Hydrogen stored in Ru/SnO₂ induces alkaline hydrogen oxidation reactions in a wide potential range

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Methods

Chemicals

All chemicals were purchased from commercial sources and used as received without further purification. Ruthenium Chloride Hydrate (RuCl₃·xH₂O, GR), Hexachloroiridium Acid Hydrate (H₂IrCl₆·xH₂O, GR), Chloroplatinic Acid Hydrate (H₂PtCl₆·xH₂O, GR), Palladium Chloride (PdCl₂, GR), were purchased from Aladdin Co. Ltd (Shanghai, China). Sodium Stannate Tetrahydrate (Na₂SnO₃·4H₂O, AR), Tin Dioxide (SnO₂, AR), Anhydrous Ethanol (C₂H₃OH, AR), Potassium Hydroxide (KOH, AR) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Deuterium oxide (D₂O, 99.8%D) was purchased from Energy Chemical (Shanghai, China). Carbon Black (Vulcan XC-72R 99.9+%) was purchased from Alfa Aesar (Shanghai, China). Nafion perfluorinated resin solution (5wt%) was purchased from Sigma-Aldrich (Beijing, China). The deionized water with the specific resistance of 18.2 M Ω cm⁻¹ was used in this study.

Materials characterization

The powder X-ray diffraction (XRD) patterns of the samples were collected from a Japan Rigaku D/MAX- γ A X-ray diffractometer equipped with Cu K α radiation (λ =1.54178Å). High-resolution transmission electron microscope (HRTEM) (JEOL-2011) was operated at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB 250 Xray photoelectron spectrometer instrument. Uv-Visible-Near infrared Spectroscopies (UV/vis-NIR) were conducted from Solid 3700. Inductively coupled plasma atomic emission spectrometer (ICP-AES) were conducted to determine the Ru and Sn concentrations of the samples with an Optima 7300 DV instrument. In situ Fourier transform infrared reflection (FTIR) were collected from Thermo Scientific Nicole iS50. ¹H Solid-State Nuclear Magnetic Resonance (NMR) spectroscopies were collected from Bruker AVANCE NEO 600 WB.

Synthesis of Ru/SnO₂

Weigh 0.5 mM of Na_2SnO_3 and dissolve it into 10 ml of deionized water, then add 3 ml of 10 mg ml⁻¹ of RuCl₃ aqueous solution, stir for half an hour, slowly pour into 30 ml of anhydrous ethanol, continue to stir for

10 minutes, then transfer the solution to the polytetrafluoroethylene kettle, the oven temperature is set to 180 °C, and the time is set to 48 h. After the oven temperature dropped to room temperature, the product is cleaned with anhydrous ethanol and centrifuged. The resulting product is annealed for 2 h in an Ar atmosphere of 500 °C to obtain Ru/SnO₂.

Synthesis of Ir/SnO₂

The preparation scheme of Ir/SnO_2 is basically the same as that of Ru/SnO_2 , except that 3 ml of 10 mg ml⁻¹ of H_2IrCl_6 aqueous solution replaces 3 ml of 10 mg ml⁻¹ of $RuCl_3$ aqueous solution.

Synthesis of Pt/SnO₂

The preparation scheme of Pt/SnO_2 is basically the same as that of Ru/SnO_2 , except that 3 ml of 10 mg ml⁻¹ of H_2PtCl_6 aqueous solution replaces 3 ml of 10 mg ml⁻¹ of $RuCl_3$ aqueous solution.

Synthesis of Pd/SnO₂

The preparation scheme of Pd/SnO₂ is basically the same as that of Ru/SnO₂, except that 3 ml of 10 mg ml⁻¹ of PdCl₂ aqueous solution replaces 3 ml of 10 mg ml⁻¹ of RuCl₃ aqueous solution.

Synthesis of Ru/C

To prepare the Ru/C catalyst, 100 mg of Vulcan XC-72R was added into 30 mL of deionized water under ultrasonic dispersion for 30 min, and then 6 ml of RuCl₃ aqueous solution (10 mg ml⁻¹) was added into the dispersion. After constant stirring 1 h, 0.2 g of NaBH₄ dissolved in 10 ml of deionized water was added into the dispersion and react for 1 h. The final product was recovered after sedimentation, centrifugation, washing and drying.

Preparation of Ir/C

To prepare the Ir/C catalyst, 30 mg of Vulcan XC-72R was added into 60 mL of EG under ultrasonic dispersion for 30 min, and then 2 ml of $H_2IrCl_6 \cdot xH_2O$ aqueous solution (10 mg ml⁻¹) was added to the dispersion, ultrasonic action was performed for 10 min, and then the dispersion was placed in an oil bath at 120 °C and continuously stirred for 2 h. The resulting product was cooled to room temperature and then centrifuged. The sediment was washed several times with water and ethanol and dried overnight under a vacuum of 60 °C. The synthesized Ir/C samples were annealed at 280 °C in Ar atmosphere. The specific experimental details were as follows: the temperature was held for 2 h at 280 °C, the heating rate was 5 °C min⁻¹, and the Ar velocity was (100 ml min⁻¹).

Electrode preparation

Before conducting electrochemical tests, glassy carbon electrode (GCE) is polished with nano-alumina to remove any remaining catalysts. Weigh 4 mg catalyst powder and mix it with 970 μ l ethanol and 30 μ l 5% Nafion perfluorinated resin solution. The solution is ultrasonic in an ice bath for 30 min to form a stable dispersed ink. For hydrogen oxidation reaction (HOR) test, 5 μ l of prepared catalyst ink was dropped onto the GCE rotating disk electrode (GCE, RDE with geometric area of 0.196 cm²) with the loading of 20 μ g_{PGM} cm⁻² (quantification by ICP-AES test).

Electrocatalytic measurements details

All electrochemical tests were carried out at the CHI 760E electrochemistry workstation. Unless otherwise specified, the GCE loaded with electrocatalysts was served as the working electrode, the platinum wire was served as the counter electrode and the Ag/AgCl electrode was used as the reference electrode. In this work, all the measured potentials were referred to the reversible hydrogen electrode (RHE) potential.

For HOR electrochemical test, 0.1 M KOH was used as the electrolyte and was saturated with pure hydrogen for at least 20 min before HOR testing. Before linear sweep voltammetry (LSV) test, cyclic voltammetry (CV)

was conducted by sweeping the potential from -0.1 V vs. RHE to 0.1 V vs. RHE and cycle 20 times at 50 mV s⁻¹ to obtain the steady voltammetry curves in H_2 -saturated electrolyte.

Then, polarization curves were recorded using a rotating disk electrode (RDE) with a rotation speed of (400 rpm, 625 rpm, 900 rpm, 1225 rpm, 1600 rpm, 2500 rpm) at a scan rate of 10 mV s⁻¹ by sweeping the potential from -0.1 V vs. RHE to 1.0 V vs. RHE in H₂-saturated electrolyte for HOR. Electrochemical impedance spectra (EIS) were recorded over the frequency range from 200 kHz to 0.1 Hz with an amplitude of applied voltage of 5 mV. The real part of the resistance was used to obtain the IR-free potential for all the potential data of HOR in this work.

The kinetic current density (j_k) was calculated by the Koutecky-Levich equation,

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{j_k} + \frac{1}{\beta c_0 \omega^{1/2}}$$

where j, j_d, β, c_0 and ω represent the current density, diffusion limited current, Levich constant, solubility of H₂ in alkaline solution and rotation speed, respectively. The exchange current density (j_0) was calculated by two methods. One is from the Butler-Volmer equation,

$$j_k = j_0 (e^{\frac{\alpha F}{RT}\eta} - e^{\frac{-(1-\alpha)F}{RT}\eta})$$

where α , *F* and *R* refer to the charge transfer coefficient, Faraday constant and the universal gas constant, respectively. Another is to perform linear fitting in micro-polarization regions via the Bulter-Volmer equation,

$$j_0 = \frac{jRT}{\eta F}$$

The stability test was performed at RDE with density of PGM is $20 \ \mu g_{PGM} \ cm^{-2}$ by sweeping the potential from -0.1 V vs. RHE to 0.1 V vs. RHE and cycle 5000 times at 50 mV s⁻¹ in H₂-saturated 0.1 M KOH solution. Polarization curves before and after 5000 CVs were recorded a scan rate of 10 mV s⁻¹ by sweeping the potential from -0.1 V vs. RHE to 1.0 V vs. RHE in H₂-saturated 0.1 M KOH solution.

DFT calculation

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 used to calculate 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 400 eV. The convergences of energy and force were set to 1×10^{-7} eV and 0.01 eV Å⁻¹, respectively. Brillouin zone sampling was employed using a Monkhorst-Packing grid with $3 \times 3 \times 1$.



Figure S1 TEM image of Ru/SnO₂.



Figure S2 Ru 3d XPS spectra of Ru/SnO_2 and Ru powder.



Figure S3 Ru K-edge XANES spectra of Ru/SnO₂, Ru foil and RuO₂.



Figure S4 VB spectra of Ru/SnO₂, SnO₂ and Ru powder.



 $Figure \ S5 \ a) \ H_{upd} \ measurement \ of \ Ru/SnO_2 \ and \ Ru \ Powder. \ b) \ CO \ stripping \ curves \ of \ Ru/SnO_2 \ and \ Ru \ Powder.$



Figure S6 UV/vis-NIR spectra of Ru/SnO₂ and SnO₂.



Figure S7 Current linear fitting in the micropolarized region.



Figure S8 a) Ru/SnO_2 polarization curve in N_2 -saturated 0.1 M KOH solution. b) SnO2 polarization curve in H_2 -saturated 0.1 M KOH solution.



Figure S9 a) HOR polarization curves of Ru/SnO_2 with Pt as CE and CR as CE. b) Tafel slope of Ru/SnO_2 with Pt as CE and CR as CE.



Figure S10 the plot of Koutechy-Levich equation.



Figure S11 Performance difference of Ru/SnO_2 and Pt/C before and after 5,000 CVs cycles.



Figure S12 Chronoamperometric curves of Ru/SnO_2 and Ru/C at 0.1 V vs. RHE.



Figure S13 HOR polarization curves of Air and 10% H₂/Ar-annealed Ru/SnO₂ in H₂-saturated 0.1 M KOH at a rotating speed of 1600 rpm.



Figure S14 DFT calculation model of H_i in Ru/SnO₂.



Figure S15 a) In-situ FTIR spectra of Ru/C, the applied potential increased from -0.12 V vs. RHE to 0.84 V vs. RHE. b) In-situ FTIR spectra of Ru/C, the applied potential decreased from 0.84 V vs. RHE to -0.12 V vs. RHE.



Figure S16 Polarization curve of Pd/SnO₂, Ir/SnO₂, Pt/SnO₂, Pd/C, Ir/C and Pt/C in H₂-saturated 0.1 M KOH solution.

Catalysts	$j_k @50 \text{ mV} (\text{mA cm}^{-2})$	Decayed potential (V	Ref.
		vs. RHE)	
Ru/SnO ₂	74.41	1	This work
Pt/C	8.08	1	
Ru/C	1.45	0.4	
$Ru/Ti_3T_2C_x$	17	0.6	1
NiRu/C	12.5	0.6	2
Ru/RuO ₂ -180	5	0.3	3
Ru@TiO ₂	2	0.9	4
$Mn_1O_x(OH)_y@Ru/C$	14.3	1	5
Ni ₄ Mo/TiO ₂	11.12	1.2	6

Table S1 Performance statistics table of Ru/SnO_2 and several of catalysts that have been reported.

Tabel S2 three vibrational modes of H_{i} in Ru/SnO_{2} calculated by DFT.

Vibrational modes ⁷	Wavenumber (cm ⁻¹)
stretch	2851.350811
in-plane	1261.092961
out-of-plane	838.645362

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