the Co-TiO₂ and TiO₂ samples. The Co coordination profiles are not only very similar under different electrochemical potentials, but they also match that of Ti. Specifically, for the first coordination shell, the Co–O bond distance is similar to that of Ti–O in TiO₂, indicating the substitution of Co in TiO₂. For the second coordination shell, the Co–Ti pathway is consistent with Ti–Ti in TiO₂ and Co-TiO₂, further verifying that Co is present as single-site substitution in the TiO₂ brookite lattice and is preserved under OER potentials.

X-ray absorption spectroscopy (XAS) with soft X-ray excitation was used to probe the electronic structure of the Co-TiO₂ material before and after thermal annealing as well as after electrochemical stability testing. For the as-synthesized Co-TiO₂, the Ti L-edge and O K-edge XAS spectra show typical TiO₂ spectral profiles, whereas the Co L-edge XAS spectrum displays a CoO-like profile (Fig. 3c–e). This indicates that the Co is doped in the TiO₂ matrix as single-site substitution; however, Co does not form strong hybridization with the O in the TiO₂ matrix at this stage. Therefore, in the as-synthesized Co-TiO₂ nanorods, the hybridization between Co and O resembles that of CoO, suggesting a 2+ oxidation state for Co that is associated with oxygen vacancies in the crystal. We also found that annealing the sample did not change the electronic structure of the Co-TiO₂, implying that annealing does not provide sufficient driving force to initiate stronger hybridization between Co and O.

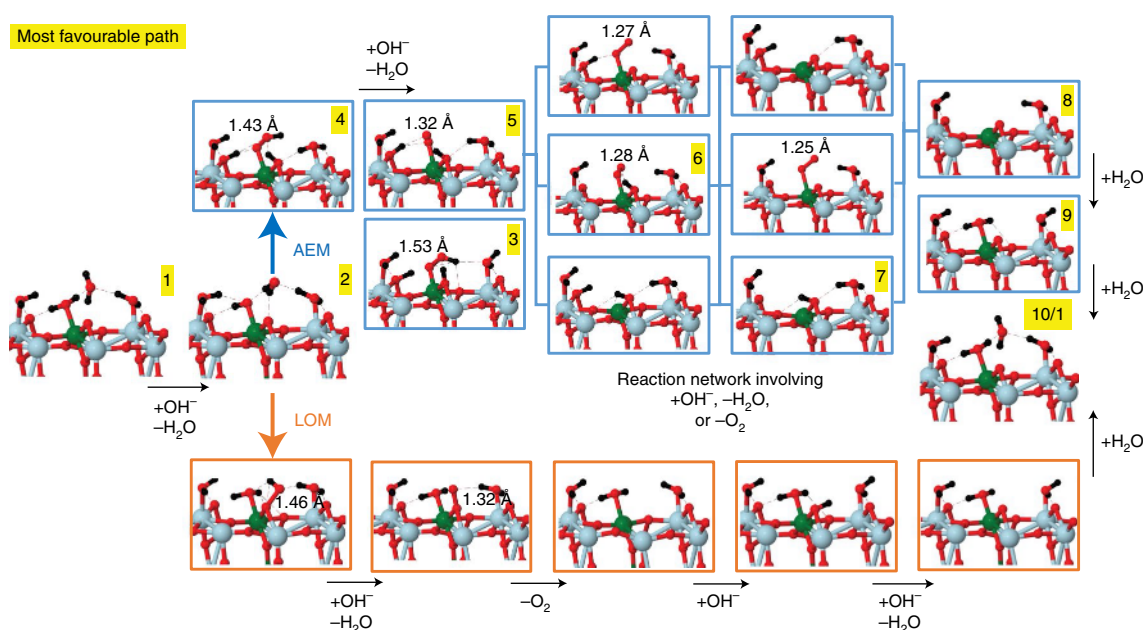


Fig. 4 | Schematic illustration of possible OER reaction mechanisms over Co-TiO₂. The pathway outlined in blue is the adsorbate evolution mechanism, and the pathway in orange is the lattice oxygen mechanism. States 1–10 (labelled with a yellow background) are the most energetically favourable and are also used in Fig. 5. The green, blue, red and black spheres in the atomic models represent Co, Ti, O and H atoms, respectively.

Interestingly, a clear change in the electronic structure of Co-TiO₂ could be seen after electrochemical testing, as indicated by the changed Co L-edge and O K-edge XAS spectra and the unchanged Ti L-edge spectrum. The unchanged Ti L-edge XAS spectrum (Fig. 3c) indicates that the TiO₂ matrix overall remains the same, whereas the changes in the O K-edge and Co L-edge XAS spectra are a clear indicator of different hybridization. The O K-edge XAS spectrum (Fig. 3d and Supplementary Fig. 18) exhibits decreased peaks in the range 528–538 eV, corresponding to a transition from O 1s to the O 2p–transition metal (TM) 3d hybridized state. Because the peak intensity is determined by the occupation of the unoccupied O 2p–TM 3d hybridized orbital, decreased peak intensity indicates the presence of more 3d electrons in the hybridized orbitals^{34–36}. Given that the Ti L-edge spectrum does not show any obvious difference, the extra accumulated 3d electrons are most likely to be from Co–O hybridization. Meanwhile, the Co L-edge spectrum (Fig. 3e and Supplementary Fig. 18) also shows a changed profile at 780 eV, confirming a strong Co–O hybridization and emptier Co 3d orbitals. Moreover, it is worth pointing out that the O K-edge spectrum of the electrochemically tested sample displays a typical TiO₂ spectral profile and is different from those of all the CoO_x species, indicating that Co–O hybridization is determined by the TiO₂ crystal electric field³⁷. Thus, we suggest that, driven by electrochemical potential, Co doped in the TiO₂ matrix presents a Ti⁴⁺-like crystal electric field property and is converted into a higher oxidation state.

Such a clear structure, single-site Co in the brookite TiO₂ (210) surface, makes it possible to precisely evaluate the intrinsic activity of the catalytic centres. First, we determined the electrochemical active surface area (ECSA) of the Co-TiO₂ catalyst by electrochemical double-layer capacitance measurements (Methods and Supplementary Figs. 19 and 20). Because (210) planes dominate the Co-TiO₂ nanorod surface and a certain proportion of surface Ti is substituted by Co, we then calculated the amount of surface Co from the ECSA, leading to subsequent analysis of the TOFs. Optimal TOFs were obtained with a Co doping level of 12%, the values being slightly higher than those of Co-TiO₂ with a lower Co content (Supplementary Fig. 21). TOFs of 6.6 ± 1.2 , 34.3 ± 9 and

181.4 ± 28 s^{−1} were observed experimentally over Co-TiO₂ nanorods (12% Co) at overpotentials of 300, 350 and 400 mV, respectively, which are among the highest for Co-based heterogeneous catalysts reported to date (Supplementary Fig. 22).

GCQM calculations. We carried out GCQM calculations on the experimentally identified brookite TiO₂ (210) surface with 12.5% Co dopant substitution (see Methods for further details). Supplementary Fig. 23 shows the constructed three double-layer slab models with inversion symmetry to avoid net dipoles in the cell. We used a 15 Å vacuum in the z direction to prevent periodic image interactions. The transition states were calculated using the climbing-image nudged elastic band method and were confirmed to have one negative frequency.

There are two types of Ti sites in the (210) surface, namely five- and six-coordinated sites. We found that placing the surface Co at a five-coordinated Ti site rather than a six-coordinated Ti site is more stable by 0.25 eV. To determine where to place the second and third layer Co, we examined the case of the second and third layer Co connecting directly to the first layer through O and the case with no connection. We found that connecting the Co dopants through O in a line is 0.15 eV more stable than having them separated (Supplementary Fig. 24). Our in situ EXAFS analysis suggested that Co is doped as single-site substitution in the brookite TiO₂ lattice; however, the two cases of single-site Co connecting in a line through O and non-connecting Co become indistinguishable in the Co K-edge EXAFS pattern, as the second coordination shell in both cases contains identical Co–Co and Co–Ti pathways with the same atomic arrangement and distance (the Co–Ti path will be primary due to concentration). We believe that these Co lines are likely to be formed at the surface under OER conditions. As revealed by XAS with soft X-ray excitation, Co²⁺ is doped in the as-synthesized nanorods coupled with an oxygen vacancy and is then converted into the higher oxidation state after electrocatalysis. Along with the increase in the Co oxidation state and the elimination of the oxygen vacancy in the surface layers at high potentials, the induced Co migration can facilitate the formation of a Co line structure that is more energetically favourable.

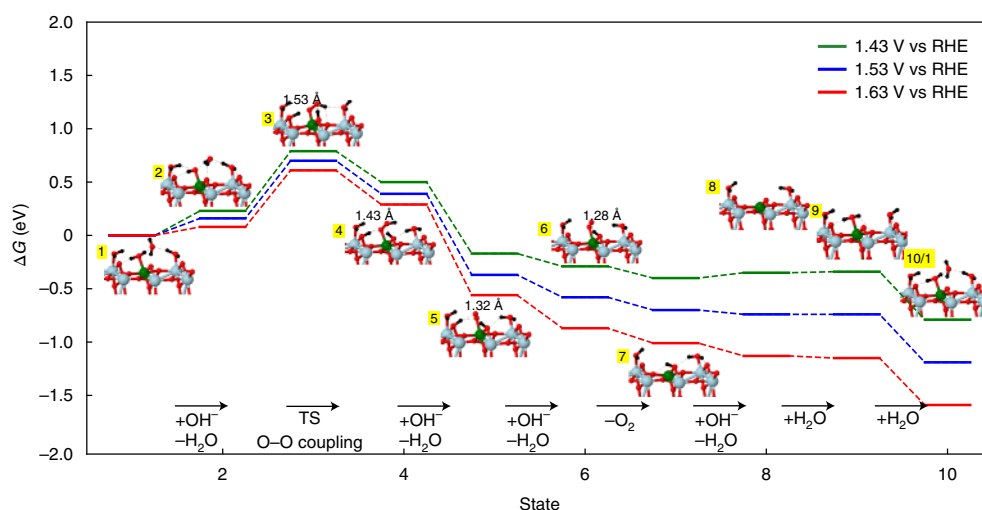


Fig. 5 | Free-energy landscape for the reaction over Co-TiO₂. Free-energy landscapes for the catalytic reaction over Co-TiO₂ at different potentials at pH = 14 showing the different states. The green, blue, red and black spheres in the atomic models represent Co, Ti, O and H atoms, respectively.

We systematically studied the most stable surface structure, including the oxidation state of the Co site and surface H₂O, under the experimental conditions (pH = 14, various potentials U) using slab models of the top three layers (Supplementary Fig. 25). We found that H₂O binds strongly to the surface with a binding energy of -1.12 eV per water molecule, consistent with previous calculations³⁸. At $U = 1.53$ V vs RHE, all the Co in the top three layers of the lattice prefer an oxidation state of 4+, leading to a d^5 configuration. This is clearly more stable than the cases with Co²⁺ and Co³⁺, which can be created using interstitial H or O vacancies in the lattice, as summarized in Supplementary Fig. 25g.

Importantly for the reaction mechanism, we found that each Co dopant introduces 0.19 unpaired spins onto the atom bridging Co and Ti. This radical character motivated us to further investigate the OER mechanism by treating this bridging O as a possible active site in addition to the Co catalytic site. Previous studies on perovskites suggested that the lattice O can interact with adsorbed OH* to form an oxygen vacancy and O₂ by a reaction pathway known as the lattice oxygen mechanism (LOM)^{19,39,40}. For some perovskites, the LOM has a higher OER activity than the adsorbate evolution mechanism (AEM)^{29,41}, which involves only the metal site and associated H₂O. This previous calculation was based on a simple scaling relation rather than the calculation of explicit barrier height⁴⁰.

We studied both the AEM and LOM in our system with the barrier heights calculated explicitly, to compare directly with our experiments, as shown in Fig. 4. We started with one monolayer of explicit H₂O solvent with one further H₂O molecule added at higher potential. The overall half reaction under strong basic conditions is $4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 4\text{e}^- + \text{O}_2$. The AEM was calculated to be the more favourable reaction pathway for our Co-TiO₂ catalyst, and each elementary step is shown in Fig. 4 with all the favourable intermediate structures labelled. Based on this reaction pathway, we plotted the free-energy landscapes for different applied potentials at pH = 14 (Fig. 5). At potentials between 1.43 and 1.63 V vs RHE, the O–O coupling (state 3) was found to be the rate-determining step (RDS), giving a linear Tafel slope in this potential range.

Direct comparison of Tafel slopes and TOFs between QM and experiment. In our previous studies of the OER on IrO₂ (ref. ²⁹) and on Fe-NiOOH (ref. ³⁰) we had to make assumptions about the surface structure, but for the Co-TiO₂ system we can be confident about the nature of the surface. In particular, we determined the

activity per active site experimentally, allowing a direct comparison of this value with the GCQM calculated results.

GCQM predicts that the TOF normalized to a Co single site in the surface can be expressed as follows:

$$\text{TOF} = \frac{kT}{h} \times \exp\left(-\frac{\Delta G^\ddagger}{kT}\right) \quad (1)$$

where k is the Boltzmann constant, T is temperature, h is Planck's constant, $\frac{kT}{h} = 6.26 \times 10^{12} \text{ s}^{-1}$, $kT = 0.0257$ eV at 298 K and $\Delta G^\ddagger$ is the calculated free-energy difference between the RDS and the resting state. The experimental and theoretical results are compared in Fig. 6. At 1.53, 1.58 and 1.63 V (300, 350 and 400 mV OER overpotential), the TOFs were calculated to be 13.7, 64.8 and 307.4 s^{-1} per site, presenting an exceedingly good agreement with the experimental values (6.6 ± 1.2 , 34.3 ± 9 and $181.4 \pm 28 \text{ s}^{-1}$, respectively).

The Tafel slope is sensitive to the reaction pathway and mechanism. Figure 6 shows clearly that the more favourable AEM mechanism leads to a Tafel Slope of 74 mV dec^{-1} , which is highly consistent with the experimental result (72 mV dec^{-1}). In contrast, the LOM mechanism leads to a reaction rate that is orders of magnitude smaller with a predicted Tafel slope of 247 mV dec^{-1} , confirming the dominant role of the AEM in our Co-TiO₂ system. It is worth noting that although our kinetic study was based on the most energetically favourable structures, the GCQM approach was also applied to the other possible single-site Co configurations that we discussed above, including Co connecting in a line and Co not connected: these possible structures with single-site Co in the (210) surface exhibited highly consistent Tafel slopes with the predicted TOFs fluctuating within QM calculation accuracy, further confirming that the reaction over our Co single-site catalytic centres follows the AEM (Supplementary Methods).

Further extension of this approach to other M-TiO₂ (M = Mn, Fe, Co, Ni, Cu) nanorods allowed us to gain an understanding of the general kinetics of the OER over well-defined single-site electrocatalysts. The M-TiO₂ nanorods were readily prepared using the same approach, leading to consistent surface facets, physical dimensions, M content and atomic arrangement³³ (Supplementary Fig. 26). Experimentally, the single-site M exhibited intrinsic activities decreasing in the order of $\text{Co} > \text{Ni} > \text{Fe}$, whereas Cu-TiO₂ and Mn-TiO₂ displayed negligible activities (Supplementary Fig. 27). For Ni-TiO₂ and Fe-TiO₂, TOFs of 2.4 ± 0.6 and $0.7 \pm 0.1 \text{ s}^{-1}$ were

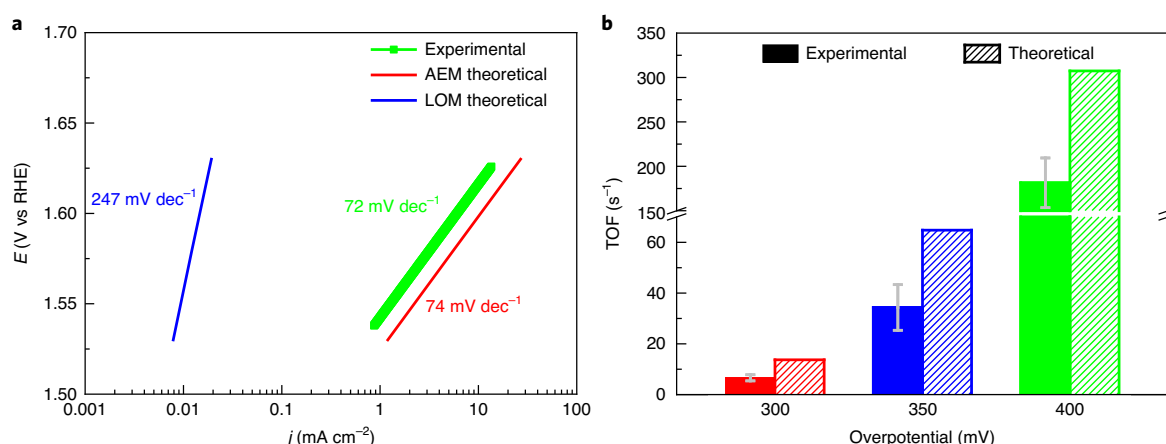


Fig. 6 | Direct comparison of the experimental results and GCQM predictions for Co-TiO₂. **a**, Tafel slope comparison of the experimental result and AEM and LOM predictions. The experimental current density of Co-TiO₂ is normalized over the ECSA. **b**, TOFs from experiment and GCQM predictions. The predicted Tafel slopes and TOFs are in excellent agreement with the experimental values. The error bars represent the standard deviation of the experimental TOFs determined from five independent samples.

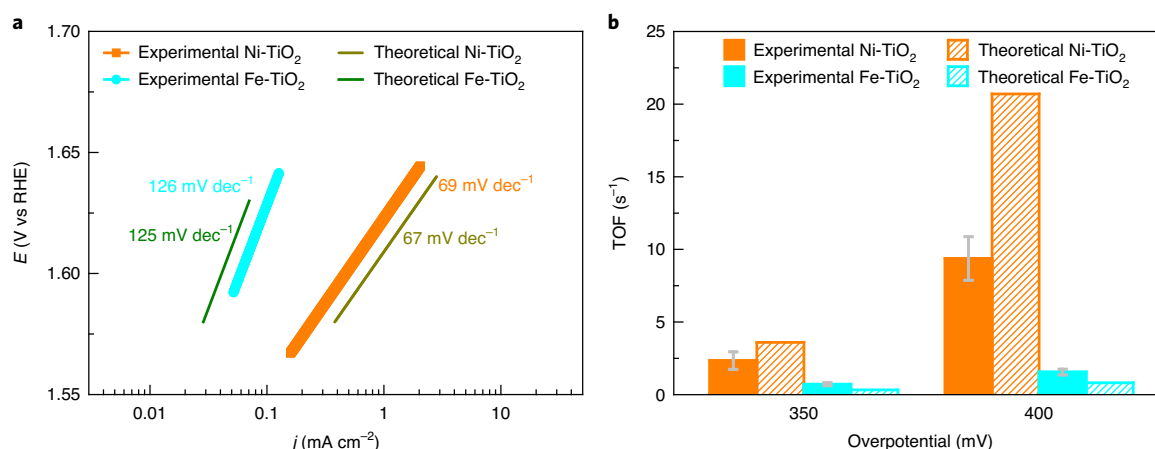


Fig. 7 | Comparison of the experimental results and GCQM predictions for Ni-TiO₂ and Fe-TiO₂. **a**, Tafel slope comparison. The experimental current density is normalized over the ECSA. **b**, TOFs from experiment and GCQM predictions. The error bars represent the standard deviation of the experimental TOFs determined from five independent samples.

experimentally observed at 350 mV overpotential, and 9.4 ± 1.5 and 1.6 ± 0.2 s⁻¹ at 400 mV overpotential, respectively. As shown in Fig. 7, our theoretical GCQM results (Tafel slopes and TOFs) are highly consistent with the experimental values. They also indicate that the seamless integration of controlled synthesis and the advanced GCQM method leads to reliable agreement between experimental observables and theoretical predictions, allowing the performance and mechanism of well-defined catalytic systems to be validated and predicted.

By comparing the free-energy landscapes of Fe-TiO₂, Co-TiO₂ and Ni-TiO₂ at the same potential (1.63 V), we found that the O–O coupling step and the resting state (that is, Co and Ni fully covered by H₂O (state 1), but Fe covered with OH (state 2), see Supplementary Fig. 28) control the overall kinetics of our single-site catalysts. Single-site Co provides a favourable combination of these steps, avoiding the resting state energy trap observed with Fe as well as the high deprotonation barrier over Ni (state 1 to state 2), which makes Co-TiO₂ the most efficient catalyst among these well-defined M-TiO₂ nanorods. The results also suggest that the screening of these initial OER steps over a broad range of Co single-site catalytic centres with different inorganic solid coordination environments

(for example, in different TiO₂ crystal phases and surface facets)⁴², coupled with controlled synthesis, will likely enable the further optimization of OER catalysts.

Conclusions

Using a catalyst with well-defined Co catalytic single-site substitution, we have demonstrated a methodological advance for the study of the OER by combining the atom-precise synthesis of nanocrystals and GCQM calculations. Our strategy for the synthesis of TiO₂ nanorods with substitutional Co doping enabled the incorporation of single-site Co into the brookite-phase TiO₂ (210) surface. The resultant Co-TiO₂ nanorods were highly efficient in catalysing the OER under basic conditions, and were stable without phase transition or segregation under the reaction conditions, as revealed by in situ and ex situ spectroscopic studies. Based on the well-characterized structure, our GCQM calculations have provided an atomistic understanding of the OER kinetics in excellent agreement with experimental observations. The accuracy of the GCQM calculations validated here will potentially allow highly accurate in silico design of rational catalysts and the controlled synthesis of optimal nanocatalysts.

Methods

Chemicals and materials. Titanium chloride (TiCl_4 , 99%) was purchased from Fluka. Cobalt carbonyl ($[\text{Co}_2(\text{CO})_8]$, stabilized in 1.5% hexane) was obtained from Stream Chemical. 1,2,3,4-Tetrahydronaphthalene (Tetralin, 98%), 1-octadecene (ODE, 90%) and cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 98%) were purchased from Acros Organics. Diethylamine (97%), oleylamine (OAm, 70%) and oleic acid (OAc, 90%) were purchased from Sigma-Aldrich. Hexanes, isopropanol and potassium hydroxide (KOH) were purchased from Fisher Scientific. Toray carbon paper 060, plain carbon cloth and iridium oxide (IrO_2) were obtained from Fuel Cell Store.

Synthesis of Co-TiO₂, Ni-TiO₂, Fe-TiO₂, Cu-TiO₂, Mn-TiO₂ and TiO₂ nanorods.

The TiO₂ and Co-TiO₂ nanorods were synthesized by an organic colloidal solution approach based on our previous publication³³. As TiCl_4 is highly sensitive to moisture, all the solvents employed in the synthesis were pre-dried at 90 °C in a vacuum using a typical Schlenk link technique. For the synthesis of the TiO₂ nanorods, a Ti precursor solution containing 0.2 M TiCl_4 and 1.0 M OAc was first prepared by dissolving TiCl_4 (2.19 ml) and OAc (31.59 ml) in ODE (66.25 ml) and stored in a N₂-filled glove box. In a four-necked reactor, ODE (10 ml), OAm (10 ml) and OAc (0.48 ml) were heated under vacuum at 90 °C for 1 hour to remove dissolved moisture and oxygen, and subsequently cooled to 60 °C under N₂. Next, 1.5 ml of Ti precursor solution was injected into the system, which was then quickly heated to 290 °C and maintained at that temperature for 10 min. Next, 8 ml of additional Ti precursor solution was added into the reactor at a rate of 0.3 ml min⁻¹. After cooling to room temperature, the TiO₂ nanorods were collected, washed with isopropanol and centrifuged at 8,000 r.p.m. for 8 min. The product was further purified twice by the addition of hexanes and isopropanol. The Co-TiO₂ nanorods were synthesized by a similar route. A Co oleate solution containing 0.2 M cobalt oleate and 1.0 M OAc was mixed with the Ti precursor solution with the desired Ti/Co ratio. Next, 1.5 ml of this solution was injected into a degassed solution containing 10 ml of ODE, 10 ml of OAm and 0.48 ml of OAc at 60 °C, and the mixture was quickly heated to 290 °C. After being held at that temperature for 10 min, another 8 ml of the mixed Ti/Co precursor solution was introduced into the system at 0.3 ml min⁻¹. The as-prepared Co-TiO₂ nanorods were collected and purified in the same way as for the TiO₂ nanorods. In this synthesis, the Co doping level was tuned by altering the Ti/Co ratio in the mixed precursor solution. Specifically, with Ti/Co molar ratios of 8:1, 8:2 and 8:3, Co doping levels of 4.2, 7.5 and 12% were achieved in the Co-TiO₂ nanorods. The Ni-TiO₂, Fe-TiO₂, Cu-TiO₂ and Mn-TiO₂ nanorods were synthesized by the same approach, using the corresponding metal oleate to substitute for Co oleate³³. The synthesis of CoO nanoparticles is described in the Supplementary Methods.

Structural characterizations. XRD patterns were collected using a Rigaku Smartlab diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). TEM images were obtained with a FEI Spirit microscope (120 kV). To obtain the TEM image of the nanorod array viewed along the longitudinal direction, the assembly method should be used, which is described in detail in the Supplementary Methods. HRTEM and STEM images were collected using a FEI Talos 200x microscope (200 kV) coupled with EELS and EDS detectors at the Center for Functional Nanomaterials at Brookhaven National Laboratory. EELS mappings and spectra were collected using a high-resolution Gatan-Enfina ER instrument with a probe size of 1.3 Å. A power law function was used for EELS background subtraction. EDS was performed with a FEI Quanta 650 scanning electron microscope.

Electrocatalytic OER measurement. All electrocatalysis studies were performed at room temperature in O₂-saturated 1.0 M KOH electrolyte using a typical three-electrode system controlled by a Bio-Logic (Model VMP3) potential station with a carbon paper working electrode, a platinum foil counter electrode and a Hg/HgO (1.0 M KOH) reference electrode. To prepare the Co-TiO₂ working electrode, the desired amount of Co-TiO₂/hexanes dispersion was airbrushed onto carbon paper with a catalyst loading of 4 mg cm⁻², followed by annealing at 200 °C overnight to remove the organic ligands. The electrode was then sealed with epoxy to give an exposed geometric area of 1 cm². The CoO nanoparticle electrode and IrO₂ electrode were also prepared by the same airbrushing technique, except that Vulcan-72 carbon-supported CoO and commercial IrO₂ were dispersed in isopropanol. All the potentials (*E*) are reported versus RHE according to the following equation:

$$E(\text{vs RHE}) = E(\text{vs HgO}) + 0.926 \text{ V} \quad (2)$$

where 0.926 V is the potential difference between the Hg/HgO (1.0 M KOH) reference electrode and RHE in 1.0 M KOH, which was calibrated by the open circuit voltage test prior to electrocatalysis. The overpotential (η) for OER could be calculated using the following equation:

$$\eta = E(\text{vs RHE}) - 1.23 \text{ V} \quad (3)$$

The OER activity was examined by LSV in the range 0.926–1.676 V vs RHE at a scan rate of 10 mV s⁻¹ with *iR* compensation. The uncompensated resistance

was measured by potentiostatic electrochemical impedance spectroscopy at a single-point high frequency (100 kHz). The fixed potential was set to 0 V versus the open circuit voltage (E_{OCV}) with a sinus amplitude of 20 mV and a delay of 0.1 period. Each test was repeated four times and average values were taken. The uncompensated resistance (R_u) in our typical cell was around 2 Ω. The *iR* drop was compensated at 85% using the Bio-Logic EC-Lab software (v11.10) with positive feedback. The catalytic stability was evaluated by chronoamperometry measurements at various potentials without *iR* correction.

To gain a deeper understanding of the OER kinetics, we calculated the ECSA using the following equation:

$$\text{ECSA} = C_{\text{dl}}/C_s \quad (4)$$

where C_s is the specific capacitance of Co-TiO₂ obtained from GCQM calculations under operando conditions (18.2 μF cm⁻², Supplementary Methods) and C_{dl} is the double-layer capacitance measured by cyclic voltammetry in the non-Faradaic region (0.526–0.726 V vs RHE). The number of Co atoms in the nanorod surface ($N_{\text{Co-atom}}$) was estimated from the ECSA and Co atom density in the Co-TiO₂ nanorods using the following equation:

$$N_{\text{Co-atom}} = \text{ECSA} \times \frac{8 \times \omega\%}{D_{\text{cell}} \times N_A} \quad (5)$$

where 8 is the number of Ti atoms in the (210) facet of a single cell of brookite TiO₂, ω is the atomic ratio of Co element in Co-TiO₂, D_{cell} is the dimension of the (210) facet in a single cell of TiO₂ ($7 \times 10^{-15} \text{ cm}^2$) and N_A is the Avogadro constant. Based on $N_{\text{Co-atom}}$, the experimental turnover frequency (TOF) was calculated from

$$\text{TOF} = \frac{j_{\text{Geo}} \times s}{4 \times N_{\text{Co-atom}} \times F} \quad (6)$$

where j_{Geo} is the geometric current density obtained from the LSV plot, s is the electrode geometric area and F is the Faraday constant.

To obtain the Faradaic efficiency of the OER, a controlled current electrolysis was performed for 12.5 hours in a gas-tight H-type cell separated by a Nafion-212 membrane and charged with 10 ml N₂-saturated 1 M KOH in each compartment. During the electrocatalysis, a steady supply of 10 cm³ min⁻¹ N₂ was introduced into the anode compartment, and the gas-phase effluent was continuously delivered to the gas-sampling loop of a gas chromatograph (Shimadzu, GC 2014) and analysed using a thermal conductivity detector (TCD). The concentration of O₂ was derived by comparing the corresponding peak area of the TCD with those of standards, and further used to calculate the Faradaic efficiency.

XAS characterization. The ex situ and in situ Co K-edge EXAFS spectra were collected at room temperature in fluorescence mode at beamline 20BM of the Advanced Photon Source at the Argonne National Laboratory using a customized electrochemical cell that is detailed in our previous publication⁴³. For in situ Co K-edge EXAFS analyses, the desired amount of Co-TiO₂ was airbrushed onto carbon cloth and annealed at 200 °C for 12 hours to serve as the working electrode, and Ag/AgCl and platinum wire were employed as the reference and counter electrodes, respectively. Cyclic voltammetry was conducted at 100 mV min⁻¹ with continuous fresh electrolyte (1.0 M KOH) pumped at a rate of 1.0 ml min⁻¹. EXAFS raw data (background subtraction, normalization and Fourier transformation by standard procedures) were processed using the ATHENA program⁴⁴. Least-squares curve-fitting analysis of the EXAFS $\chi(k)$ data was conducted using the ARTEMIS program. The model was built by substitution of the central Ti atom in brookite-phase TiO₂ with a Co atom. The effective curved-wave backscattering amplitude ($F(k)$), the photoelectron mean free path for all paths (λ , measured in Å) and phase shifts ($\phi(k)$) were calculated using the ab initio code FEFF 9.05. Soft X-ray XAS was performed at beamline 8.0.1 of the Advanced Light Source at the Lawrence Berkeley National Laboratory. The signals collected were of the total electron yield, measuring the drain current from the ground. The energy scale of each spectrum was calibrated using reference samples. The soft XAS raw data (background subtraction and normalization) were processed using the ATHENA program.

SRXRD characterization. In situ SRXRD measurements on Co-TiO₂ were conducted at beamline 17BM ($\lambda = 0.24141 \text{ \AA}$) of the Advanced Photon Source at the Argonne National Laboratory using the same set-up as described for the in situ EXAFS characterization. The two-dimensional diffraction patterns were collected with a PerkinElmer silicon flat panel detector, which was set 200 mm behind the sample, and processed using the GSAS-II software⁴⁵ to obtain plots of intensity versus 2θ .

GCQM calculations. All QM calculations were performed using the spin-polarized PBE exchange correlation functional together with DFT-D2 (ref. ⁴⁶) pair potential London dispersion corrections as implemented within the Vienna ab initio simulation package (VASP)⁴⁷. To locate the transition states for the various steps of the reaction, we used the climbing image-nudged elastic band method, as implemented in VASP⁴⁸. The k -point grid was $2 \times 3 \times 1$ and the energy cut-off was

500 eV in all calculations. We grouped the five- and six-coordinated Ti/Co as one double layer so that the unit cell has three double layers. The water binding energy on the brookite TiO_2 (210) surface was calculated to be 1.12 eV, which compares well with the value of 1.1 eV for the six double layer reported in the literature³⁸.

To convert the QM energies into Gibbs free energies at 298 K, we calculated the phonon vibrational density of states using density functional perturbation theory⁴⁹. The vibrational contributions to the free energies were included for both surfaces and molecules. To compute the free-energy change of the elementary reaction steps involving gaseous or liquid molecules, such as water and hydrogen, we considered the contributions of rotation, translation and vibration⁵⁰ to the free molecule, which we obtained from the Jaguar package⁵¹, as well as the solvation energy of the water molecule in liquid water (2.05 kcal mol⁻¹). The free energy of gas-phase O_2 ($G[\text{O}_2]$) was derived from

$$G[\text{O}_2] = 4.92(\text{eV}) + 2G[\text{H}_2\text{O}] - 2G[\text{H}_2] \quad (7)$$

by using the experimental Gibbs free energy of the reaction $2\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 2\text{H}_2(\text{g})$ in standard conditions. To obtain the free energies as a function of applied potential U , we used the CANDLE⁵² implicit solvation model as implemented in JDFTx⁵³. This has been used successfully in previous OER studies, including with IrO_2 (ref. 29), Fe-doped γ - NiOOH (ref. 30) and other metals doped into NiOOH (ref. 32).

We calculated the geometries using VASP with the VASPsol (ref. 54) solvation model for various numbers of charges on the surface, and then we transformed the optimized geometries using the grand canonical potential kinetics (GCP-K)⁵⁵ formulation along with the CANDLE implicit solvation model to obtain the free energies as a function of U . This allowed the charged surfaces to be effectively screened by the ionic response in solution. A specific example of such a transformation is provided in Supplementary Methods. This GCQM approach was also used for Ni- TiO_2 and Fe- TiO_2 with the same structure, surface facet and reaction conditions. The atomic coordinates of the optimized models are provided in Supplementary Data 1.

Data availability

All data generated or analysed during this study are included in this published article (and its Supplementary Information files) or can be obtained from the corresponding authors upon reasonable request.

Code availability

All computational structures are included in this published article (and its Supplementary Data and Supplementary Information files). The code and script for GCQM computation and analysis are provided as part of the JDFTx constant charge calculations and can be accessed at <https://jdfx.org/index.html> or obtained from the corresponding authors upon reasonable request.

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References

- McCrory, C. C. L. et al. Benchmarking hydrogen evolving reaction and oxygen evolving reaction electrocatalysts for solar water splitting devices. *J. Am. Chem. Soc.* **137**, 4347–4357 (2015).
- Spanos, I. et al. Standardized benchmarking of water splitting catalysts in a combined electrochemical flow cell/inductively coupled plasma–optical emission spectrometry (ICP-OES) setup. *ACS Catal.* **7**, 3768–3778 (2017).
- Liu, B. et al. Large-scale synthesis of transition-metal-doped TiO_2 nanowires with controllable overpotential. *J. Am. Chem. Soc.* **135**, 9995–9998 (2013).
- An, L. et al. Heterostructure-promoted oxygen electrocatalysis enables rechargeable zinc–air battery with neutral aqueous electrolyte. *J. Am. Chem. Soc.* **140**, 17624–17631 (2018).
- Li, Y. et al. Advanced zinc–air batteries based on high-performance hybrid electrocatalysts. *Nat. Commun.* **4**, 1805 (2013).
- Liu, J. et al. Metal-free efficient photocatalyst for stable visible water splitting via a two-electron pathway. *Science* **347**, 970–974 (2015).
- Wang, H. et al. Bifunctional non-noble metal oxide nanoparticle electrocatalysts through lithium-induced conversion for overall water splitting. *Nat. Commun.* **6**, 7261 (2015).
- Burke, M. S., Kast, M. G., Trotochaud, L., Smith, A. M. & Boettcher, S. W. Cobalt–iron (oxy)hydroxide oxygen evolution electrocatalysts: the role of structure and composition on activity, stability, and mechanism. *J. Am. Chem. Soc.* **137**, 3638–3648 (2015).
- Seitz, L. C. et al. A highly active and stable $\text{IrO}_2/\text{SrIrO}_3$ catalyst for the oxygen evolution reaction. *Science* **353**, 1011–1014 (2016).
- Zhang, B. et al. Homogeneously dispersed multimetal oxygen-evolving catalysts. *Science* **352**, 333–337 (2016).
- Chen, J. Y. C. et al. Operando analysis of NiFe and Fe oxyhydroxide electrocatalysts for water oxidation: detection of Fe^{4+} by Mössbauer spectroscopy. *J. Am. Chem. Soc.* **137**, 15090–15093 (2015).
- Liu, W. et al. Amorphous cobalt–iron hydroxide nanosheet electrocatalyst for efficient electrochemical and photo-electrochemical oxygen evolution. *Adv. Funct. Mater.* **27**, 1603904 (2017).
- Kim, J., Chen, X., Shih, P.-C. & Yang, H. Porous perovskite-type lanthanum cobaltite as electrocatalysts toward oxygen evolution reaction. *ACS Sustain. Chem. Eng.* **5**, 10910–10917 (2017).
- Suntivich, J., May, K. J., Gasteiger, H. A., Goodenough, J. B. & Shao-Horn, Y. A perovskite oxide optimized for oxygen evolution catalysis from molecular orbital principles. *Science* **334**, 1383–1385 (2011).
- Wu, T. et al. Iron-facilitated dynamic active-site generation on spinel CoAl_2O_4 with self-termination of surface reconstruction for water oxidation. *Nat. Catal.* **2**, 763–772 (2019).
- Li, C. et al. Phase and composition controllable synthesis of cobalt manganese spinel nanoparticles towards efficient oxygen electrocatalysis. *Nat. Commun.* **6**, 7345 (2015).
- Gupta, S. et al. Highly active and stable graphene tubes decorated with FeCoNi alloy nanoparticles via a template-free graphitization for bifunctional oxygen reduction and evolution. *Adv. Energy Mater.* **6**, 1601198 (2016).
- Toma, F. M. et al. Efficient water oxidation at carbon nanotube–polyoxometalate electrocatalytic interfaces. *Nat. Chem.* **2**, 826–831 (2010).
- Roy, C. et al. Impact of nanoparticle size and lattice oxygen on water oxidation on NiFeO_xH_y . *Nat. Catal.* **1**, 820–829 (2018).
- Laio, A. & Parrinello, M. Escaping free-energy minima. *Proc. Natl Acad. Sci. USA* **99**, 12562–12566 (2002).
- Iannuzzi, M., Laio, A. & Parrinello, M. Efficient exploration of reactive potential energy surfaces using Car-Parrinello molecular dynamics. *Phys. Rev. Lett.* **90**, 238302 (2003).
- Cheng, T. et al. Mechanism and kinetics of the electrocatalytic reaction responsible for the high cost of hydrogen fuel cells. *Phys. Chem. Chem. Phys.* **19**, 2666–2673 (2017).
- Cheng, T., Xiao, H. & Goddard, W. A. Reaction mechanisms for the electrochemical reduction of CO_2 to CO and formate on the Cu(100) surface at 298 K from quantum mechanics free energy calculations with explicit water. *J. Am. Chem. Soc.* **138**, 13802–13805 (2016).
- Cheng, T., Xiao, H. & Goddard, W. A. Full atomistic reaction mechanism with kinetics for CO reduction on Cu(100) from ab initio molecular dynamics free-energy calculations at 298 K. *Proc. Natl Acad. Sci. USA* **114**, 1795–1800 (2017).
- Qian, J., An, Q., Fortunelli, A., Nielsen, R. J. & Goddard, W. A. Reaction mechanism and kinetics for ammonia synthesis on the Fe(111) surface. *J. Am. Chem. Soc.* **140**, 6288–6297 (2018).
- Qian, J. et al. Initial steps in forming the electrode–electrolyte interface: H_2O adsorption and complex formation on the Ag(111) surface from combining quantum mechanics calculations and ambient pressure X-ray photoelectron spectroscopy. *J. Am. Chem. Soc.* **141**, 6946–6954 (2019).
- Ye, Y. et al. Dramatic differences in carbon dioxide adsorption and initial steps of reduction between silver and copper. *Nat. Commun.* **10**, 1875 (2019).
- Cheng, T., Wang, L., Merinov, B. V. & Goddard, W. A. Explanation of dramatic pH-dependence of hydrogen binding on noble metal electrode: greatly weakened water adsorption at high pH. *J. Am. Chem. Soc.* **140**, 7787–7790 (2018).
- Ping, Y., Nielsen, R. J. & Goddard, W. A. The reaction mechanism with free energy barriers at constant potentials for the oxygen evolution reaction at the IrO_2 (110) surface. *J. Am. Chem. Soc.* **139**, 149–155 (2017).
- Xiao, H., Shin, H. & Goddard, W. A. Synergy between Fe and Ni in the optimal performance of (Ni,Fe)OOH catalysts for the oxygen evolution reaction. *Proc. Natl Acad. Sci. USA* **115**, 5872–5877 (2018).
- Sundararaman, R., Goddard, W. A. & Arias, T. A. Grand canonical electronic density-functional theory: algorithms and applications to electrochemistry. *J. Chem. Phys.* **146**, 114104 (2017).
- Shin, H., Xiao, H. & Goddard, W. A. In silico discovery of new dopants for Fe-doped Ni oxyhydroxide ($\text{Ni}_{1-x}\text{Fe}_x\text{OOH}$) catalysts for oxygen evolution reaction. *J. Am. Chem. Soc.* **140**, 6745–6748 (2018).
- Zhang, Z. et al. Generalized synthetic strategy for transition-metal-doped brookite-phase TiO_2 nanorods. *J. Am. Chem. Soc.* **141**, 16548–16552 (2019).
- Ye, Y. et al. X-ray spectroscopies studies of the 3d transition metal oxides and applications of photocatalysis. *MRS Commun.* **7**, 53–66 (2017).
- Ye, Y. et al. Strong O 2p–Fe 3d hybridization observed in solution-grown hematite films by soft X-ray spectroscopies. *J. Phys. Chem. B* **122**, 927–932 (2018).
- Kronawitter, C. X. et al. Electron enrichment in 3d transition metal oxide hetero-nanostructures. *Nano Lett.* **11**, 3855–3861 (2011).
- Li, J. et al. Tracking the local effect of fluorine self-doping in anodic TiO_2 nanotubes. *J. Phys. Chem. C* **120**, 4623–4628 (2016).
- Holmström, E. et al. Hydration structure of brookite TiO_2 (210). *J. Phys. Chem. C* **121**, 20790–20801 (2017).
- Grimaud, A. et al. Activating lattice oxygen redox reactions in metal oxides to catalyse oxygen evolution. *Nat. Chem.* **9**, 457 (2017).

40. Yoo, J. S., Rong, X., Liu, Y. & Kolpak, A. M. Role of lattice oxygen participation in understanding trends in the oxygen evolution reaction on perovskites. *ACS Catal.* **8**, 4628–4636 (2018).
41. Rossmeisl, J., Qu, Z. W., Zhu, H., Kroes, G. J. & Nørskov, J. K. Electrolysis of water on oxide surfaces. *J. Electroanal. Chem.* **607**, 83–89 (2007).
42. Li, X., Rong, H., Zhang, J., Wang, D. & Li, Y. Modulating the local coordination environment of single-atom catalysts for enhanced catalytic performance. *Nano Res.* **13**, 1842–1855 (2020).
43. Zhang, Z. et al. Revealing structural evolution of PbS nanocrystal catalysts in electrochemical CO₂ reduction using in situ synchrotron radiation X-ray diffraction. *J. Mater. Chem. A* **7**, 23775–23780 (2019).
44. Ravel, B. & Newville, W. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Rad.* **12**, 537–541 (2005).
45. Toby, B. H. & Von Dreele, R. B. GSAS-II: the genesis of a modern open-source all purpose crystallography software package. *J. Appl. Cryst.* **46**, 544–549 (2013).
46. Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **27**, 1787–1799 (2006).
47. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).
48. Henkelman, G., Uberuaga, B. P. & Jónsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *J. Chem. Phys.* **113**, 9901–9904 (2000).
49. Baroni, S., de Gironcoli, S., Dal Corso, A. & Giannozzi, P. Phonons and related crystal properties from density-functional perturbation theory. *Rev. Mod. Phys.* **73**, 515–562 (2001).
50. Sprowl, L. H., Campbell, C. T. & Árnadóttir, L. Hindered translator and hindered rotor models for adsorbates: partition functions and entropies. *J. Phys. Chem. C* **120**, 9719–9731 (2016).
51. Bochevarov, A. D. et al. Jaguar: a high-performance quantum chemistry software program with strengths in life and materials sciences. *Int. J. Quantum Chem.* **113**, 2110–2142 (2013).
52. Sundararaman, R. & Goddard, W. A. The charge-asymmetric nonlocally determined local-electric (CANDLE) solvation model. *J. Chem. Phys.* **142**, 064107 (2015).
53. Sundararaman, R. et al. JDFTx: software for joint density-functional theory. *SoftwareX* **6**, 278–284 (2017).
54. Mathew, K., Sundararaman, R., Letchworth-Weaver, K., Arias, T. A. & Hennig, R. G. Implicit solvation model for density-functional study of nanocrystal surfaces and reaction pathways. *J. Chem. Phys.* **140**, 084106 (2014).
55. Huang, Y., Nielsen, R. J. & Goddard, W. A. Reaction mechanism for the hydrogen evolution reaction on the basal plane sulfur vacancy site of MoS₂ using grand canonical potential kinetics. *J. Am. Chem. Soc.* **140**, 16773–16782 (2018).

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Author contributions

The project was conceived by C.L. and J.Q. under the supervision of T.B.G., W.A.G. and S.Z. Catalyst synthesis, structural characterization and catalysis measurements were performed by C.L., C.S. and Z.Z. GCQM calculations were finished by J.Q. and H.S. In situ XRD and in situ EXAFS experiments were conducted by C.L., H.Z., C.-J.S., Z.Z. and G.W. Soft XAS experiments were conducted by Y.Y., Y.S.L. and J.G. STEM elemental mapping was performed by S.L. and S.H. All the spectra were analysed and interpreted by C.L., Z.Z. and Y.Y. All authors contributed to the writing of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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