Supporting Information

Acetate promotes the formation of NiRu/NiO towards efficient hydrogen evolution

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1. Experimental Section

1.1 Materials

All chemicals, including N, N-Dimethylformamide (DMF), 1,4-benzenedicarboxylic acid (H₂BDC), anhydrous ethanol, nickel(II) chloride hexahydrate (NiCl₂·6H₂O), Ruthenium(III) chloride hydrate (RuCl₃·H₂O), sodium acetate trihydrate (CH₃COONa·3H₂O), Ru/C (20 wt% Ru on Vulcan XC-72), Nafion D520 (5 wt%), carbon black (Ketjenblack), were purchased and directly used without further purification. Milli-Q water with a resistance of 18.2 MΩ was used in all experiments.

1.2 Synthesis of NiRu/Ni(OH)₂ and NiRu/NiO

The NiRu/Ni(OH)₂ was prepared by an acetate-assisted solvothermal method. In detail, 10 mL DMF, 10 mL ethanol, and 10 mL water were firstly mixed in a glass bottle. Then, 2.0 mL CH₃COONa·3H₂O solution (3M) and 0.15 mmol H₂BDC were added in the bottle. After the solution was sonicated for 10 mins, 0.4 mmol NiCl₂·6H₂O and 0.12 mmol RuCl₃·H₂O were added into the solution, and stirred for 10 mins. Afterwards, the obtained solution was transferred to a Teflon-lined stainless steel autoclave (50 mL). Then the autoclave was sealed and heated at 120°C for 12 h. After the autoclave was naturally cooled down to room temperature, the product was collected via centrifugation, washed with water for three times, and ethanol once, and finally dried by vacuum freeze-drying.

Then, NiRu/NiO was fabricated by annealing treatment of NiRu/Ni(OH)₂. In detail, the obtained NiRu/Ni(OH)₂ sample was put in a tubular furnace. Then under the protection of Ar, the furnace was elevated to 300 °C at a ramping rate of 2 °C min⁻¹ and held at this temperature for 3 h, and cooled to ambient temperature naturally to obtain NiRu/NiO.

1.3 Synthesis of NiRu-BDC and NiRu-BDC-D

The NiRu-BDC was prepared by a traditional solvothermal method. In detail, 10 mL DMF, 10 mL ethanol, and 10 mL water were firstly mixed in a glass bottle. Then, 0.15 mmol H₂BDC was added in the bottle. After the solution was sonicated for 10 mins, 0.4 mmol NiCl₂·6H₂O and 0.12 mmol RuCl₃·H₂O were added into the solution, and stirred for 10 mins. Afterwards, the obtained solution was transferred to a Teflon-lined stainless steel autoclave (50 mL). Then the autoclave was sealed and heated at 120°C for 12 h. After the autoclave was naturally cooled down to room temperature, the product was collected via centrifugation, washed with water for three times, and ethanol once, and finally dried by vacuum freeze-drying.

Then, NiRu-BDC-D was fabricated by annealing treatment of NiRu-BDC. In detail, the obtained NiRu-BDC sample was put in a tubular furnace. Then under the protection of Ar,

the furnace was elevated to 300 °C at a ramping rate of 2 °C min⁻¹ and held at this temperature for 3 h, and cooled to ambient temperature naturally to obtain NiRu-BDC-D.

1.4 Characterizations

The morphology of the samples was characterized by field emission scanning electron microscopy (FESEM, Zeiss GeminiSEM 300) equipped with an energy dispersive spectrometer (EDS), and transmission electron microscopy (TEM, Tecnai G2 F30). The powder X-ray diffractometer (XRD) data was collected using a Rigaku MiniFlex 600 with Cu K α radiation at a scan rate of 1° min⁻¹. XPS measurements were carried out on an ESCALab250 using Al K α radiation. Inductively coupled plasma optical emission spectrometry (ICP-OES) was conducted on Agilent 5110.

1.5 Electrochemical Measurements

Electrocatalyst inks were prepared by mixing active materials with carbon black and Nafion. Specifically, 5 mg NiRu/NiO was dispersed in 1 mL H₂O, then 300 μ L carbon black (3 mg ml⁻¹) and 35 μ L Nafion (5 wt%) were added in the solution and sonicated over 1 h. Then, 10 μ L of the electrocatalyst ink was drop-cast onto the glassy carbon electrode (0.196 cm²), and the electrocatalyst layer was dried naturally. For comparison, NiRu-BDC-D, Ru/C were also prepared by the same method on glassy carbon electrode, except that no carbon black was added for Ru/C.

Electrochemical tests were carried out on a workstation (CHI 760D Instruments) by using a standard three-electrode glass cell (Pine Research Instruments, USA). Ag/AgCl (4 M KCl) electrode and carbon rod were used as the reference and counter electrodes, respectively, while 1.0 M KOH aqueous solution was used as the electrolyte. The reversible hydrogen electrode (RHE) potentials were obtained by the following equation: E(RHE) = E(Ag/AgCl)+ 0.205 + 0.059 × pH. A flow of N₂ was maintained in the electrolyte during the test.

Linear sweep voltammetry (LSV) curves were recorded with a scan rate of 5.0 mV s⁻¹. The obtained current densities were normalized to the geometrical surface area. Electrochemical impedance spectroscopy (EIS) was measured in the frequency range from 0.1 Hz to 100 kHz with an initial potential of -1.08 V vs. Ag/AgCl. IR*70% compensation of LSV curves was performed using the solution resistance estimated from EIS results. The electrical double layer capacitor (C_{dl}) of the samples were obtained from CV plots in a small potential range (from -0.4 to -0.5 V vs. Ag/AgCl). The electrode durability was tested by the galvanostatic method, which was conducted at 10 mA cm⁻² for 20 hours. All the electrochemical measurements were carried out at ambient temperature.

2. Supplementary Figures and Tables



Figure S1. XPS survey spectrum of NiRu-BDC.



Figure S2. XPS survey spectrum of NiRu/Ni(OH)₂.



Figure S3. SEM image of NiRu/Ni(OH)₂.



Figure S4. XRD pattern of the material prepared by the same method for NiRu/Ni(OH)₂, except that no ethanol was added.

As displayed in figure S4, when ethanol is not used, NiRu is still fabricated, and the typical peak at 9.3 degree for NiRu-MOF (JCPDS No.035-1677) is not observed. The broad (001) peak of Ni(OH)₂ indicates its relatively low crystallinity, while (100), (101), (110) peaks of Ni(OH)₂ disappeared, demonstrating the importance of ethanol for the formation of NiRu/Ni(OH)₂.



Figure S5. The enlarged XRD pattern of NiRu/NiO.



Figure S6. SEM image of NiRu/NiO.



Figure S7. SEM image and the corresponding elemental mapping of NiRu/NiO.



Figure S8. EDX spectrum of NiRu/NiO.



Figure S9. TEM image of NiRu/NiO.



Figure S10. TEM image of NiRu/NiO, where SAED pattern of NiRu/NiO was obtained.



Figure S11. (a) HAADF-STEM image, and (b-d) the corresponding elemental mapping of NiRu/NiO.



Figure S12. XPS Ru 3p spectrum of NiRu/Ni(OH)₂.



Figure S13. SEM image of NiRu-BDC-D.



Figure S14. XRD pattern of NiRu-BDC-D.

The XRD pattern in figure S14 shows that the obtained NiRu-BDC-D sample contains both NiRu-BDC and NiRu species. The observed characteristic peaks of NiRu-BDC (JCPDS No.035-1677) indicates that the pristine structure of NiRu-BDC was well preserved even after the annealing treatment, while three newly appeared peaks can be well indexed to (111), (200) and (220) planes of metallic NiRu.



Figure S15. (a) XPS Ni 2p spectrum of NiRu-BDC-D. (b) XPS Ru 3p spectrum of NiRu-BDC-D.

The Ni 2p XPS spectrum of NiRu-BDC-D (figure S15a) shows two main peaks positioned at 856.1 and 873.7 eV, which are assigned to Ni²⁺ 2P_{3/2} and Ni²⁺ 2P_{1/2}, together with two corresponding satellite peaks located at 861.7 and 880.5 eV (Chem. Commun., 2017, 53, 10906–10909). The Ru 3p XPS spectrum (figure S15b) displays that NiRu-BDC-D has two peaks located at 463.5 and 485.7 eV, corresponding to Ru $3P_{3/2}$ and Ru $3P_{1/2}$ of oxidized Ru species, respectively (Nat Commun., 2017, 8, 14969).



Figure S16. LSV curves of NiRu/NiO samples synthesized by different mol ratios of Ni and Ru precursors (10:3, 5:1, and 10:1, respectively) in 1.0 M KOH electrolyte.

As shown in figure S16, NiRu/NiO (10:3) sample has higher HER activity than that of NiRu/NiO (5:1), and NiRu/NiO (10:1). Therefore, NiRu/NiO (10:3) sample is well studied in this work, and the term "NiRu/NiO" in the manuscript refers to NiRu/NiO with the mol ratios of Ni and Ru precursors (10:3).



Figure S17. LSV curves of NiRu/NiO, and NiRu-BDC in 1.0 M KOH electrolyte.

The alkaline HER performance of pristine NiRu-BDC was also investigated. The LSV curves in figure S17 show that NiRu-BDC requires an overpotential of 135 mV to achieve the current density of 10 mA cm⁻², much larger than that of NiRu/NiO (18 mV).



Figure S18. CV curves for NiRu/NiO at scan rates from 20 to 100 mV s⁻¹.



Figure S19. CV curves for NiRu-BDC-D at scan rates from 20 to 100 mV s⁻¹.



Figure S20. ECSA-normalized LSV curves of NiRu/NiO, and NiRu-BDC-D in 1.0 M KOH electrolyte.

Electrochemical active surface area (ECSA) is obtained by the following equation: ECSA= C_{dl}/C_s . The specific capacitance(C_s) for a flat surface is generally in the range of 20-60 µF cm⁻², and here 40 µF cm⁻² is used (Angew. Chem. Int. Ed., 2014, 53, 14433–14437; Chem. Sci., 2017, 8, 2769–2775; J. Mater. Chem. A, 2022, 10, 12438– 12446). Therefore, ECSAs of NiRu/NiO, NiRu-BDC-D were calculated to be 139.25, and 90.25 cm²_{ECSA}, respectively. The ECSA-normalized LSV curves in figure S20 show that NiRu/NiO, and NiRu-BDC-D have quite close intrinsic HER activities, suggesting that the better HER performance of NiRu/NiO is mainly attributed to its larger ECSA, which can provide more active sites towards HER.