Enhanced oxygen evolution over dual corner-shared cobalt tetrahedra

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Developing efficient catalysts is of paramount importance to oxygen evolution, a sluggish anodic reaction that provides essential electrons and protons for various electrochemical processes, such as hydrogen generation. Here, we report that the oxygen evolution reaction (OER) can be efficiently catalyzed by cobalt tetrahedra, which are stabilized over the surface of a Swedenborgite-type YBCo$_4$O$_7$ material. We reveal that the surface of YBaCo$_4$O$_7$ possesses strong resilience towards structural amorphization during OER, which originates from its distinctive structural evolution toward electrochemical oxidation. The bulk of YBaCo$_4$O$_7$ composes of corner-sharing only CoO$_4$ tetrahedra, which can flexibly alter their positions to accommodate the insertion of interstitial oxygen ions and mediate the stress during the electrochemical oxidation. The density functional theory calculations demonstrate that the OER is efficiently catalyzed by a binuclear active site of dual corner-shared cobalt tetrahedra, which have a coordination number switching between 3 and 4 during the reaction. We expect that the reported active structural motif of dual corner-shared cobalt tetrahedra in this study could enable further development of compounds for catalyzing the OER.

A sustainable society relies upon renewable energy resources instead of fossil fuel combustion to generate electricity, reducing emissions of pollutants. Meanwhile, several eco-friendly energy conversion systems, such as water electrolyzers and metal-air batteries, have been explored to store energy from renewable resources. In these systems, the oxygen evolution reaction (OER) is an essential step. The complex four-electron transfer process makes OER occur at a large overpotential and thus generally consumes considerable energy. In the last years, various transition-metal-based complex compounds have been intensively explored for catalyzing the OER efficiently. However, the design of advanced catalysts with high activity and sustainability is still challenging owing to limited choices.

The OER active site in octahedral geometry (or square pyramidal geometry for an undercoordinated surface site) has been dominant and is generally regarded as a promising local structure with a coordination number switching between 5 and 6 during the OER. Active transition-metal with lower coordination numbers (in trigonal bipyramidal geometry) has also been reported with a coordination number switching between 4 and 5 during the OER. These active sites in a reduced coordinate environment possess unique electronic and structural characteristics, which are found beneficial for the charge-transfer and adsorption of intermediates during the electrochemical reaction.

Till now, little attention has been paid to the possible active sites of tri/tetra-oxygen-coordinated (in tetrahedral geometry), which have the potential to enable efficient OER. Compared with the octahedral moieties, the tetrahedral moieties are more flexible, and the tetrahedral units are easier of deformation and rotation, which can be
beneficial for the formation of surface-active sites for a promoted OER\textsuperscript{26,27}. A few complex materials, such as spinel, wurtzite, and phosphates, containing tetrahedral sites, have been considered for catalyzing OER\textsuperscript{26,27,31}. These tetrahedral sites, however, are generally found inactive and are prone to transform to actual catalytic sites with higher coordination numbers (5 or 6)\textsuperscript{2,26,27,31}. Nevertheless, the formation of a stable tri-oxygen-coordinated site on the surface from the material containing tetrahedral moieties is possible. For instance, an active tri-oxygen-coordinated aluminum site has been observed from the surface of gamma alumina, which contains tetrahedra and has been extensively used as the catalyst or catalyst support in the petroleum industry\textsuperscript{24,25}.

In this work, we demonstrate that tri-oxygen-coordinated cobalt can be stabilized over the surface of a \(\text{YBaCo}_4\text{O}_7\) (YBC4) material, which is composed of corner-shared \(\text{CoO}_4\) tetrahedra\textsuperscript{26}. An active motif of dual corner-shared cobalt tetrahedra can efficiently catalyze the OER as well as the cobalt in an octahedral geometry.

**Results and discussion**

**Cobalt tetrahedra over YBC4 surface**

The corner-shared \(\text{CoO}_4\) tetrahedra in YBC4 are packed along the c-direction (Fig. 1a) with alternated Triangular and Kagome layers. The Y and Ba cations occupy octahedral and anticuboctahedral cavities within the \(\text{Co}_4\text{O}_{12}\) tetrahedra, respectively. An averaged valence state of +2.25 for Co is expected in \(\text{YBaCo}_4\text{O}_7\). A sol-gel method was applied to synthesize the \(\text{YBaCo}_4\text{O}_7\). The as-prepared \(\text{YBaCo}_4\text{O}_7\) shows a high oxygen-coordinated aluminum site has been observed from the surface of gamma alumina, which contains tetrahedra and has been extensively used as the catalyst or catalyst support in the petroleum industry\textsuperscript{24,25}.

**Fig. 1 | Cobalt tetrahedra over YBC4 surface.** a Crystal structure of YBC4 and the arrangements of corner-shared \(\text{CoO}_4\) tetrahedra in the Triangular layer and the Kagome layer. b The top view of the \(\text{YBaCo}_4\text{O}_7\) (110) facet with tri-oxygen-coordinated cobalt (marked in orchid). c O 1s core spectra from temperature-dependent XPS of an as-prepared YBC4 sample. d O K-edge EELS spectra from the sub-surface (-9 nm and -1.5 nm) and the surface of YBC4. All spectra are aligned to Fermi energy (\(E_F\)) with 0 eV. e Extracted intensities of \(\alpha\) peaks from sub-surface to surface. A linear background is applied to subtract the background adsorption. f A typical OH-adsorbed site, including adjacent Co from the Kagome layer and the Triangular layer, over the (110) facet. The O from adsorbed OH group is highlighted in green. g PDOS of unoccupied Co 3d states from sub-surface (dot line) and surface (dash line). The solid lines are the corresponding integrated PDOS of unoccupied Co 3d states.
The OER activity and stability. a) IR-corrected and oxides surface area normalized OER currents at a scan rate of 10 mV/s. The inset is the turnover frequency (TOF) for YBC4, BSCF, CoAl2O4, and IrO2 at an overpotential of 300 mV. b) A consecutive CV scanning test for YBC4.

OER activity and stability

The OER activity of YBC4 was measured using the rotating-disk electrode (RDE) technique in 0.1 M KOH (pH = 12.82). The result is compared with spinel-type CoAl2O4, perovskite-type BSCF, and rutile-type IrO2. The high phase purity of as-prepared CoAl2O4 and BSCF is confirmed by XRD (Fig. S14). The IR-corrected and oxide surface area contributed to the increased intensity of α peak from the surface O K-edge spectra.

Enhanced stability by the flexible structure

To pinpoint the root cause for the observed stability in YBC4, HR-TEM, XRD, ICP-MS, XPS, and XAS were conducted to characterize the bulk and surface before, during, and after the electrochemical tests. Figure 3a and Fig. S20 show the TEM images from the surfaces of YBC4 before and after CV cycling. The as-prepared YBC4 shows well-crystallized surfaces. Correspondingly, the dissolution of Y and Ba is also found negligible in the electrolyte used for the CV testing (Table S3). From the evolution of Co 2p core spectra after CV cycling (Fig. S21 and Table S4), the YBC4 is electrochemically oxidized during OER. As reflected by the right shift of the peaks (Fig. 3b, c) in the XRD pattern of YBC4 after CV cycling, the YBC4 lattice contracts during the electrolyte oxidation and partial cobalt atoms will coordinate with the intercalated oxygen.

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introduce the ionic size mismatch and strain within the lattice, leading to structural instability. For example, in perovskite, a highly oxidized state with ionic size mismatch induces structural collapse and cation exclusion (See Fig. S23 for additional discussions). Similarly, surface structural amorphization and/or transformation are observed in typical catalysts, such as perovskite-type BSCF and spinel-type Co$_3$O$_4$, when a sufficient high overpotential (a highly oxidizing environment) is applied for catalyzing OER. For a better understanding of the electrochemical oxidation of YBC4 during OER, we performed additional XAS analysis on three YBC4 samples, which had been electrochemically oxidized at 1.6, 1.75, and 2 V (vs. RHE) for 500 mins, respectively. From the XANES spectra of Co K-edge extraction of large Y and Ba, which occurs in perovskites, is then alleviated in YBC4 during the OER tests.

OER mechanism over cobalt tetrahedra
It has been proposed that the Co octahedra are responsible for the OER catalytic activity in a more oxidized YBaCo$_{3.5}$O$_{7.5}$ catalyst. Because of the oxygen nonstoichiometry ($\delta = 0.18$), in as-prepared YBC4, a few Co atoms (~4%) are in an octahedral geometry. These Co octahedra, however, are found cannot be the key to the catalytic activity of as-prepared YBC4. This is because the catalytic activity of a stoichiometric YBC4 ($\delta = 0$) is as good as the as-prepared YBC4 (Fig. S26). Thus, the measured activity of as-prepared YBC4 originates from the dominant Co tetrahedra, or more specifically, surface tri/tetra-oxygen-coordinated Co.

To depict our hypothesis on how OER is catalyzed over the surface Co tetrahedra, DFT calculations were performed with a computational hydrogen electrode (CHE) mode to explore the possible interactions between surface tri-oxygen-coordinated Co and OER intermediates.
The possible OER paths over the Co tetrahedra are illustrated in Fig. S27. Figure 4a presents the free energy diagrams for the most likely OER process, and the detailed OER steps are expressed with the following equations:

\[
\left( \triangle^* \text{OH} \cdots \triangle^* \text{OH} \right) + \text{OH}^- \rightarrow \left( \triangle^* \text{O} \cdots \triangle^* \text{OH} \right) + \text{H}_2\text{O} + e^- \tag{1}
\]

\[
\left( \triangle^* \text{O} \cdots \triangle^* \text{OH} \right) + \text{OH}^- \rightarrow \left( \triangle^* \text{OOH} \cdots \triangle^* \text{OH} \right) + e^- \tag{2}
\]

\[
\left( \triangle^* \text{OOH} \cdots \triangle^* \text{OH} \right) \rightarrow \left( \triangle^* \text{OH} \cdots \triangle^* \text{OH} \right) + \text{H}_2\text{O} + \text{O}_2 \tag{3}
\]

\[
\left( \triangle^* \text{OH} \cdots \triangle^* \text{OH} \right) + \text{OH}^- \rightarrow \left( \triangle^* \text{OH} \cdots \triangle^* \text{OH} \right) + e^- \tag{4}
\]

\[
\left( \triangle^* \text{OH} \cdots \triangle^* \text{OH} \right) + \text{OH}^- \rightarrow \left( \triangle^* \text{OH} \cdots \triangle^* \text{OH} \right) + e^- \tag{5}
\]

Where \((\triangle^* \text{OH} \cdots \triangle^* \text{OH})\) represents the initial active sites of adjacent OH-adsorbed Co tetrahedra. \(\triangle^*\) and \(\triangle^*\) correspond to the surface tri-oxygen-coordinated Co sites from the Kagome and the Triangular layer, respectively. In this mechanism, the OER starts from the adjacent Co sites with mono-\(\mu\)-oxo-bridged CoO\(_3\)(OH) in a tetrahedral geometry \((\triangle^* \text{OH} \cdots \triangle^* \text{OH})\). In the first proton-coupled electron transfer (PCET) step, the deprotonation occurs at the \(\triangle^* \text{OH}\) site. Then, an OO bond is formed \((\triangle^* \text{OOH})\) after the nucleophilic attack. And the \((\triangle^* \text{OOH} \cdots \triangle^* \text{OH})\) is stabilized by the strong hydrogen bonding interaction between \(\triangle^* \text{OOH}\) and \(\triangle^* \text{OH}\). Subsequently, the \(\text{O}_2\) releases from the \(\triangle^* \text{OOH}\) coupled with the formation of adjacent tri-oxygen-coordinated Co \((\triangle^* \cdots \triangle^*)\). By bonding with another two OH groups through the PCET mechanism, the \((\triangle^* \cdots \triangle^*)\) resets to the initial status \((\triangle^* \text{OH} \cdots \triangle^* \text{OH})\). Overall, this OER process shows a theoretical overpotential of 510 mV, which is 50 mV lower than a calculated overpotential of 560 mV from BSCF. Note that an experimental overpotential difference of 50 mV may indicate an OER current change by several times. However, a theoretical overpotential difference of 50 mV can be related to the error of DFT calculation. Based on the proposed mechanism, the enhanced OER can be ascribed to the unique surface-active site of mono-\(\mu\)-oxo-bridged Co tetrahedra, which originates from the arrangement of CoO\(_2\) tetrahedra in YBC4 (Fig. 1a and Fig. S28).

The particularity of mono-\(\mu\)-oxo-bridged Co in tetrahedral geometry is further studied by comparing it with Co in octahedral geometry, which has been extensively explored for catalyzing OER. Through an in-depth comparison of two coordination geometries, a single CoO\(_2\) tetrahedron in YBC4 is found non-optimal toward catalyzing the OER, which unlike many state-of-the-art catalysts with the finely tuned octahedral active site (Supplementary Discussion, Table S6). The measured activity of mono-\(\mu\)-oxo-bridged Co in tetrahedral geometry (dual corner-shared cobalt tetrahedra) is attributed to its unique geometry structure (Supplementary Discussion, Fig. S29, and S30), which enables the proposed OER mechanism. Specifically, Fig. 4b presents the mono-\(\mu\)-oxo-bridged Co in tetrahedral geometry, and three typical interatomic distances of adjacent O in a single Co polyhedron, adjacent Co, and two terminal O from adjacent Co are marked. Firstly, it is found that the relatively large interatomic distances of adjacent and two terminal O atoms make the coupling of adjacent and two terminal O atoms unfavorable, and, as a result, a water nucleophilic attack induced O–O bond formation (adsorption evolution mechanism, AEM) is preferred (Fig. 4c). Secondly, the adjacent Co-Co distance is short enough to allow the interaction of intermediates from two Co centers, i.e., hydrogen bonding stabilized...
The room temperature XPS tests for the sample before and after electrochemical tests were performed on PHIS000 VersaProbe spectrometer including an Al Kα X-ray source. For the HT-XPS characterization, Omicron® Mg Kα source (hv = 1253.6 eV) and hemisphere analyzer were used with a fixed passing energy of 20 eV for each element. The system was calibrated to the Fermi level without additional adjustment as the samples had good electric conductivity. For the sample preparation, the YBC4 powder (approximately 1 g) was pressed into a pellet (10 mm in diameter). The sample pellet was then degassed in the ultrahigh vacuum (UHV) chamber where both the consequent heat-treatment and XPS measurements were carried out. All the data were fitted by the XPSPEAK software package. Linear-type background subtraction was applied, and the spectra were fitted using a combined Lorentzian-Gaussian line shape. The Co 2p binding energy values reported by Gautiera et al. were used while fitting the Co 2p spectrum.

The surface areas were characterized by nitrogen adsorption-desorption tests (ASAP Tri-star II 3020) with the Brunauer-Emmett-Teller (BET) method.

**Electrode preparation and electrochemical characterization**

Glassy carbon (rotating disk) electrode with an area of 0.196 cm$^2$ was pre-polished with 50 nm Al$_2$O$_3$ powder and then sonicated in deionized water for at least three times to remove the residual Al$_2$O$_3$ particles. The catalyst ink with a concentration of 5 mg mL$^{-1}$ was prepared by ultra-sonically dispersing 5 mg oxide catalyst and 2 mg acetylene black (Alfa Aesar) in a water (750 μL) isopropanol (225 μL)-Nafion (25 μL) solution, 10 μL of well-dispersed ink was dropped onto the glassy carbon and dried overnight. The electrochemical experiments were carried out in a 150 mL glass cell at room temperature with an RDE system (Pine Instrument). An SP-150 workstation was applied to perform cyclic voltammetry scanning, chrono potentiometric tests, and electrochemical impedance spectroscopy analysis. A rotation speed of 1600 rpm was used. Before tests, the glassware was boiled in water to remove contaminants. The tests were performed in a 0.1 M KOH solution, which was purged with ultra-pure oxygen before each measurement for 30 min. A Pt wire was used as the counter electrode and a saturated calomel electrode (SCE) was used for reference. The evolution of oxygen and the Faradic efficiency were evaluated with rotating ring disk electrode (RRDE) experiments. The loading of the YBC4 catalyst was identical to the case in RDE experiments. During the measurements, the potential of the Pt-ring disk was maintained at a constant potential of 0.3 V (vs RHE) and, to minimize the bubble formation, an RRDE rotation rate of 3000 rpm was used.

For CV cycling tests, a graphite paper (∼2.5 cm × 2.5 cm) was used as the support and the catalyst loading amount is 0.25 mg cm$^{-2}$. The test was performed in a homemade electrochemical polyethylene cell with a Pt wire as the counter electrode and a mercuric oxide electrode as the reference electrode. The concentration of dissolved cations during electrochemical cycling in the electrolyte is measured with an induc-tively coupled plasma mass spectrometer (ICP-MS, Elan DRC-e). For the tests of electrochemical oxidation of YBC4 with chronocoulometry, a graphite paper (∼1 cm × 2 cm) was used as the support and the loading amount of catalyst increased to 0.5 mg cm$^{-2}$.

**Calculation of turnover frequency (TOF)**

The TOF was calculated from the equation:

$$\text{TOF} = \frac{j \times \Delta A_{\text{OX}}}{4 \pi \epsilon \times N_A}$$

where $j$ is the BET surface area normalized current density at an overpotential of 300 mV, $\Delta A_{\text{OX}}$ is the total surface area of the catalyst deposited on the GC electrode. $\epsilon$ is the electric charge carried by a single electron. $N_A$ is the number of active sites. While calculating the
Computation details
First principles calculations were conducted based on the spin-polarized Generalized Gradient Approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) exchange and correlation functionals implemented in Density Functional Theory (DFT)\textsuperscript{49}. We utilized a plane-wave basis set with a cutoff energy of 1.3 times the maximum cutoff specified by the pseudopotentials of the elements. Interaction potentials of core electrons were replaced by the Projector-Augmented Wave (PAW) method as parameterized in the Vienna ab initio simulation package (VASP)\textsuperscript{50}. The Hubbard $U$ parameter (GGA + $U$) was adopted to enhance the description of correlation effects and to alleviate the self-interaction error\textsuperscript{51}. The optimized effective interaction parameter $U_{\text{eff}}$ ($U_{\text{eff}} = U - J$) of 3.32 eV was used for Co transition metal which has been widely adopted in the Materials Project\textsuperscript{52}. All atoms and cell parameters of each model structure were fully relaxed until the total energy was approached within 10$^{-4}$ eV. A gamma point mesh was performed with 2×2×1 k-points for YBaCo$_4$O$_7$ (110) slab models to sample the Brillouin zone. We used the tetrahedron smearing method with Blöchl corrections\textsuperscript{53}. The periodic boundary condition was imposed on the unit cell where a vacuum size was almost twice larger (> 20 Å) than the thickness of YBaCo$_4$O$_7$ (110)'s slab to prohibit interactions between the top and bottom surface.

Surface structure calculation. The Gibbs energy of different surface termination was calculated with the equation of

$$
\sigma = \frac{1}{A} [E_{\text{slab}} - nE_{\text{bulk}}]
$$

where $E_{\text{slab}}$ is the energy of slab, $E_{\text{bulk}}$ is the energy of bulk YBC4 per formula unit, $n$ is the number of the formula unit in the slab, $A$ is the surface area. All the surface atoms were fully relaxed during the surface structure optimization.

Wulff structure simulation. The simulation of Wulff shapes was done with the software SOWOS, an open-source program for the three-dimensional Wulff construction\textsuperscript{54}. The simulated Wulff structure of YBC4 that matched the corresponding relative surface energies as listed in Fig. S4. In comparison with that of the (001) and (111) facets, the surface energies of the (110) facet decreased rapidly.

Crystal orbital overlap calculation. The crystal overlap population scheme of the LOBSTER method (version 2.2.1) was employed to study bonding and chemical interaction properties\textsuperscript{55}. The “completeness” of the basis functions in representing the valence electronic configuration of the POTCAR files used in the VASP calculations was verified with a small absolute charge spilling value of 0.56%–0.83%. To match the number of bands in the VASP calculations with the number of orbitals used in the LOBSTER projection scheme, the VASP input parameter NBANDS was set to 216 for all model systems. Symmetry was switched off (ISYM = -1) for all VASP calculations. Crystal orbital overlap population (COOP) is very powerful in understanding chemical bonding by showing the bonding (COOP > 0) and antibonding (COOP < 0) character of each studied chemical bond.

Calculation of OER free energy. The reaction pathway of OER on the surface of YBC was analyzed by considering all the possible reaction intermediates. In the YBC4 (110) facet, the cobalt-terminated surface enables the exposure of adjacent cobalt sites. The case that all the surface cobalt sites are occupied by an adsorbed OH species was chosen as the starting point of OER. For each elementary step, the reactant OH could attack either the Triangular or the Kagome cobalt site. Therefore, both cases need to be evaluated and the thermodynamically more feasible one was considered as the real elementary step. The free energy change for each step was defined as the change of chemical potentials between the products and the reactants. Taking the elementary step of

$$
\left( \frac{\Delta}{k} \text{OH} \cdots \frac{\Delta}{t} \text{OH} \right) + \text{OH}^- \rightarrow \left( \frac{\Delta}{k} \text{O} \cdots \frac{\Delta}{t} \text{OH} \right) + \text{H}_2\text{O} + e^-
$$

as an example, the free energy change is calculated as

$$
\Delta G = \mu \left( \frac{\Delta}{k} \text{O} \cdots \frac{\Delta}{t} \text{OH} \right) + \mu (\text{H}_2\text{O}) - \mu \left( \frac{\Delta}{k} \text{OH} \cdots \frac{\Delta}{t} \text{OH} \right) - \mu (\text{OH}^-)
$$

The chemical potentials of each species were calculated by standard DFT techniques, as described by Peterson et al.\textsuperscript{60}. Solvation correction was included in the initial state where two terminal OH were adsorbed on Co tetraheda to address the stabilization of hydroxyl adsorbates.

Data availability
The data that support the findings of this study are provided in the Main Text and Supplementary Information.

Code availability
The analysis codes that support the findings of the study are available from the corresponding authors upon reasonable request.

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Author contributions
Z.X., Y.S.M., and Y.C. proposed the research and wrote the manuscript. Y.C. and Z.X. designed the experiments. Y.C. prepared the samples and carried out electrochemical measurements. J.S., Y.S., T.W., M.O., M.Z., J.G., and Y.S.M. conducted DFT modeling and simulation. J.W. performed TEM measurements. S.X., M.W., Y.D., and Z.F. performed XAS measurements. K.Y. and W.C. performed HT-XPS measurements. M.W. and Z.X. performed synchrotron-based XRD measurements. Y.C., J.W., S.X., Y.D., K.Y., M.W., A.F., S.D., L.H., and H.G. performed the data analysis. All authors commented on the manuscript.

Competing interests
The authors declare no competing interests.

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