

Electronic Supplementary Information

Homogenous mixed coating enabled significant stability and capacity enhancement of iron oxide anode for aqueous nickel-iron batteries

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Experimental section

Synthesis of Fe₃O₄@MoO₂-C Nanorod Film Anode

The Fe₃O₄@MoO₂-C nanorod film on the CC was prepared by a three-step method including hydrothermal process, electrodeposition and annealing treatment. Firstly, 0.946 g FeCl₃·6H₂O and 0.497 g Na₂SO₄ were dissolved in 70 mL deionized water to get a mixed aqueous solution, which, with a piece of CC current collector immersed in, was maintained at 160 °C for 6 h. Before this, the CC was ultrasonicated in hydrochloric acid, acetone, ethanol and deionized water for 20 min, respectively. When the autoclave cooling to room temperature, the CC covered with FeOOH precursor was taken out and then cleaned in ethanol and deionized water, dried at 60 °C. Then, the electrodeposition was carried out on a CS310 electrochemical workstation with a three-electrode model using FeOOH nanorod film as the working electrode (WE), a Pt foil as the counter electrode (CE), saturated calomel electrode (SCE) as the reference electrode (RE) and the mixed 0.05 M (NH₄)₆Mo₇O₂₄ and 0.05 M glucose as the electrolyte. The electrodeposition was performed using cyclic voltammetry within 0 to -1 V at a scan rate of 20 mV s⁻¹ for 10, 20, 40, and 60 cycles. Finally, after the electrodeposition, the product was annealed at 450 °C for 1 h in Ar gas to obtain Fe₃O₄@MoO₂-C electrode. The mass loading of the Fe₃O₄@MoO₂-C electrode is ~2.7 mg cm⁻².

Synthesis of Ni_{0.49}Cu_{0.51}O Nanowire Array Cathode

The Ni_{0.49}Cu_{0.51}O nanowire array cathode was first prepared by a one-step hydrothermal method to obtain the precursor of (Ni_{0.49}Cu_{0.51})₂(OH)₂CO₃ nanowire array, and then annealed in a tubular furnace. The detail experimental process is as reported in our previous work.²⁸

Fabrication of Ni_{0.49}Cu_{0.51}O//Fe₃O₄@MoO₂-C Aqueous Alkaline Batteries

The aqueous alkaline battery was constructed with Fe₃O₄@MoO₂-C anode and Ni_{0.49}Cu_{0.51}O cathode in opposition to each other and using the cellulose membrane soaked with 3 M KOH electrolyte as the separator. The cell was encapsulated by flexible plastic film with two pieces of platinum connected to the edges of the two electrodes.

Characterizations

The electrode samples were characterized by SEM (JSM-6700F, 10 kV) with EDS equipment, TEM (JEM-2010FEF, 200 kV), XRD (Bruker D-8 Avance) and XPS (Thermo Electron, VG ESCALAB 250 spectrometer). The mass of active materials was measured by using a Mettler Toledo ME204E Balance (max= 220 g; d=0.1 mg).

Electrochemical measurements

All the electrochemical measurements were tested on a CS310 electrochemical workstation at room temperature. For individual working electrodes, the electrochemical performance was performed by the standard three-electrode system, with all the prepared Fe₃O₄@MoO₂-C as the WE, Pt foil as the CE and the Hg/HgO as the RE in a 3 M KOH electrolyte. For the full cell testing, a two-electrode mode was used with one Ni_{0.49}Cu_{0.51}O connected to the WE and one Fe₃O₄@MoO₂-C as the CE.

The frequency range and amplitude of the EIS measurement are 0.1 Hz-100 kHz and 5 mV s⁻¹, respectively. The EIS measurement was carried out at open circuit potential without bias potential.

The capacity can be calculated based on the discharging curves according to:

$$Q = \frac{I \Delta t}{S}$$

where I , Δt and S represent the constant discharging current, the discharging time, the geometrical area or the active mass of the electrode/device, respectively.

The energy and power densities of the device were calculated based on the following equations:

$$E = \frac{I \int V(t) dt}{T}$$

$$P = E / \Delta t$$

where I is the discharging current, $V(t)$ is the discharging voltage at t , dt is the time differential, T is the device volume (including the current collector, anode, cathode and electrolyte) or the total mass of active materials, and Δt is the discharging time.

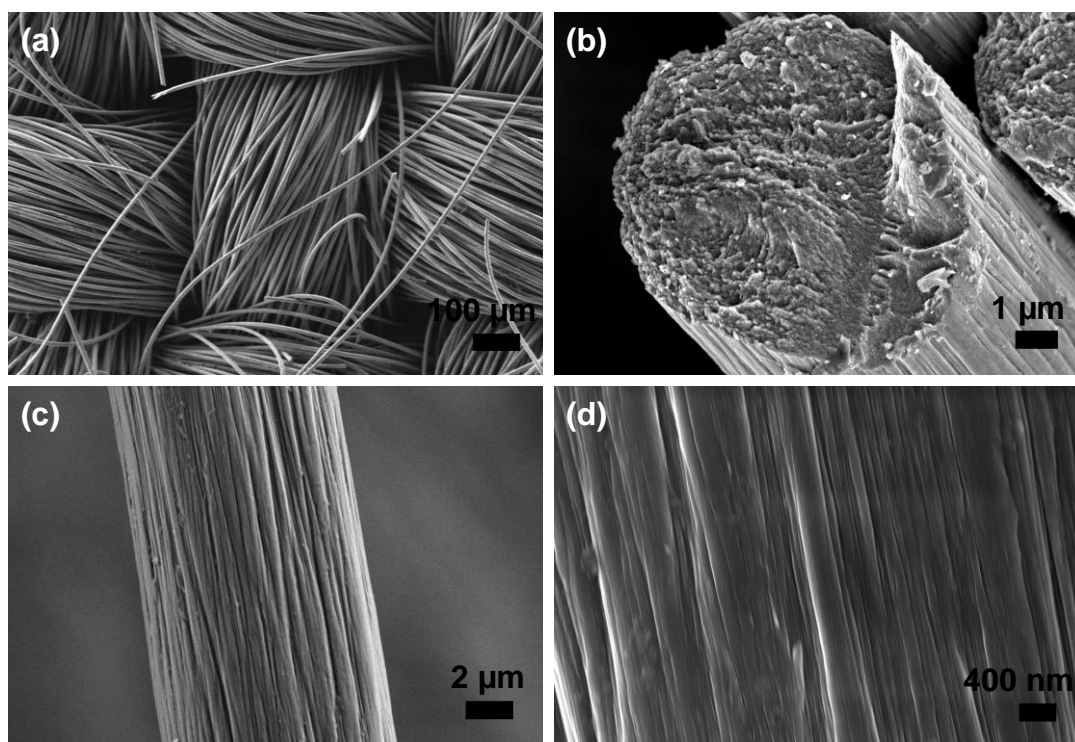


Fig. S1 (a) Top-view SEM image of carbon cloth. (b) The cross-sectional SEM image of one carbon fiber. (c-d) Surface morphologies of the fiber. It seems that the carbon fiber is composed of numerous densely packed tiny ribbons.

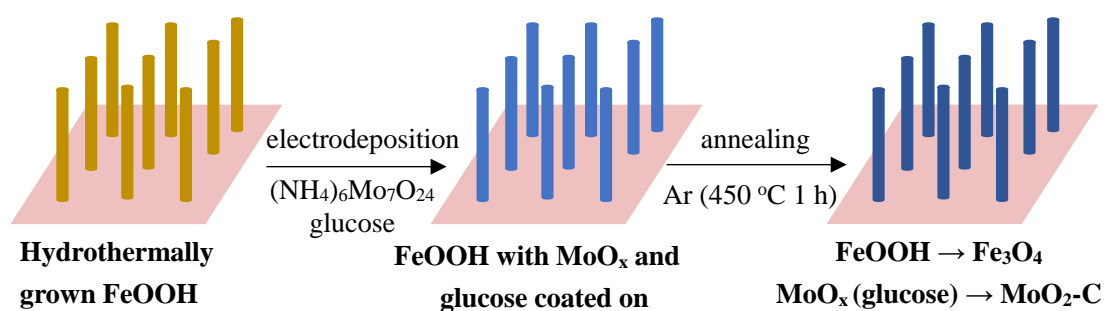


Fig. S2 Schematic illustration of the synthesis process of $\text{Fe}_3\text{O}_4@\text{MoO}_2\text{-C}$ nanorod film anode. It should be noted that the glucose in the electrolyte for electrodeposition was *in-situ* adsorbed and simultaneously deposited with Mo oxides onto the Fe oxide surface, which was subsequently carbonized into carbon. The generated carbon can further reduce metal oxide to some extent. As a result, the Fe_3O_4 surface was finally coated with $\text{MoO}_2\text{-C}$.

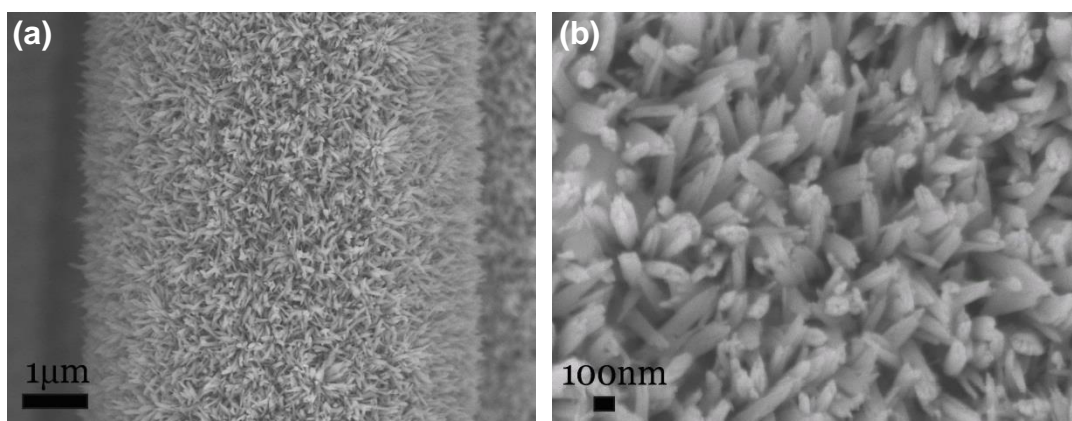


Fig. S3 (a-b) SEM images of FeOOH nanorod film (precursor) with different magnifications.

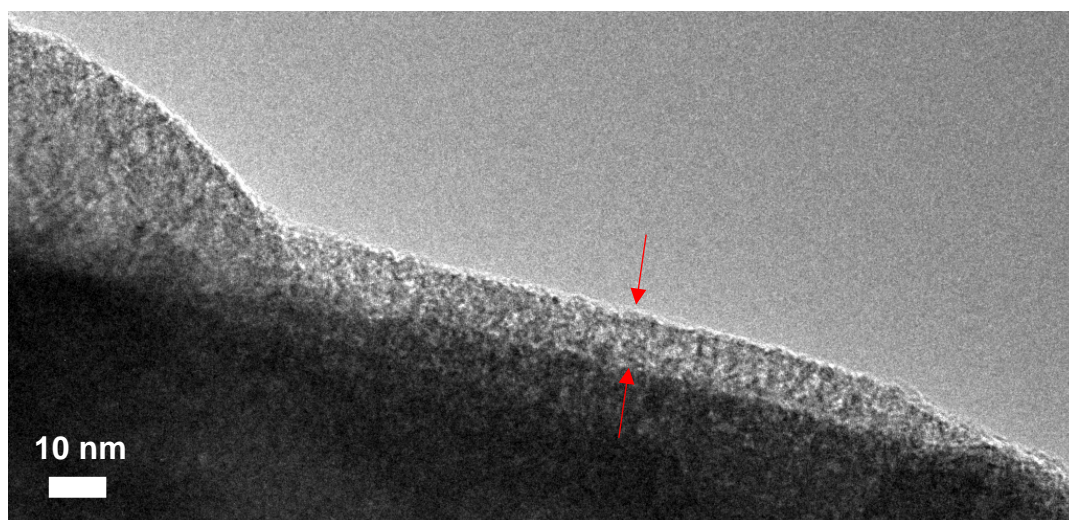


Fig. S4 Enlarged picture of Figure 1h, showing the continuous interface between Fe₃O₄ nanorod and MoO₂-C layer.

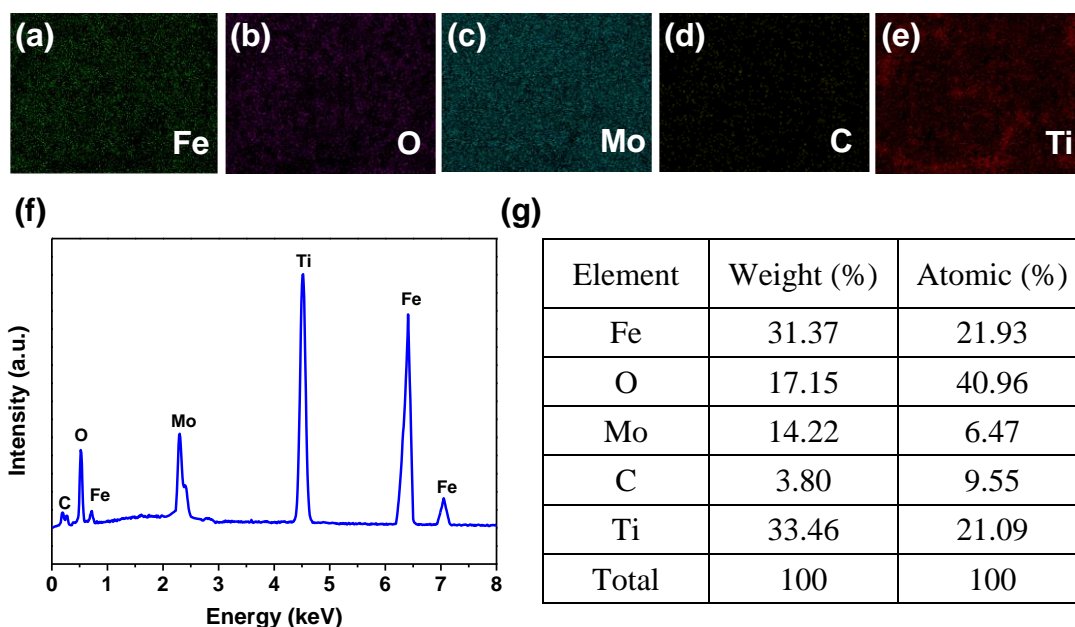


Fig. S5 In order to determine the carbon content in $\text{Fe}_3\text{O}_4@\text{MoO}_2\text{-C}$ and avoid the influence of carbon cloth current collector, we synthesized one sample using Ti substrate under otherwise the same synthetic conditions. (a-e) EDS elemental mapping results of Fe, O, Mo, C and Ti, respectively. (f-g) EDS curve and elemental contents. As can be seen, the gravimetric content ratio of Fe:Mo:O:C is 31.37:14.22:17.15:3.80, thus the carbon content in $\text{Fe}_3\text{O}_4@\text{MoO}_2\text{-C}$ is ~5.71 wt%.

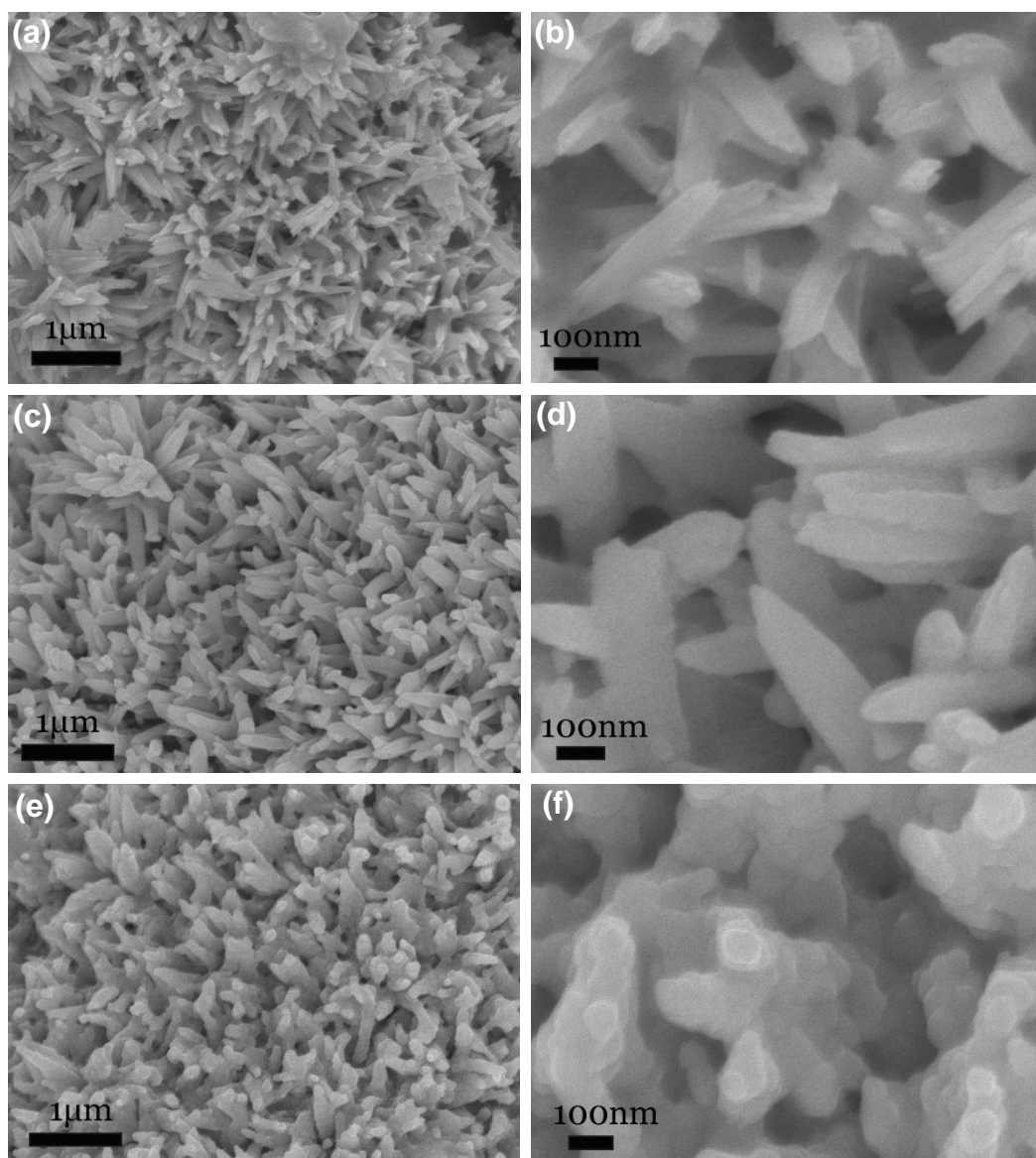


Fig. S6 SEM images of Fe₃O₄@MoO₂-C anodes with (a-b) 10 cycles; (c-d) 20 cycles; and (e-f) 60 cycles of electrodeposition.

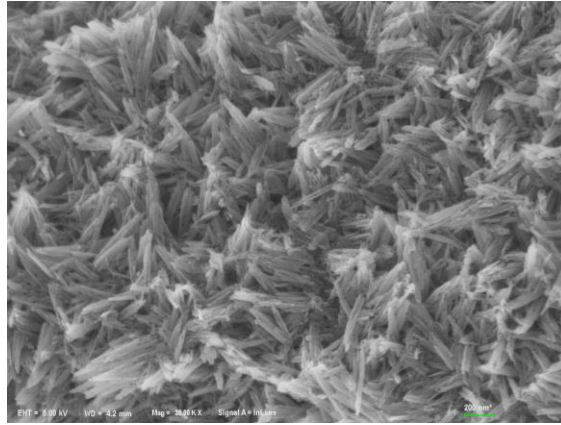


Fig. S7 SEM image of the optimized Fe₃O₄@MoO₂-C anode after 200 electrochemical cycles.