Supporting Information

Oxide passivated CoNi@NC-supported Ru(OH)ₓClᵧ cluster as highly efficient catalysts for the oxygen and hydrogen evolution

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Methods

All chemicals of analytical grade were purchased from Macklin Ltd (Shanghai, China). They were used without further purification.

Synthesis of the CoNi@NC

40 mL Co(NO$_3$)$_2$ (0.6 mol/L), Ni(NO$_3$)$_2$ (0.6 mol/L) and Na$_4$EDTA (0.6 mol/L) mixed aqueous solution and 20 mL methanol was enclosed into a 80 mL stainless steel autoclave followed by processing at 200 °C for 24 h. After cooling to room temperature, the generated precipitates were filtered and washed in deionized water followed by drying at 60 °C. The obtained complex was denoted as EDTA-CoNi. Then, CoNi@NC samples were prepared by annealing the EDTA-CoNi at a temperature 550 °C for 3 h in N$_2$ atmosphere.

Synthesis of Ru-CoNi@NC-X

50 mg CoNi@NC was dispersed in 5mL RuCl$_3$·xH$_2$O ethanol solution with stirring and ultrasound. Then, the solution was enclosed into a 20 mL stainless steel autoclave and followed by processing at 80 °C for 2 h. Then, the obtained products were cleaned with deionized water by repeated centrifugation, and dried at 60 °C for 12 h in a vacuum. The Ru-CoNi@NC-1 and Ru-CoNi@NC-2 were obtained when the concentration of RuCl$_3$·xH$_2$O was 0.02mol/L and 0.04mol/L, respectively.

Synthesis of Ru-Ni foam-X

The synthesis of Ru-Ni foam-X was similar to that described above for Ru-CoNi@NC-X, except that CoNi@NC was replaced by Ni foam.
The synthesis of Ru-CoNi@NC-2-X was similar to that described above for Ru-CoNi@NC-2, except that the reaction time is 0.5h and 8h (The obtained products are denoted as Ru-CoNi@NC-2-0.5 and Ru-CoNi@NC-2-8).

Characterization

The morphology and microstructure of the samples were characterized by field-emission scanning electron microscopy (FE-SEM, JSM–6700F). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained using transmissions electron microscopy (TEM, JEOL–2100F). Atomic resolved STEM images were performed on a probe aberration-corrected STEM (FEI, Titan Cubed Themis G2 300, USA) operated at 300 kV. The phase composition of the samples were determined by X-ray diffraction (XRD, Rigaku D-max-γA XRD with Cu Kα radiation, λ = 1.54178 Å) from 5° to 80°. Thermogravimetric analysis (TGA, Netzsch STA449C) was performed in air over temperatures ranging from room temperature to 900 °C, at a heating rate of 5 °C·min⁻¹. The X-ray photoelectron spectroscopy (XPS) analysis was implemented on a Perkin-Elmer PHI 550 spectrometer with Al Kα (1486.6 eV) as the X-ray source. Nitrogen adsorption/desorption isotherms were measured at 77 K with a micrometrics ASAP 2020 analyzer. Particlesize distribution of the nanoparticles were measured by using a Malvern Nanosizer instrument (Zetasizer Nano ZS90, Malvern Instruments Company, UK).

Electrochemical Measurement

Electrochemical measurements of the samples were conducted on an electrochemical
station (CHI 760E) using a three-electrode system with a graphite rod and a silver chloride electrode (SCE) as the counter and reference electrode. A glassy carbon electrode coated with catalysts as the working electrode. All the electrochemical data were tested without iR compensation.

Typically, 4 mg catalyst was suspended in 750 uL water and 250 uL ethanol with 30 μL Nafion solution (5 wt.%, Du Pont) to form a homogeneous ink assisted by ultrasound. Then, 5 μL of the ink was spread onto the surface of glassy carbon by a micropipette and dried under room temperature. The electrolyte was 1 M KOH (OER) and 0.5 M H₂SO₄ (HER) solution, which was purged by nitrogen for 30 min. The Linear sweep voltammetry (LSV) was performed with a scan rate of 5 mV s⁻¹ at the room temperature. The electrochemical surface area (ECSA) was compared by estimating the electrochemical double layer capacitances (C_{dl}) with cyclic voltammetry (CV). CV curves were performed at a potential range of 0.1-0.2 V vs RHE. The electrochemical impedance spectra were recorded at the overpotential of 100 mV in the frequency range of 0.01Hz-100 kHz. The two-electrode system was built by employing two Ru-CoNi@NC-2 electrodes.

TOF is the number of reactants transformed at an active site in per unit time.

\[ \text{TOF} = \frac{\text{the number of all oxygen turnovers in per second}}{\text{the number of all active sites}} \]

The number of active sites was quantified by the cyclic voltammetry (CV) method. All CV measurements were conducted in the potential range of 0-0.6 V vs. RHE at a fixed scan rate of 50 mV s⁻¹ in PBS solution (pH=7). The surface charge (Qₛ) was then calculated to be the half of the integrated charge over the whole potential range. The
TOF value was calculated based on the number of active sites for each catalyst (considering the total metal loading in the catalyst) using the following formula:

**HER:** \[ \text{TOF} = \frac{j S_{\text{geo}}}{2Fn} \]  

**OER:** \[ \text{TOF} = \frac{j S_{\text{geo}}}{4Fn} \]  

\( j \) is the current density at a given overpotential; \( S_{\text{geo}} \) is the geometric surface area of the electrode; \( F \) is the Faraday constant (96485.3 C/mol); \( n \) (mol) = \( Qs/F \) is the number of active sites.

Figure S1. SEM image of CoNi–EDTA precursor.
Figure S2. XRD spectrum of CoNi–EDTA precursor

Figure S3. TG curve of of CoNi–EDTA precursor.
Figure S4. XRD spectrum of CoNi@NC.

Figure S5. The photographs depicting structural color change of Ni foam after being treated in the ethanol solution of RuCl$_3$·xH$_2$O.

Figure S6. The comparison of $\eta_{20}$ and $\eta_{50}$ of various catalysts.
Figure S7. Cyclic voltammetry curves of (a) CoNi@NC, (b) Ru-CoNi@NC-1, and (c) Ru-CoNi@NC-2 in 1.0 M KOH with different scan rates.

Figure S8. SEM image of Ru-CoNi@NC-2 after 20h OER testing.

Figure S9. The comparison of XRD spectra of Ru-CoNi@NC-2 before and after 20 h OER testing.
Figure S10. SEM image of Ru-CoNi@NC-2 after 20h HER testing.

Figure S11. The polarization curves of Ru-CoNi@NC-2, Ru-CoNi@NC-2-0.5 and Ru-CoNi@NC-2-8 for (a) OER in 1 M KOH, (c) HER in 1 M KOH, (e) HER in 0.5
M H₂SO₄; Tafel slopes of Ru-CoNi@NC-2, Ru-CoNi@NC-2-0.5 and Ru-CoNi@NC-2-8 for (b) OER in 1 M KOH, (d) HER in 1 M KOH, (f) HER in 0.5 M H₂SO₄.

Figure S12. The comparison of XRD spectra of Ru-CoNi@NC-2 before and after 20 h HER test in 0.5 M H₂SO₄.