New Journal of Chemistry

Electronic Supplementary Information

Improved electronic interaction and dispersing effect derived from the F-doped TiO$_2$ support on RuO$_x$ to boost the electrocatalytic oxygen evolution performance

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1. Experimental Section

1.1. Materials

The chemical reagents $RuCl_3$ xH_2O (x = 3), TiO_2 (5-10 nm, Anatase), NH_4F, $CO(NH_2)_2$, NaH_2PO_2 H_2O and $NaBH_4$ were purchased from the Aladdin Co., Ltd. Ethanol and H_2SO_4 solutions were purchased from the Beijing Chemical Co. and used without further purification. 5 wt% Nafion® ionomer was purchased from the DuPont Co. Commercial IrO_2 denoted as $IrO_2(CM)$ was purchased from the Alfa Aesar Chemical Co., Ltd. Commercial Pt/C (20 wt%Pt) denoted as Pt/C(CM) was purchased from the Johnson Matthey Company. $F-SnO_2$ (FTO) conductive glass was purchased from the NSG Co., Ltd. All solutions in this work were modulated using Millipore-MiliQ water (resistivity: $\rho > 18$ MΩ*cm).

1.2. Catalysts Preparation

A series of F-doped TiO_2 (F-TiO_2) supports were synthesized through high-temperature heating TiO_2 with NH_4F, the calcination temperatures were 300, 350, 400 and 500 ℃, the mass ratios of TiO_2 : NH_4F = 1:5, 1:10, 1:15, 1:20. In detail, the TiO_2 powder was firstly grounded with NH_4F powder. Then, the powder mixture was placed in a tubular oven and reacted for 2 h under the N_2 atmosphere to obtain F-TiO_2. The N-TiO_2 and P-TiO_2 counterparts were also synthesized through the similar procedure except for the different dopants, including $CO(NH_2)_2$ and NaH_2PO_2, the synthesis conditions refer to the F-TiO_2 support.

The supported RuO_x/F-TiO_2 catalyst with Ru content of 50 wt% was prepared through a $NaBH_4$ reduction route. Firstly, 50 mg F-TiO_2 was ultrasonically dispersed in 100 mL deionized water for 1 h. Then, a certain amount of $RuCl_3$ $3H_2O$ was added to the resulting suspension and stirred for 1 h. Subsequently, a certain amount of aqueous $NaBH_4$ solution ($nNaBH_4$: $nRuCl_3$ = 8:1) was quickly injected into the above suspension and stirred continuously for 3 h. Finally, the suspension was filtered and washed with deionized water and ethanol, then dried at 60 ℃ in the oven overnight to obtain the target catalyst. RuO_x/N-TiO_2 and RuO_x/P-TiO_2 catalysts were prepared through the similar procedure. Pure RuO_x catalyst denoted as RuO_x(hm) was

prepared through the similar procedure except for the addition of support. IrO_2(CM) catalyst was adopted as comparison.

1.3. Physical Characterization

Electrical Conductivity Measurement: The electrical conductivity of $F-TiO_2$ support was measured by the four-point probe technique (RTS-8, China).

X-ray Diffraction (XRD): The phase composition of the catalysts was investigated by XRD characterization using D8-Advance X-ray diffractometer (BRUKER Company, Germany) with the Cu K_α (l ¼1.5405 Å) as radiation source operating at 40 kV and 200 mA. Diffraction peaks were recorded in the range of 2θ = 20-90 ° at the scanning rate of 2 ° min^{-1}.

X-ray Photoelectron Spectroscopy (XPS): The surface elemental composition, chemical state and electronic structure of the catalysts were investigated by XPS spectrometer (Kratos Ltd. XSAM-800, UK) with Al K_α monochromatic source. All the binding energies were calibrated using the C 1s binding energy peak (284.6 eV) as the reference.

Transmission Electron Microscopy (TEM): The morphology and composition of the catalysts were characterized with TEM, high-resolution transmission electron microscopy (HRTEM), high-angle annular dark-field scanning TEM (HAADF-STEM), elemental mapping analysis and energy-dispersive X-ray spectroscopy (EDX) by Tecnai G2 F20 S-TWIN electron microscope (FEI Company, USA) working at an accelerating voltage of 200 kV.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES): ICP-OES (X Series 2, Thermo Scientific USA) analysis was applied to quantify the electrooxidative-dissolution of Ru after the stability test.

1.4. Electrochemical Measurement

Three-electrode test: Electrochemical performance measurements were firstly investigated with conventional three-electrode setup operated on Princeton Applied Research Model273 Potentiostat/Galvanostat. The electrolyte solution was 0.5 mol L^{-1} H_2SO_4 purged with high-purity N_2 for at least 30 min. The working electrode

substrate, counter electrode and reference electrode were glassy carbon electrode (GC, 3 mm diameter), Pt plate and saturated calomel electrode (Hg/Hg$_2$Cl$_2$; SCE), respectively. All the potentials reported were calibrated with the reversible hydrogen electrode (RHE) that E (RHE) = E (SCE) + 0.242 V + 0.059*pH. To prepare the working electrode: firstly, 3 mg of the catalyst was ultrasonically dispersed in 315 μL solutions containing of 15 μL Nafion® solution and 300 μL ethanol solution for at least 30 min; secondly, 2.23 μL catalyst inks was pipetted and spread on the glassy carbon substrate; lastly, the electrode was obtained after the solvent volatilized with the catalyst loading was 0.3 mg cm^{-2}.

The outer charge (Q_{outer}) was calculated through fitting the cyclic voltammetry (CV) curves (0.40-1.40 V) obtained at the scanning rate of 300 mV s^{-1}.

Linear sweep voltammetry (LSV) curves for OER were recorded in a potential window between 1.10 and 1.70 V at the scanning rate of 5 mV s^{-1} in N$_2$-saturated H$_2$SO$_4$ solution at room temperature. All data were corrected for 95% iR potential drop, R is the solution resistance.

The mass activity was normalized with the equation as follows:

$$i_{\text{Mass activity}} = \frac{i_{\text{Measured}}}{m_{\text{Ru}}} \tag{1}$$

where m_{Ru} is the mass loading for all the Ru element.

The electrochemical impedance spectra (EIS) measurements were conducted on an Autolab potentiostat in the frequency range from 0.1 Hz to 10 kHz at the potential of 1.50 V, a 10 mV amplitude of sinusoidal potential perturbation was employed during the measurements.

The galvanostatic tests were measured using the FTO conductive glass as the working electrode substrate. Testing conditions included a constant current density of 10 mA cm^{-2} in N$_2$-saturated H$_2$SO$_4$ solution at room temperature, and the catalyst loading was also 0.3 mg cm^{-2}.

Two-electrode test: Two-electrode overall water splitting tests were performed with RuO$_x$/F-TiO$_2$, RuO$_x$(hm) or IrO$_2$(CM) as the anode catalyst, and Pt/C(CM) as the cathode catalyst. FTO was used as the working electrode substrate. The anode catalyst

loading was 0.3 mg cm^{-2}, and the cathode catalyst loading was 0.1 mg cm^{-2}. LSV experiments were performed with the voltage window ranged from 1.0 to 2.0 V at the scanning rate of 5 mV s^{-1} in 0.5 M H$_2$SO$_4$ at room temperature. The galvanostatic test was performed at the constant current density of 10 mA cm^{-2} for 20 h.

2. Figures and Tables
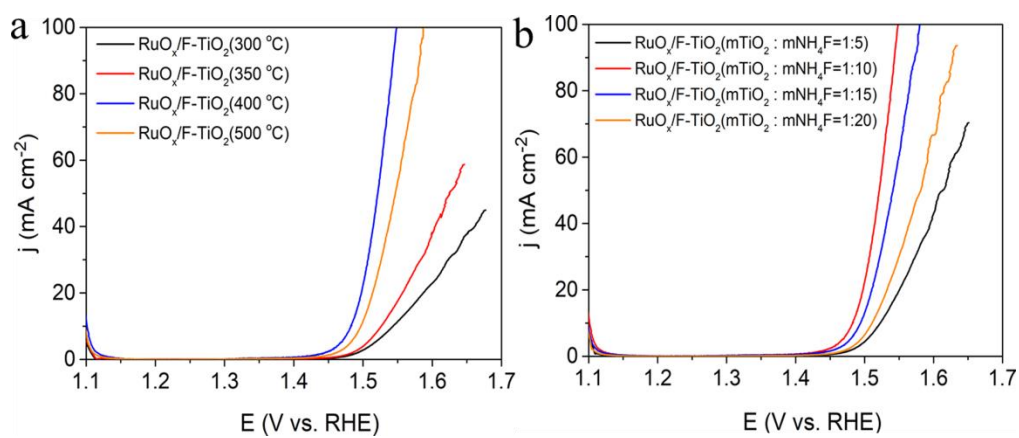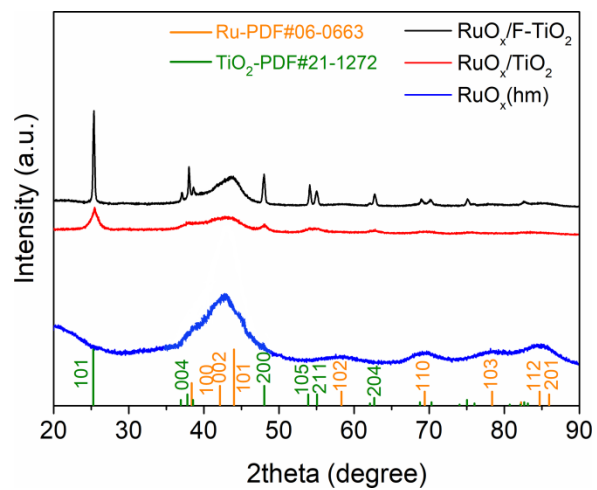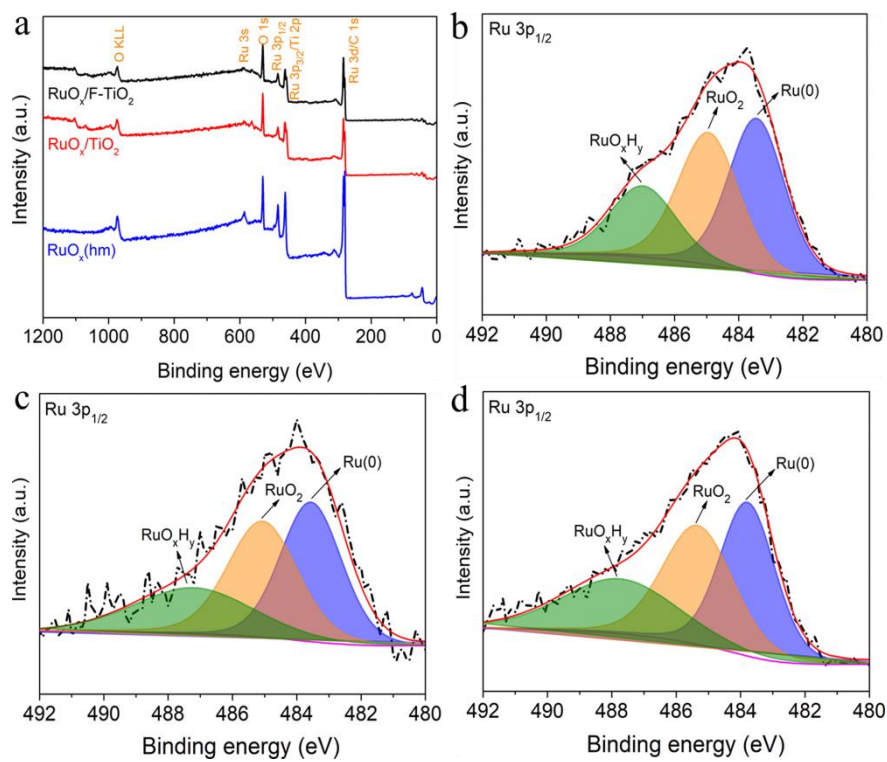

Fig. S1 LSV curves of $RuO_x/F-TiO_2$ with varying (a) calcination temperature of $F-TiO_2$ and (b) mass ratio of $TiO_2 : NH_4F$.
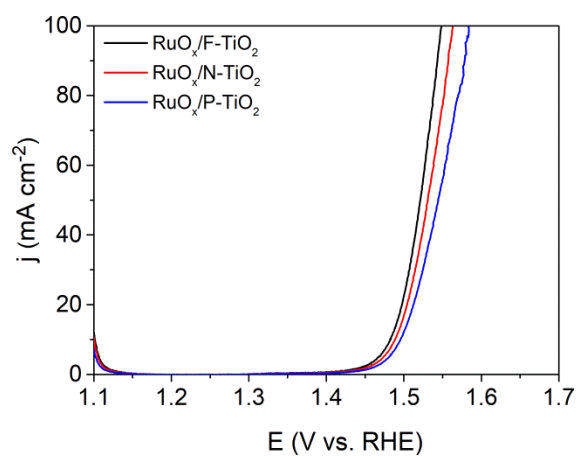
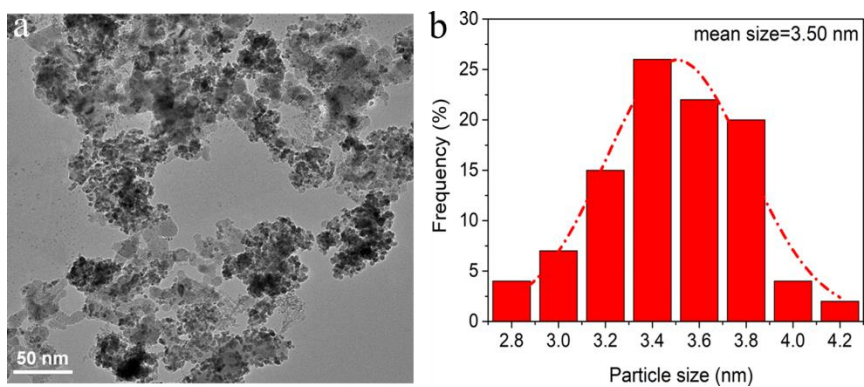**Fig. S2** LSV curves of $RuO_x/F-TiO_2$, $RuO_x/N-TiO_2$ and $RuO_x/P-TiO_2$.

Fig. S3 XRD patterns of $RuO_x/F\text{-}TiO_2$, RuO_x/TiO_2 and $RuO_x(hm)$.
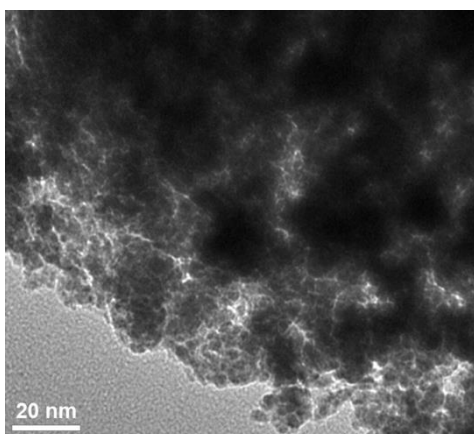
Fig. S4 (a) XPS survey spectra. High-resolution XPS spectra of the deconvoluted Ru $3p_{1/2}$ for (b) $RuO_x/F\text{-}TiO_2$, (c) RuO_x/TiO_2 and (d) $RuO_x(hm)$.
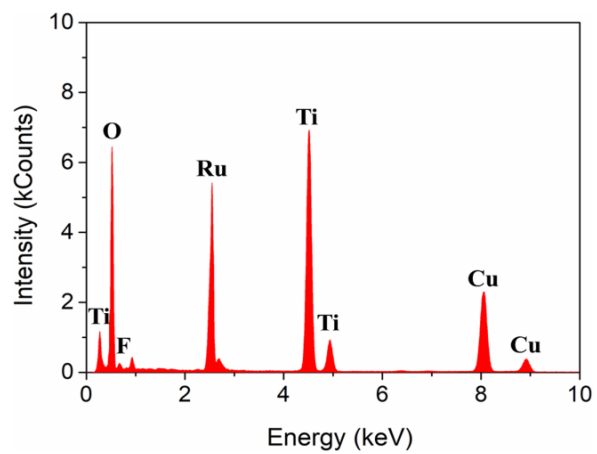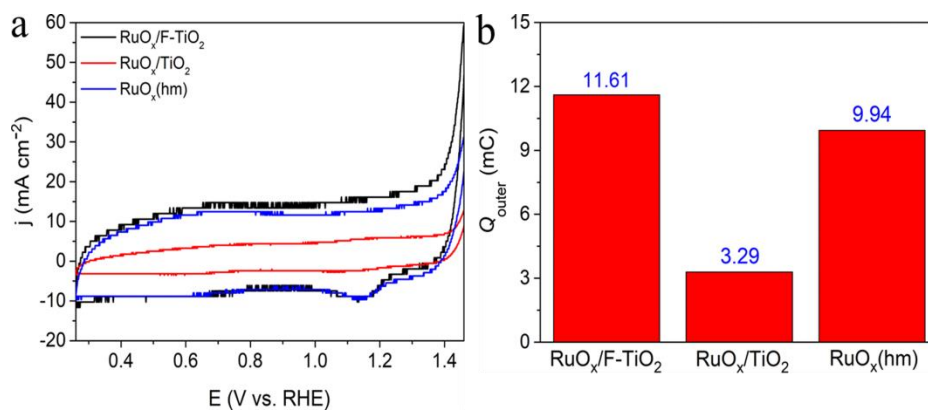
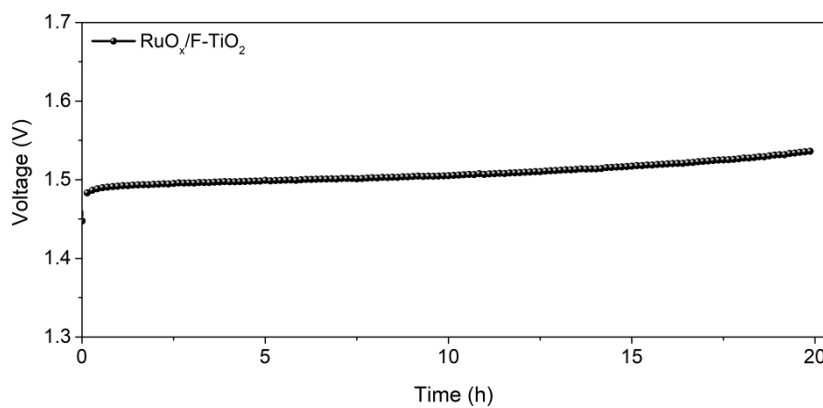**Fig. S5** (a) TEM image of RuO$_x$/TiO$_2$ and (b) corresponding histogram of the particle size distribution.

Fig. S6 TEM image of RuO$_x$(hm).

Fig. S7 EDX spectrum of $RuO_x/F-TiO_2$.

Fig. S8 (a) CV curves at the scanning rate of 300 mV s^{-1} in N$_2$-saturated 0.5 M H$_2$SO$_4$ solution. (b) Histograms of the outer charge.

Fig. S9 Galvanostatic test of RuO$_x$/F-TiO$_2$ at the constant current density of 10 mA cm^{-2} for 20 h.

Table S1 XPS analysis of the catalysts.

Catalyst	Binding energy (Ru 3p$_{1/2}$; eV)	Binding energy (eV) and Relative content (%) of Ru species		
		Ru(0)	RuO$_2$	RuO$_x$H$_y$
RuO$_x$/F-TiO$_2$	483.80	483.439; 40.82%	484.943; 37.32%	486.983; 21.86%
RuO$_x$/TiO$_2$	484.00	483.559; 38.17%	485.061; 36.88%	487.202; 24.95%
RuO$_x$(hm)	484.15	483.785; 36.49%	485.329; 36.25%	487.747; 27.26%

Table S2 R_s and R_{ct} values fitted from the EIS.

Catalyst	R_s (Ω)	R_{ct} (Ω)
RuO$_x$/F-TiO$_2$	5.5	21.2
RuO$_x$/TiO$_2$	5.8	41.3
RuO$_x$(hm)	5.5	32.8
IrO$_2$(CM)	5.6	44.0