Electronic Supplementary Material (ESI) for Materials Advances.

Macroporous NiMo alloy Self-Supporting Electrode for Efficient Hydrogen Evolution at Ultrahigh Current Densities

Yudan Chen[a], Lin Chen[b], Ying Xiong[b], Xinxin Yu[a], Kun Tang[a*], Lixin Zhang[c]

Mingzai Wu[a*]

[a]Key Laboratory of Structure and Functional Regulation of Hybrid Materials, Ministry of Education, Anhui University, Hefei 230601, China;

[b]School of Materials Science and Engineering, Southwest University of Science and Technology

[c]Shanxi Provincial Key Laboratory for High Performance Battery Materials and Devices

Email: wumz@ahu.edu.cn, tangkun0214@163.com

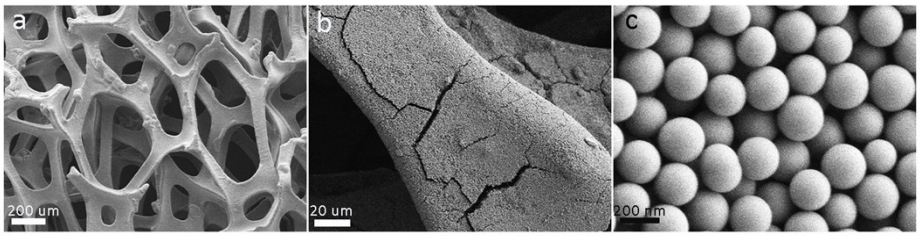

figure S1 SEM images of the Deposited SiO_2 spheres on the surface of foam nickel.

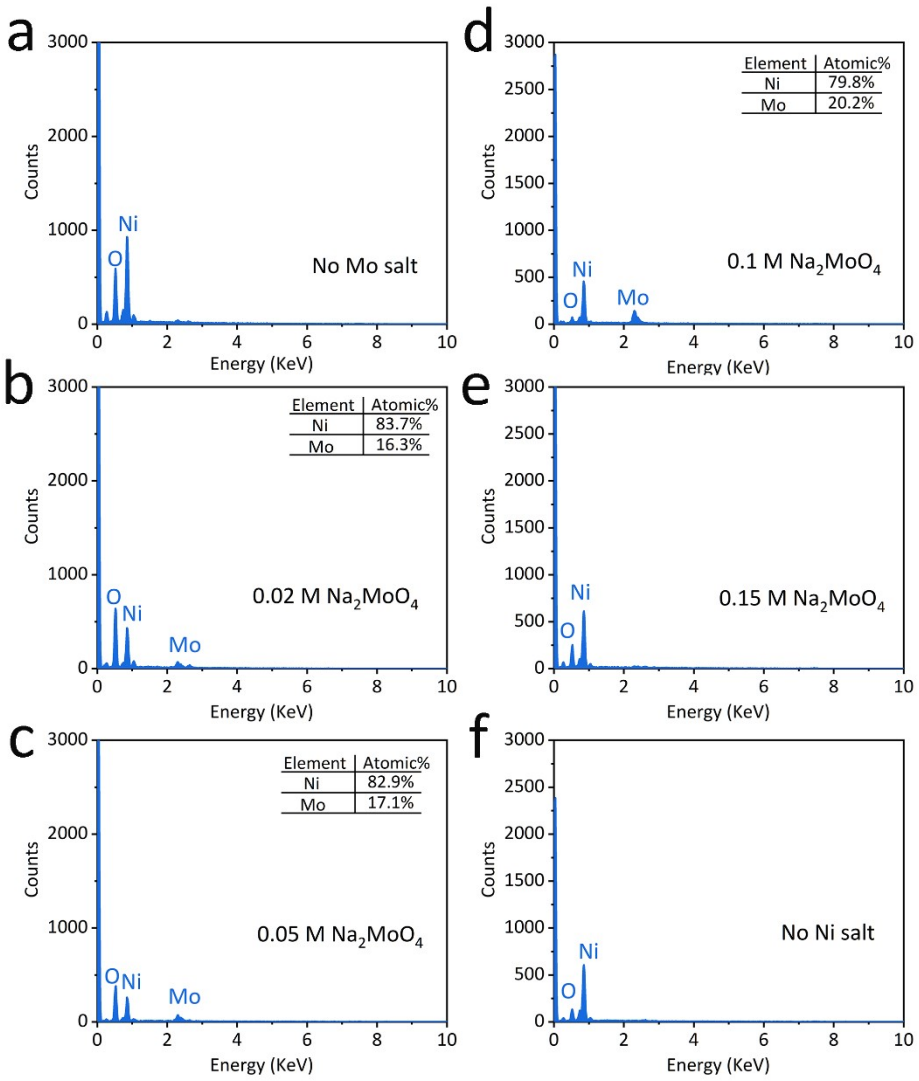

Figure S2. EDS spectra of NiMo@NF electrodes prepared with different concentrations of Mo salt: (a) 0.02 M; (b) 0.05 M; (c) 0.1 M; (d) 0.15 M

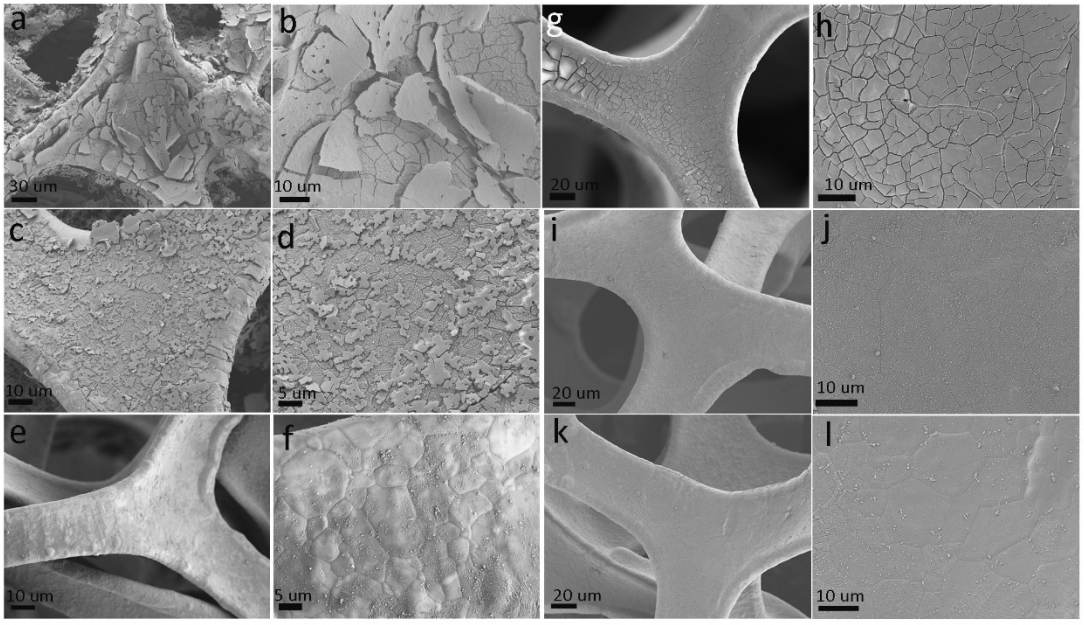

Figure S3. SEM images of (a,b) Ni@NF (without Mo); (c,d) NiMo@NF (0.02 M Na_2MoO_4); (e,f) NiMo@NF (0.05 M Na_2MoO_4); (g,h) NiMo@CC (0.1 M Na_2MoO_4). (i,j) SEM images of the obtained NF when the Mo salt reaches 0.15 M. (k,l) SEM images of the obtained NF when no Ni salt was added.

The content of Mo in NiMo alloy was determined by energy dispersive X-ray spectroscopy (EDS). With the increase of Na_2MoO_4 concentration in the bath, the Mo content was determined to be 16.3, 20.2 and 21.4 wt%. It was not until the concentration of Na_2MoO_4 reached more than 0.15 M that Mo signal was not displayed in EDS (Figure S2).

In addition, scanning electron microscope (SEM) showed the morphology of NiMo@NF electrode with different Ni/Mo ratios. For pure Ni@NF, a large area of disordered nickel flakes grew on the surface of nickel foam, while NiMo@NF (0.02 M Na_2MoO_4), NiMo@NF (0.05M Na_2MoO_4) and NiMo@NF (0.1 M Na_2MoO_4) showed tiny nanoparticles with gradually sparse distribution (Figure S3). These results show that the particle size of NiMo alloy can be adjusted by adding molybdenum salt. At the same time, if there is only Mo salt without Ni salt, metal Mo cannot be electrodeposited. Finally, we chose 0.05M Na_2MoO_4 as the electroplating solution, and obtained the small-particle NiMo alloy. These results show that Mo can't be electrodeposited without the induction of Ni salt, but NiMo alloy with small size particles can be obtained by adjusting Ni/Mo ratio.

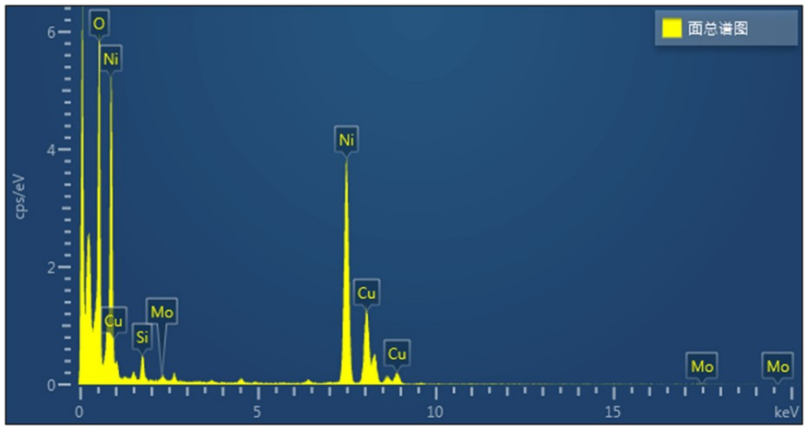

figure S4 EDX spectra of the NiMo PA@NF. the average atomic ratio of Ni to Mo is about 4: 1.01.

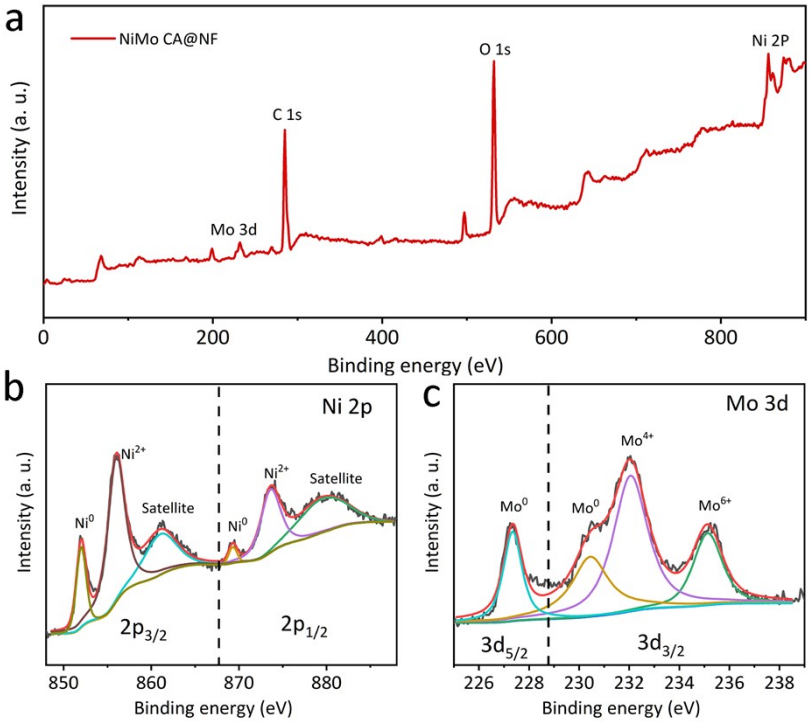

Figure S5 (a)The XPS pattern of as-obtained NiMo CA@NF. The NiMo PA@NF is composed of Ni, Mo and O elements. (b) The high-resolution XPS pattern of Ni 2p for NiMo PA@NF. the peaks at 855.8 eV, 861.7 eV, 873.7 eV and 881.4 eV are ascribed to Ni^{2+} $2p_{3/2}$, Ni^{2+} $2p_{3/2}$ satellite, Ni^{2+} $2p_{1/2}$ and Ni^{2+} $2p_{1/2}$ satellite, respectively. Ni^{0} $2p_{3/2}$ and Ni^{0} $2p_{1/2}$ are observed at 852.6 eV and 869.5 eV, respectively. (c) The high-resolution XPS pattern of Mo 3d for the NiMo PA@NF. The peaks located at 232.5 eV and 235.4 eV belong to Mo^{4+} $3d_{3/2}$ and Mo^{6+} $3d_{3/2}$, respectively. The Mo^{0} $3d_{5/2}$ is detected at 227.3 eV.

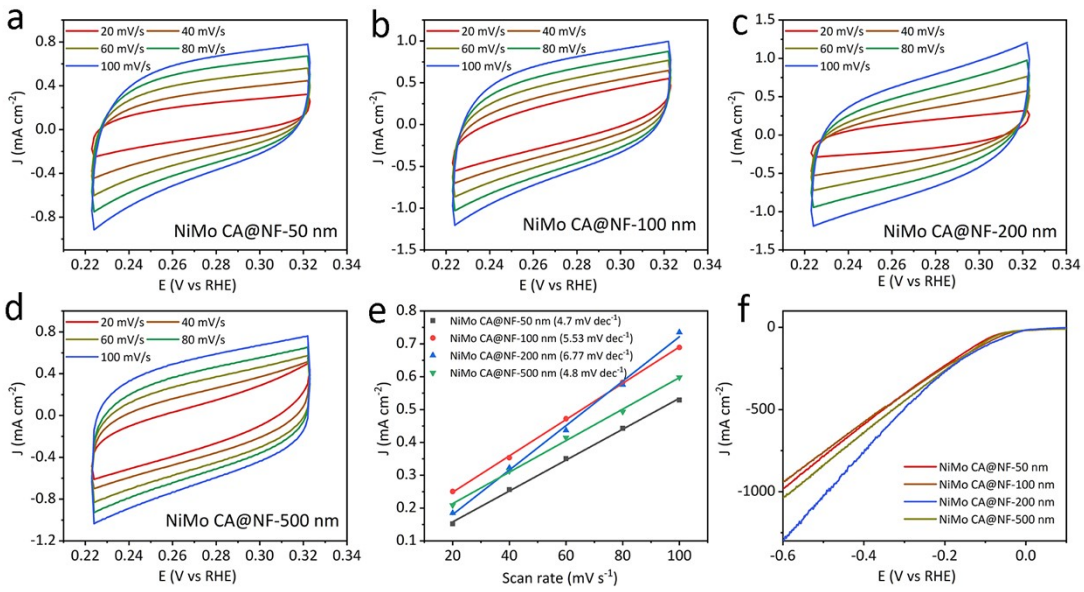

Figure S6 The electrochemically active surface area of NiMo PA@NF electrodes using silica spheres as template with diameters of 50 nm (a), 100 nm (b), 200 nm (c), 500 nm (d) and (e) the corresponding electrochemical double-layer capacitance; (f) the LSV curves of NiMo PA@NF electrodes with different pore diameters.

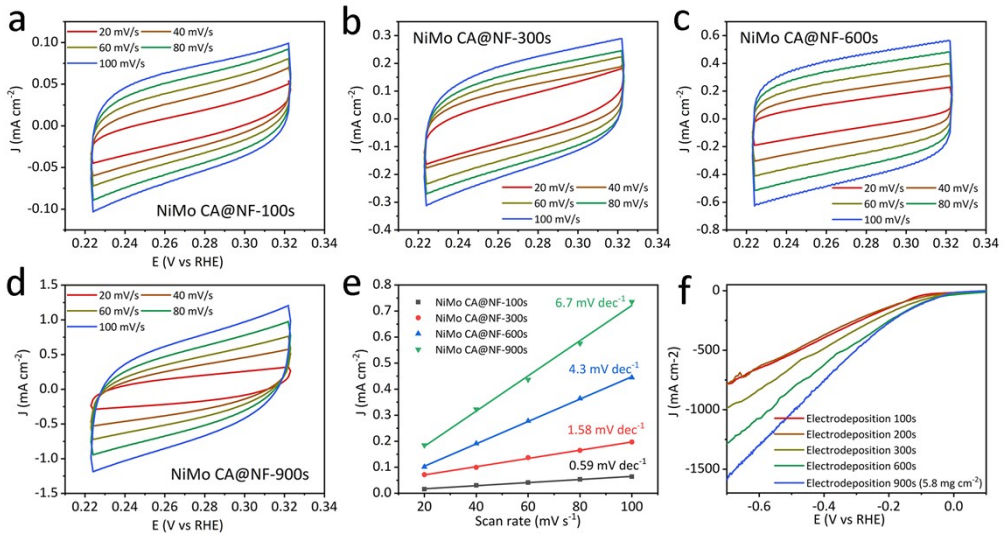

Figure S7. The mass load of the NiMo PA@NF electrode using silica sphere of 200 nm in diameter as template with plating time of (a)100s, (b) 300s, (c) 600s, (d) 900s and (e) the corresponding electrochemical double-layer capacitance; (f) LSV polarization curves of NiMo PA@NF with different mass loads.

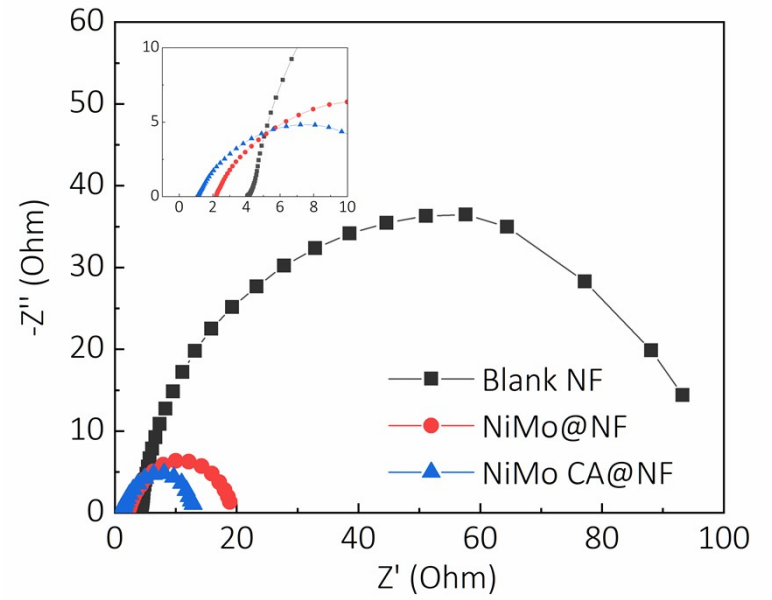

Figure S8. Nyquist plots of Blank NF, NiMo@NF and NiMo PA@NF.

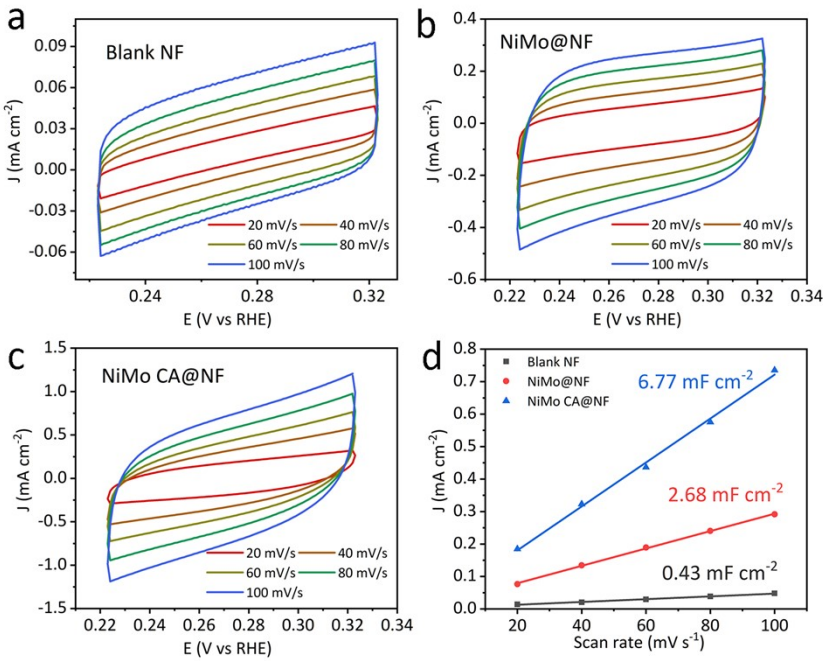

Figure S9. Cyclic voltammetry curves of (a) Blank NF, (b) NiMo@NF and (c) NiMo PA@NF catalysts under the potential of 0.224-0.324 V vs. RHE at different scan rates from 20 mV s^{-1} to 100 mV s^{-1}.

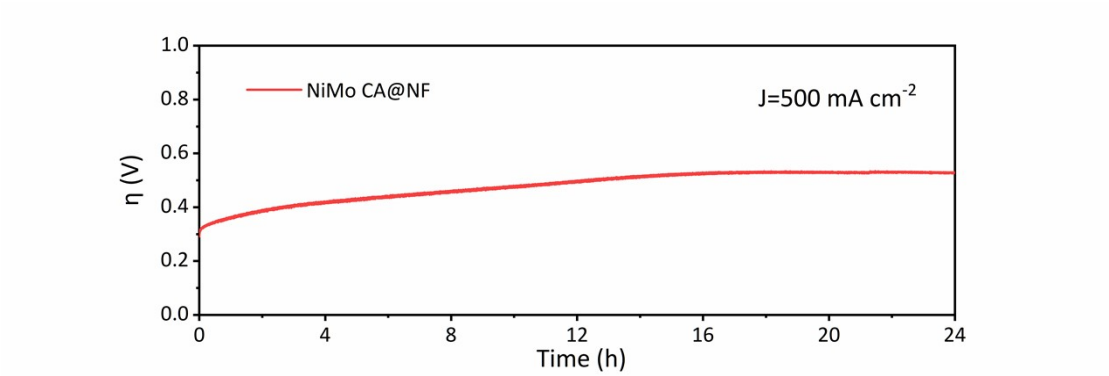

Figure S10. The stability of NiMo PA@NF evaluated by static current technique at a current density of 500 mA cm^{-2} for 24 h.

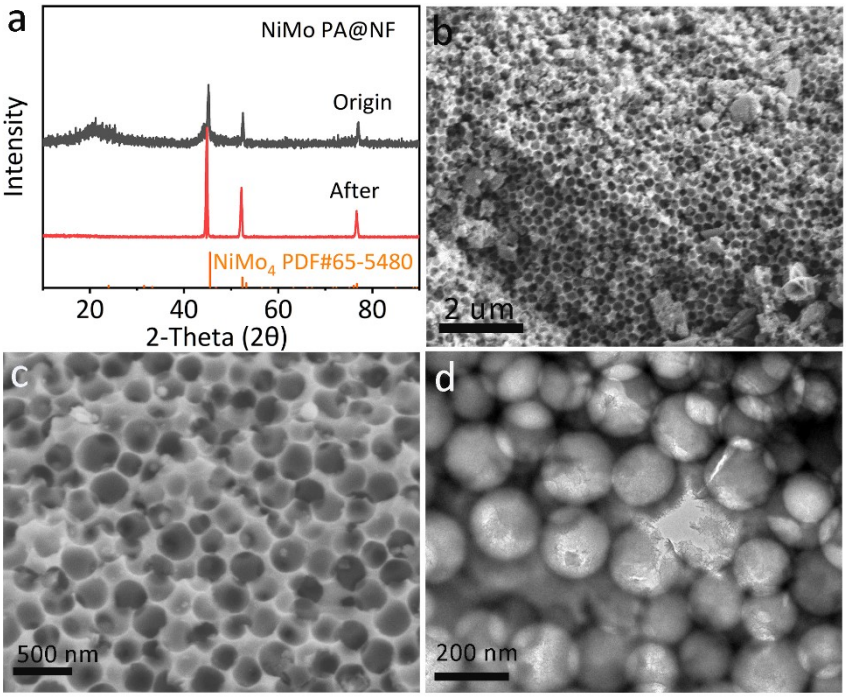

Figure S11. (a) XRD patterns, (b, c) SEM images and (d) TEM images of the employed NiMo PA@NF after the galvanostatic stability test