1 Oxygen-vacancy-rich CeO₂/Ru nanoparticles enable a high-

2 performance catalyst for alkaline hydrogen oxidation

3 Experimental section

4 Synthesis of RuCeCu-MOF.

5 In a typical preparation of the CuRuCe-MOF, 0.2416 g of Cu(NO₃)₂·3H₂O, 0.1086 g 6 of Ce(NO₃)·6H₂O and 50 mg of RuCl₃·xH₂O were dissolved in 13 mL of ethanol to 7 obtain solution A, 0.3022 g of 1,3,5-benzenetricarboxylic acid dissolved in 13 mL of 8 DMF to obtain solution B. Then solution B was dropped into solution A and stirred 9 for half an hour, and then transferred to a Teflon-lined 50 mL autoclave at 85 °C and 10 heated for 24 hours. The product was collected, washed several times with ethanol, 11 and dried under vacuum.

12

13 Synthesis of Ru/CeO₂(v)/C.

14 Using the obtained CuRuCe-MOF as the precursor, the catalyst was prepared by the 15 temperature-programmed pyrolysis method. The CuRuCe-MOF was placed in a 16 crucible in the center of the tube furnace. Under H_2/Ar mixed atmospheres, heat to 17 600 °C at a heating rate of 5 °C/min for 2 hours, then cool to room temperature, and 18 then take out the crucible from the furnace. Subsequently, the calcined product was 19 dissolved in 0.2 M hydrochloric acid solution and stirred for 24 hours to remove 20 copper species to obtain the final product. After centrifugation, the obtained product 21 was washed twice with water and once with ethanol.

22

23 Physical characterization.

The powder X-ray diffraction (XRD) patterns of the samples were collected from a 24 25 Japan Rigaku D/MAX-yA X-ray diffractometer equipped with Cu Ka radiation $(\lambda = 1.54178 \text{ Å})$. Scanning electron microscopy (SEM) images were recorded on a 26 27 JEOLJSM-6700 M scanning electron microscope. Transmission electron microscopy (TEM) images were recorded with a Hitachi H-7650 transmission electron 28 microscope using an accelerating voltage of 200 kV, and a high resolution 29 30 transmission electron microscope (HRTEM) (JEOL-2011) was operated at an 31 acceleration voltage of 200 kV. The specific surface area was evaluated at 77 K using 32 the Brunauer-Emmett-Teller (BET) method (Micromeritic TriStar II 3020 V1.03 instrument), while the pore volume and pore size were calculated according to the 33 34 Barrett-Joyner-Halenda (BJH) formula applied to the adsorption branch. Raman 35 spectra were obtained using a LabRAM HR Raman spectrometer. TG-DTA was 36 carried out using a SDT Q600 (V20.9 Build 20) equipment (TA Company, USA). 37 Electron paramagnetic resonance (EPR) spectroscopy was collected from electron Paramagnetic Resonance Spectrometer (JES-FA 200 (JEOL)). X-ray photoelectron 38 spectroscopy (XPS) was conducted on an ESCALAB 250 X-ray photoelectron 39

40 spectrometer instrument. The content of Ru and Ce were obtained via the inductively 41 coupled plasma-atomic emission spectrometer (ICP-AES) (Optima 7300 DV). ¹H 42 MAS NMR experiments was recorded on a Bruker AVANCE NEO 600 WB 43 spectroscope at 600 MHz. In situ infrared absorption spectroscopy (IRAS) were 44 obtained using a Nicolet iS50 FT-IR spectrometer. The X-ray absorption near edge 45 structure (XANES) and the extended X-ray absorption fine structure (EXAFS) were 46 investigated at BL08U1A and BL14W1 beamline of Shanghai Synchrotron Radiation 47 Facility (SSRF).

48

49 Ultraviolet Photoemission Spectroscopy.

50 Ultraviolet emission spectroscopy (UPS) measurements were performed at the 51 Catalysis and Surface Science Terminal of the National Synchrotron Radiation 52 Laboratory (NSRL) in Hefei, China. As the excitation source, synchrotron radiation 53 has a photon energy of 40 eV, and the valence band spectrum was measured. The 54 valence band spectrum refers to the Fermi level determined from the Au sample. 55 Apply a sample bias of -10 V to observe the secondary electron cut-off.

56

57 Electrochemical measurements.

58 Electrochemical tests were all carried out in the three-electrode system on the 59 electrochemical workstation CHI760E.

60 For the HOR electrochemical test, 0.1 M KOH was used as the electrolyte. The 61 working electrode was a glassy carbon (GC) electrode (diameter: 5 mm), and the 62 counter electrode was a platinum wire, Ag/AgCl (filled with 3M KCl solution) electrode as reference electrode. In this work, all potentials measured by HOR were 63 referred to as reversible hydrogen electrode (RHE) potentials using Pt as the working 64 electrode in the H₂-saturated electrolyte for calibration. The solution resistance was 65 measured using AC-impedance spectroscopy from 200 kHz to 100 mHz and 10 mV 66 voltage perturbation, and the polarization curves were corrected for the solution 67 68 resistance. In order to prepare a working electrode, 1 mg of catalyst and 30 μL of 69 Nafion solution (Sigma Aldrich, 5 wt%) were dispersed in 470 ml of ethanol, and then 70 sonicated to form a homogeneous ink. The glassy carbon (GC, diameter 5 mm) electrode was polished with γ -Al₂O₃ powder slurry to obtain a clean surface, and then 71 72 ultrasonically cleaned with ultrapure water and ethanol. Subsequently, the dispersion was dropped on the glassy carbon electrode (All of the catalysts with a loading of 10 73 $\mu g_{NM} \operatorname{cm}_{disk}^{-2}$). Before the HOR test, cyclic voltammetry (CV) was performed in an 74 H₂-saturated electrolyte to obtain a stable voltammetry curve. Then, a rotating disk 75 electrode (RDE) was used to record the polarization curve at a scan rate of 1 mV s⁻¹. 76

77

78 Electrochemically active surface area (ECSA) measurement.

The electrochemically active surface area (ECSA) of various samples was measured according to the Cu-UPD method reported in the previous literature.¹ The catalyst modified electrode was stabilized after cycling between 0 and 0.95 V in Ar-saturated 0.1 M H_2SO_4 . The voltammogram obtained at a sweep rate of 5 mV s⁻¹ was used as the background of the corresponding Cu_{upd} stripping voltammogram. Cu_{upd} stripping 84 voltammetry (0.25–0.95 V, 5 mV s⁻¹) was performed in an Ar-saturated 0.1 M H_2SO_4

solution containing 2 mM CuSO₄ after Cu deposition at 0.25 V for 100 s. The value of Γ

86 ECSA can be calculated by the following equation:

$$ECSA(\frac{cm_{metal}^{2}}{g_{metal}}) = \frac{Q_{Cu}}{M_{metal} 420 \,\mu C \, cm^{-2}}$$

87 88

89 Kinetic current density j_k and exchange change density j_0 .

90 The kinetic current density (j_k) could be obtained by the Koutecky-Levich equation:

91
$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d}$$

$$\eta_d = \frac{RT}{2F} ln^{[i0]} (1 - \frac{j_d}{j_l})$$

92

93 Where η_d is the diffusion overpotential, j_d is the diffusional current density, j_l is the 94 hydrogen mass transport limited current density and j is the measurement current 95 density. R is the ideal gas constant, T is the experimental temperature in Kelvin., and 96 F is the Faradaic constant.

97 The exchange current (j_0) was obtained by fitting the kinetic current (j_k) to the Butler-

98 Volmer equation:

$$j_k = j_0 \frac{\eta F}{RT}$$

99

100 Where η is the overpotential, R is the ideal gas constant, T is the experimental 101 temperature in Kelvin, and F is the Faradaic constant.

102

103 CO stripping experiments.

104 CO stripping was performed by holding the electrode potential at 0.1 V versus RHE 105 for 10 min in the purged CO to adsorb CO on the metal surface, followed by N_2 106 purging for another 30 min to remove residual CO in the electrolyte. The CO-107 stripping current was obtained via cyclic voltammetry in a potential region from 0 to 108 1.2 V at a sweep rate of 20 mV s⁻¹.

109

110 Calculation details.

All the calculations were based on density functional theory by using the Vienna Ab Initio simulation package (VASP). The generalized gradient approximation (GGA) with the function of Perdew-Becke-Ernzerhof (PBE) was employed to describe the electron interaction energy of exchange correlation. The projector augmented wave was applied to describe the electron-ion interaction and the plane-wave energy cutoff was set to 450 eV. The convergences of energy and force were set to 1×10^{-5} eV and 0.02 eV/Å, respectively. Brillouin zone sampling was employed using a Monkhorst-Packing grid with $3 \times 3 \times 1$ for structural optimization and $9 \times 9 \times 2$ for DOS calculation.

120 where the symbol "*" represented the active site.

- 121 The HBE were calculated by:
- 122 HBE = $E_{*H} E_* 1/2 E_{H2}$
- 123 The OHBE were calculated by:
- 124 OHBE= $E_{*OH} E_* E_{OH}$
- 125 The symbol "*" represented the active site. The E_{*H} and E_{*OH} represent the energy of
- 126 catalysts with the adsorbed H and OH species; while E_* and E_{H2} stand for the energies
- 127 of the clean surface of catalysts and the H_2 molecules. As to the $\mathrm{E}_{\mathrm{OH}},$ it can be
- 128 obtained by $E_{OH} = E_{H2O} 1/2 E_{H2}$.
- 129



Scheme S1. Schematic representation of the formation of Ru/CeO₂(v)/C. (a) a nanopolyhedron of RuCeCu-MOF precursor, (b) ultrasmall Ru, CeO₂(v) and Cu₂₊₁O nanoparticles embedded in the carbon skeleton, (c) ultrasmall Ru/CeO₂(v) nanoparticles embedded in the amorphous carbon skeleton after removing $Cu_{2+1}O$, (d) enlarged model of Ru/CeO₂(v) nanoparticles are supported on a highly conductive graphene-like layer.



Figure S1. SEM and TEM images of RuCeCu-MOF.



144 Figure S2. XRD patterns of RuCeCu-MOF and Cu-MOF.



147 Figure S3. Typical XRD pattern of the intermediate product.148



150 Figure S4. TGA curve of the RuCeCu-MOF under argon atmosphere.151



153 Figure S5. Typical XRD pattern of $Ru/CeO_2(v)/C$.



156 Figure S6. SEM and TEM images of $Ru/CeO_2(v)/C$.



159 Figure S7. High-resolution XPS spectrum of Ru/CeO₂(v)/C for Cu 2p.160



162 Figure S8. STEM image and EDS maps of elemental Ru and Ce in $Ru/CeO_2(v)/C$.



164 Figure S9. Nitrogen adsorption/desorption isotherms of Ru/CeO₂(v)/C.165



166

167 Figure S10. Pore size distribution of Ru/CeO₂(v)/C.168



169

170 Figure S11. XRD pattern of Ru/C.



173 Figure S12. The Raman spectra of $Ru/CeO_2(v)/C$ and CeO_2 .



176 Figure S13. High-resolution spectrum of XPS of $Ru/CeO_2(v)/C$ for Ce 3d.



179 Figure S14. High-resolution Ce 3d XPS spectra of Ru/CeO₂(v)/C and CeO₂(v)/C.
180





Figure S15. Onset level (E_{onset}) of the UPS spectra for Ru/CeO₂(v)/C and Ru/C.



Figure S16. Polarization curves of $Ru/CeO_2(v)/C$ in H_2 and N_2 saturated 0.1 M KOH at a scan rate of 1 mV s⁻¹ and rotation rate of 1600 rpm.



189 Figure S17. EIS Nyquist plots of CeO₂, Ru/C and Ru/CeO₂(v)/C. EIS was also 190 conducted, which can provide information on the solution resistance (R_s) and charge 191 transfer resistance (R_{ct}).² The results showed that CeO₂ has very poor electronic

192 conductivity. In Ru/CeO₂(v)/C, Ru and CeO₂(v) are supported on highly conductive 193 graphene-like carbon. Compared with that of CeO₂, the charge transfer resistance of 194 Ru/CeO₂(v)/C was much lower. Notably, Ru/CeO₂(v)/C exhibited similar charge 195 transfer to Ru/C, leading to excellent HOR activity. 196



197

198 Figure S18. EPR images of Ru/CeO₂(v)/C and Ru/CeO₂/C.199



200

201 Figure S19. HOR polarization curves of Ru/CeO2(v)/C and Ru/CeO2/C in H2-

202 saturated 0.1 M KOH at a scan rate of 1 mV s^{-1} and a rotation speed of 1600 rpm.





206 Ru/CeO₂(v)/C-700. 207



208

209 Figure S21. HOR polarization curves of Ru/CeO2(v)/C-500, Ru/CeO2(v)/C-600 and

210 Ru/CeO₂(v)/C-700 in H₂-saturated 0.1 M KOH with a scan rate of 1 mV s⁻¹ at a 211 rotating speed of 1600 rpm.

212



215 Ru/CeO₂(v)/C-60.

216



- 218 Figure S23. HOR polarization curves of Ru/CeO₂(v)/C-40, Ru/CeO₂(v)/C-50 and
- 219 Ru/CeO₂(v)/C-60 in H₂-saturated 0.1 M KOH with a scan rate of 1 mV s^{-1} at a

220 rotating speed of 1600 rpm.



222

223 Figure S24. Cu stripping curves of Ru/CeO₂(v)/C, PtRu/C and Pt/C in Ar-saturated 224 solution (2 mM CuSO₄ + 0.1 M H₂SO₄) at a scan rate of 5 mV s⁻¹.

225



Figure S25. linear current potential region around the equilibrium potential of HOR/HER of Ru/CeO₂(v)/C, PtRu/C and Pt/C conducted in H₂-saturated 0.1 M KOH at a scan rate of 1 mV s⁻¹ with the rotation speed at 1600 rpm after iR compensation.



232 Figure S26. (a) TEM and (b) XRD images of $Ru/CeO_2(v)/C$ after the stability test. 233 High-resolution XPS spectra of (c) Ru 3p in $Ru/CeO_2(v)/C$ before and after the

233 High-resolution XPS spectra of (c) Ru 3p in Ru/CeO₂(v)/C before 234 stability test and (b) Ce 3d in Ru/CeO₂(v)/C after the stability test.



237 Figure S27. (a-e) HAADF-STEM image and maps of elemental Ru (b), Ce (c), O (d), 238 and C (e) in Ru/CeO₂(v)/C. (f, g) HRTEM images after the stability test of

239 Ru/CeO₂(v)/C.240



241

242 Figure S28. CVs of Ru/CeO₂(v)/C and Ru/C in N₂-saturated 0.1M KOH solution at a

243 scan rate of 20 mV s⁻¹.

244



245

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246 Figure S29. CO stripping voltammograms of Ru/CeO<sub>2</sub>(v)/C and Pt/C in N<sub>2</sub>-saturated
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247 0.1 M KOH with a scan rate of 20 mV s⁻¹.



250 Figure S30. In situ infrared absorption spectra. *H bands recorded for $Ru/CeO_2(v)/C$

251~ and Ru/C in a H_2-saturated 0.1 M KOH solution.

252



Figure S31. HOR polarization curves of Ru/CeO₂(v)/C, Ru/C and CeO₂(v)/C in H₂saturated 0.1 M KOH at a scan rate of 1 mV s⁻¹ and a rotation speed of 1600 rpm.



Figure S32. ¹H NMR spectra of oxygen-vacancy-rich CeO₂.



Figure S33. Optimized structures of H* adsorbed on Ru both from (a) side view and (b) top view, OH* adsorbed on Ru both from (c) side view and (d) top view, the white, blue and red spheres represent H, Ru and O atoms, respectively.









269 Figure S35. H*: adsorption site 2 (-0.54 eV).

270





272 Figure S36. H*: adsorption site 3 (-0.82 eV).





275 Figure S37. OH*: adsorption site 1 before optimization.



278 Figure S38. OH*: adsorption site 2 before optimization.



281 Figure S39. OH*: adsorption site 3 before optimization.282



283

284 Figure S40. Optimized structures of (a) H^* (site 2), (b) OH^* adsorbed on $Ru/CeO_2(v)$

285 interface from top view, the white, yellow, blue and red spheres represent H, Ce, Ru

286 and O atoms, respectively.

287



288

289 Figure S41. Adsorption of H^* in the Ru/CeO₂ model.



292 Figure S42. Adsorption of OH* in the Ru/CeO_2 model.



295 Figure S43. The projected DOS of Ru atoms in the $Ru/CeO_2(v)$ and Ru cluster 296 models.

298 Table S1

299 ICP-AES results for the actual contents of Ru, Ce and Cu in the $Ru/CeO_2(v)/C$ 300 catalyst.

	Catalyst	Ru (wt. %)	Ce (wt. %)	Cu (wt. %)
Ru	$1/CeO_2(v)/C$	25.40	5.22	0.14%

Table S2

303 ICP-AES results showing the actual contents of Ru and Ce in Ru/CeO₂(v)/C-40, 304 Ru/CeO₂(v)/C-50 and Ru/CeO₂(v)/C-60.

Catalyst	Ru/CeO ₂ (v)/C-40	Ru/CeO ₂ (v)/C-50	Ru/CeO ₂ (v)/C-60
Ru (wt. %)	15.7	25.4	30.1
Ce (wt. %)	4.7	5.2	5.5
Ru/Ce	3.3/1	4.9/1	5.5/1

310 **Table S3**

311 The mass activities and specific activities for Ru/CeO₂(v)/C, PtRu/C, and Pt/C

Catalyst	ECSA (m ² g _{NM} ⁻¹)	$ \begin{array}{c} \dot{j}_{k,m} \\ \eta = 50 \text{ mV} \\ (\text{A mg}_{NM}^{-1}) \end{array} $	<i>j</i> _{0,s} (mA cm _{NM} ⁻²)
Ru/CeO ₂ (v)/C	39.11	8.06	2.85
PtRu/C	128.58	3.45	0.34
Pt/C	116.01	0.41	0.14

312

313 Table S4

- 314 Summary of the mass activity at an overpotential of 50 mV and ECSA-normalized
- 315 exchange current density of selected HOR electrocatalysts in alkaline media.

Catalyst	$j_{k,m}$ $\eta = 50 \text{ mV}$ $(\text{A mg}_{\text{NM}}^{-1})$	<i>j</i> _{0,s} (mA cm _{NM} ⁻²)	Scan rate (mV/s)	Reference
Ru/CeO ₂ (v)/C	8.06	2.85	1	This work
Ru/C (3.1 nm)	0.063	0.082	10	1
P-Ru/C	-	0.72	10	3
Ir1Ru1 NWs/C	1.416 A	0.126	10	4
IO-Ru–TiO2/C	0.907	1.13	10	5
PdCu/C-500 °C	0.552	-	1	6
Pt ₆ NCs/C	3.658	1.546	5	7
RhMo NSs	6.96	-	5	8
Rh2Sb NBs	3.254	0.506	5	9
IrNi@Ir/C	1.12	1.22	10	10
RuNi1	2.70	-	10	11
hcp/fcc-Ru	1.016	0.664	10	12
Sn-Ru/C	1.79	0.47	10	13

316

317 Table S5

318 Calculated optimal binding energy of ΔE_{H^*} and ΔE_{OH^*} on various models.

Models	$\Delta E_{\mathrm{H}^{*}}\left(\mathrm{eV}\right)$	$\Delta E_{OH^*} (eV)$
Ru cluster	-0.96	-1.12
$Ru/CeO_2(v)$	-0.54	-0.81
Pt (111)	-0.40	0.92

319 320

J. Ohyama, T. Sato, Y. Yamamoto, S. Arai and A. Satsuma, J. Am. Chem. Soc., 2013, 135,
 8016-8021.

323 2. Y. Duan, Z. Y. Yu, L. Yang, L. R. Zheng, C. T. Zhang, X. T. Yang, F. Y. Gao, X. L. Zhang,

X. X. Yu, R. Liu, H. H. Ding, C. Gu, X. S. Zheng, L. Shi, J. Jiang, J. F. Zhu, M. R. Gao and S.
H. Yu, *Nat. Commun.*, 2020, 11, 4789.

- 326 3. Y. M. Zhao, X. W. Wang, G. Z. Cheng and W. Luo, ACS Catal., 2020, 10, 11751-11757.
- 327 4. B. W. Qin, H. M. Yu, X. Q. Gao, D. W. Yao, X. Y. Sun, W. Song, B. L. Yi and Z. G. Shao, J.

328		Mater. Chem. A, 2018, 6, 20374-20382.
329	5.	J. X. Jiang, S. C. Tao, Q. He, J. Wang, Y. Y. Zhou, Z. Y. Xie, W. Ding and Z. D. Wei, J
330		Mater Chem A, 2020, 8, 10168-10174.
331	6.	Y. Qiu, L. Xin, Y. W. Li, I. T. McCrum, F. M. Guo, T. Ma, Y. Ren, Q. Liu, L. Zhou, S. Gu,
332		M. J. Janik and W. Z. Li, J. Am. Chem. Soc., 2018, 140, 16580-16588.
333	7.	X. N. Wang, L. M. Zhao, X. J. Li, Y. Liu, Y. S. Wang, Q. F. Yao, J. P. Xie, Q. Z. Xue, Z. F.
334		Yan, X. Yuan and W. Xing, Nat. Commun., 2022, 13, 1596.
335	8.	J. T. Zhang, X. Z. Liu, Y. J. Ji, X. R. Liu, D. Su, Z. B. Zhuang, Y. C. Chang, C. W. Pao, Q.
336		Shao, Z. W. Hu and X. Q. Huang, Nat. Commun., 2023, 14, 1761.
337	9.	Y. Zhang, G. Li, Z. L. Zhao, L. L. Han, Y. G. Feng, S. H. Liu, B. Y. Xu, H. G. Liao, G. Lu, H.
338		L. Xin and X. Q. Huang, Adv. Mater., 2021, 33, 2105049.
339	10.	D. Liu, S. Q. Lu, Y. R. Xue, Z. Guan, J. J. Fang, W. Zhu and Z. B. Zhuang, Nano Energy,
340		2019, 59 , 26-32.
341	11.	J. J. Mao, C. T. He, J. J. Pei, Y. Liu, J. Li, W. X. Chen, D. S. He, D. S. Wang and Y. D. Li,
342		Nano Lett., 2020, 20 , 3442-3448.
343	12.	Y. B. Li, C. Y. Yang, J. C. Yue, H. J. Cong and W. Luo, Adv. Funct. Mater., 2023, 33,
344		2211586.
345	13.	L. Q. Wu, L. X. Su, Q. Liang, W. Zhang, Y. Men and W. Luo, ACS Catal., 2023, 13, 4127-
346		4133.
347		