Hexagonal NiMoO$_4$-MoS$_2$ Nanosheets heterostructure as a Bifunctional Electrocatalyst for urea oxidation assisted Overall Water Electrolysis

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1. Experimental Section

1.1 Chemicals

The reagents required for the experiment were: absolute ethanol(C$_2$H$_6$O), nickel nitrate hexahydrate((Ni(NO$_3$)$_2$·6H$_2$O), urea (CO(NH$_2$)$_2$), potassium hydroxide (KOH) Sodium molybdate dihydrate (Na$_2$MoO$_4$·2H$_2$O), Pt/C/NF, IrO$_2$/NF and Hex ammonium molybdate ((NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O) were commercially available from Aladdin Chemistry, Thioacetamide (CH$_3$CSNH$_2$) purchased from Tianjin Guangfu, nickel foam (1 × 2 cm$^2$), ultrapure water (18.25 MΩ·cm) was prepared using a purified system UPC-1-10 T purification system.

1.2 Preparation of MoS$_2$/NF

Disperse 0.6 mmol (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O and 9.0 mmol thioacetamide (CH$_3$CSNH$_2$) in 60 mL deionized water, and stir magnetically for 60 min at room temperature. Subsequently, the obtained transparent solution was transferred to the PTFE lining of a 100 mL stainless steel autoclave, which contained pre-treated nickel foam (1×2 cm$^2$). The nickel foam was respectively used with 5 % hydrochloric acid solution, ethanol, alternate ultrasonic cleaning with deionized water for 30 min to obtain pretreated nickel foam. Keep it in a blast drying oven at 200 °C for 20 h. After it is naturally cooled to room temperature, it is washed several times with deionized water and absolute ethanol, and finally dried in an oven at 60 °C for 12 h. Obtained MoS$_2$/NF nanosheets.

1.3 Preparation of NiMoO$_4$/NF

The NiMoO$_4$/NF is prepared by the following steps. Usually 3 mmol Ni(NO$_3$)$_2$·6H$_2$O and 3 mmol Na$_2$MoO$_4$·2H$_2$O are dissolved in 30 mL ultra-pure water and 30 mL absolute ethanol to form a uniform German solution. Ultrasonic treatment for 20 min. Then, a piece of pretreated NF is immersed in the above solution and transferred to the lining. In a 100 mL stainless steel autoclave with Teflon, heated at 150 °C for 6 h. After cooling to room temperature, the obtained NiMoO precursor (NiMoO/NF) grown on NF was cooled to room temperature. Wash with water and ethanol several times, and then dry in a vacuum drying oven at 60 °C for 6 h. Annealed at 350 °C for 2 h in Ar atmosphere to prepare NiMoO$_4$/NF electrodes.

1.4 Preparation of NiMoO$_4$-MoS$_2$/NF

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Dissolve 3 mmol Ni(NO$_3$)$_2$·6H$_2$O and 3 mmol Na$_2$MoO$_4$·2H$_2$O in 30 mL ultrapure water and 30 mL absolute ethanol to form a homogeneous mixed solution. Ultrasonic treatment for 20 min. Then, Dip MoS$_2$/NF into the above solution, transfer it to a 100 mL stainless steel autoclave lined with Teflon, and heat it at 150 °C for 6 h. Wash with water and ethanol several times, and then dry in a vacuum drying oven at 60 °C for 6 h. Finally, the NiMoO$_4$-MoS$_2$/NF heterostructure was obtained by annealing at 350 °C for 2 h in Ar atmosphere.

1.5 Preparation of Pt/C/NF and IrO$_2$/NF

The electrodes were prepared by the drop casting method. Initially, 5 mg of Pt/C/NF was dispersed in 1 mL of ethanol-water mixture at a volume ratio of 1: 4 and with 20 μL of Nafion to obtain a homogeneous dispersion solution of the catalyst. This solution was then uniformly applied to a 1 x 1 cm$^2$ piece of NF and dried at room temperature for 1 h, Loaded at 5mg/cm$^2$. The preparation method of IrO$_2$/NF is the same as above.

1.6 Characterization

Micrographs were taken using a Titan ETEM (U.S.A., FEI Co., G280-300) equipment, and the accelerating voltage was 300 kV. Energy-dispersive spectroscopy (EDS) mapping and scanning electron microscopy (SEM) micrographs were obtained by a SU8220 (Hitachi Corp., Japan) with the voltage of 5 kV. X-ray diffraction (XRD) patterns were acquired by an X-ray facility (Cu Kα radiation, λ = 0.154056 nm, Smart Lab, Rigaku Corp.D8 Advance, Japan). X-ray photoelectron spectroscopy (XPS) patterns were taken by an X-ray photoelectron spectroscopy instrument equipped with Al Kα source (ESCALAB 250Xi, Thermo Fisher Scientific, USA). JC2000DM precision type contact angle measuring instrument.

1.7 Electrochemical measurements

A standard three-electrode system was used to evaluate the electrochemical impedance spectroscopy (EIS) and the linear sweep voltammetry (LSV) experiments of the catalyst. It consists of a reference electrode (reversible hydrogen electrode - RHE), a counter electrode (graphite rod), and a working electrode (the as-prepared catalysts) (the area of each catalyst immersed in the electrolyte was 0.5 cm$^2$). Furthermore, the above system was tested in 1.0 M KOH with 0.5 M urea and 1.0 M KOH solution, with a scan speed of 5 mV·s$^{-1}$. Then, prepared electrodes of noble metal Pt/C/NF and IrO$_2$/NF were tested with an area of 0.5 cm$^2$. The tests potentials of both HER and UOR were corrected by the equation:

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 \text{pH} + 0.098 \text{V}$$

0.5 M urea +1.0 M KOH solution, with a scan speed of 5 mV·s$^{-1}$. The EIS was applied in a frequency domain between $10^5$ to $10^{-1}$ Hz, with 5 mV of amplitude. Potentials were IR compensated by the following equation: (1) $E_{\text{corr}} = E_{\text{mea}} - \text{IRs}$, The Tafel slope was converted from the LSV curve according to the following equation:

$$\eta = a + b \log (j)$$

Water splitting test was carried out in a two-electrode system. NiMoO$_4$-MoS$_2$/NF (1 cm *0.5 cm) are used both as cathode and anode in a single liquid cell. LSV curves were obtained with the scan rate of 5 mV s$^{-1}$, and the stability was performed by chronoamperometry at 1.445 V corresponding to the current density of 10 mA·cm$^{-2}$ for 24 h.
Fig. S 1 The NiMoO₄/NF (a-c) SEM images and (e, f) EDS energy spectra at different magnifications.

Fig. S 2 The MoS₂/NF (a-c) SEM images and (e, f) EDS at different magnifications.

Fig. S 3 (a) Polarization curves before and after 1000 cycles of CV scanning in 1 M KOH with 0.5 M Urea; (b-d) Cyclic voltammetry curves of NiMoO₄-MoS₂/NF, MoS₂/NF and NiMoO₄/NF at different scanning rates (20-100 mV·s⁻¹).
Fig. S4 (a) Polarization curves before and after 1000 cycles of CV scanning in 1 M KOH with 0.5 M Urea; (b-d) Cyclic voltammetry curves of NiMoO$_4$/NF, MoS$_2$/NF, NiMoO$_4$-MoS$_2$/NF at different scanning rates (20-100 mV·s$^{-1}$).

Fig. S5 After tested for 24 h of NiMoO$_4$-MoS$_2$/NF (a-c) SEM; (d) EDS images; (e) XRD patterns of the NiMoO$_4$-MoS$_2$/NF after the 24 UOR test.

Table S1 Performance comparison of some bifunctional materials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Current density (mA·cm$^{-2}$)</th>
<th>UOR Potential (V)</th>
<th>HER Potential (mV)</th>
<th>Urea–water electrolysis (V)</th>
<th>References</th>
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<tr>
<td>Co$_3$P/N-C/NF</td>
<td>10</td>
<td>1.351</td>
<td>65</td>
<td>1.35</td>
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<tr>
<td>Ni@NCNT</td>
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<td>1.56</td>
<td>76.3</td>
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<td>NiMoO</td>
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<td>90</td>
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<td>MoS$_2$/Ni$_3$S$_2$</td>
<td>10</td>
<td>1.45</td>
<td>99</td>
<td>1.45</td>
<td>4</td>
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References
1890-1897.