

Electronic Supplementary Information

Mn₃O₄ nano-octahedrons on Ni foam as an efficient three-dimensional oxygen evolution electrocatalyst

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I. Experimental Section

Chemicals. Manganese (II) chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) and tetramethylammonium hydroxide (TMAH) were purchased from Shanghai Chemical Reagent Co. Ltd. The iridium oxide (IrO_2) power was a commercial product purchased from Acros. Nafion (5 wt%) was obtained from Sigma-Aldrich. Ultrapure water ($18.2 \Omega \text{ cm}^{-2}$ resistivity) was used for all aqueous solution. All chemicals were of analytical grade and used as received.

Preparation of Mn_3O_4 nano-octahedrons. In a typical procedure, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.4 mmol) was dissolved in 20 mL of deionized (DI) water in ice bath and stirred to form a clear solution. 4 mL of 25 wt% tetramethylammonium hydroxide solution was added slowly into the solution. The mixed solution was under vigorous stir in ice bath for 24 h. Product was collected by centrifugation at 5000 rpm for 5 min, washed with DI water and ethanol and dried at 60 °C for 8 h. The products obtained above were calcined at different temperature for 1 h.

Fabrication of $\text{Mn}_3\text{O}_4/\text{NF}$ electrode. Mn_3O_4 nano-octahedrons on Ni foam, referred to as $\text{Mn}_3\text{O}_4/\text{NF}$, were prepared by a simple dip-coating method. The as prepared solution was to serve as the coating substance. Nickel foam (about 1 cm × 3 cm) was carefully cleaned with 3.5 M HCl solution in an ultrasound bath for 10 min in order to remove the surface NiO layer, and then DI water and ethanol were used for 15 min each to ensure the surface of the Ni foam was well cleaned. The cleaned Ni foam was immersed in the as-prepared coating solution for 5 min, and withdrew at a rate of 0.6 cm min⁻¹. The obtained Ni foam was then calcined at 150 °C for 1 h.

Electrochemical measurements. All electrochemical studies were performed using a CHI 660 pontentionstat (CH Instruments, China) in a three-electrode setup in 1 M KOH aqueous solution. The reference electrode and counter electrode were Ag/AgCl electrode (3.5 M KCl) and platinum wire, respectively. The $\text{Mn}_3\text{O}_4/\text{NF}$ electrodes were directly used as the anodes for electrochemical characterizations. For comparison on Ni foam electrode, working electrodes comprised of 0.5 cm × 0.5 cm pieces of nickel foam loaded with IrO_2 . 10 mg of IrO_2 was dispersed in 10 mL of DI water and 40 μl of Nafion solution (5 wt%) with sonication treatment followed by deposition of this solution on Ni foam electrode, and final evaporation of the water.

For comparison on GC electrode, Mn_3O_4 was loaded on GC electrode for electrochemical measurement. 4 mg of catalyst powder and 40 μl Nafion solution (5 wt%) were dispersed in 1 mL of 4:1 v/v water/ethanol by at least 30 min sonication to form a homogeneous ink. Then 5 μl of the catalyst ink was loaded onto a glassy carbon electrode of 3 mm in diameter (loading 0.285 mg cm⁻²). Finally, the as-prepared catalyst film was dried at room temperature.

The electrocatalytic activity of the catalysts towards OER was examined by

polarization curves using linear sweep voltammetry (LSV) from 0 to 0.8 V with a sweep rate of 5 mV s⁻¹ in 1 M KOH at room temperature. All of the potentials in our manuscript were calibrated to a reversible hydrogen electrode (RHE).

Characterizations. The morphology and structure of the samples were characterized by scanning electron microscopy (SEM, Hitachi S4800) and transmission electron microscopy (TEM, JEM 2100, 200 kV). Brunauer-Emmett-Teller (BET) surface area measurements were performed at 77K on a Micromeritics ASAS 2460 adsorption analyzer in N₂-adsorption mode. The sample was degassed at 150 °C for 24 h under vacuum prior to the measurements. The crystal structure was determined by X-ray diffraction (XRD, D/max2550V). Further, the chemical states of the elements in catalysts were studied by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD), and the binding energy of C 1s peak at 284.8 eV was taken as an internal standard.

II. Supporting Figures

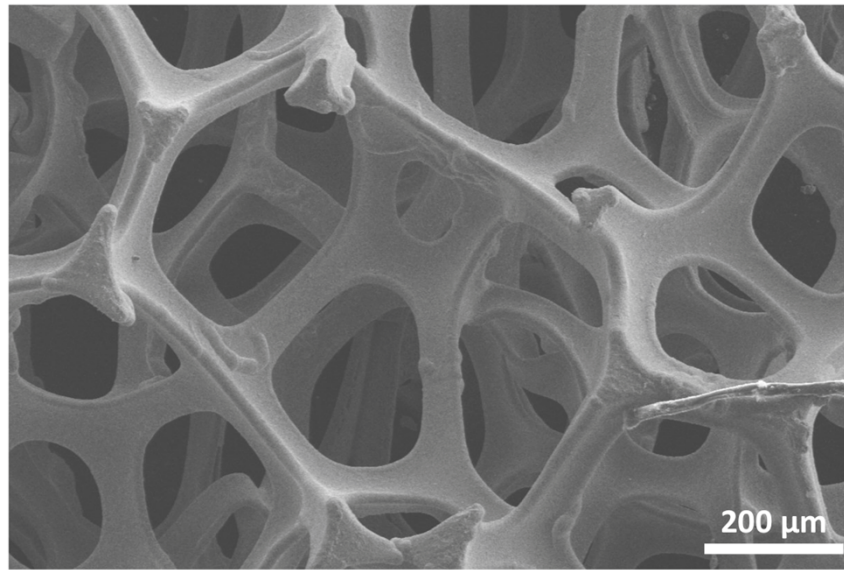


Figure S1. SEM image of the bare Ni foam.

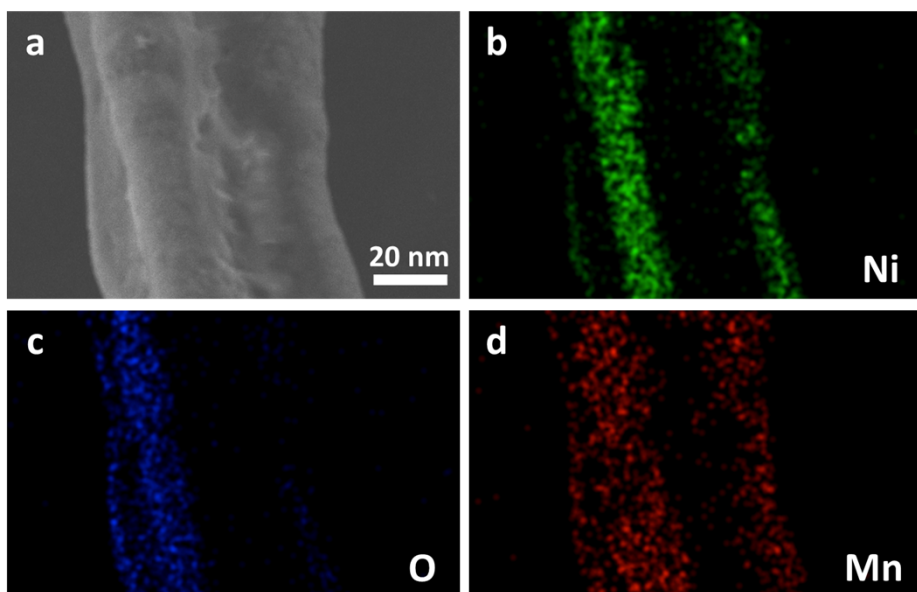


Figure S2. SEM image of Mn₃O₄/Ni foam (a), and corresponding EDX mapping of Ni (b), O (c), and Mn (d), respectively.

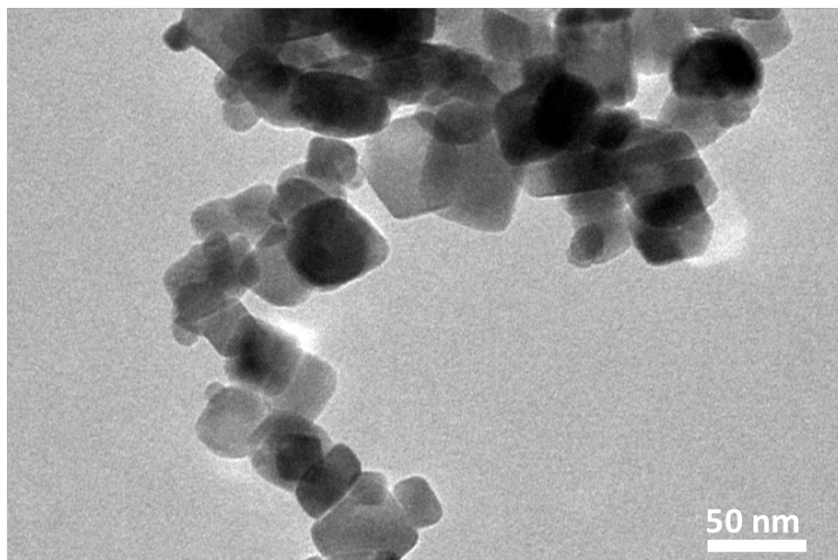


Figure S3. TEM image of the Mn₃O₄ nano-octahedrons.

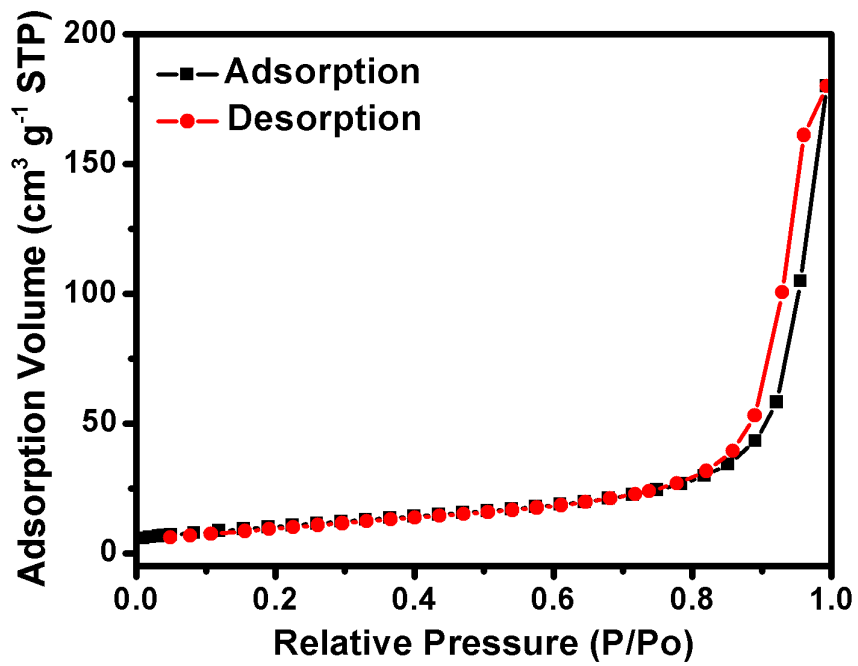


Figure S4. Nitrogen adsorption/desorption isotherm of Mn₃O₄ nano-octahedrons. The surface area for Mn₃O₄ nano-octahedrons was calculated from the adsorption isotherm by the Brunauer-Emmett-Teller (BET) method. The tested BET surface area for Mn₃O₄ nano-octahedrons is 39.7 m² g⁻¹.

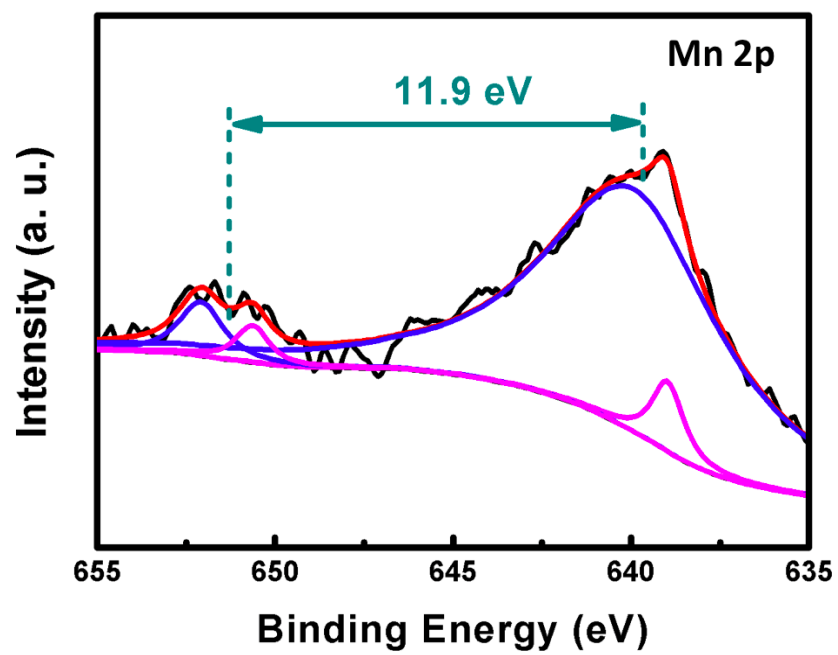


Figure S5. XPS Mn 2p spectrum of Mn₃O₄/Ni foam electrode.

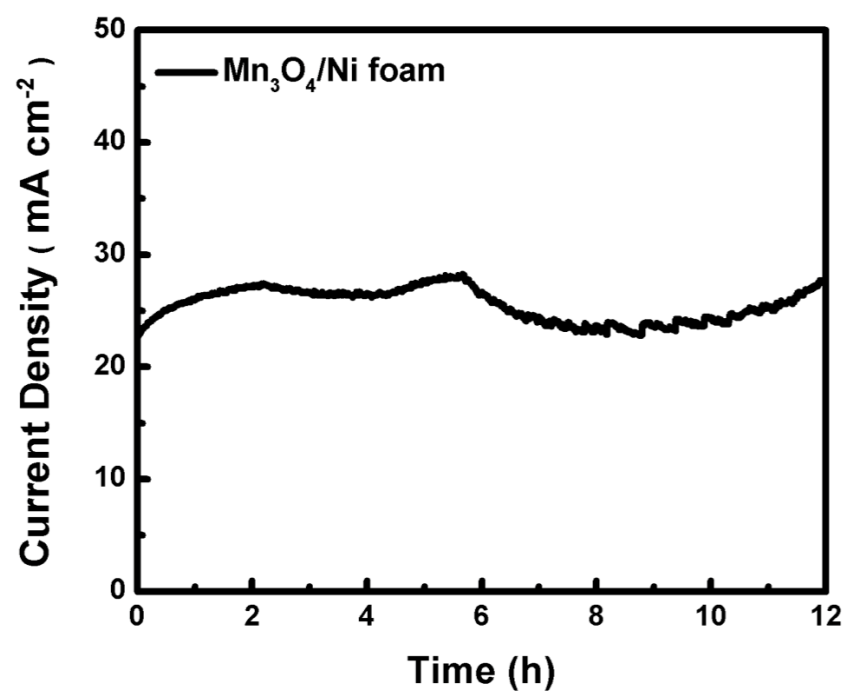


Figure S6. Current-time plot of Mn₃O₄/Ni foam with the applied overpotential at 320 mV.

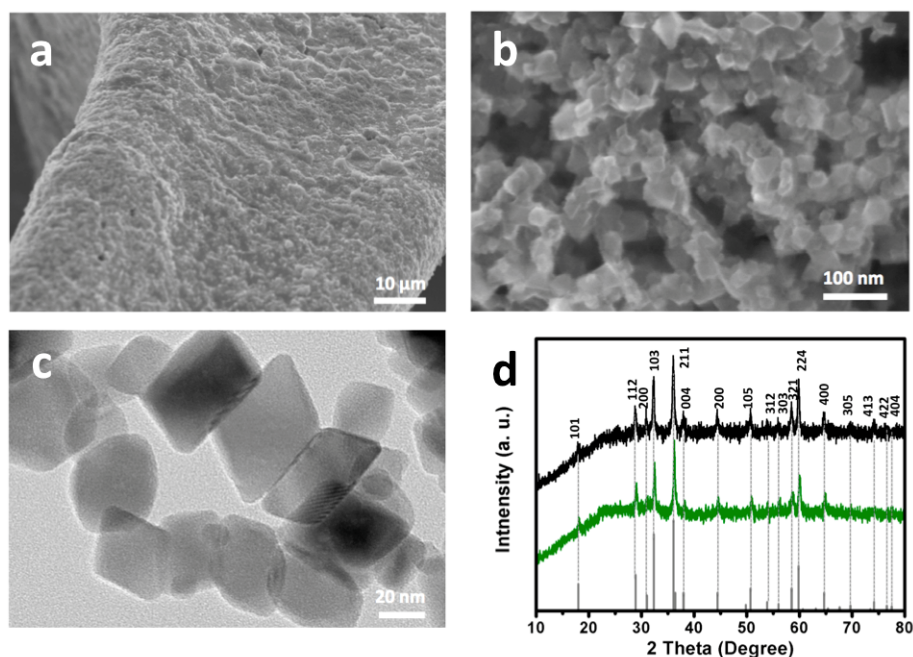


Figure S7. (a) Low-magnification and (b) high-magnification SEM images of the $\text{Mn}_3\text{O}_4/\text{NF}$ electrode after stability test. (c) HRTEM image of the Mn_3O_4 sample ultrasonicated from the $\text{Mn}_3\text{O}_4/\text{NF}$ electrode after stability test. (d) XRD pattern of the as-prepared coprecipitacional products (black) and Mn_3O_4 sample ultrasonicated from the $\text{Mn}_3\text{O}_4/\text{NF}$ electrode after stability test (olive). Mn_3O_4 , JCPDS no. 24-0734 (grey).

After the long-term stability test, the Mn_3O_4 nano-octahedrons were characterized by SEM, TEM and XRD. As shown in Fig. S7a and S7b, the surface of Ni foam is still uniformly covered by small nanoparticles, and the Mn_3O_4 nano-octahedrons (Fig. S7c) didn't lose contact with the electrode, indicating the strong bonding between Mn_3O_4 and nickel foam. In addition, the Mn_3O_4 nano-octahedrons were ultrasonicated off the electrode and the corresponding XRD spectrum shows clear diffraction peaks of Mn_3O_4 , displays no significant difference with the XRD spectrum of the as-prepared products. These suggest that Mn_3O_4 nano-octahedrons are stable for OER.