Electronic Supplementary Information

Ru₄Se@MoS₂ hybrid as a highly efficient electrocatalyst toward hydrogen evolution reaction

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Experimental

Materials

Na₂MoO₄, thiourea, RuCl₃ and Se powder were purchased from Energy Chemical Ltd. (Shanghai, China). Hydrazine hydrate (85 wt%) and KOH were purchased from Aladdin Ltd. (Shanghai, China). All chemical reagents used were of analytical grade and used without further purification. Carbon fiber paper (CFP) was bought from Shanghai Hesen Corp. Commercial 20% Pt/C catalysts were purchased from Shanghai Macklin Biochemical Co., Ltd.

Synthesis of MoS₂ nanosheets on carbon fiber paper

Prior to the synthesis, the carbon fiber paper was cut into small pieces (3
cm × 1.5 cm) and then washed with ultrapure water, ethanol and acetone by ultrasonication, respectively. The cleaned carbon fiber papers were dried at room temperature before further use. MoS	extsubscript{2} nanosheets were grown on the carbon fiber paper through a hydrothermal reaction. Typically, 1 mmol Na	extsubscript{2}MoO	extsubscript{4} and 4 mmol thiourea were dissolved in 30 mL ultrapure water by stirring. The mixture solution was transferred into a 50 mL Teflon–lined autoclave, and a piece of carbon fiber paper was immersed in. Then the autoclave was put into a oven and kept at 200 °C for 24 h. After naturally cooling down to room temperature, the carbon fiber paper was taken out and washed thoroughly with ultrapure water and ethanol, and then dried at room temperature.

**Synthesis of Ru\textsubscript{x}Se@MoS	extsubscript{2}**

0.042 g Se powder and 0.0363 g RuCl\textsubscript{3} were mixed in deionized water (35 mL). After vigorous stirring for 10 min, 2 mL hydrazine hydrate (85 wt%) was dropped into the above solution under constant stirring. The resulting solution was transferred into a 50 mL Teflon–lined autoclave, and the carbon fiber paper covered with MoS\textsubscript{2} nanosheets was immersed into the solution. Then the autoclave was sealed and maintained at 120 °C for 12 h. After naturally cooled to room temperature, the carbon fiber paper was taken out and washed thoroughly with deionized water and ethanol, and finally dried in vacuum at 60 °C overnight.

**Material characterizations**

X-ray diffraction (XRD) patterns were recorded at room temperature on a Bruker D8 Advance X-ray diffractometer using a Cu Kα radiation (λ=1.5416 Å) with 2θ scan range between 5° and 80°. The surface morphology of the samples was investigated by field-emission scanning electron microscopy (FESEM, FEI Quanta FEG 250) and Transmission electron microscopy (TEM, FEI Tecnai G2 F20). X-ray photoelectron spectroscopy (XPS) measurements were carried out with a ThermoFisher K-Alpha X-ray photoelectron spectrometer with an Al Kα source. All the binding energies were calibrated to the standard C 1s emission signal (284.8 eV) of the contaminant carbon during the measurement.
**Electrochemical measurements**

20% Pt/C catalysts were loaded on carbon fiber paper (CFP) through a drop-casting method. Briefly, 10 mg of the catalyst were dispersed in 480 μL of water–ethanol solution at volume ratio of 250:230. Then 20 μL of Nafion solution (5 wt%, DuPont) was added. The obtained mixture was ultra-sonicated for 3 h to form a homogenous ink. Then 50 μL catalyst ink was dropped onto a piece of carbon fiber paper (CFP, 1 cm×1cm) and left to dry at room temperature overnight.

The electrochemical measurements were performed using a standard three-electrode cell system with a CHI660E electrochemical workstation. The high-purity N$_2$-saturated 0.5 M H$_2$SO$_4$ and 1 M KOH solution were used as the electrolytes. In the basic media, a Hg/HgO electrode and a graphite rod were used as the reference electrode and counter electrode, respectively. The polarization curves for HER were measured with a potential window of -0.8 V~1.6 V vs Hg/HgO at a scan rate of 2 mV/s. All the potentials were referenced to a reversible hydrogen electrode (RHE) using $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.935$. In the acidic electrolyte, an Ag/AgCl (saturated KCl) was used as the reference electrode. The polarization curves for HER were measured with a potential window of 0.1 V~0.8 V vs Ag/AgCl at a scan rate of 2 mV/s. All the potentials were converted to the RHE using $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197$. In order to reveal the intrinsic electrocatalytic behavior of the catalysts, a 90% IR compensation was applied to all the polarization curves based on the ohmic resistance of the solution determined by electrochemical impedance spectroscopy (EIS). EIS measurements were carried out with a frequency range of 100 mHz to 100 kHz and an amplitude of 5 mV. Z-view software was used to fit the EIS spectra. The long-term stability of the catalyst was evaluated by continuously cyclic voltammetry (CV) measurement between -0.8 V~ -1.3 V (vs Hg/HgO) in basic media and 0.1~0.5 V (vs Ag/AgCl) in acidic media for 1000 cycles at a scan rate of 100 mV/s$^{-1}$, and the polarization curves before and after CV measurement were recorded. Chronopotentiometry test was conducted at the corresponding potential to deliver a current density of -20 mA cm$^{-2}$ to monitor the long-term potential-time response during the HER process.
Figure S1 XRD pattern of Ru\textsubscript{x}Se calcinated at 400 °C and the standard pattern for crystalline RuSe\textsubscript{2} (PDF No. 65-3328).

Figure S2 SEM images of MoS\textsubscript{2} and Ru\textsubscript{x}Se@MoS\textsubscript{2}, indicating the nanoflowers grown on the vertically aligned nanosheets.
Figure S3 EDX spectrum of Ru$_x$Se@MoS$_2$ and the atomic fraction of different elements

| Element | Atomic Fraction (%) |
|---------|---------------------|
| Mo      | 20.9                |
| S       | 6.83                |
| Se      | 4.24                |
| Ru      | 0.72                |

Figure S4 HRTEM image (a) of Ru$_x$Se@MoS$_2$ and two magnified images (b, c) to illustrate the interplanar space of 0.27 nm corresponding to (100) plane of 2H-MoS$_2$. 
Figure S5 TEM image of Ru₅Se

Figure S6 SEM images of Ru₅Se@MoS₂ after a long-term HER test.
Figure S7 TEM images of Ru$_x$Se@MoS$_2$ after a long-term HER test.

Figure S8 Time-dependent potential curves of commercial 20% Pt/C catalyst operated at a current density of -20 mA cm$^{-2}$
Table S1 The overpotential at the current density of 10 mA/cm², Tafel slope for MoS₂-based HER electrocatalysts in alkaline media.

| Catalysts                                      | η@10 mA cm⁻² (mV) | Tafel slope (mV dec⁻¹) | Ref.                      |
|------------------------------------------------|-------------------|------------------------|--------------------------|
| MoS₂ intercalated with Co(OH)₂ nanoparticles   | 89                | 53                     | ACS Nano, 2018, 12:4565-4573 |
| Nickel Hydr(oxy)oxide nanoparticles on metallic MoS₂ nanosheets | 73                | 75                     | Adv. Sci., 2018, 5:1700644 |
| Ni(OH)₂/MoS₂ heterostructure                   | 80                | 60                     | Nano Energy, 2017, 37:74-80 |
| Ni-doped MoS₂ nanosheets                       | 98                | 60                     | Energy Environ. Sci., 2016, 9:2789-2793 |
| Ni(OH)₂/MoS₂ heterostructures                  | 227               | 105                    | Nanoscale, 2018, 10:19074-19081 |
| Amorphous nickel-cobalt complexes hybridized with 1T-phase MoS₂ | 70                | 38.1                   | Nat. Commun., 2017, 8:15377 |
| Aligned MoS₂/Ni₃S₂ Nanoarrays on Ni foam       | 76                | 56                     | ACS Appl. Mater. Interfaces, 2018, 10:1752-1760 |
| MoS₂/Ni₃S₂ Heterostructures                    | 110               | 50                     | Angew. Chem. Int. Ed. Engl., 2016, 55:6702- |
| System Description                                                                 | Potential (V) | Current (mA/cm²) | Reference                                      |
|-----------------------------------------------------------------------------------|---------------|------------------|------------------------------------------------|
| MoS₂ nanosheet arrays vertically aligned on graphene-mediated 3D Ni networks       | >600          | 98               | Adv. Funct. Mater., 2014, 24:6123-6129          |
| Interlaced NiS₂-MoS₂ Nanoflake-Nanowires                                           | ~120          | 70               | J. Mater. Chem. A, 2016, 4:13439-13443          |
| MoS₂-NiCo LDH hybrid                                                              | 78            | 76.6             | Joule, 2017, 1:383-393                          |
| Co₃O₄@MoS₂ Heterostructures                                                        | 207           | 59.5             | J. Mater. Chem. A, 2018, 6:2067-2072            |
| Ni–Fe-LDH–MoS₂ nanohybrids                                                         | >330          | 67               | ACS Energy Lett., 2018, 3:952-960               |
| MoS₂–Ni₃S₂ Heteronanorods                                                          | 98            | 61               | ACS Catal., 2017, 7:2357-2366                   |
| NiS-Ni(OH)₂@MoS₂₋ₓ                                                                | 226           | 81               | Adv. Funct. Mater., 2016, 26, 7386              |
| CoS-Co(OH)₂@MoS₂₋ₓ                                                               | 143           | 68               |                                                 |