Supplementary Materials

Plasma-sprayed-enabled microcosmic explosion to construct Ni

mesh-based electrodes for water splitting

Experimental section

Chemicals

All reagents were analytical grade and used without further purification. Potassium hydroxide and ethanol were purchased from Shanghai LingFeng Chemical Reagent Co., Ltd. Iron (III) nitrate nonahydrate [Fe(NO₃)₃·9H₂O] was purchased from Sinopharm Chemical Reagent Co., Ltd. All experimental water was purified by the Millipore system catalyst.

Preparation of PS-NM Electrode

Ni mesh (NM) was cleaned by sonicating in acetone solution for 20 min. Then repeatedly washed with ethanol to remove the lipids on the metal surface. NM was placed in HCl solution with a concentration of 4 mol L^{-1} for 10 min, and then left for 15 min, repeatedly washed with distilled water to remove the oxide layer on the metal surface. After that, the mixed powder of Ni and Al was sprayed onto the cleaned NM surface by plasma thermal spraying. The specific technological parameters for the preparation are shown as follows.

Under the working current, Ar mixed with a small amount of H₂ (5 vol.%) will form the plasma gas due to the ionization excitation. The inlet pressure of the forming gas is 3.5 MPa. The temperature of the plasma gas is higher than 4000 °C. The plasma gas will be quickly ejected through the spray gun. At the same time, the mixed Ni, Al powders are transported to the plasma flame flow by a 1.6 MPa N₂, then rapidly melted, and finally brought to the surface of the substrates by high-speed plasma gas to form PS-NM electrodes. The flow rate of cooling water is 5 L s⁻¹. The distance from the nozzle to substrate is 40 cm.

The obtained sample was then immersed in aqueous solution of 30% NaOH for 24 h, and then repeatedly washed with distilled water. After that, the sample (1×2 cm) was activated overnight by soaking in 1 M KOH solution again. Finally, the PS-NM electrode is obtained after several times of water washing and a vacuum drying under 40 °C for 6 h. The purpose of the thorough alkaline solution soaking is to avoid the interference of Al impurities. The specific result is shown in Fig. S1.

Preparation of me-PS-NM Electrode

As for *me*-PS-NM, all other experimental operations were the same as abovementioned, except for replacing the mixed Ni, Al powders with the Ni-coated Al composite metal powders.

Preparation of Fe³⁺-me-PS-NM Electrode

The *me*-PS-NM sample was put into the mixed solution of $0.06 \text{ g Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 5 mL ethanol, and 15 mL deionized water for 24 h under room temperature. Then, the sample was washed with distilled water and then dried in a drying oven at 60 °C for 4 h to obtain the Fe³⁺-*me*-PS-NM electrode.

Preparation of Fe³⁺-NM Electrode

As for Fe³⁺-NM, all other experimental operations were the same as abovementioned, except for replacing the *me*-PS-NM precursor with pure NM.

Characterizations

The morphology of the electrodes was observed by Zeiss Ultra 55 field emission scanning electron microscope (SEM), and elemental analysis was performed by energy

dispersive X-ray (EDX) spectrum. Transmission electron microscopy (TEM, JAPAN-JEOL-JEM 2100 F), High-resolution TEM (HRTEM), and selected area electron diffraction (SAED) images were characterized at 200 kV accelerating voltage. Bruker Dimension Icon was used for atomic force microscopy (AFM) imaging, and the thickness of the nanosheets was analyzed. The content of Fe was determined by inductively coupled plasma-mass spectrometry (ICP-MS). The X-ray photoelectron spectroscopy (XPS) analysis was carried out on ESCALab MKII spectrometer, which uses Mg Ka X-ray as the source of excitation. X-ray diffraction (XRD) measurements were carried out on Rigaku SmartLab by Cu Kα radiation in the range from 5° to 80°.

Electrochemical Measurement

All electrochemical tests were carried out with CHI 660E. Hg/HgO was used as the reference electrode and Pt sheet as the counter electrode. Fe³⁺-*me*-PS-NM, *me*-PS-NM, PS-NM, and NM were used as the working electrode. The scanning rate of linear scanning voltammetry (LSV) was 5mV s⁻¹. Measurements were conducted in 1 M KOH solution, and the working electrode was controlled at 1×1 cm. Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range from 100 kHz to 0.01 Hz with an AC voltage of 5 mV, and tests at a fixed potential of -250 mV (vs. RHE) for HER and 1.6 V (vs. RHE) for OER. The electrochemical active surface area (ECSA) curve was measured by different scanning rates (50, 60, 70, 80, and 100mV s⁻¹). There was no Faraday reaction in the voltage range from 0.723 to 0.825 V. The capacitive current of the cyclic voltammetry curve ($\Delta J_{IJa-Jcl}/2$) was drawn to fit the double layer capacitance (C_{dl}). ECSA and ECSA current density $q^{j}ECSA$) are calculated according to Eq.1 and Eq.2:

$$ECSA = \frac{C_{dl} \text{ (mA cm}^2)}{0.04 \text{ (mA cm}^2)} \times A$$

$$j_{ECSA} = \frac{I \text{ (mA)}}{ECSA \text{ (cm}^2)}$$
Eq.2

where A is the geometric area of the electrode (in this case, 1 cm²). The specific capacitance of a flat surface is normally between 0.02 mF cm⁻² to 0.06 mF cm⁻². Therefore, we added the C_{dl} value of NM (0.04 mF cm⁻²) as the criterion for estimating the ECSA.^{1,2}

All presented potentials were corrected against the ohmic potential drop with 85% iR compensation.

Supplementary Figures



Fig. S1 XPS patterns of Al 2p of PS-NM before and after activation.



Fig. S2 XPS patterns of Al 2p of me-PS-NM before and after activation.

In the Al 2p spectrum of Fig. S1 and S2, the peaks at 73.9 eV and 69 eV correspond to Al³⁺ and Al-Ni bonds, respectively.^{3, 4} However, no Al peak is detected in the activated electrodes, which confirm that there is no residual Al in the electrodes.



500µm

Fig. S3 EDS element mapping images of Ni, and O for the me-PS-NM.

Element	Content (At%)
Ni	66.1
0	33.9

Fig. S4 EDS element distribution of *me*-PS-NM.



Fig. S5 The LSV curve of HER mass activity in KOH.



Fig. S6 Nyquist plots of different electrodes for HER (inset: the equivalent circuit Nyquist plot).



Fig. S7 Long-term stability test of *me*-PS-NM at the current density of 100 mA cm⁻² (inset: LSV plots of *me*-PS-NM after stability test)



Fig. S8 The EDS element map of *me*-PS-NM after the stability test.

Element	Content (At%)	
Ni	79.1	
0	20.9	

Fig. S9 EDS element distribution of me-PS-NM after stability test.



Fig. S10 LSV curve of different Fe content.



Fig. S11 The LSV curve of OER mass activity in KOH.



Fig. S12 Nyquist plots of different electrodes for OER (inset: the equivalent circuit Nyquist plot).



Fig. S13 CV curves measured at different scan rates from 50, 60, 70, 80, and 100 mV s⁻¹ (the color changes from light to dark) of (a) NM, (b) PS-NM, (c) *me*-PS-NM, and (d) Fe³⁺-*me*-PS-NM.



Fig. S14 The C_{dl} plots for extraction ECSA of different electrodes.

The electrochemical active surface area (ECSA) of the different electrodes was evaluated by measuring the CV curves at different scanning rates (Fig. S11). The double-layer capacitance (C_{dl}) trends to the positive correlation between ECSA. The C_{dl} value is derived by the ECSA of each electrode (Fig. S12).^{5, 6} Fe³⁺-*me*-PS-NM exhibits the highest C_{dl} value (3.68 mF cm⁻²), which is 2 times higher than *me*-PS-NM (1.59 mF cm⁻²), 4 times higher than PS-NM (0.91 mF cm⁻²), and 12 times higher than NM (0.29 mF cm⁻²). It can be seen that the target electrode has the most abundant active sites.



Fig. S15 SEM images of Fe³⁺-*me*-PS-NM.



Fig. S16 EDS element mapping images of Ni, Fe, and O for the Fe³⁺-*me*-PS-NM.

Element	Content (At%)	
Ni	18.3	
Fe	4.2	
0	77.5	

Fig. S17 EDS spectrometer data for the Fe^{3+} -*me*-PS-NM.



Fig. S18 TEM image of Fe³⁺-me-PS-NM nanosheet.



Fig. S19 AFM images of different regions of Fe³⁺-*me*-PS-NM.



Fig. S20 (a) HRTEM image and corresponding (b) SAED pattern of Fe³⁺-me-PS-NM.



Fig. S21 EDX element mapping images of Ni, Fe, and O of Fe^{3+} -*me*-PS-NM.



Fig. S22 Long-term stability test of Fe³⁺-*me*-PS-NM at the current density of 100 mA cm⁻² (inset: LSV plots of Fe³⁺-*me*-PS-NM after stability test



Fig. S23 The EDS element map of Fe^{3+} -me-PS-NM after the stability test.

Element	Content (At%)
Ni	17.2
Fe	4.7
0	78.1

Fig. S24 EDS element distribution of Fe³⁺-me-PS-NM after stability test.



Fig. S25 SEM images of Fe³⁺-NM.



Fig. S26 OER LSV curves of Fe³⁺-me-PS-NM and Fe³⁺-NM in 1.0 M KOH.



Fig. S27 (a) CV curves with various scan rates (50, 60, 70, 80, 100 mV s⁻¹) for Fe³⁺-NM. (b) Derived C_{dl} comparison of Fe³⁺-*me*-PS-NM and Fe³⁺-NM.



Fig. S28 Polarization curves of Fe³⁺-*me*-PS-NM and Fe³⁺-NM with current densities normalized to ECSA.

Firstly, the microscopic morphology of Fe³⁺-NM is analyzed by SEM. Fig. S25 shows that NiFe LDH nanosheets are successfully grown on the surface of NM. In Fig.

S26, at a current density of 10 mA cm⁻², the overpotential of Fe³⁺-me-PS-NM is 220 mV, which is much less than the overpotential of Fe^{3+} -NM (326 mV). Even when the current density is increased to 100 mA cm⁻², the overpotential of Fe³⁺-me-PS-NM is only 260 mV, which is still much lower than the overpotential of F Fe³⁺-NM (398 mV). This is owing to the synergistic effect between *me*-PS-NM and NiFe LDH that endows the catalyst with excellent electrocatalytic properties against OER. To further clarify the difference in OER performance between Fe³⁺-me-PS-NM and Fe³⁺-NM. Fig. S27b presents the C_{dl} calculate from the corresponding CV curves (Fig. S27a). The C_{dl} of Fe³⁺-me-PS-NM is 7 times that of Fe³⁺-NM. This shows that plasma-spraying-induced microcosmic explosion strategy can increase the ECSA value and further increase the number of exposed active sites.⁷ To verify this result, we calculate the ECSA of the electrodes. The results are shown in Table S1, the high ECSA of Fe³⁺-me-PS-NM confirms the advantages of the sufficient electrocatalytic active sites. To assess the activity of the catalysts more fairly, the normalized polarization curve of ECSA shown in Fig. S28.^{8,9} The Fe³⁺-me-PS-NM catalyst has a higher ECSA normalized current density at the same test potential, proving that the Fe³⁺-me-PS-NM catalyst has a satisfactory intrinsic activity over Fe³⁺-NM. The above results confirm that synergistic effect between *me*-PS-NM and NiFe LDH enhance the properties of OER.



Fig. S29 SEM images of me-PS-NM after OWS stability test.



Fig. S30 SEM images of Fe³⁺-me-PS-NM after OWS stability test.



Fig. S31 XRD characterization of Fe³⁺-me-PS-NM after OWS stability test.



Fig. S32 High-resolution XPS spectra of (a) Ni 2p and (b) Fe 2p after OWS stability test.

Supplementary Tables

	electro	catalysis.		
Catalyst	Electrolyte	Overpotential at 10 mA cm ⁻² (mV vs RHE)	Tafel slope (mV dec ⁻¹)	Reference
me-PS-NM	1M KOH	76	88.9	This work
NiFeLDH/NF	1M KOH	120	134	10
NiFe-MOF-5/NF	1M KOH	163	139	11
FeC1-NF-AO	0.1M KOH	161	126	12
Ni-Fe-V-S/NF	1M KOH	161	96	13
NiP/NF	1M KOH	102	90	14
Ni-Fe-P/NF	1M KOH + 1M ethanol	156	101	15
Mn _{0.52} Fe _{0.7} Ni-MOF-74	1M KOH	99	103.8	16
FeTPP@NiTPP/NF	1M KOH	170	172.4	17
FeS/NiS/NF	1M KOH	144	120	18
Ni-Fe ₂ B/NF	1M KOH	115	123	19

 Tab. S1 Comparison the HER performance of *me*-PS-NM electrode to several recently reported

 electrocatalysts

1	,		
	Overpotential	Tafel slope	
Electrolyte	at 10 mA cm ^{-2}	$(mV dec^{-1})$	Reference
	(mV vs RHE)		
1M KOH	220	43.4	This work
1M NaOH	305	65.3	20
1M KOH	328	62	21
30wt.%	306	77.1	22
КОН			23
1M KOH	223	71.6	23
1M KOH	261	85.8	24
1M KOH	255	55	25
30wt.%	253	62.3	26
1M KOH	280	68	27
1M KOH	240	65	28
1M KOH	244	80	29
	Electrolyte 1M KOH 1M NaOH 1M KOH 30wt.% KOH 1M KOH 1M KOH 30wt.% KOH 1M KOH 1M KOH	Electrolyte Overpotential All O mA cm ⁻² (mV vs RHE) IM KOH 220 IM NaOH 305 IM KOH 328 30wt.% 306 KOH 223 IM KOH 223 IM KOH 261 IM KOH 255 30wt.% 253 S0wt.% 253 IM KOH 280 IM KOH 280 IM KOH 240	Overpotential at 10 mA cm ⁻² (mV vs RHE) Tafel slope (mV dec ⁻¹) (mV dec ⁻¹) 1M KOH 220 43.4 1M NaOH 305 65.3 1M KOH 328 62 30wt.% 306 77.1 KOH 223 71.6 1M KOH 223 71.6 1M KOH 261 85.8 1M KOH 255 55 30wt.% 253 62.3 1M KOH 280 68 1M KOH 280 68 1M KOH 280 65

 Tab. S2 Comparison the OER performance of Fe³⁺-me-PS-NM electrode to several recently reported electrocatalysts.

Electrode	Ni (at%)	Fe (at%)	O (at%)
Fe ³⁺ - <i>me</i> -PS-NM	25.91	3.98	70.11

Tab. S3 The at% content of Ni, Fe, and O elements were obtained by XPS results.

Tab. S4 Inductively coupled plasma-mass spectrometry (ICP-MS) results of Fe³⁺-me-PS-NM

Flaatrada	Element	Concentration	Fe element	Ni element
Electrode	Element	(mg L ⁻¹)	content (%)	content (%)
E_{a}^{3+} and B_{a}^{a} NM	Fe	1.762	8 2	80.67
Fe ³⁷ -me-PS-NM	Ni	17.262	0.2	00.07

Tab. S5 The C_{dl} and ECSA values of Fe3+-*me*-PS-NM and Fe3+-NM

	Catalysts	
	Fe ³⁺ -NM	Fe ³⁺ - <i>me</i> -PS-NM
C_{dl} (mF cm ⁻²)	0.5	3.68
ECSA	12.5	92

Catalyst	Electrolyte	water splitting cell voltage (V) at 10 mA cm ⁻²	Substrate	Reference
Fe ³⁺ - <i>me</i> -PS-NM	1M KOH	1.54	NM	This work
me-PS-NM				
Fe-Ni ₃ S ₂ /NF	1M KOH	1.59	NF	30
Fe-Ni ₃ S ₂ /NF				
NiFe _{0.8} Ce _{0.2} /NF	1M KOH	1.59	NF	31
NiFe _{0.8} Ce _{0.2} /NF				
Ni-Fe-P/NF	1M KOH	1.63	NF	32
Ni-Fe-P/NF				
Fe-Ni-OH/Ni	1M KOH	1.57	NF	33
Fe-Ni-OH/Ni				
NiFe-MOF-5/NF	1M KOH	1.57	NF	11
NiFe-MOF-5/NF				
Ni _{0.75} Fe _{0.25} LDHs/NF	1M NaOH	1.64	NF	34
Ni _{0.75} Fe _{0.25} LDHs/NF				
FN LDH/FNF-60	1M KOH	1.62	FNF	24
Ni(OH) ₂ /FNF-25				
Fe, Rh-Ni ₂ P/NF	1M KOH	1.62	NF	35
Fe, Rh-Ni ₂ P/NF				
Ni-P foam	1M KOH	1.65	FeNi foam	36
FeNi@FeNiB-700				
Ag@NiFe/NF	1M KOH	1.56	NF	37
Ag@NiFe/NF				

Tab. S6 Comparison the Overall water splitting performance of Fe³⁺-*me*-PS-NM || *me*-PS-NM bifunctional electrodes to several recently reported bifunctional catalysts.

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