Supporting information

Amorphous-Crystalline RuTi Nanosheets Enhancing OH

Species Adsorption for Efficient Hydrogen Oxidation Catalysis

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METHODS

Chemicals. Ruthenium acetylacetonate (Ru(acac)₃) and titanium acetylacetonate (TiO(acac)₂) were purchased from Alfa Aesar Co. Ltd., China. Sodium chlorides (NaCl), potassium hydroxide (KOH), isopropanol (C₃H₈O, AR) and ethanol (C₂H₆O, AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Commercial Pt/C (20 wt.%) was obtained from Johnson Matthey (JM). Water (18 M Ω cm⁻¹) used in all the experiments was obtained by passing through an ultra-pure purification system (Aqua Solutions). All the chemicals were used as received without further purification.

Materials synthesis. Typically, 10 mg Ru(acac)₃ and 2.2 mg TiO(acac)₂ were mixed in 1 mL water and 4 mL ethanol containing 15 mg NaCl. After ultrasonic treatment at room temperature for 30 min, the blight red solvent was slowly evaporated. The dried solid was pyrolyzed at 250 °C in air for 90 min. The product (marked with a/c-Ru/Ti-RuO₂) was washed with water and ethanol three times and collected by centrifugation. The a/c-Ru/RuO₂ and c-RuO₂ were prepared with a similar procedure except for the absence of TiO(acac)₂ under 250 °C and 300 °C, respectively. The c-Ti-RuO₂ was obtained by treating a/c-Ru/Ti-RuO₂ in air at 300 °C for 90 min. The a/c-Ru/Ti-RuO₂ with different Ti contents (marked as a/c-Ru/Ti-RuO₂-61 and a/c- Ru/Ti-RuO₂-32) were obtained by changing the amounts of TiO(acac)₂ to 1.1 mg and 4.4 mg, respectively.

Characterizations. Transmission electron microscopy (TEM) was operated on JEOL electron microscope at an accelerating voltage of 100 kV. High-resolution TEM (HRTEM) and energy dispersive X-ray spectroscopy elemental mapping were operated on FEI Tecnai F30 TEM with an accelerating voltage of 300 kV. Scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) were conducted on HITACHI S-4800 with an accelerating voltage of 15 kV. X-ray diffraction spectroscopy (XRD) was conducted on Rigaku with Cu Ka ($\lambda = 1.54$ Å). X-ray photoelectron spectrum (XPS) was conducted on SSI S-Probe XPS spectrometer. The thickness of sample was determined by atomic force microscope (AFM, Dimension Fast Scan). Thermogravimetric (TG) curves were obtained through a STA209 PC (Netzsch, Germany) instrument from 25 to 900 °C. The electron paramagnetic resonance (EPR) was carried out at 300 K with a JEOL JES-FA200 EPR spectrometer. XAS was operated on NSRRC TPS44A.

Electrochemical measurements. All the electrochemical measurements were performed at CHI660 electrochemical workstation (Chenhua, shanghai) with a typical three-electrode system. A rotating disk electrode (RDE) with diameter of 5 mm, graphite rod, and a saturated calomel electrode (SCE) were used as working electrode, counter electrode and reference electrode, respectively. For the preparation of the working electrode, RuTi nanosheets were loaded on carbon black (VXC-72R) by ultrasound 1 h. The loading content of Ru on carbon powder was estimated from TG analysis and EDS composition. The carbon supported RuTi nanosheets (1 mg), isopropanol (495 μ L), and Nafion solution (5 μ L, 5 wt.%) were added into a glass vial and then ultrasonicated for 1 h to make a homogenous ink. Then, 10 μ L electrocatalyst ink was dropped onto the RDE surface. All electrochemical performance of catalysts was tested after activating for 100 cycles at a scan rate of 0.5 V s⁻¹ during potential range from -0.2 to 0.4 V vs. RHE. Linear sweep voltammetry (LSV) was carried out at the scan rate of 5 mV s⁻¹ and rotation speed of 1600 rpm. All the polarization curves were corrected 95% IR compensation by workstation. The kinetic current density (*j_k*) can be calculated by the Koutecky-Levich (K-L) equation:

$$1/j=1/j_k+1/j_d$$

Where *j* is current density and j_d is diffusion-limited current density, which can be collected by the Levich equation:

$$j_d = 0.62 n F D^{3/2} v^{-1/6} C_0 \omega^{1/2} = B C_0 \omega^{1/2}$$

where *n* is the number of electrons involved in the HOR, *F* is the Faraday constant, *D* is the diffusion coefficient of the reactant, *v* is the viscosity coefficient of electrolyte, C_0 is the solubility of H₂ in the electrolyte, ω is the rotating speed, and *B* is the Levich constant.

The exchange current density j_0 can be obtained from the Butler-Volmer (B-V) equation:

$$j_k = j_0(e^{\alpha F/RT} - e^{(-\alpha)F\eta/RT})$$

where α is the transfer coefficient, F is the Faraday constant, R is the universal gas constant, T is the temperature, and η is the overpotential.

Electrochemically active surface areas (ECSAs) were tested by Cu underpotential deposition (Cu_{UPD}) stripping. Typically, CV on each catalyst was first carried out at a scan rate of 50 mV s⁻¹ in Ar-purged 0.5 M H₂SO₄ solution to obtain a steady voltammogram as the background. Then, Cu_{UPD} stripping was performed at a scan rate of 50 mV s⁻¹ in Ar-purged 0.5 M H₂SO₄ solution containing 5 mM CuSO₄ after Cu deposition at about 0.25 V for 100 s. The value of ECSA (cm²) can be calculated by equation:

$$ECSA=Q_{Cu}/Q_{s}$$

Where Q_{Cu} is the measured integral charge, Q_s is the surface charge density of 420 μ C cm_{metal}⁻² which is assumed for a monolayer adsorption of Cu_{UPD} on metal.

The cyclic voltammogram (CV) was performed in Ar-saturated 0.1 M KOH. CO stripping test was performed in 0.1 M KOH solution. First, the electrode was held at a certain potential for 100 s in CO-saturated 0.1 M KOH solution to adsorb CO. Then, the electrode was transferred rapidly to the Ar-saturated 0.1 M KOH solution, and CV curves were collected in the potential range from 0 to 1 V vs. RHE at a scan rate of 0.05 V s⁻¹. The obtained first forward scan is considered as the stripping of a monolayer of CO.

Electrochemical measurement of *in-situ* Fourier transform infrared spectroscopy (FTIR). Electrochemical *in-situ* Fourier transform infrared spectroscopy experiments were carried out on a Nicolet 8700 FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT-A detector. A thin-layer IR cell with a CaF₂ prism was used. During the external reflection FTIR measurement, a thin layer structure (~10 µm) is formed between the electrode and the IR window, and the signal is acquired during the process using a multi-step FTIR spectroscopy (MSFTIR) program. In the attenuated total reflection (ATR) FTIR experiment, the catalyst was directly dropped on the Si prism coated with Au film as the working electrode. The resulting spectra were reported as the relative change in reflectivity at each potential, that is, $\Delta R/R = R(E_S) - R(E_R) / R(E_R)$, where $R(E_S)$ and $R(E_R)$ are single-beam spectrum collected at the sample potential E_S and reference potential E_R , respectively. The E_S was switched from lower to higher potentials during the measurements. To improve the signal to noise ratio, 300 singlebeam spectra were collected and co-added for each resulting spectrum at a spectral resolution of 8 cm⁻¹.



Fig. S1. (a) SEM image and (b) EDS profile of $a/c-Ru/Ti-RuO_2$.



Fig. S2 (a, b) TEM images and (c, d) HRTEM images of a/c-Ru/Ti-RuO₂.



Fig. S3 XRD pattern of a/c-Ru/RuO₂.



Fig. S4 (a, b) TEM images and (c) HRTEM image of $a/c-Ru/RuO_2$. (d) IFFT and FFT images of $a/c-Ru/RuO_2$ transformed by (c). The scale bars of FFT and IFFT images are 1/2 nm and 1 nm, respectively.



Fig. S5 XRD patterns of c-Ti-RuO₂ and c-RuO₂.



Fig. S6 (a) SEM image, (b) SEM-EDS profile, and (c, d) TEM images of c-Ti-RuO₂.



Fig. S7 EPR spectra of c-Ti-RuO₂ and c-RuO₂.



Fig. S8 XPS survey spectra of a/c-Ru/Ti-RuO₂ and c-Ti-RuO₂.



Fig. S9 (a) HOR polarization curves of a/c-Ru/Ti-RuO₂, a/c-Ru/Ti-RuO₂-61, and a/c-Ru/Ti-RuO₂-32. (b) XRD patterns of a/c-Ru/Ti-RuO₂-61 and a/c-Ru/Ti-RuO₂-32.



Fig. S10 Polarization curves of a/c-Ru/Ti-RuO₂ in H₂-saturated and Ar-saturated 0.1 M KOH.



Fig. S11 Polarization curves of (a) c-Ti-RuO₂, (b) a/c-Ru/RuO₂, and (c) commercial Pt/C at different rotating speeds. (d) Koutecky-Levich plot of c-Ti-RuO₂, a/c-Ru/RuO₂, and commercial Pt/C.



Fig. S12 TG curves of a/c-Ru/Ti-RuO₂/C and c-Ti-RuO₂/C.



Fig. S14 Summary of mass activities of reported catalysts for HOR.



Fig. S14 Cu stripping voltammograms of (a) $a/c-Ru/Ti-RuO_2$, (b) $c-Ti-RuO_2$, (c) $a/c-Ru/RuO_2$, and (d) Pt/C.



Fig. S15 (a-c) TEM images and (d) SEM-EDS profile of a/c-Ru/Ti-RuO₂ after stability test for 12000 s.



Fig. S16 HOR polarization curves of (a) $a/c-Ru/Ti-RuO_2$, (b) $c-Ti-RuO_2$, (c) $a/c-Ru/RuO_2$, and (d) commercial Pt/C in H₂-staturated and 1000 CO ppm + H₂-staturated 0.1 M KOH electrolytes.



Fig. S17 CV curves of (a) a/c-Ru/Ti-RuO₂, (b) a/c-Ru/RuO₂, (c) c-Ti-RuO₂, and (d) commercial Pt/C before and after activating for 100 cycles at 0.5 V s⁻¹.



Fig. S18 (a, b) TEM images, (c) XRD pattern, (d) SEM-EDS profile, (e) Ru 3d spectra, and (f) normalized XANES spectra of a/c-Ru/Ti-RuO₂ before and after activating for 100 cycles at 0.05 V s⁻¹.



Fig. S19 CV curves of (a) c-Ti-RuO₂, (b) a/c-Ru/RuO₂, and (c) commercial Pt/C before and after activating for 100 cycles at 0.05 V s⁻¹ in 0.1 M KOH. (d) CV peaks comparison of a/c-Ru/RuO₂ and Pt/C.



Fig. S20 HOR polarization curves of (a) $a/c-Ru/Ti-RuO_2$ and (b) commercial Pt/C collected in 0.1 M KOH and 0.1 M KOD.



Fig. S21 *In-situ* FTIR spectra recorded at potential from 0.2 to -0.15 V vs. RHE in H₂-saturated 0.1 M KOH electrolyte for (a) a/c-Ru/Ti-RuO₂ and (b) c-Ti-RuO₂.



Fig. S22 CO-stripping curves of (a) a/c-Ru/Ti-RuO₂, (b) c-Ti-RuO₂, (c) a/c-Ru/RuO₂, and (d) commercial Pt/C collected in 0.1 M KOH at 0.05 V s⁻¹.



Fig. S23 *In-situ* FTIR spectra of a/c-Ru/Ti-RuO₂, c-Ti-RuO₂, and a/c-Ru/RuO₂ at 0.65 V vs. RHE.

Valence proportion	Ru ⁰ 3d	Ru ⁴⁺ 3d	Ru-O/Ti-O	Ru–O _{BRI}	Ru–O _{cus}
a/c-Ru/Ti-RuO ₂	27.9%	46.9%	24.5%	41.2%	34.3%
c-Ti-RuO ₂	25.9%	40.0%	40.0%	31.2%	28.8%

Table S1 Analysis on Ru 3d and O 1s XPS spectra.

Catalyst		Mass activity	D. (
	Electrolyte	/ A mg ⁻¹	Ket.
a/c-Ru/Ti-RuO ₂	0.1 M KOH	4.16	This work
RuFe _{0.1}	0.1 M KOH	0.23	Small 2022, 18, 2202404
RuNi	0.1 M KOH	4.34	CCS Chem. 2023, 10, 1931–1941
P-Ru/C	0.1 M KOH	0.90	ACS Catal. 2020, 10, 11751–11757
d-RuNi MLNS	0.1 M KOH	1.79	Adv. Funct. Mater. 2023, 33, 2210328
RuNi ₁	0.1 M KOH	2.70	Nano Lett. 2020, 20, 3442-3448
<i>fcc</i> Ru/C	0.1 M KOH	0.12	J. Energy Chem. 2021, 61, 15–22
Ru/RuO ₂ -180	0.1 M KOH	0.025	Adv. Mater. 2022, 35, 2208821
O-RuNi@C-400	0.1 M KOH	0.60	ACS Materials Lett. 2022, 4, 2097–2105
Ir ₁ Ru ₃ NWs	0.1 M KOH	3.346	J. Mater. Chem. A 2018, 6, 20374–20382
Mo-Ru NSAs	0.1 M KOH	2.45	Energy Environ. Sci. 2023, 16, 157–166

 Table S2 Comparison between a/c-RuTi and other reported catalysts for alkaline HOR.