Supporting Information

Engineering intense Ru-TiO₂ interaction for robust hydrogen oxidation reaction

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Experimental Section

Materials

Titanium trichloride solution (15%~20% TiCl₃ dispersed in 30% HCl) and Nafion solution (5 wt%) were purchased from Aladdin. Sodium nitrate (NaNO₃), potassium hydroxide (KOH), copper sulfate pentahydrate (CuSO₄·5H₂O) and ethylene glycol (EG) were purchased from Macklin. Trihydrate ruthenium trichloride (RuCl₃·3H₂O) was purchased from RHAWN, and anhydrous ethanol was purchased from Sinopharm Chemical Reagent Co. Ltd. The water used in all experiments was ultrapure deionized water with a resistivity of 18.2 M Ω cm⁻¹ at room temperature.

Synthesis of D-TiO₂

In a typical synthesis of D-TiO₂, 3 mL TiCl₃, 1 mL deionized water and 30 mL ethylene glycol were thoroughly mixed and transferred into a hydrothermal reactor with a PTFE inner liner. After reacting at 150°C for 4 hours, the products were centrifuged and washed three times with deionized water and ethanol, then dried overnight at 80°C in a vacuum oven. The dried products were calcined at 500°C for 2 hours in a 10% H₂/Ar atmosphere (5°C min⁻¹) to obtain D-TiO₂.

Synthesis of Ru/TiO₂

To obtain a series of Ru/TiO₂ electrocatalysts, 20 mg D-TiO₂ and 37.6 μ L aqueous RuCl₃ solution (1 mol L⁻¹) were mixed in 20 mL deionized water. After ultrasonication for 30 minutes, 2 g NaNO₃ was added into the solution. Then the above mixture was stirred in an 80°C water bath until evaporated. The dry mixture was calcined at 350°C for 1 hour at a heating rate of 5°C min⁻¹. Calcination products were washed three times with deionized water and ethanol, then dried overnight at 80°C to get RuO₂/TiO₂ precursor. Ru/TiO₂ electrocatalysts were finally obtained by annealing RuO₂/TiO₂ precursors at 200, 300, 400, and 450°C for 1 hour in a 10% H₂/Ar atmosphere (5°C min⁻¹), and they were designated as Ru/TiO₂-200, Ru/TiO₂-300, Ru/TiO₂-400, and Ru/TiO₂-450, respectively.

Synthesis of Ru/TiO₂-H

Comparison sample Ru/TiO₂-H was synthesized by a hydrothermal approach. In a typical synthesis process, 20 mg D-TiO₂ and 37.6 μ L aqueous RuCl₃ solution (1 mol L⁻¹) were mixed with 30 mL of ethylene glycol and transferred to a hydrothermal reactor after stirring for 1 hour. The reaction was carried out at 180°C for 2 hours. After cooling to room temperature, the products were centrifuged and washed three times with deionized water and ethanol, then dried overnight at 80°C to acquire

final products Ru/TiO_2 -H.

Synthesis of Ru/TiO₂-P

Comparison sample Ru/TiO₂-P was synthesized through a pyrolysis process. 40 mg D-TiO₂ and 75.2 μ L aqueous RuCl₃ solution (1 mol L⁻¹) were mixed with 20 mL deionized water. After ultrasonication for 30 minutes, the mixture solution was stirred in an 80°C water bath until evaporated. The dried mixture was calcined at 500°C for 2 hours in a 10% H₂/Ar atmosphere (5°C min⁻¹). The pyrolyzed products were collected and washed three times with deionized water and ethanol to remove possible residual ions, and then dried overnight at 80°C to acquire final products Ru/TiO₂-P.

Characterizations

The X-ray diffraction patterns were collected by a Rigaku MiniFlex600 X-ray diffractometer with Cu K α radiation (λ = 1.5418 Å). TEM and HRTEM images were obtained through a JEOL JEM2100F electron microscope. XPS spectra were collected with American Thermo Scientific K-Alpha spectrometer equipped with Al K α photon source. ICP-OES testing was conducted with a Thermo Fisher iCAP PRO spectrometer. The XAS spectra of Ru-K edge were collected at beamline BL14W1 in Shanghai Synchrotron Radiation Facility (SSRF), China. Data processing was performed with Athena and Artemis modules. A Fortran HAMA was used for wavelet transformation (WT).

Electrochemical Measurements

All electrochemical measurements were performed in a standard three-electrode cell system with an electrochemical workstation (Chi 760E and IVIUMnSTAT). A graphite rod and an Hg/HgO electrode were used as the counter electrode and reference electrode, respectively. The Hg/HgO electrode was calibrated against the reversible hydrogen electrode (RHE). The working electrode was prepared by coating catalyst ink (10 μ L) on the glass carbon electrode (GCE). A typical composition of catalyst ink was as follows: 2 mg electrocatalyst and 1 mg carbon black were dispersed in a solution containing 400 μ L ethanol, 80 μ L deionized water and 20 μ L Nafion solution (5 wt%). The above mixture was ultrasonically dispersed for 30 minutes to obtain a homogeneous ink before being coated on the electrode. HOR tests were conducted in H₂-saturated 0.1 M KOH solution at a rotation speed of 1600 rpm and a scan rate of 5 mV s⁻¹ with 95% iR compensation. The durability of samples was evaluated by chronoamperometry on a rotating disk electrode (catalyst loading: 0.2 mg cm⁻²).

The kinetic current density (j_k) was calculated based on the Koutechy-Levich equation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} \#(1)$$

where *j* is the measured current density and j_d is the diffusion current density. j_d can be obtained based on Nernstian diffusion overpotential equation:

$$j_d = j_l \left(1 - e^{-\frac{2F\eta}{RT}}\right) \#(2)$$

where j_{l} is the diffusion-limited current density and η is the overpotential.

The specific exchange current density (j_0) was obtained through fitting j_k with Butler-Volmer equation:

$$j_k = j_0 \left(e^{\frac{\alpha F}{RT}\eta} - e^{\frac{-(1-\alpha)F}{RT}\eta} \right) \#(3)$$
 where α is the charge transfer coefficient, *F* is the Faraday's Constant

(96485 C mol⁻¹), *R* is the universal gas constant (8.314 J mol⁻¹ K⁻¹), and *T* is the temperature (K), α and j_0 were set as variables.

The electrochemically active surface area (ECSA) of the electrocatalysts was determined by copper underpotential deposition (Cu_{UPD}). Firstly, cyclic voltammetry was performed at the potential range of 0-0.85 V (vs. RHE) in an Ar-saturated 0.5 M H₂SO₄ solution to obtain the background, with a scan rate of 50 mV s⁻¹. Then the electrode was polarized at 0.25 V (vs. RHE) for 100 s in an Ar-saturated 0.5 M H₂SO₄ solution containing 5 mM CuSO₄ to deposit a monolayer of Cu. Subsequently, the Cu_{UPD} dissolution voltammetry curve was collected with a potential range of 0.25-0.85 V (vs. RHE) and a scanning rate of 50 mV s⁻¹. The ECSA (10⁴ cm² mg_{metal}⁻¹) can be calculated by following equation (4) and (5):

$$Q_{Cu} = \frac{\int idE}{v} \#(4)$$
$$ECSA = \frac{Q_{Cu}}{Q_s} \#(5)$$

where Q_{Cu} is the measured integral charge (C), *v* is the scan rate (mV s⁻¹), and Q_s is the surface charge density which is assumed to be 420 μ C cm_{metal}⁻² for a monolayer adsorption of Cu on the catalyst. The measurement of underpotential deposited hydrogen (H_{UPD}) was conducted in the potential range of 0.02-0.6 V (vs. RHE) at a scan rate of 50 mV s⁻¹ in Ar-saturated 0.1 M KOH solution. For CO stripping tests, the working electrode was firstly held at 0.1 V (vs. RHE) for 10 minutes in CO-saturated 0.1 M KOH solution to adsorb CO. Then the electrode was transferred into an Ar-saturated 0.1 M KOH solution and cyclic voltammetry was performed at the range of 0-1.1 V (vs. RHE) at a scan rate of 50 mV s⁻¹ to obtain the CO stripping curve.



Figure S1 (a, b) HRTEM images of RuO₂/TiO₂.



Figure S2 Electron microscopy images of Ru/TiO_2 -200. (a) HRTEM image. (b, c) Enlarged images of white dashed rectangular regions in (a). (d-g) The corresponding FFT and inverse FFT patterns of yellow dashed rectangular regions in (b) and (c), respectively.



Figure S3 Electron microscopy images of Ru/TiO_2 -300. (a) HRTEM image. (b, c) Enlarged images of white dashed rectangular regions in (a). (d-g) The corresponding FFT and inverse FFT patterns of yellow dashed rectangular regions in (b) and (c), respectively.



Figure S4 Electron microscopy images of Ru/TiO_2 -450. (a) HRTEM image. (b, c) Enlarged images of white dashed rectangular regions in (a). (d-g) The corresponding FFT and inverse FFT patterns of yellow dashed rectangular regions in (b) and (c), respectively.



Figure S5 Size statistics of Ru nanoparticles. (a-d) HRTEM images of Ru/TiO_2 -200, Ru/TiO_2 -300, Ru/TiO_2 -400, and Ru/TiO_2 -450. (e-h) The corresponding histogram of Ru nanoparticles size distribution for the above samples.



Figure S6 X-ray photoelectron spectroscopy spectra of Ru/TiO_2 -200 and Ru/TiO_2 -300. (a) C 1s and Ru 3p spectra. (b) Ti 2p and Ru 3p spectra.



Figure S7 Ru K-edge EXAFS spectra and the corresponding fitting results of Ru foil, shown in (a) k^3 weighted *k*-space, (b) k^3 weighted *R*-space (FT magnitude and imaginary, without phase correction).



Figure S8 Ru K-edge EXAFS spectra and the corresponding fitting results of Ru/TiO₂-200, shown in (a) k^3 weighted *k*-space, (b) k^3 weighted *R*-space (FT magnitude and imaginary, without phase correction).



Figure S9 Ru K-edge EXAFS spectra and the corresponding fitting results of Ru/TiO₂-300, shown in (a) k^3 weighted *k*-space, (b) k^3 weighted *R*-space (FT magnitude and imaginary, without phase correction).



Figure S10 Ru K-edge EXAFS spectra and the corresponding fitting results of Ru/TiO₂-400, shown in (a) k^3 weighted *k*-space, (b) k^3 weighted *R*-space (FT magnitude and imaginary, without phase correction).



Figure S11 Ru K-edge EXAFS spectra and the corresponding fitting results of Ru/TiO₂-450, shown in (a) k^3 weighted *k*-space, (b) k^3 weighted *R*-space (FT magnitude and imaginary, without phase correction).



Figure S12 Wavelet transforms for the k^3 -weighted EXAFS for RuO_2/TiO_2 , Ru/TiO_2 -200, Ru/TiO_2 -300, and Ru/TiO_2 -450.



Figure S13 LSV curves of Ru/TiO₂ samples in H₂-saturated and Ar-saturated 0.1 M KOH solution.



Figure S14 Cu-UPD stripping voltammograms curves (colored lines) of (a) Ru/TiO₂-200, (b) Ru/TiO₂-300, (c) Ru/TiO₂-400, and (d) Ru/TiO₂-450 together with their background curves (black lines) obtained in the absence of CuSO₄.



Figure S15 Chronoamperometry response of Ru/TiO_2 electrocatalysts at an over potential of 100 mV operated on RDE.



Figure S16 CO stripping voltammograms of Ru/TiO₂-200, Ru/TiO₂-300, Ru/TiO₂-400, and Ru/TiO₂-450.



Figure S17 HRTEM images of (a, b) Ru/TiO₂-H and (c, d) Ru/TiO₂-P.



Figure S18 LSV curves of Ru/TiO_2 -H and Ru/TiO_2 -P in H₂-saturated 0.1 M KOH at a rotation rate of 1600 rpm.



Figure S19 Ti 2p and Ru 3p XPS spectra of Ru/TiO₂-H and Ru/TiO₂-P.



Figure S20 (a) Ru K-edge XANES spectra of Ru/TiO₂-400, Ru/TiO₂-H, Ru/TiO₂-P, and reference materials (Ru foil and RuO₂). (b) Fourier-transformed k³-weighted χ (k)-function of the Ru K-edge EXAFS spectra of Ru/TiO₂-400, Ru/TiO₂-H, Ru/TiO₂-P, and reference materials (Ru foil and RuO₂). (c, d) Wavelet transforms for the k³-weighted EXAFS for Ru/TiO₂-H and Ru/TiO₂-P.



Figure S21 (a) HER polarization curves of RuO_2/TiO_2 , Ru/TiO_2 , and Pt/C in 1.0 M KOH. (b) HER overpotentials at 10 mA cm⁻² for RuO_2/TiO_2 , Ru/TiO_2 , and commercial Pt/C. (c) Tafel slope of RuO_2/TiO_2 , Ru/TiO_2 , Ru/TiO_2 , and commercial Pt/C.

Sample	Shell	CNa	R(Å) ^b	$\sigma^2(\text{\AA}^2)^c$	$\Delta E_0(eV)^d$	R factor ^e
Ru/TiO ₂ -200	Ru-Ru	6.6	2.67	0.004	4.60	0.013
	Ru-O	3.6	1.96	0.009		
Ru/TiO ₂ -300	Ru-Ru	7.8	2.67	0.004	4.58	0.009
	Ru-O	2.9	1.96	0.008		
Ru/TiO ₂ -400	Ru-Ru	8.3	2.67	0.004	4.46	0.010
	Ru-O	2.3	1.95	0.007		
Ru/TiO ₂ -450	Ru-Ru	9.2	2.67	0.004	4.91	0.010
	Ru-O	1.9	1.96	0.006		
Ru foil	Ru-Ru	12	2.67	0.003	4.63	0.010

Table S1 The fitting parameters of Ru K-edge EXAFS for as-prepared samples.

CN was fixed as 12 for fitting the Ru K-edge EXAFS of Ru foil, thus determining the value of S_0^2 as 0.727. Then S_0^2 was set to 0.727 for following fitting.

a: CN is the coordination number;

b: R is interatomic distance;

c: σ^2 is Debye-Waller factor;

d: ΔE_0 is edge-energy shift;

e: R factor is the goodness of fit.

Sample	j ₀ (mA cm ⁻²)	j _{0,m} (A mg⁻¹ _{Ru})	j _{0,s} (mA cm ⁻² _{ECSA})	j _{k,m} (A mg⁻¹ _{Ru})	j _{k,s} (mA cm ⁻² _{ECSA})
Ru/TiO ₂ -200	2.51	0.102	0.235	0.282	0.648
Ru/TiO ₂ -300	3.04	0.124	0.243	0.384	0.752
Ru/TiO ₂ -400	4.01	0.163	0.484	0.559	1.657
Ru/TiO ₂ -450	5.92	0.242	0.921	1.529	5.824
Pt/C	4.87	0.119	0.100	0.272	0.229

 Table S2 Performance comparison of various samples.

Sample	Ru content (wt%)
Ru/TiO ₂ -200	10.461
Ru/TiO ₂ -300	10.996
Ru/TiO ₂ -400	12.035
Ru/TiO ₂ -450	12.207
Average	11.42

Table S3 The ICP-OES test results of Ru content for Ru/TiO_2 series samples.