Interphase-oxidized ruthenium metal with half-filled d-orbitals for

hydrogen oxidation in an alkaline solution

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1. Experimental Section

1.1 Materials

Ruthenium chloride (RuCl₃>99.5%, Ru 46.2%), tetrabutyl titanate (TBOT, analytical reagent > 98.5%), carbon black (Vulcan XC-72R), ethanol (CH₃CH₂OH, analytical reagent > 99.7%), ammonia (NH₃.H₂O, analytical reagent, 25%-25%), deionized water (18.25 M Ω cm⁻¹), nafion solution (5 wt%), potassium hydroxide (KOH, analytical reagent > 85.0%). All other chemicals were used as received without further purification.

1.2 Methods

Functionalization of Vulcan XC-72R

Vulcan XC-72R was pretreated with concentrated nitric acid to improve its water dispersion and to remove metal impurities. Typically, 320 mL concentrated nitric acid solution containing 8 g Vulcan XC-72R carbon was heated under reflux for 4~5 h. After dilution with water and filtration, Vulcan XC-72R carbon was obtained in the solid remaining after filtration. Then, the Vulcan XC-72R carbon was washed with water until the pH of the filtrate was close to 7. Finally, the functionalized XC-72R carbon was obtained after heating in a muffle furnace at 300 °C for 0.5 h.

Synthesis of IO-Ru-TiO₂/C catalyst

RuCl₃ and TBOT were chosen as the Ru and TiO₂ precursors, respectively. Typically, a 100 ml suspension of functionalized XC-72R carbon (0.16 g) in ethanol was formed by ultrasonication and stirring for 30 minutes, and then a concentrated ammonia solution (0.30 mL, 28 wt %) was added to the suspension under stirring. After stirring for 30 minutes, TBOT was added dropwise in 5 minutes, and the reaction was allowed to proceed for 24 h in a 45 °C water bath under continuous mechanical stirring. Then, a RuCl₃ solution was added dropwise in 5 minutes under vigorous stirring, and the mixture was continuously stirred for 24 h in a sealed container at room temperature and dried at 70 °C in a water bath. The obtained solid was annealed at 500 °C for 2 h in a tube furnace under a 1:6 H₂:Ar gas flow. After washing with deionized water and ethanol, and drying at 60 °C under vacuum for 24 h, the IO-Ru TiO_2/C catalyst was obtained. The metal precursor molar ratio of Ru: TiO_2 was 1:3.8, and the total mass fraction of Ru and TiO_2 was 20 wt%.

Synthesis of the Ru-TiO₂/C catalyst

In a typical synthesis of the Ru-TiO₂/C catalyst, a 100 ml suspension of functionalized XC-72R carbon (0.16 g) in ethanol was formed by ultrasonication and stirring for 30 minutes, and then a RuCl₃ solution was added dropwise in 5 minutes under vigorous stirring; the mixture was continuously stirred for 24 h in a sealed container at room temperature and dried at 70 °C in a water bath. The obtained solid was redispersed in 100ml ethanol with ultrasonication, and then concentrated ammonia (0.30 mL, 28 wt %) was added to the suspension under stirring. After stirring for 0.5 h, TBOT was added dropwise in 5 minutes, and the reaction was allowed to proceed for 24 h in a 45 °C water bath and then dried at 70 °C under continuous mechanical stirring. The obtained solid was then annealed at 500 °C for 2 h in a tube furnace under a 1:6 H₂:Ar gas flow. After washing with deionized water and ethanol and drying at 60 °C under vacuum for 24 h, the Ru-TiO₂/C catalyst was obtained.

Synthesis of the TiO₂/C catalyst

In a typical synthesis of the TiO_2/C catalyst, a 100 ml suspension of functionalized XC-72R carbon (0.16 g) in ethanol was formed by ultrasonication and stirring for 30 minutes, and then a concentrated ammonia solution (0.30 mL, 28 wt %) was added to the suspension under stirring. After stirring for 30 minutes, TBOT was added dropwise in 5 minutes, and the reaction was allowed to proceed for 24 h in a 45 °C water bath; the solution was then dried at 70 °C under continuous mechanical stirring. The obtained solid was then annealed at 500 °C for 2 h in a tube furnace under a 1:6 H₂:Ar gas flow. After washing with deionized water and ethanol and drying at 60 °C under vacuum for 24 h, the TiO_2/C catalyst was obtained.

Synthesis of Ru/C catalyst

In a typical synthesis of the Ru/C catalyst, a 100 ml suspension of functionalized XC-72R carbon (0.16 g) in ethanol was formed by ultrasonication and stirring for 30 minutes, and then a RuCl₃ solution was added dropwise in 5 minutes under vigorous stirring; the mixture was continuously stirred for 24 h in a sealed container at room temperature and dried at 70 °C in a water bath. The obtained solid was then annealed at 500 °C for 2 h in a tube furnace under a 1:6 H₂:Ar gas flow. After washing with deionized water and ethanol and drying at 60 °C under vacuum for 24 h, the Ru/C catalyst was obtained.

1.3 Characterization

Transmission electron microscopy

The morphology of the catalyst particles was observed by transmission electron microscopy (TEM). TEM measurements including high-resolution TEM (HRTEM) imaging, were conducted using an FEI Tecnai G² F20 S-TWIN instrument operating at 200 kV, in conjunction with energy-dispersive X-ray spectroscopy (EDS). The samples were prepared by dropping their ethyl alcohol dispersion onto carbon film TEM grids using pipettes and drying under ambient conditions.

X-ray diffraction experiments

X-ray diffraction (XRD) experiments were performed on an XRD-6000 (Japan) equipped with a secondary graphite monochromator with a Cu K α (λ = 0.15418 nm) radiation source. XRD patterns were acquired at a 2 θ range of 10° to 90° and a scan speed of 5°min⁻¹. The microstructural parameters of the samples were determined using JADE6 software.

X-ray photoelectron spectroscopy

The chemical composition of the near surface area of the sample was obtained by X-ray photoelectron spectroscopy (XPS) measurements. XPS analysis was conducted using a Kratos XSAM800 instrument equipped with a monochromatic AI X-ray source (AI KR, 1.4866 keV). The XPS analysis chamber pressure was maintained at 10⁻⁷ Pa or lower during data collection. Each spectrum was constructed by averaging two scans. During data analysis, the binding energy (BE) of the core level C 1s peak was set at 284.8 eV to compensate for surface-charging effects. The Shirley background was subtracted, and the satellite peaks for all element peaks were removed before curve fitting. Experimental spectra were fitted to a Gaussian line shape. Surface elemental compositions were determined by the ratios of peak areas that had been corrected with empirical sensitivity factors.

X-ray absorption fine structure measurement

The X-ray absorption fine structure data were collected at the BL14W1 station in the Shanghai Synchrotron Radiation Facility (SSRF). The electron storage ring of SSRF was operated at 3.5 GeV with a maximum current of 250 mA. The spectra were recorded in the transmission mode for the Ru K-edge by using a Si (311) double-crystal monochromator. The XAFS data were collected under ambient conditions. Standard compounds, Ru foil (edge energy 22117 eV) and the sample for energy calibration were tested simultaneously by utilizing the third ionization chamber. The obtained XAFS data were processed in Athena (version 0.9.25) for background, pre-edge line and post-edge line calibrations. Then Fourier transform fitting was carried out in Artemis (version 0.9.25). The models of Ru foil and RuO₂ were used to calculate the scattering paths.

The coordination numbers of the model samples (Ru foil) were fixed as the standard values. The obtained So² of Ru foil was 0.784, and this value was fixed in the subsequent fitting of Ru K-edge data for IO-Ru-TiO₂/C, Ru-TiO₂/C, RuO₂ and Ru/C. The internal atomic distances R, the edge-energy shift ΔE_0 , and the Debye-Waller factor σ^2 were permitted to work separately. The obtained parameters of the Ru K-edge are listed in Table S2, and the curve-fitting results are shown in Figure S4.

1.4 Electrochemical measurement

All electrochemical experiments were performed by using an electrochemical workstation (VersaSTAT 3F) in a standard three-electrode cell at room temperature. The cell consisted of a glassy carbon (GC) working electrode (5 mm in diameter, PINE: AFE3T050GC), a Ag/AgCl (3 M KCl) reference electrode, and a graphite rod counter electrode. The reference electrode was calibrated to a reversible hydrogen electrode (RHE) in the same electrolyte before each measurement. The working electrodes were prepared by applying catalyst ink onto GC disk electrodes. In brief, the electrocatalyst was dispersed in ethanol and Nafion solution (5 wt %) and then ultrasonicated for 30 minutes to form a uniform catalyst ink. The well-dispersed catalyst ink was deposited onto a prepolished GC disk and the resulting electrodes were dried at room temperature before electrochemical testing. For all electrochemical experiments on the RDE, the specific loading of the precious metal (Pt or Ru) was 25.48 μ g cm⁻². All potentials in this study are given relative to the RHE. Cyclic voltammograms (CVs) for the catalysts were

obtained in 0.1 mol L⁻¹ N₂-purged KOH from 0.0 to 0.9 V versus RHE at 50 mV s⁻¹. Hydrogen oxygen reaction (HOR) measurements were conducted in 0.1 mol L⁻¹ KOH electrolyte, which was saturated with H_2 by continuous purging.

The CO adsorption was conducted by holding the electrode in the 0.1 mol L⁻¹ KOH solution under the bubbling of CO gas for 15 min. Then, the cyclic voltammograms experiments was performed in the fresh 0.1 mol L⁻¹ KOH solution at a scan rate of 50 mVs⁻¹ in the potential between 0 and 1.2 V. The CO stripping CV curve and blank CV curve can be obtained from two consecutive scan cycles. Specifically, the ECSA

values of Pd in the catalysts was calculated as: $ECSA = \frac{Q_{CO}}{C_p * m}$, where Q_{CO} (mC) is the charge due to CO adsorption/desorption in the CO stripping region, 0.42 mC cm⁻² is the electrical charge associated with CO monolayer adsorption, and m is the loading of precious metal on the working electrode.

The kinetic current densities (j_k) associated with the intrinsic activity of the catalysts can be obtained

$$j_k = \frac{j_d * j}{j_i - j}$$

by the following equation: $\int_{d} \int_{d} \int_{d} d = \int_{d}$

by the following equation: $MA = \frac{J_k}{m} * 0.19625$, *where* m is the precious metal loading, and the 0.19625(cm²) is the electrode area.

The specific activity (SA) can be obtained according to the equations: $SA = \frac{ik}{ECA}$, $ECA = \frac{Q_{co}}{C_p}$, Where i_k (mA) is the kinetic current at 0.05 V, Q_{co} is 0.42mC/cm², C_p is the charge due to CO adsorption/desorption in the CO stripping region.

2. Supplementary Figures



Figure S1. (a) Schematic of the traditional mechanism for Ru metal in alkaline solution. A considerable amount of OH* was absorbed on the surface of the metal, which hindered H adsorption and decreased OH desorption. (b) Mechanism illustrations for IO-Ru-TiO₂/C modified by TiO₂. The adsorption of OH on the metal surface was decreased.



Figure S2. TEM images and particle size distribution histograms for (a, b) Ru/C, (c, d) Ru-TiO₂/C. and (e, f) IO-Ru-TiO₂/C.



Figure S3. Ru 3d XPS spectra for (a) Ru/C, (b) Ru-TiO₂/C and (c) IO-Ru-TiO₂/C. (d) Ti 3p XPS spectra for TiO₂/C, Ru-TiO₂/C and IO-Ru-TiO₂/C.



Figure S4. Fitting results of the EXAFS spectra of the (a) Ru foil (FT range: 3-14.050 Å⁻¹, fitting range: 1-3 Å). (b) RuO₂ (FT range: 3-14 Å⁻¹, fitting range: 1.05-3.8 Å). (c) IO-Ru-TiO₂/C (FT range: 4-14 Å⁻¹, fitting range: 1.1-3 Å). (d) Ru-TiO₂/C (FT range: 4-14 Å⁻¹, fitting range: 1-3 Å). (e) Ru/C (FT range: 3.5-14 Å⁻¹, fitting range: 1.05-2.7 Å).



Figure S5. The exchange current (i₀) for PtRu/C (278.35 uA), IO-Ru-TiO₂/C (436.59 uA), Ir/C (124.94 uA), Ru/C (228.98 uA), Pt/C (89.06 uA), Pd/C (11.63 uA) and Ru-TiO₂/C (158.48 uA), in 0.1 M H₂-saturated KOH aqueous solution at scan rates of 10 mV s⁻¹ and 1600 rpm min⁻¹. The metal loading is 25.48 ug cm⁻² on rotating disk electrode. The exchange current density was calculated by tafel curve extrapolation, and the exchange current density (j₀) was normalized by ECSA for comparison. The j₀ for IO-Ru-TiO₂/C was detected to be 108.85 μ A cm⁻², which is greatest among the produced catalysts, including PtRu/C (108.58 μ A cm⁻²), Ir/C (63.3 μ A cm⁻²), Ru/C (105.78 μ A cm⁻²), Pt/C (42.04 μ A cm⁻²), Pd/C (6.05 μ A cm⁻²) and Ru-TiO₂/C (63.7 μ A cm⁻²) in a 0.1 M H₂-saturated KOH solution.



Figure S6. The polarization curves of HOR for IO-Ru-TiO₂/C and Ru/C with a rotation rate of 2500, 1600, and 900 rpm, respectively. The metal loading is 25.48 ug cm⁻² on rotating disk electrode.



Figure S7. Relative current-time (i-t) chronoamperometric responses of Ru/C and IO-Ru-TiO₂/C at 0.6 V and 0.3V vs. RHE in 0.1 M H₂ - saturated KOH solution. The metal loading is 25.48 ug cm⁻² on rotating disk electrode. The stability difference is more obvious at 0.6 V vs. RHE than 0.3 V vs. RHE, indicating a higher stability for IO-Ru-TiO₂/C at high potential.

3. Supplementary Tables

| Table S1. | Comparison | of alkaline | HOR activity. |
|-----------|------------|-------------|---------------|
|-----------|------------|-------------|---------------|

| Electrocatalyst | Electrolyte | Mass activity (A.g ⁻¹) | Ref |
|--|-------------|------------------------------------|-----------|
| Pt(pc) | 0.1 M KOH | 240Pt/@50 mV | 1 |
| Ru/C (3.1 nm) | 0.1 M NaOH | 82/Ru @50 mV | 2 |
| Pt/Cu NWs | 0.1 M KOH | 650/Pt @50 mV | 3 |
| Pd/Cu NWs | 0.1 M KOH | 330/Pd @50 mV | 4 |
| Ru ₁ @Pt ₁ (2 ML) | 0.1 M KOH | 480/Pt+Ru @50 mV | 5 |
| Ru _{0.20} Pt _{0.80} /C | 0.1 M KOH | 696/Pt @50 mV | 6 |
| PtNb/NbOx-C | 0.1 M KOH | 360/Pt @50 mV | 7 |
| Ir ₉ Ru₁/C | 0.1 M KOH | 370/Ru+Ir @10 mV | 8 |
| Ru₃lr₂/C | 0.1 M NaOH | 612/Ru+Ir @50 mV | 9 |
| Pdir/C | 0.1 M KOH | 79/Pd+Ir @50 mV | 10 |
| IrNi@PdIr/C | 0.1 M KOH | 850/lr @50 mV | 11 |
| lr₃Pd₁Ru ₆ /C | 0.1 M KOH | 340/Ir+Pd+Ru @10 mV | 12 |
| Ir₀Ru₁/C | 0.1 M KOH | 370/Ru+lr @ 10mV | 12 |
| Ru/C-H ₂ O/CH ₃ CH ₂ OH | 0.1 M KOH | 41.1/Ru @ 10mV | 13 |
| O-PdFe@Pt/C | 0.1 M KOH | 247.9/Pt+Pd @ 50mV | 14 |
| Pt/Cu nanowire | 0.1 M KOH | 650/Pt @50 mV | 15 |
| Ru-Ir/C | 0.1 M NaOH | 620/Ru+lr @50 mV | 16 |
| Ni/SC | 0.1 M KOH | 11/Ni @50 mV | 17 |
| CeO ₂ /Ni | 0.1 M KOH | 12.28@50 mV /Ni | 18 |
| Ni/N-CNT | 0.1 M KOH | 9.3/Ni@50 mV | 19 |
| Ni/NiO/C-700 | 0.1 M KOH | 5/Ni@50 mV | 20 |
| Ni₃N/C | 0.1 M KOH | 24.38/Ni@50 mV | 21 |
| Ru/C | 0.1 M KOH | 52@50 mV | This work |
| PtRu/C | 0.1 M KOH | 604@50 mV | This work |
| IO-Ru-TiO ₂ /C | 0.1 M KOH | 907@50 mV | This work |

| Sample | Scattering pair | CN | R (Å) | ^{2 -3 2 c} σ (10 Å) | ΔE ₀ (eV) ^d | R factor |
|---------------------------|-----------------|---------|-----------|----------------------------------|-----------------------------------|----------|
| Ru foil | Ru-Ru | 12 | 2.67±0.03 | 3.6±0.4 | -7.8±0.8 | 0.016 |
| IO-Ru-TiO ₂ /C | Ru-Ru | 3.7±0.8 | 2.68±0.03 | 9.9±1.6 | -7.3±2.1 | 0.012 |
| | Ru-O | 5.9±0.8 | 2.02±0.10 | 8.9±1.8 | -0.7±2.3 | |
| Ru-TiO ₂ /C | Ru-Ru | 3.8±0.7 | 2.68±0.03 | 7.2±1.1 | -7.3±1.8 | 0.013 |
| | Ru-O | 5.1±1.0 | 2.01±0.09 | 9.5±2.6 | -0.9±3.2 | |
| Ru/C | Ru-Ru | 7.4±1.1 | 2.68±0.03 | 4.9±0.7 | -7.0±1.5 | 0.007 |
| | Ru-O | 1.9±1.0 | 1.99±0.08 | 4.3±5.4 | -2.4±8.8 | |
| RuO ₂ | Ru-Ru-1 | 2 | 3.15±0.04 | 0.6±0.4 | -3.1±2.9 | 0.012 |
| | Ru-Ru-2 | 8 | 3.59±0.04 | 12.1±1.0 | 3.1±1.8 | |
| | Ru-O | 6 | 1.98±0.06 | 3.4±0.4 | -0.1±1.0 | |

 Table S2. Structural parameters obtained from the curve-fitting analysis of the EXAFS spectra.

^a CN is the coordination number;

^bR is the interatomic distance, that is, the bond length between the central Pd atoms and surrounding coordination atoms;

 $^{c}\sigma^{2}$ is the Debye-Waller factor, a measure of thermal and static disorder in absorber-scatterer distances;

 $^{d}\Delta E_{0}$ is the edge-energy shift, which is the difference between the zero kinetic energy value of the sample and that of the theoretical model.

SO₂=0.784

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