Activating lattice oxygen by defect-engineered Fe2O3-CeO2 nano-heterojunction for efficient electrochemical water oxidation

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Experimental Section

Materials

All chemical regents were analytically pure. Nickel foam (NF) was bought from Shenzhen Green and Creative Environmental Science and Technology Co, Ltd. Ferric sulfate hydrate (Fe₂(SO₄)₃·xH₂O; Aladdin), terephthalic acid (C₈H₆O₄, TPA; Aladdin), cerous nitrate (Ce(NO₃)₃·6H₂O; Aladdin), ammonium hydroxide (NH₃·H₂O; Aladdin), hydrochloric acid (HCl; Aladdin), N,N-dimethylformamide Chemical), hydroxide (DMF; Beijing potassium (KOH: Macklin), Tetramethylammonium hydroxide (TMAOH; Macklin), cerium dioxide (CeO₂; Macklin), iron trioxide (Fe₂O₃; Macklin), heavy water (H₂¹⁸O; Isotope) ruthenium oxide (RuO₂; Aladdin), nafion (C₁₀H₇OH; Beijing Chemical), ethanol and deionized water were used as received.

Cleanse of NF

NF was cut into small pieces with the size of 3 cm \times 4 cm, immersed in hydrochloric acid (concentrated HCl : H₂O = 1 : 3 in v/v) and sonicated for 15 min. The cleansed NF was washed with large amount of deionized water, then rinsed with deionized water and ethanol under sonication for several times until neutral condition was achieved for the solvent. The as-cleansed NF pieces were immersed in ethanol and sealed for reserve to prevent oxidation.

Preparation of RuO₂

22.5 mg of RuO₂ powder was mixed with 245 μ L of ethanol, 245 μ L of water and 20 μ L (5 wt%) of Nafion solution by room temperature ultrasonication for 60 min to make the RuO₂ dispersed uniformly in the solvent, and conFig.d as RuO₂ ink. According to the loading amount of the material, the same RuO₂ was loaded on pure nickel foam by pipetting gun with a drop-coating area of 0.5×0.5 cm², and finally vacuum dried to obtain the RuO₂ electrode material.

Preparation of MIL-53

Firstly, 0.400 g (1 mmol) of $Fe_2(SO_4)_3 \cdot xH_2O$ was added to 35 mL of DMF, and then 0.495 g (3 mmol) of TPA was added. The mixture was stirred for 30 minutes before added with 2.5 mL of ethanol and 2.5 mL of water. The solution was stirred for 30 min and poured into a 100 ml autoclave. A piece of fresh NF (3 × 4 cm) was immersed in the homogeneous solution. The reaction kettle was then sealed and placed in an oven at 125 °C for reaction for 12 hours and then naturally cooled to ambient temperature. The material was rinsed several times with deionized water and dried in a vacuum oven at 60 °C.

Preparation of CeO₂

Firstly, 0.434 g (1 mmol) of Ce(NO₃)₃·6H₂O was added to 40 mL of deionized water, and then added with 2.5ml of NH₃·H₂O. The mixture was stirred for 30 min and poured into a 100 ml autoclave. A piece of fresh NF (3×4 cm) was immersed in the homogeneous solution. The reaction kettle was then sealed and placed in an oven at 180 °C for reaction for 6 hours and then naturally cooled to ambient

temperature. The material was rinsed several times with deionized water and dried in a vacuum oven at 60 $^{\circ}$ C.

Preparation of Fe₂O₃

Firstly, 0.400 g (1 mmol) of $Fe_2(SO_4)_3 \cdot xH_2O$ was added to 35 mL of DMF, and then added with 0.495 g (3 mmol) of TPA. The mixture was stirred for 30 minutes before added with 2.5 mL of ethanol and 2.5 mL of water. The solution was stirred for 30 min and poured into a 100 ml autoclave. A piece of fresh NF (3 × 4 cm) was immersed in the homogeneous solution. The reaction kettle was then sealed and placed in an oven at 180 °C for reaction for 6 hours and then naturally cooled to ambient temperature. The material was rinsed several times with deionized water and dried in a vacuum oven at 60 °C.

Preparation of Fe_2O_3 (a) CeO_2

Firstly, 0.434 g (1 mmol) of Ce(NO₃)₃·6H₂O was added to 40 mL of deionized water, and then added to 2.5ml of NH₃·H₂O. The mixture was stirred for 30 min and poured into a 100 ml autoclave. A piece of MIL-53 sample loaded on NF (3×4 cm) was immersed in the homogeneous solution. The reaction kettle was then sealed and placed in an oven at 180 °C for reaction for 6 hours and then naturally cooled to ambient temperature. The material was rinsed several times with deionized water and dried in a vacuum oven at 60 °C.

Preparation of Fe_2O_3 (a) CeO_2-O_V

A piece of $Fe_2O_3@CeO_2$ on NF was placed in a porcelain crucible, calcined at 350 °C for 2 h under argon atmosphere with a heating rate of 5 °C min⁻¹, then naturally cooled to ambient temperature to obtain $Fe_2O_3@CeO_2-O_V$.

Materials Characterization

Powder X-ray diffraction (PXRD) analysis was carried out on a MiniFlex600 X-ray diffractometer within the range of $2\theta = 2 \sim 80^{\circ}$. The morphology of the as-prepared Fe₂O₃@CeO₂-O_V, Fe₂O₃@CeO₂, Fe₂O₃, CeO₂ and MIL-53 was characterized using scanning electron microscope (SEM, ZEISS Gemini 300) and transmission electron microscope (TEM, FEI TF20). Elemental mapping was performed by field emission scanning electron energy-dispersive X-ray spectroscopy (ZEISS Gemini 300) and field transmittance electron energy dispersive spectroscopy (FEI TF20). The chemical element composition and states were investigated using X-ray photoelectron spectroscopy (XPS) spectra (Shimazu AXIS Supra) equipped with monochrome Al Ka anode. Fourier-transform infrared (FT-IR) spectroscopy measurements were carried out by Bruker Vertex 70 spectrometer. Raman spectra were collected with Renishaw inVa spectrometer. Electron Paramagnetic Resonance (EPR) spectra were collected by a Bruker A300 EPR Spectrometer.

X-ray absorption fine structure (XAFS)

The X-ray absorption fine structure (XAFS) spectra of Fe K-edge and Ce L_3 -edge were collected at a laboratory X-ray spectrometer easyXAFS300 (easyXAFS LLC, American). The obtained XAFS data were processed in Athena (version 0.9.26) for background, pre-edge line and post-edge line calibrations, and then Fourier transformed

fitting was carried out in Artemis (version 0.9.26).¹ For Wavelet Transform analysis, the $\chi(k)$ exported from Athena was imported into the Hama Fortran code.

Pair distribution function (PDF)

PDF analyses were performed on a Rigaku SmartLab (9kW) diffractometer. Powder samples were placed in a boro-silicate capillary with an outer diameter of 0.5 mm and a wall thickness of 0.01 mm. Rotating Ag anode was used to produce X-rays with a wavelength of 0.056 nm and a beam size of 8mm×0.4mm. The sample scanning speed is 0.5° per minute and the scanning range is from 3° to 150°, corresponding to a scattering vector Q range of 0.59 (1/A°) to 21.87 (1/A°).

Electrochemical Tests

Electrochemical performance was measured using a CHI 660E electrochemical working station. Electrochemical tests were performed on all samples at room temperature using a three-electrode setup. The self-supporting electrodes of samples loading on NF (Fe₂O₃@CeO₂-O_V, Fe₂O₃@CeO₂, Fe₂O₃, CeO₂ and MIL-53) were directly used as working electrodes. A graphite plate was used as the counter electrode, and Hg/HgO electrode was used as the reference. Except otherwise noted, the electrolyte used was 1.0 M KOH solution with the pH value of 14. Linear sweep voltammetry (LSV) was performed at a scan rate of 5 mV s⁻¹ with 90%-iR correction manually compensated. Potential E_{RHE} and overpotential (η) were calculated using the following equations:

$$E_{RHE} = E_{Hg/HgO} + (0.098 + 0.059 \times \text{pH}) \text{ V}$$

 $\eta = E_{RHE} - 1.23 \text{ V}$

Electrochemical surface area (ECSA)

Electrochemical surface areas (ECSAs) were evaluated by measuring the double-layer capacitance (C_{dl}) via cyclic voltammetry (CV). CV curves were measured at various scan rates from 10 to 60 mV s⁻¹ within the potential window of 1.07-1.17 V. According to the following equation, the ECSA values of the catalysts are calculated:

$$ECSA = C_{dl}/C_s$$

where C_s is the specific capacitance per unit area for samples under identical electrolyte conditions. For our estimates of surface area, we use the general specific capacitances of $C_s = 0.040 \text{ mF} \cdot \text{cm}^{-2}$ in 1.0 M KOH as previously reported. The ECSA-normalized current density j_{ECSA} for as-prepared catalysts was calculated by:²

$$j_{ECSA} = j/ECSA$$

where *j* is the current density.

Turnover frequency (TOF)

Turnover frequency (TOF) can be calculated to further estimate the intrinsic activity of catalysts, which follows the equation:

$$TOF = \frac{J \times A}{4 \times F \times m}$$

where J is the current density (A cm⁻²) at a given overpotential, A and m are the area of the electrode (0.25 cm⁻²) and the number of loading moles of the active substance

on the substrate, respectively. The number 4 represents a four-electron transfer process of OER. F is the Faraday constant (96485 C mol⁻¹).³

Electrochemical stability test

Multiple current step chronopotentiometry (MCSCP) tests were performed by setting the current density step increment as 4 mA cm⁻² and retention time as 500 s for 12 steps. Accelerated degradation tests (ADT) were applied by CV cycling within the potential window of 1.20 to 1.50 V for 1000, 5000 and 10000 cycles, respectively. The long-term durability of Fe₂O₃@CeO₂-O_V was assessed by chronoamperometry (i-t) tests in 1.0 M KOH at the constant potential of 1.424 and 1.509 V (with the starting current density around 10 and 100 mA cm⁻², respectively) for continuous 100 h.

Faraday efficiency (FE) measurement

Faraday efficiency (FE) was calculated using a rotating ring-disk electrode (RRDE) with glassy carbon disk electrode and Pt ring electrode on the RRDE Instrument (Pine Instruments). The glass carbon part of the disk electrode is 5mm in diameter, and the overall collecting efficiency N is 0.37. Powder of $Fe_2O_3@CeO_2-O_V$ was scratched from the self-supporting NF pieces and loaded onto the glassy carbon disk electrode as working electrode. RRDE tests were conducted in N₂-saturated 1.0 M KOH solution with a constant ring potential of 0.45V (vs. RHE) to induce the oxygen reduction reaction (ORR). FE was calculated according to the following equation:

$$FE = \frac{I_{ring}}{N \times I_{disk}}$$

where I_{ring} is the ring electrode current, I_{disk} is the disk electrode current, N is the overall collecting efficiency (N = 0.37).⁴

For FE calculation by the water drainage method, a three-electrode system was measured using a CHI 660E electrochemical analyzer. Fe₂O₃@CeO₂-O_V was used as the working electrode, Hg/HgO was used as the reference electrode, and a graphite rod was used as the counter electrode. A 5 mL measuring cylinder was used to collect oxygen precipitation on the working electrode during the test by drainage method, and the Faraday efficiency of OER was calculated by recording the time required for the precipitation of the same volume of oxygen. The current density was constant at 100 mA cm⁻² and 500 mA cm⁻² during the test.

Membrane-electrode flow cell tests

The homemade anion exchange membrane water electrolysis (AEMWE) flow cell system was consisted of the anode, cathode and anion exchange membrane (AEM, Fumasep FAA-3-50, Dioxide Materials). The self-supporting Fe₂O₃@CeO₂-O_V on Ni foam (thickness: 0.15 mm) was pressed at 15 MPa for 10 s and used as the anode electrode. The cathode electrode was prepared by loading commercial Pt/C (20 wt %) with the loading of 1 mg cm⁻² on carbon paper. The membrane electrode assembly (MEA) was prepared by pressing both anode and cathode electrodes to the two sides of the AEM. The fastening pressure of the AEMWE cell was 5 N m⁻¹. The performance of AEMWE with an active area of 2 cm × 2 cm was evaluated by CV in the range of 1.0 to 2.0 V at a scan rate of 5 mV s⁻¹. Stability tests were performed by

chronopotentiometry at different current densities (0.5 and 1.0 A cm⁻²) in 1.0 M KOH at room temperature.

DEMS Experiments

The operando DEMS experiments were performed using a QAS 100 mass spectrometer (Linglu Instruments, Shanghai) with a custom-made electrochemical cell, in which Pt wire and Ag/AgCl electrode served as the as counter electrode and the reference electrode, respectively. The working electrode was prepared by drop-casting the catalyst ink on a gold disk electrode with 9 mm diameter and loading of 0.5 mg cm⁻². To prepare the catalysts ink, the activated catalysts on Ni foam were first ultrasonically treated to obtain powdery catalysts. 3 mg powder was then ultrasonically dispersed in the mixture solution of 1 mL ethanol and 30 µL Nafion (5 wt%) to form a homogeneous ink. The mass signals were detected when the electrodes were subjected to potential cycling without iR correction. The 0.1 M KOH solution made with heavy oxygen water (98% ¹⁸O, Wuhan Isotope Technology Co., Ltd.) was utilized for isotopic labeling. The electrodes were firstly activated by CV between 1.29-1.75 V vs. RHE for 5 cycles and then immersed for 10 min. The ¹⁸O-labelled electrodes were rinsed with H₂¹⁶O to wash off the surface of H₂¹⁸O. ¹⁸O-labelled electrodes were measured by CV in the potential range of 1.29-1.75 V. vs. RHE for 10 cycles in 0.1 M KOH using H₂¹⁶O as solvent. DEMS and CV analyses were performed simultaneously during the cyclic tests. The time scale of the mass spectrum was converted to the potential scale according to the scan rate CV (5 mV s⁻¹).

ρ^{RHE} calculation

Proton reaction orders ρ^{RHE} were derived from LSV curves measured under different pH values of 12.5, 13.0, 13.5 and 14.0. The current density values at the fixed potential of 1.50 V (vs. RHE) were plotted in log scale against pH values, and the ρ^{RHE} values were extracted as the slopes of the linear fitting according to the equation $\rho^{\text{RHE}}=\partial \text{logj}/\partial \text{pH}$. An ideally zeroth order of proton reaction at the REH scale ($\rho^{\text{RHE}}=0$) is expected for completely concerted proton-electron transfer process, typical in the AEM pathway, while ρ^{RHE} larger than 0 indicates pH-dependent behaviors and non-cooperative proton-electron transfer.⁵⁻⁷

DFT calculation

Within the framework of periodic boundary condition, the spin-polarized density functional theory (DFT) calculation was implemented using VASP code.⁸ The ion-core electron interaction was described by the Projected augmented wave method,⁹ while the exchange and correlation interactions of elections were described by PBE functional.¹⁰The dispersion interactions were considered by involving the Grimme's D3 corrections.¹¹ As this system is considerably large (periodic box of 14.84Å×15.13Å×25.00 Å, Fig. S39), the Gamma point k-point sampling was used with the energy cutoff of 400 eV. During the calculations, the DFT + U approach was applied with Hubbard term (U_{eff} = U - J) describing the on-site coulombic interactions, which improved the description of localized states in Fe and Ce. According to the previous literatures, the value of U_{eff} = 4.3 eV¹²⁻¹⁴ was adopted on Fe 3*d* orbital, while the value

of $U_{eff} = 5.0 \text{ eV}^{15-17}$ was adopted on Ce 4*f* orbital. The convergence criterion for total energies was $2 \times 10^{-6} \text{ eV}$ with the Fermi smearing scheme, while the forces acting on the atoms were smaller than 0.05 eV/Å for geometry optimization. The α -Fe₂O₃ support was organized as its stable (104) surface characterized in XRD with the 2 × 3 supercell. The CeO₂ nanoparticle was described as the Ce₁₀O₂₀ cluster obtained from the lattice of CeO₂. The detailed model was shown in Fig. S43.



Fig. S1 (a) XRD pattern, (b) FT-IR and (c) Raman spectra of MIL-53 powder sample.



Fig. S2 Rietveld refining X-ray diffraction patterns of (a) CeO_2 , (b) Fe_2O_3 , (c) $Fe_2O_3@CeO_2$ and (d) $Fe_2O_3@CeO_2-O_V$.



Fig. S3 (a) FT-IR and (b) Raman spectra of $Fe_2O_3@CeO_2-O_V$, $Fe_2O_3@CeO_2$, Fe_2O_3 and CeO_2 .



Fig. S4 SEM images of MIL-53.



Fig. S5 SEM images of Fe₂O₃@CeO₂.



Fig. S6 SEM images of Fe₂O₃.



Fig. S7 SEM images of CeO₂.



Fig. S8 SEM images of Fe_2O_3 @CeO₂-O_V.



Fig. S9 TEM, HRTEM and SAED images of $Fe_2O_3@CeO_2-O_V$.



Fig. S10 TEM, HRTEM and SAED images of CeO_2 .



Fig. S11 TEM, HRTEM and SAED images of Fe_2O_3 .



Fig. S12 TEM, HRTEM and SAED images of Fe₂O₃@CeO₂.



Fig. S13 EDS mapping images of CeO_2 samples.



Fig. S14 EDS mapping images of Fe₂O₃ samples.



Fig. S15 EDS mapping images of Fe₂O₃@CeO₂.



Fig. S16 XPS spectra of samples: (a) survey spectra; (b) O 1s; (c) Ce 3d; (d) Fe 2p.



Fig. S17 Fourier-transformed k^3 -weighted magnitudes of Fe K-edge EXAFS signals with fitting curves for Fe₂O₃@CeO₂-O_V, Fe₂O₃@CeO₂, Fe₂O₃ and reference Fe foil samples. (a-d) *k* space; (e-h) *R* space. Solid line: experimental signals; dashed lines: fitting curves.



Fig. S18 Fe K-edge WT-EXAFS contour plots for Fe_2O_3 @CeO₂-O_V, Fe_2O_3 @CeO₂, Fe_2O_3 and reference Fe foil samples.



Fig. S19 Fourier-transformed k^2 -weighted magnitudes of Ce L₃-edge EXAFS signals with fitting curves for Fe₂O₃@CeO₂-O_V, Fe₂O₃@CeO₂, CeO₂ and reference CeO₂ samples. (a-d) *k* space; (e-h) *R* space. Solid line: experimental signals; dashed lines: fitting curves.



Fig. S20 Ce L₃-edge WT-EXAFS contour plots for Fe_2O_3 @CeO₂-O_V, Fe_2O_3 @CeO₂, CeO₂ and reference CeO₂ samples.



Fig. S21 The pair distribution function G(r), the corresponding raw powder diffraction data, and the total scattering function S(Q) data of (a-c) CeO₂, (d-f) Fe₂O₃, (g-i) Fe₂O₃@CeO₂, and (j-l) Fe₂O₃@CeO₂-O_V.



Fig. S22 (a) The simulated partial pair distribution function $G_{o-o}(r)$, $G_{Ce-o}(r)$, and $G_{Ce-Ce}(r)$ of CeO₂. (b) Interatomic distances of O-O, Ce-O, and Ce-Ce identified in the pair distribution function G(r) of Fe₂O₃@CeO₂ and Fe₂O₃@CeO₂-O_V. (c) The crystal structure of CeO₂. (d) Schematic of the distances between atoms in the CeO₂ lattice.



Fig. 23 CV curves collected at various scan rates (10, 20, 30, 40, 50 and 60 mV s⁻¹) for double layer capacitance (C_{dl}) calculations of (a) RuO₂, (b) CeO₂, (c) Fe₂O₃, (d) Fe₂O₃@CeO₂, (e) Fe₂O₃@CeO₂-O_V and (f) MIL-53 in 1.0 M KOH.



Fig. S24 77 K N₂ adsorption-desorption isotherms and calculated BET surface area values for (a) Fe_2O_3 , (b) CeO_2 , (c) Fe_2O_3 @CeO₂ and (d) Fe_2O_3 @CeO₂-O_V.



Fig. S25 ECSA-normalized LSV curves of samples. (a) positive scans and (b) negative scans.



Fig. S26 Calculation of TOF values from CV curves at different scan rates for (a) CeO_2 , (b) Fe_2O_3 , (c) $Fe_2O_3@CeO_2$ and (d) $Fe_2O_3@CeO_2-O_V$; (e) TOF-normalized LSV curves of samples.



Fig. S27 The MCSCP curve of Fe_2O_3 @CeO₂-O_V without iR correction. 4 mA cm⁻² current density increment was applied for 500 s for each step.



Fig. S28 SEM images of Fe_2O_3 @CeO₂-O_V after (a) 1000, (b) 5000 and (c) 10000 ADT cycles. SEM images of Fe_2O_3 @CeO₂ after (d) 1000, (e) 5000 and (f) 10000 ADT cycles.



Fig. S29 Chronoamperometric stability test of Fe_2O_3 @CeO₂-O_V at 1.424 V, with the starting current density around 10 mA cm⁻².



Fig. S30 (a) X-ray diffraction patterns and (b) Raman spectra of $Fe_2O_3@CeO_2-O_V$ before and after OER tests.



Fig. S31 XPS spectra of Fe₂O₃@CeO₂-O_V before and after OER test: (a) survey spectra; (b) O 1s; (c) Ce 3d, and (d) Fe 2p.



Fig. S32 SEM images of $Fe_2O_3@CeO_2-O_V$ after OER test.



Fig. S33 TEM and HRTEM images of Fe_2O_3 (@CeO_2-O_V after OER test.



Fig. 34 Photographic image of the AEMWE cell.



Fig. S35 LSV curves of (a) RuO_2 , (b) CeO_2 , (c) Fe_2O_3 , (d) $Fe_2O_3@CeO_2$ and (e) $Fe_2O_3@CeO_2-O_V$ in alkaline electrolytes with different pH. (f) LSV curves of $Fe_2O_3@CeO_2-O_V$ and $Fe_2O_3@CeO_2$ in 1.0 M KOH and 1.0 M TMAOH.



Fig. S36 Linear-fitting calculation of ρ^{RHE} values for quantification of pH-dependence of Fe₂O₃@CeO₂-O_V and Fe₂O₃@CeO₂.



Fig. S37 Calculation of contribution ratios of the capacitive and diffusion-controlled current densities: CV curves at various scan rates from 1 to 5 mV s⁻¹ for (a) $Fe_2O_3@CeO_2$ and (b) $Fe_2O_3@CeO_2-O_V$; corresponding linear-fitting calculation of b values for (c) $Fe_2O_3@CeO_2$ and (d) $Fe_2O_3@CeO_2-O_V$.



Fig. S38 DEMS signals of O₂ products for (a) $Fe_2O_3@CeO_2$ and (b) $Fe_2O_3@CeO_2-O_v$ in the electrolyte using $H_2^{18}O$ as the solvent during three times of LSV in the potential range of 1.29–1.75 V versus RHE, with a 5 mV s⁻¹ scan rate. OER mechanism analysis based on operando DEMS with the isotope labeling measurements.



Fig. S39 The DFT calculations on the models of the Fe₂O₃@CeO₂ catalyst. (a) The comparative calculation on choosing the Fe-terminating surface or the O-terminating surface to support the Ce₁₀O₂₀ cluster. (b) The O_V formation energies at different places of the Fe₂O₃@CeO₂ catalyst, including on CeO₂ cluster, at interface and on Fe₂O₃ surface. The above part shows the O about to be removed (marked in blue). The O_V formation over the top of CeO₂ shows to be the most favorable.



Fig. S40 Geometric 3D configurations of key reaction intermediate states during LOMbased OER on top of CeO₂ cluster for (a) $Fe_2O_3@CeO_2-O_V$ and (b) $Fe_2O_3@CeO_2$. The color code is the same as in Fig. 6 in the manuscript.



Fig. S41 Geometric 3D configurations of key reaction intermediate states during LOMbased OER at the CeO₂/Fe₂O₃ oxide interface for (a) Fe₂O₃@CeO₂-O_V and (b) Fe₂O₃@CeO₂. The color code is the same as in Fig. 6 in the manuscript.



Fig. S42 The free energy profiles for LOM-based OER steps for the case that initial O_V locates at the CeO₂/Fe₂O₃ oxide interface. The dotted lines represent the O₂ desorption step. This interfacial reaction site is inferior to that on top of CeO₂ cluster in Fig. 6.



Fig. S43 PDOS of O 2*p* during the O₂ desorption step of LOM for (a) $Fe_2O_3@CeO_2-O_V$ and (b) $Fe_2O_3@CeO_2$.

For the case of Fe₂O₃@CeO₂ without O_V, during the O₂ desorption step of LOM, when an extra oxygen vacancy (* \Box) forms, CeO₂ cluster is reduced to form Ce(III), and both Ce 5d and O 2p bands upshift, while the Fe 3d band does not show obvious change as shown in Fig. S37b (in the Fig. shows the PDOS of Fe 3d band of surficial Fe atoms). In this case, the interaction between CeO₂ cluster and Fe₂O₃ support is not strong enough to induce the shape change of the CeO₂ cluster, and the heterojunction effect is only electronic.

For the case of Fe₂O₃@CeO₂-O_V, counter-intuitively, when * \Box is generated during O₂ desorption of LOM, O 2*p* downshifts instead. The reason is that when an extra oxygen vacancy (* \Box) is generated with the presence of an already existed oxygen vacancy O_V, the as-formed CeO_{2-x} cluster (with two oxygen vacancies) presents an ultra-electronrich strong-reduction state, which interacts so strongly with the Fe₂O₃ support, leading to the collapse of the CeO_{2-x} cluster onto the Fe₂O₃ support (experimentally this situation would be like "a piece of cold butter melt on a hot pan", where the interfacial contact area is increased as the CeO_{2-x} cluster is "squashed" onto the support). From a theoretical point of view, this cluster-support exchange in oxide-heterojunction system is quite similar to the electronic metal-support interaction (EMSI) at the metal/oxide interface.^[18-19] The only difference is here the electron transfer takes place at oxide/oxide interface. The strong interfacial interaction transports the additional electrons on CeO_{2-x} cluster to the Fe₂O₃ support. In this case, although the Ce 5*d* band still upshifts slightly, due to the strong interaction and bonding between surficial Fe and O atoms from the CeO_{2-x} cluster, both Fe 3*d* and O 2*p* downshift.

In simple words, the stronger interaction between CeO_2 cluster and Fe_2O_3 support compensates the endergonic formation energy cost of an extra oxygen vacancy, thus contributing to the higher catalytic performance of Fe $_2O_3@CeO_2-O_V$ for LOM-based OER.

Sample	shell	CN	R(Å)	σ^2	ΔE_0	R factor
Name	Shen					
Fe foil	Fe-Fe	8	2.47±0.01	0.0051	6.4±0.9	0.0032
	Fe-Fe	6	2.85±0.01	0.0065		
Fe ₂ O ₃	Fe-O	5.9±0.4	1.94±0.01	0.0102	-5.6±1.9	0.0100
	Fe-Fe	1.2±0.2	2.88±0.02	0.0010		
	Fe-Fe1	4.8 ± 0.8	3.37±0.02	0.0049		
	Fe-Fe2	7.3±1.7	3.63±0.02	0.0124		
Fe ₂ O ₃ @ CeO ₂	Fe-O	6.3±0.4	1.99±0.01	0.0111		
	Fe-Fe	9.6±0.9	3.00±0.01	0.0167	0.7±1.2	0.0082
	Fe-Fe1	2.4±0.2	3.33±0.01	0.0015		
Fe ₂ O ₃ @	Fe-O	5.0±0.2	2.07±0.01	0.0084	12 4+1 0	0.0064
CeO ₂ -O _V	Fe-Fe	0.7 ± 0.1	2.66±0.01	0.0043	12.4±1.0	

Table S1. EXAFS fitting parameters extracted from the Fe K-edges of all the catalysts.

^{*a*}CN: coordination numbers; ^{*b*}R: bond distance; ^{*c*} σ^2 : Debye-Waller factors; ^{*d*} ΔE_0 : the inner potential correction. *R* factor: goodness of fit. S_0^2 was set to 0.77, according to the experimental EXAFS fit of Fe foil reference by fixing CN as the known crystallographic value.

Sample	shell	CN	R(Å)	σ^2	ΔE_0	R factor
Name						
CeO ₂	C - O	0	2 22 10 02	0.0040		0.0227
Standard	Ce-U	8	2.32±0.03	0.0040	6.6±2.8	0.0227
Fe ₂ O ₃ @	Ce-O	8.4±1.5	2.28±0.04	0.0049	77129	0.0192
CeO ₂	Ce-O1	3.9±1.9	2.54±0.09	0.0035	/./±2.8	
Fe ₂ O ₃ @	Ce-O	6.2±1.0	2.24±0.03	0.0045		0.0174
CeO ₂ -O _V	Ce-O1	4.7±2.6	3.16±0.08	0.0046	3.0±2.1	
	Ce-O	7.1±0.5	2.33±0.01	0.0023		
CeO ₂	Ce-Ce	2.5±0.5	3.00±0.02	0.0010	8.2±1.2	0.0231
	Ce-Ce1	7.3±1.0	3.89±0.02	0.0013		

Table S2. EXAFS fitting parameters extracted from the Ce L₃-edges of all the catalysts. ^{*a*}CN: coordination numbers; ^{*b*}R: bond distance; ^{*c*} σ^2 : Debye-Waller factors; ^{*d*} ΔE_0 : the inner potential correction. *R* factor: goodness of fit. S_0^2 was set to 0.63, according to the experimental EXAFS fit of CeO₂ reference by fixing CN as the known crystallographic value.

Catalyst	<i>j</i> (10 mA cm ⁻²)	η (mV)	References	
Fe ₂ O ₃ @CeO ₂ -O _v	10	172	This work	
Fe ₂ O ₃ @CeO ₂	10	217	This work	
CoFeCuOOH	10	170	[20]	
Ni _{0.3} Fe _{0.7} -LDH	10	184	[21]	
Mo ₁ -NiFeO _x H _y	10	193	[22]	
(Ni,Mn)-(Co)tet- (Co ₂)octO ₄ NSs	10	281.6	[23]	
ZnCo ₂ O ₄ -xF _x	10	350	[24]	
SNFM	10	260	[25]	
S-FeOOH/IF	10	244	[26]	
Zn _{0.2} Co _{0.8} OOH	100	241	[27]	
BM/BiFeO _x H _y	10	232	[28]	
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.2}Mn_{0.2}$ $Ni_{0.2}Mg_{0.2}O_{3}$	10	320	[29]	
CoVFeN@NF	10	212	[30]	
Fe–NiSOH	10	207	[31]	

Table S3. Comparisons of OER performance for other transition metal catalysts with

 $Fe_2O_3@CeO_2-O_V \text{ in } 1.0 \text{ M KOH.} (j = 10 \text{ mA cm}^{-2}).$

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