Supporting Information

Graphene aerogel-supported NiFe alloy for efficient anion exchange membrane water electrolysis

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Experimental Section

Materials

Iron (III) chloride ($FeCl_3$, analytical grade) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Nickel (II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, analytical grade) and potassium hydroxide (KOH, 90%) were purchased from Macklin Biochemical Co., Ltd. Nafion solution (5 wt%) was purchased from Sigma-Aldrich. Carbon paper (Sigracet 22 BB) was purchased from SGL Carbon. Ethanol (C_2H_5OH, 99.7%) were purchased from Macklin and Shanghai Aladdin, respectively. High-purity N_2 (≥99.999%) were supplied by Cixi Sanjiang Gas Co., Ltd. Commercial graphene oxide (GO, analytical grade) was purchased from Suzhou TanFeng Technology Co., Ltd. Ultrapure water (18.2 MΩ·cm) was used throughout all experiments.

Preparation of Graphene Aerogel (GA)

Graphene aerogel (GA) was prepared via hydrothermal self-assembly followed by freeze-drying. Briefly, 90 mg of commercial graphene oxide (GO) was dispersed in 18 mL ultrapure water in a 50 mL centrifuge tube. The mixture was ultrasonicated for 90 min to obtain a homogeneous and stable GO colloid. The resulting suspension was transferred into a Teflon-lined stainless-steel autoclave and heated at 180 °C for 12 h. After cooling to room temperature, a porous monolithic graphene hydrogel (GH) was obtained. The GH was washed with ultrapure water by centrifugation for 5-6 cycles to thoroughly remove residual species. The cleaned hydrogel was then freeze-dried to yield a porous graphene aerogel (GA).

Thermal Annealing of GA (GA-250/300/350)

To further remove residual oxygen-containing functional groups and enhance electrical conductivity, the freeze-dried GA precursor was annealed under N_2 protection. Typically, 50 mg of GA was uniformly spread in a square ceramic boat and placed in the quartz tube of a tubular furnace. The furnace was purged with high-purity N_2 for 30 min prior to heating. The sample was heated at a ramp rate of 5 °C min^{-1} to 250 °C, 300 °C, 350 °C and held for 2 h under flowing N_2, followed by natural cooling to room

temperature to obtain GA-250, GA-300, GA-350 respectively, and GO-300 were prepared by using commercial GO directly to anneal at 300 °C for 2h with the same procedure.

Synthesis of NiFe Alloy Nanoparticles on GA (NiFe@GA)

NiFe@GA were synthesized via drop infiltration of metal precursors followed by rapid microwave-induced alloying. NiFe bimetal precursor solutions were prepared using $NiCl_2 \cdot 6H_2O$ and anhydrous $FeCl_3$ with Ni:Fe molar ratios of 4:0, 3:1, 2:2, 1:3, and 0:4, denoted as Ni4, Ni3Fe, Ni2Fe2, NiFe3, and Fe4, respectively. For each composition, the total metal-ion concentration was adjusted to 0.5, 1.0, or 2.0 mM. Typically, 2.0 mg of GA-300 was placed in a glass Petri dish. 100 μL precursor solution was added dropwise onto the GA-300 scaffold until it was fully wetted. The impregnated sample was dried in a vacuum oven at 60 °C for 12 h to remove the solvent. The dried composite was then transferred into an Ar-filled glovebox and irradiated in a microwave reactor at 1000 W for 3 min to induce rapid alloying. After microwave treatment, the sample was naturally cooled to room temperature and stored for further characterization and electrochemical tests. By systematically varying both the Ni:Fe ratio and the total metal-ion concentration, the effects of bimetallic synergy and metal loading on electrocatalytic performance were investigated.

Materials Characterization.

XRD patterns were collected on a D8 Advance diffractometer (Bruker, Germany) with Cu Kα radiation (λ = 1.5406 Å), and Raman spectra were recorded on a Renishaw inVia system (UK) using a 532 nm laser to identify the phase features. In-situ Raman spectra were recorded using 50× objective, 5 mW laser power, and an 1800 grooves mm^{-1} grating. A commercial MSL-III electrochemical Raman cell containing 1.0 M KOH was employed. The synthesized catalyst was used directly as the working electrode (electrically contacted by a copper strip), with Pt wire as the counter electrode and Ag/AgCl as the reference electrode. Sample morphology and microstructure were characterized by field-emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan) and high-resolution transmission electron microscopy (HRTEM, JEM-

2100F, JEOL, Japan) coupled with EDX analysis (Quantax-STEM, Bruker, Germany). Elemental compositions and oxidation states were determined by X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific, USA), with the C 1s signal at 284.6 eV used for binding-energy calibration. Nitrogen adsorption–desorption measurements were carried out on an Anton Paar Autosorb 6100 (FKM MP-MP) instrument. Before measurement, the samples were degassed under vacuum at 120 °C for 8 h. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method, and the pore-size distribution/pore volume was derived from the adsorption–desorption isotherms using the BJH model.

Electrochemical Measurements.

All OER measurements were carried out in 1.0 M KOH using a CHI760E electrochemical workstation (CH Instruments, Shanghai, China) with a standard three-electrode configuration. A graphite rod served as the counter electrode and a Hg/HgO electrode (1.0 M KOH) was used as the reference electrode. All potentials were converted to the reversible hydrogen electrode (RHE) scale. A catalyst ink was prepared and drop-cast onto nickel foam (1 × 1 cm^2) as the working electrode. Specifically, 1.0 mg of catalyst powder and 19 μL of Nafion solution (5 wt%) were dispersed in 70 μL ethanol, followed by ultrasonication for 30 min to form a homogeneous ink. Then 18 μL of the ink was uniformly pipetted onto a pre-cleaned nickel foam substrate (ultrasonically cleaned) and dried under a mercury lamp. The catalyst loading was controlled at 1 mg cm^{-2}. For comparison, commercial RuO_2 was prepared using the same procedure with a loading of 100 μg cm^{-2}. Cyclic voltammetry (CV) was used for electrode activation and for assessing redox features and capacitive behavior. Linear sweep voltammetry (LSV) for OER activity was recorded at a scan rate of 5 mV s^{-1}. Unless otherwise noted, LSV curves are presented in the range of 1.2-1.8 V (vs. RHE). Tafel analysis was conducted based on the LSV data using the Tafel equation. Electrochemical impedance spectroscopy (EIS) was performed at 0.60 V (vs. RHE) over a frequency range of 100 kHz-0.01 Hz (or 0.1 Hz, as specified) with an AC amplitude of 10 mV to evaluate charge-transfer behavior.

For AEMWE measurement, commercial Pt/C (50 wt%) was used as the cathode catalyst with a Pt loading of 0.5 mg_{Pt} cm^{-2}. The catalyst and Kmem-A50 ionomer (catalyst/ionomer mass ratio = 85:15) were dispersed in a water/methanol mixture (mass ratio 1:3) and stirred for 1 h at room temperature. The suspension was then ultrasonicated for 2 h in an ultrasonic bath equipped with a low-temperature circulating thermostat to avoid overheating, yielding a homogeneous catalyst ink. The ink was deposited onto carbon paper using an ultrasonic spray coater. The anode ink was prepared following the same procedure, except that NiFe@GA-300 was used as the anode catalyst. The anode catalyst ink was drop-cast onto nickel felt using a micropipette and dried completely. The catalyst loading on both electrodes was controlled at 2 mg cm^{-2}. The Kmem-A50 membrane (50 μm) was sandwiched between the cathode and anode without hot pressing to form the MEA. The geometric active area of the MEA was 1 cm^2. Prior to electrolysis measurements, the MEA was soaked in 1.0 M KOH for 24 h to complete hydroxide ion exchange. The MEA was then assembled into the electrolyzer cell for AEMWE testing. The electrolyte temperature was set to the corresponding testing temperature during polarization measurements.

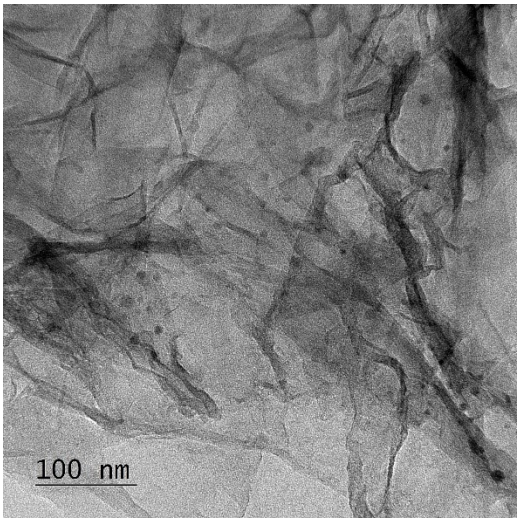

Fig. S1. TEM image of Ni_2Fe_2 alloy nanoparticles on GA-300.

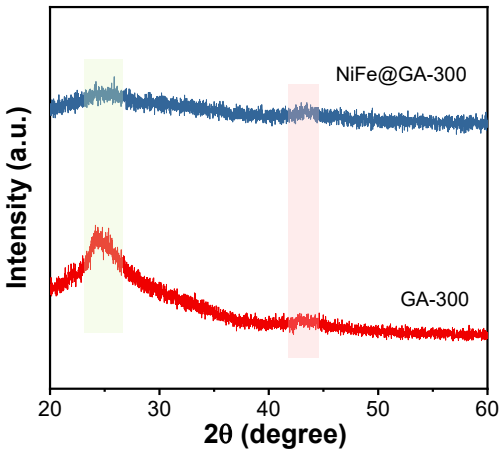

Fig. S2. XRD patterns of GA-300 and NiFe@GA-300.

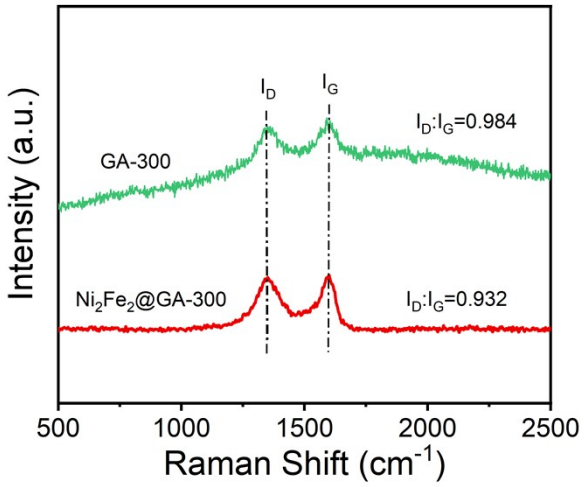

Fig. S3. Raman spectra of GA-300 and Ni_2Fe_2@GA-300.

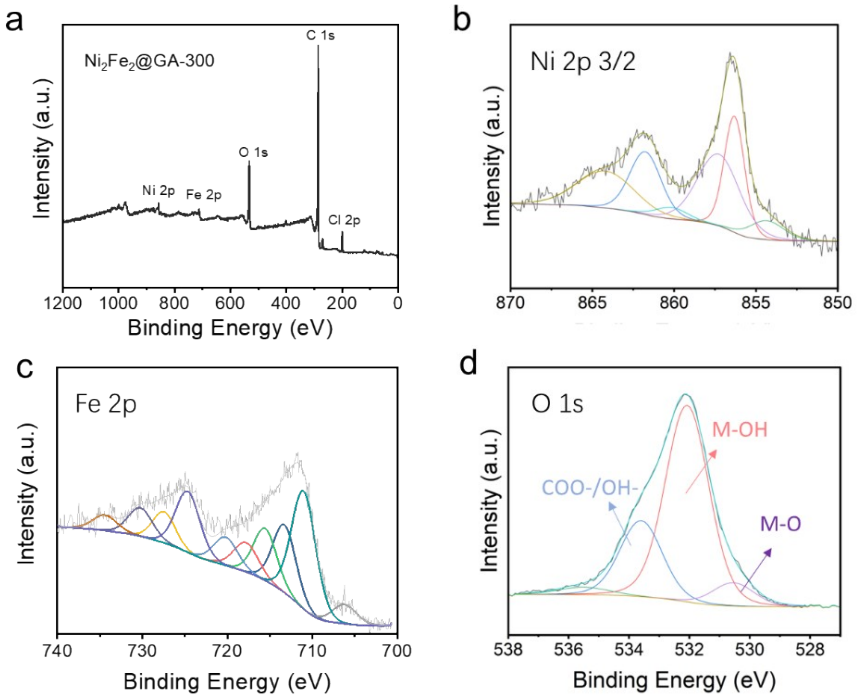

Fig. S4. XPS full spectra of Ni_2Fe_2@GA-300 and their high-resolution of Ni, Fe and O elements.

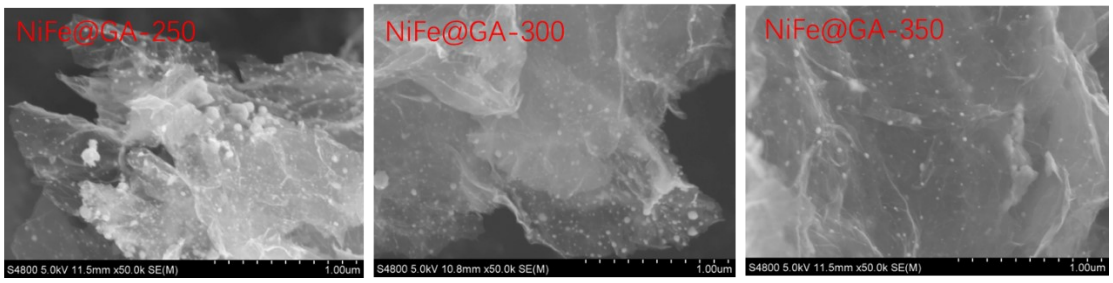

Fig. S5. SEM images of NiFe alloy nanoparticles on various GA samples annealed at different temperatures (250 °C, 300 °C, 350 °C)

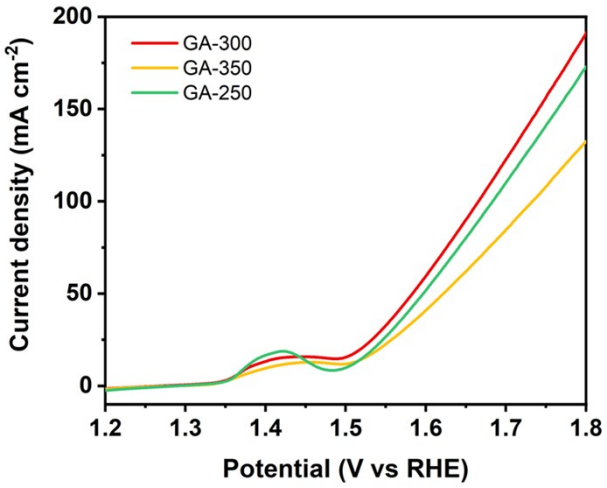

Fig. S5. OER LSV curves of NiFe@GA-*X* under GA annealing with different temperatures.

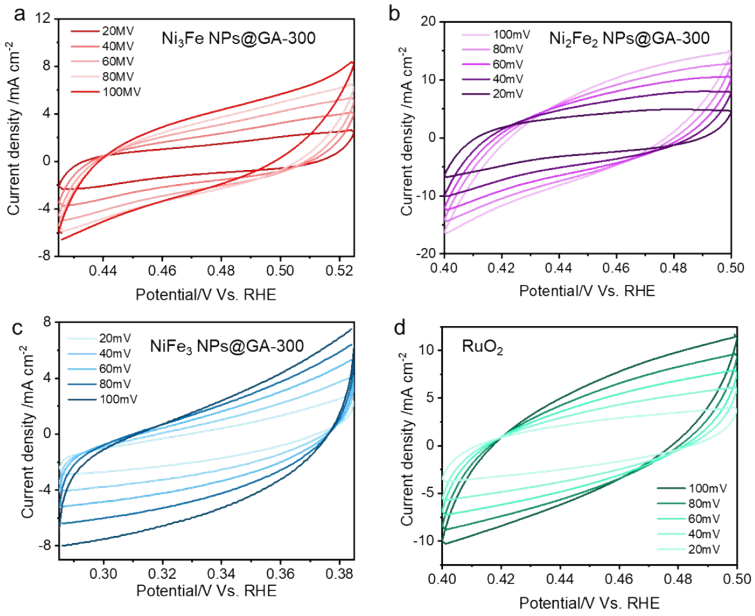

Fig. S7. CV cycles in the non-Faradic window of different NiFe@GA-300 samples at various scan rates.

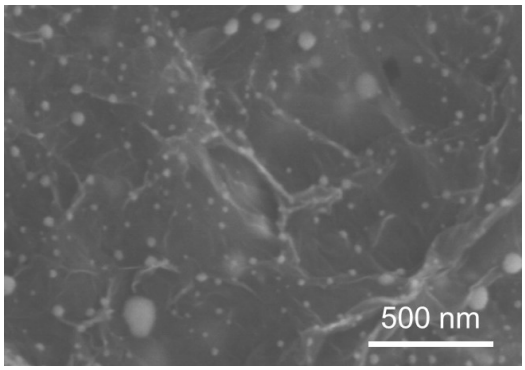

Fig. S8. SEM image of NiFe alloy nanoparticles on GO-300.

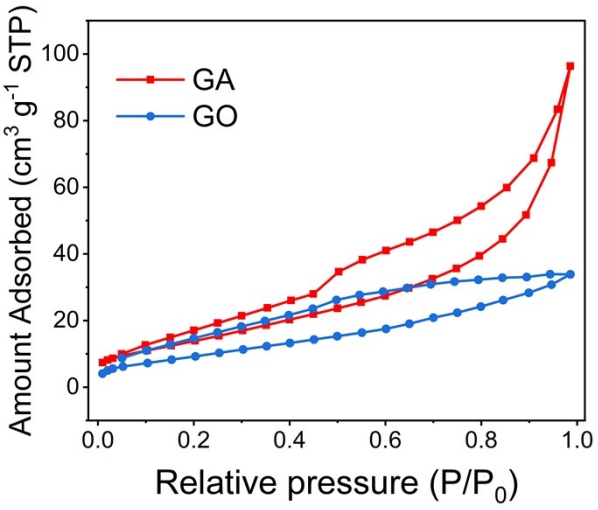

Fig. S9. N_2 adsorption and desorption curves of GA and GO.

Table S1. The fitted charge-transfer resistance (R_{ct}) of the electrodes.

Anodes	R_{ct} (Ω)
Ni_2Fe_2@GA-300	24.2
Ni_2Fe_2@GO-300	38.7
RuO_2	65.6

Table S2. The textural properties of the GA and GO supports.

Supports	Specific Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Average Pore Diamter (Å)
GA	54.1	0.1494	110.52
GO	36.3	0.0525	57.918

Table S3. Comparison of AEMWE performance with other OER non-precious metal catalysts.

Anode (loading)	Cathode (loading)	Membrane	T (°C) Electrolyte	*j* (mA cm^{-2}) @Voltage	Stability	Ref.
Ni_2Fe_2@GA-300 (2 mg cm^{-2})	**Pt/C (0.5 mg_{Pt} cm^{-2})**	**Kmem-A50**	**65 °C 1M KOH**	**1 A cm^{-2} @1.66 V**	**100 h @1 A cm^{-2} 0.9 mV h^{-1}**	**This work**
$CoCrO_x$ (1 mg cm^{-2})	Pt/C (1.5 mg_{Pt} cm^{-2})	PiperION-A60-HCO3	60 °C 1M KOH	1.5 A cm^{-2} @2.1 V	120 h @0.5 A cm^{-2} <4.9 mV h^{-1}	Nat. Commun. (2024) 15:3416
$(FeCoNiCrCu)Se_x$（HEMS）	Pt/C (N.A.)	HELITE AEM01(eChemStore）	60 °C 1M KOH	1.5 A cm^{-2} @2.4 V	120 h @0.5 A cm^{-2} No decay	Joule (2024) 8, 2342–2356, Angew. Chem. Int. Ed. (2024) e202404418
Nei-Ir_1/CoGaOOH	Pt/C (N.A.)	N.A.	80 °C 1M KOH	1 A cm^{-2} @2.1 V	50 h @1 A cm^{-2} No decay	Adv. Mater. (2024) 36, 2314211
Bi/$BiCeO_{1.8}$H	Pt/C (N.A.)	Sustainion X37-50（Dioxide Materials）	50 °C 1M KOH	1 A cm^{-2} @1.79 V	100 h @1 A cm^{-2} 2.2% drop	Adv. Funct. Mater. (2025) e17292
RuVCoCuZnW	RuVCoCuZnW	N.A.	80 °C 1M KOH	0.5 A cm^{-2} @1.66 V	N.A.	Chem. Eng. J. (2025) 522 167795
Co-CE30	PtRu/C (N.A.)	HQPC-TMA (50 μm)	70 °C Pure water	1 A cm^{-2} @2.15 V	40 h @1 A cm^{-2} 0.9 mV h^{-1}	Adv. Funct. Mater. (2025) 2506656
NiFeS (1.0 mg cm^{-2})	Pt/C (2 mg_{Pt} cm^{-2})	PiperION-A60-HCO3	60 °C 1M KOH	1.84 A cm^{-2} @2 V	300 h @1 A cm^{-2} 0.26 mV h^{-1}	

B-MOF-Zn-Co	Pt/C (N.A.)	Alkyer W-25	50 °C 1M KOH	1 A cm^{-2} @2.04 V	300 h @0.2 A cm^{-2} 0.23 mV h^{-1}	Small (2024) 20, 2308517
S-HEO	Pt/C (N.A.)	LDPE-VBC-TMA	60 °C 1M KOH	1 A cm^{-2} @2.16 V	40 h @2 V 16% drop	Small (2024) 20, 2402241
CuNiFe-LDH (1.0 mg cm^{-2})	$NiFe_2O_4$ (1.0 mg cm^{-2})	Sustainion X37-50 RT	50 °C 1M KOH	1.131 A cm^{-2} @1.85 V	120 h @0.6 A cm^{-2} 0.25 mV h^{-1}	Appl. Catal. B: Environ. (2024) 340, 123187
NiFeW (2 mg cm^{-2})	PtRu/C (0.5 mg cm^{-2})	PiperION-A40-HCO3	70 °C 1M KOH	2.12 A cm^{-2} @2 V	N.A.	ACS Catal. (2026) 16, 4449−4462