Engineering NiMoP Nanosheets on Hollow Cu₃P

Nanotube Arrays as Efficient Electrocatalyst for Hydrogen

Evolution Reaction

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Reaction mechanism of NiMoP@Cu3P/CF:

The color changes of the samples from orange to light blue, green, and finally to brownish black were clearly observed, as shown in Figure S1. The specific reaction mechanism is as follows¹⁻⁵:

(1) Preparation of Cu(OH)₂/CF electrode:

 $\mathrm{Cu} + \mathrm{S_2O_8^{2-}} + 4\mathrm{OH^-} + 2\mathrm{NH_4^+} \rightarrow \mathrm{Cu}(\mathrm{OH})_2 + 2\mathrm{SO_4^{2-}} + 2\mathrm{NH_3} + 2\mathrm{H_2O}$

(2) Preparation of NiMo LDH@Cu(OH)₂/CF electrode:

$$CO(NH_2)_2 + 3H_2O \rightarrow 2NH_4^+ + 2OH^- + CO_2$$
$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O$$
$$2Ni^{2+} + 2OH^- + CO_3^{2-} \rightarrow Ni_2(OH)_2CO_3$$
$$Mo^{6+} + 4OH^- + CO_3^{2-} \rightarrow Mo(OH)_4 CO_3$$
$$Cu^{2+} + 2OH^- + CO_3^{2-} \rightarrow Cu_2(OH)_2CO_3$$

(3) Preparation of NiMoP@Cu₃P/CF electrode:

 $Ni_{2}(OH)_{2}CO_{3} \rightarrow 2NiO+H_{2}O+CO_{2}$ $Mo(OH)_{4}CO_{3} \rightarrow MoO_{3}+2H_{2}O+CO_{2}$ $Cu_{2}(OH)_{2}CO_{3} \rightarrow 2CuO+H_{2}O+CO_{2}$ $6NiO+4PH_{3} \rightarrow 3Ni_{2}P+P+6H_{2}O$ $MoO_{3}+2PH_{3} \rightarrow MoP+P+3H_{2}O$ $3CuO+2PH_{3} \rightarrow Cu_{3}P+P+3H_{2}O$



Figure S1. From left to right are photos of foamed copper, Cu(OH)₂/CF, NiMo LDH@Cu(OH)₂, NiMoP@Cu₃P/CF.



Figure S2. XRD patterns of NiMoP@Cu₃P/CF



Figure S3. SEM images of Cu(OH)₂/CF (a, b, c).



Figure S4. CV curves for CF (a), NiMo LDH/CF (b) Cu(OH)₂/CF (c), NiMo LDH@Cu(OH)₂/CF (d), NiMoP/CF (e), Cu₃P/CF (f) and NiMoP@Cu₃P/CF (g) under different scan rates increasing from 20 mV s⁻¹ to 100 mV s⁻¹ in 1 M KOH. The C_{dl} (h) of CF, NiMo LDH/CF, Cu(OH)₂/CF, NiMo LDH @Cu(OH)₂/CF, NiMoP/CF, Cu₃P/CF and NiMoP@Cu₃P/CF.



Figure S5. XRD patterns of the NiMoP@Cu₃P/CF after HER test.

Figure S6. XPS survey spectrum of NiMoP@Cu₃P/CF after long cycles of HER : survey (a), Cu 2p (b), Ni 2p (c), Mo 3d (d), and P 2p electrons for NiMoP@Cu₃P/CF core level spectra.

Table S1. Comparison of the HER catalytic performance of NiMoP@ Cu_3P /CF with other previously reported electrocatalysts.

Catalyst	Phosphorus source	Overpotential (mV)	Tafel slope (mV dec ⁻¹)	Ref.
NiMoP@Cu ₃ P	NaH ₂ PO ₂	81	133.1	This work
NiMo LDH@Cu(OH) ₂	-	111	188.1	This work
Ni ₅ P ₄ nanosheets on Ni foil	red phosphorus	150	53	[6]
MoP/Ni ₂ P/NF	NaH ₂ PO ₂	75	100.2	[⁷]
NiCu-P	red phosphorus	175	53	[8]
MoP@NCF	H ₃ PO ₄	129.5	72.4	[9]
Cu ₃ P NW/CFa	NaH ₂ PO ₂	143 /0.5M H ₂ SO ₄	67	[¹⁰]
NiMoP ₂ NW/CC	NaH ₂ PO ₂	199/ ₁₀₀	112	[¹¹]
Mn-NiP ₂ NSs/CC	NaH ₂ PO ₄	97	61	[¹²]
Ni ₂ P-Cu ₃ P/NiCuC	NaH ₂ PO ₂	78	177	[¹³]

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