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Supporting Information

Facile synthesis of three-dimensional wrinkled cobalt doped MoP/FeP₄ nanospheres for boosted hydrogen evolution reaction

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Material

Sodium hypophosphite (NaH₂PO₂·H₂O) were purchased from Aladdin. Dopamine hydrochloride (C₈H₁₁NO₂·HCl), Cobalt nitrate (Co(NO₃)₂·6H₂O), Ammonium molybdate (H₈MoN₂O₄), Ammonium hydroxide (NH₃·H₂O), Absolute ethanol (C₂H₆O) and 5 wt % Nafion were provided by Sinopharm Chemical Reagent Co, Ltd, China. Commercial 10 wt % Pt/C was available from Aladdin. Potassium ferricyanide (K₃[Fe(CN)₆])was purchased from Yantai Shuangshuang Chemical Co, Ltd. All chemicals are of analytical grade and can be used directly.

Synthesis of Co-MoP/FeP₄ heterojunction

0.2 g (NH₄)₆Mo₇O₂₄·4H₂O and 0.2 g C₈H₁₁NO₂·HCl were dissolved in 8 mL deionized water to obtain a transparent solution. After continuous stirring for 10 min, 0.08 g K₃[Fe(CN)₆] was added until dissolved. Then 20 mL ethanol was quickly added to the above solution under vigorous stirring. After stirring for 30 min, 1000 μ L NH₃·H₂O was added to initiate polymerization, and finally 0.02 g of Co(NO₃)₂·6H₂O solution (Co(NO₃)₂·6H₂O was dissolved in 3 mL of water) was added dropwise. After continued stirring for 2 h, the Mo-Fe-Co precursor was isolated by centrifugation, washed several times with ethanol, and dried in an oven at 40°C. The obtained Mo-Fe-Co precursor and 3.0 g NaH₂PO₂ were then placed upstream and downstream in a tube furnace, respectively, and annealed at 300°C for 2 h at the heating rate of 2°C min⁻¹ in N₂ atmosphere, and then annealed at 800°C at the heating rate of 5°C min⁻¹ for 1 h. Co-MoP/FeP₄ obtained after cooling to room temperature.

Synthesis of MoP/FeP₄ heterojunction

For further comparison, the synthetic method of MoP/FeP₄ was similar to the above method of the Co-MoP/FeP₄. The MoP/FeP₄ was fabricated without introducing $Co(NO_3)_2 \cdot 6H_2O$.

Synthesis of MoP nanospheres

For further comparison, the synthetic method of MoP was similar to the above method of the MoP/FeP₄. The MoP was fabricated without introducing $K_3[Fe(CN)_6]$ and $NH_3 \cdot H_2O$.

Sample Characterization

The structures and morphologies of samples were sequentially assessed via transmission electron microscopy (TEM, FEI TECNAI G² F₂₀, America) and fieldemission scanning electron microscopy (FE-SEM, Carl Zeiss Ultra Plus, Germany). The elemental mappings and chemical compositions of the samples were characterized via energy-dispersive X-ray spectroscopy (EDX, Oxford, England) equipped with an Aztec-X-80. The crystal structures and interlayer spacings were determined via X-ray powder diffraction (XRD, X'Pert PRO, Netherlands) with Cu K α radiation. X-ray photoelectron spectroscopy (XPS) analyses were collected on a PHI-5702 multifunctional photoelectron spectromete (America) equipped with monochromated Al K α radiation source. The surface area and pore size distribution of the samples were determined via the Brunauer-Emmett-Teller (BET) instrument (Autosorb-iQ2-MP, USA). The Raman spectra was performed with a 632.8 nm excitation laser wavelength (Renishaw invia, England).

Electrochemical measurements

All electrochemical tests were carried out an Autolab PGSTAT128N (Switzerland) electrochemical workstation using a standard three-electrode system. A glassy carbon electrode (GCE) with a diameter of 5 mm was used as the working electrode, graphite rod as the counter electrode, both Hg/HgO and Ag/AgCl electrode as the reference electrode. All the potentials were converted into the reversible hydrogen electrode (vs. RHE) by the Nernst equation:

The aqueous solutions of 1.0 M KOH and 0.5 M H_2SO_4 were used separately as the electrolyte. The working electrode was fabricated as follows: 5 mg of catalyst was dispersed in a mixture solution of 450 µL ethanol, 500 µL water, and 50 µL Nafion solution (5 wt %). The mixture was ultrasonized for 50 min to form uniformly catalyst ink. Then, 5 µL of catalyst ink was dropped on GCE, and dried at room temperature (catalyst loading ~0.127 mg cm⁻²). The linear sweep voltammograms (LSV) were obtained in the potential region from 0.0 to - 0.8 V at a scan rate of 5 mV s⁻¹. The Tafel slopes were measured by fitting the linear region of the Tafel plot using Tafel equation. The long-term stability tests were carried out in a range from -0.7 to -0.05 V (vs. RHE) for 2000 cycles. The double-layer capacitances (C_{dl}) were determined by cyclic voltammetry (CV) curves at different scan rates from 20 to 160 mV s⁻¹. The electrochemical impedance spectroscopy (EIS) measurements were conducted in the

frequency range of 50 kHz to 0.01 Hz. All the polarization curves were corrected by iR compensation to eliminate interference of the ohmic resistance.



Scheme S1 Preparation for Co-MoP/FeP₄ heterojunction.



Fig. S1 (a) TEM and (b) HRTEM images of the MoP/FeP₄ heterojunction.



Fig. S2 (a) TEM and (b) HRTEM images of the MoP.



Fig. S3 EDS elemental mapping of Mo, Fe, P and C for MoP/FeP₄ heterojunction.



Fig. S4 CV curves of (a) Mo-Fe-Co precursor, (b) MoP nanospheres, (c) MoP/FeP₄ heterojunction and (d) Co-MoP/FeP₄ heterojunction in 1M KOH.



Fig. S5 CV curves of (a) Mo-Fe-Co precursor, (b) MoP nanospheres, (c) MoP/FeP₄ heterojunction and (d) Co-MoP/FeP₄ heterojunction in H₂SO₄.

Catalyst	$\eta_{10}(mV)$	Tafel slope (mV dec ⁻¹)	C _{dl} (mF cm ⁻²)	Rct (Ω)	
Co-MoP/FeP ₄	161.7	67.99	7.97	26.2	
MoP/FeP ₄	204.65	75.74	3.61	47.4	
Mo-Fe-Co	410.7	93.43	1.07	84.5	
MoP	241.73	89.31	2.36	53.9	

Table S1 HER parameters of various as-prepared catalysts in 1 M KOH

Catalyst	η ₁₀ (mV)	Tafel slope (mV dec ⁻¹)	C _{dl} (mF cm ⁻²)	Rct (Ω)
Co-MoP/FeP ₄	142.2	67.81	4.81	25.6
MoP/FeP ₄	180.3	79.36	2.41	50.3
Mo-Fe-Co	497.4	155.25	0.26	111.1
MoP	273.2	95.01	0.45	70.6

Table S2 HER parameters of various as-prepared catalysts in 0.5 M H_2SO_4

Catalysts	Overpotential			
	$\eta_{10}/\ mV$	Tafel/ mV dec ⁻¹	Electrolyte	Reference
Co-MoP/FeP ₄	161.7	67.99	alkaline	This work
Co-MoP/FeP ₄	142.2	67.81	acidic	This work
MoP/NPG	126	49	alkaline	[S1]
MoP/NPG	148	56	acidic	[S1]
MoP-rGO	150	66	alkaline	[S2]
MoP-rGO	117	62	acidic	[S2]
Mo ₂ C/MoP@NPC	169	65	alkaline	[S3]
Mo ₂ C/MoP@NPC	228	75	acidic	[S3]
Mn-MoP	198	50	alkaline	[S4]
Mn-MoP	199	49	acidic	[S4]
Ni-MoP/rGO	122	71.4	alkaline	[85]
Ni-MoP/rGO	/	/	acidic	[\$5]
FeP	185	93	alkaline	[S6]
FeP	110	57	acidic	[S6]
Mn-FeP	173	95	alkaline	[S7]
Mn-FeP	69	59	acidic	[S7]
FeCo-P/CC	130	57.2	alkaline	[S8]
FeCo-P/CC	/	/	acidic	[S8]

 Table S3. Comparison of the (Mo/Fe)P-based catalysts HER activity in alkaline and acidic electrolyte.

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