

Sn-induced electronic structure engineering of NiFe LDH for stable and efficient oxygen evolution reaction and urea oxidation reaction

Xiaohe Zhang^a, Xiaoqing Wu^{b*} and Xiaoqiang Du^{b*}

^a School of Energy and Power Engineering, North University of China, Taiyuan 030051, China

^b School of Chemistry and Chemical Engineering, North University of China, Xueyuan road 3, Taiyuan 030051, People's Republic of China. E-mail: duxq16@nuc.edu.cn

Experimental Section

All used materials in this work were of analytical grade, and used without further treatment. Reagents for the electrolyte synthesis, FeCl₂·4H₂O, SnCl₂·2H₂O, CO(NH₂)₂, NH₄F, KOH were bought from Sinopharm Chemical Reagent (Co., Ltd). Ni foam (NF) was obtained Shenzhen Green and Creative Environmental Science and Technology Co. Ltd. Ethanol was bought from Aladdin Ltd. (Shanghai, China).

Synthesis of Sn-NiFe LDH/NF, Sn₆O₄(OH)₄@NiFe LDH/NF-1 and Sn₆O₄(OH)₄@NiFe LDH/NF-2

The NF was cut into an area of 2 × 4 cm². In order to remove the surface oxidized layer from the NF before employing it as a substrate, it was washed with 3 M hydrochloric acid for 10 min under ultrasonication, and then rinsed with ethanol and water 3–5 times, before being further dried to obtain fresh NF. After that, Sn₆O₄(OH)₄@NiFe LDH/NF-1 was synthesized by a one-step solvothermal method. Typically, FeCl₂·4H₂O (1.2 g), SnCl₂·2H₂O (0.45 g), ammonium fluoride (0.12 g), and urea (0.54 g) were adequately dissolved in 8 mL anhydrous ethanol and 40 mL DI water under sonication and continuous magnetic stirring for 15 min to form a homogeneous solution. A piece of prepared NF was added to the aforementioned solution in a 100 mL Teflon-lined stainless steel autoclave, which was then sealed and kept at 120 °C for 8 h. After the high-pressure reactor had cooled to room temperature, the resulting foam was carefully extracted, and DI water was used to flush out any unreacted materials attached on the surface, before drying at 60 °C for 12 h. The syntheses of Sn-NiFe LDH/NF and Sn₆O₄(OH)₄@NiFe LDH/NF-2 were similar to that of Sn₆O₄(OH)₄@NiFe LDH/NF-1 but were done according to the molar amounts of SnCl₂·2H₂O of 1 mmol (0.225g) and 3 mmol(0.675g) at constant molar amounts of FeCl₂·4H₂O, ammonium fluoride and urea, respectively. The loading amount of Sn-NiFe LDH/NF catalysts on nickel foam is 2.6 mg/cm².

Material characterization

X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS, ThermoFisher Scientific ESCALAB) were also performed to research the composition and oxidation state of samples. To investigate the morphology of electrodes, a field emission scanning electron microscopy (FESEM, Hitachi, Japan) was carried out. An energy-dispersive X-ray spectroscope (EDS) was employed to research the elemental percentage and mapping of Ni, Sn, Fe and O on the Sn-NiFe LDH electrocatalysts.

Electrochemical measurements

An electrochemical workstation (Shanghai Chenhua) was applied to perform all the electrocatalytic measurement. A typical three-electrode device, where, graphite and Hg/HgO were acted as the counter and reference electrode, Ni foams with the resulting materials were employed as working electrode. Electrochemical tests electrolyte was the 1.0 M KOH for OER and 1.0 M KOH with 0.50 M urea for UOR. Moreover, all electrocatalytic measurement was carried out at 25 °C. To investigate the electrochemical performance of electrodes, the linear sweep voltammetry (LSV) was done at the scanning rate of 5 mV s⁻¹ by iR-compensation of 70%. What is noteworthy is that the each of the LSV tests was performed three times in order to ensure the reliability of the data. The electrochemical impedance spectroscopy (EIS) was provided in the frequency ranging from 100 kHz to 0.01Hz to study the electrochemical impedance and electrical conductivity of electrodes. Chronoamperometry tests were provided at current densities of 30 mA cm⁻² for 13 h to assess long-term electrocatalytic stability of UOR for Sn-NiFe LDH electrocatalysts. The used potentials were converted versus the reversible hydrogen electrode (RHE) based on the following formula 1: $V_{\text{RHE}} = V (\text{vs. Hg/HgO}) + 0.098 + 0.059 * \text{pH}$ (1)

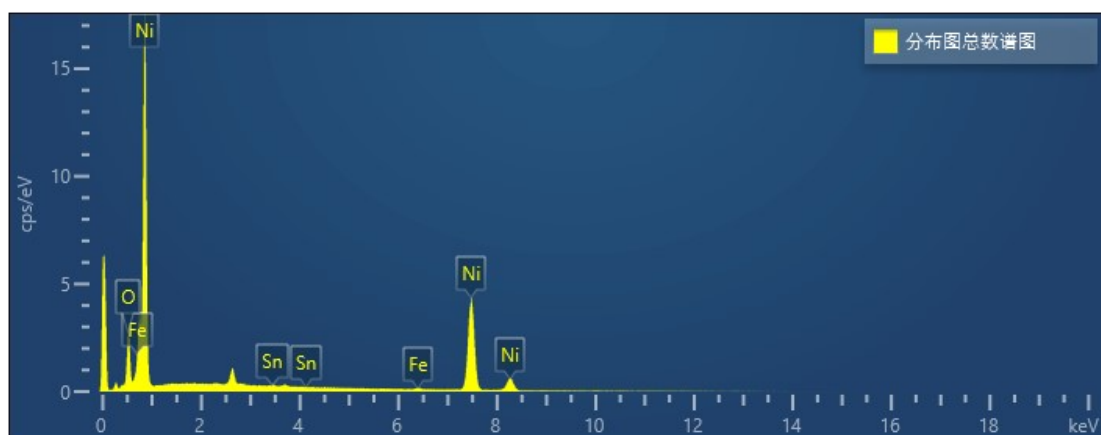


Fig. S1 EDS analysis of the Sn-NiFe LDH/NF nanostructure.

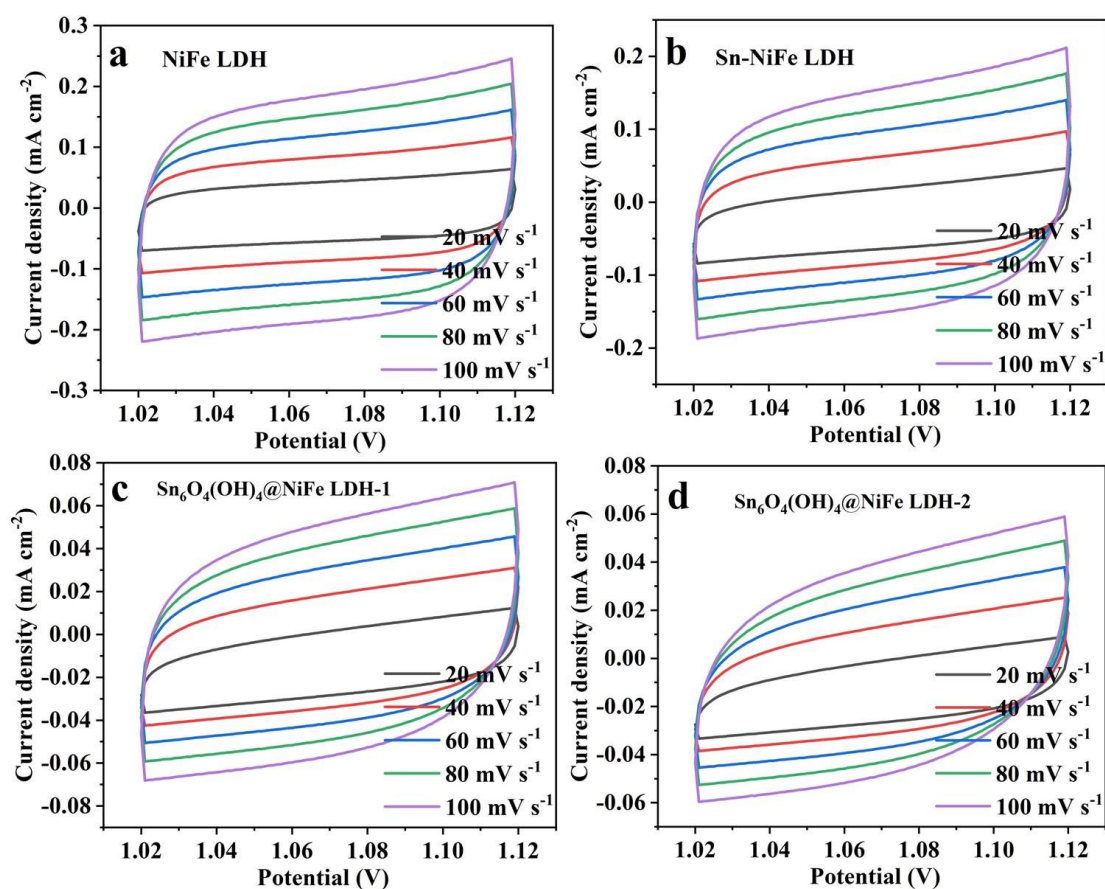


Fig. S2 CV curves with different scan rates for OER, NiFe LDH/NF (a), Sn-NiFe LDH/NF (b), $\text{Sn}_6\text{O}_4(\text{OH})_4@$ NiFe LDH/NF-1 (c) and $\text{Sn}_6\text{O}_4(\text{OH})_4@$ NiFe LDH/NF-2 (d).

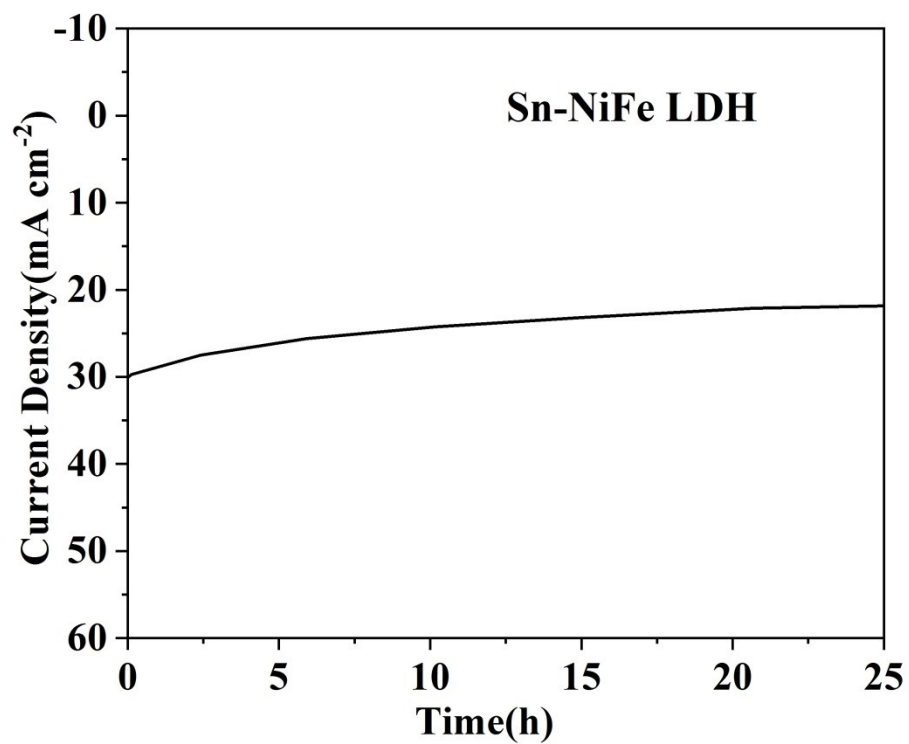


Fig. S3 (a) Chronoamperometry test of Sn-NiFe LDH/NF at 1.51 V for OER.

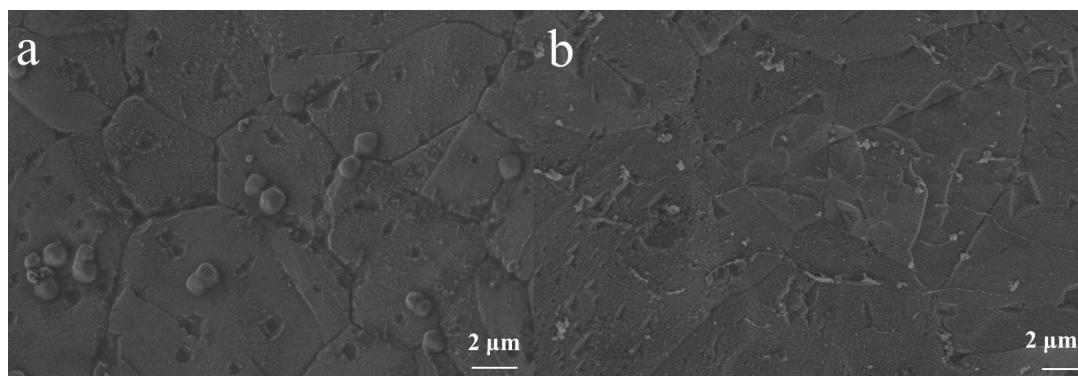


Fig. S4 SEM of fresh (a) and recovered (b) Sn-NiFe LDH/NF for OER.

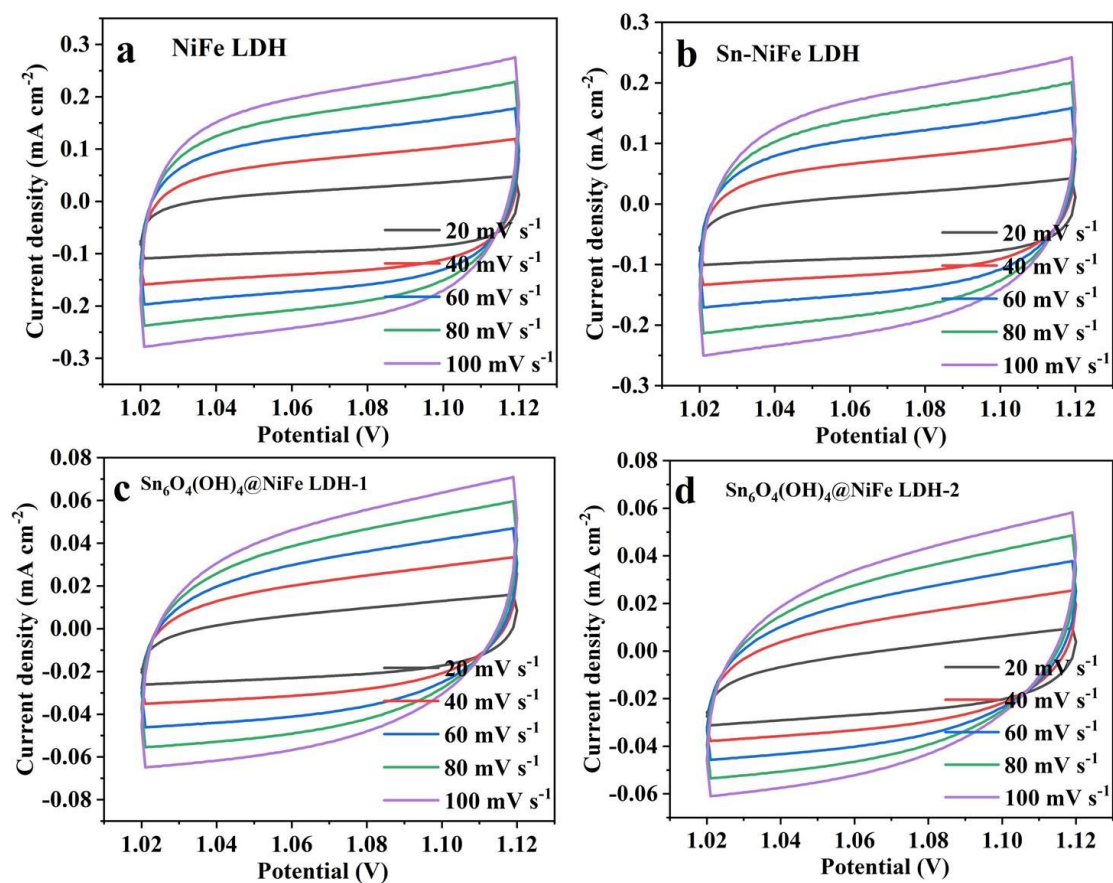


Fig. S5 CV curves with different scan rates for UOR, NiFe LDH/NF (a), Sn-NiFe LDH/NF (b), Sn₆O₄(OH)₄@NiFe LDH/NF-1 (c) and Sn₆O₄(OH)₄@NiFe LDH/NF-2 (d).

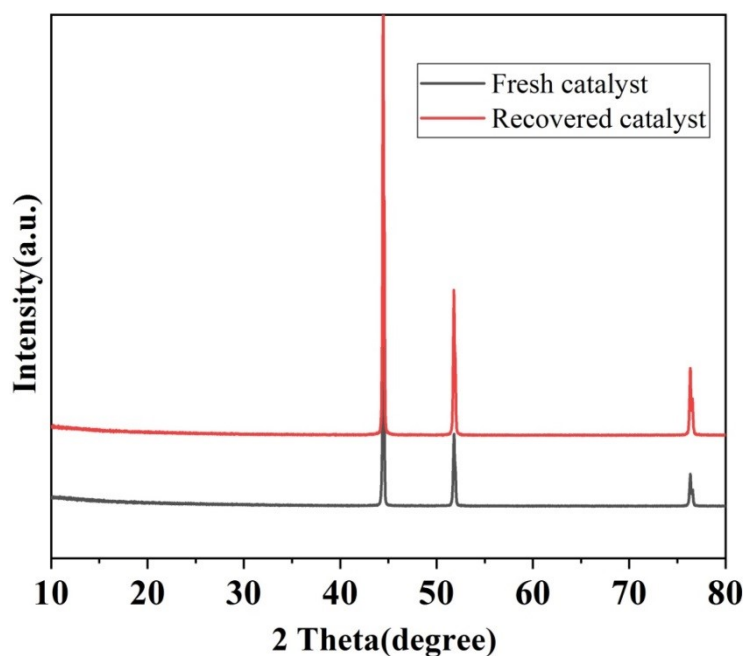


Fig. S6 XRD of fresh and recovered Sn-NiFe LDH/NF for UOR.

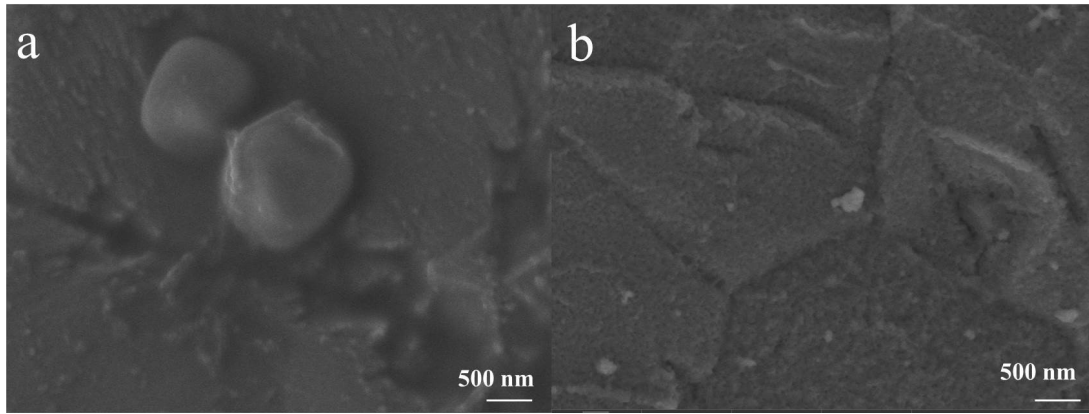


Fig. S7 SEM of fresh (a) and recovered (b) Sn-NiFe LDH/NF for UOR.