Supporting Information

Atomic layer deposited Al_2O_3 layer confinement: an efficient strategy to synthesize durable MOF-derived catalysts toward oxygen evolution reaction

Hang Lei[a], Yongyin Liang[b], Guobiao Cen[b], Bo-tian Liu[b,c], Shaozao Tan[a]*, Zilong Wang[a,b]*, Wenjie Mai[b]*

a. Guangdong Engineering & Technology Research Centre of Graphene-like Materials and Products, Department of Chemistry, College of Chemistry and Materials Science, Jinan University, Guangzhou 510632, China.

b. Siyuan Laboratory, Guangdong Provincial Engineering Technology Research Center of Vacuum Coating Technologies and New Energy Materials, Department of Physics, Jinan University, Guangzhou, Guangdong 510632, P. R. China.

c. Guangxi Key Laboratory of Electrochemical and Magneto-chemical Functional Materials, Department of Chemistry and Biological Engineering, Guilin University of Technology, Guilin 541004, P.R. China.

*E-mail addresses: zilong@email.jnu.edu.cn (Prof. Wang), tsztan@jnu.edu.cn (Prof. Tan), wenjiemai@email.jnu.edu.cn (Prof. Mai)

1. Experimental Section

1.1 Preparation of Ti/NiFe LDH

The NiFe LDH was prepared using a method which was reported by previous literature.[1] In a typical experiment, 1.54 mmol Nickel(II) nitrate hexahydrate, 0.22 mmol Iron(III) nitrate nonahydrate, 8 mmol urea and 3.2 mmol ammonia fluoride were dissolved in 32 mL distilled water, and then under vigorous stirring for 30 min. After that, the mixture was transferred into a 50 mL Teflon-hydrothermal kettle and a cleaned Ti mesh with the size 1×1 cm^2 was immersed into above solution. The Teflon-hydrothermal kettle was transferred to vacuum drying oven and maintained at 120 ºC for 6 h. After the system was cooled to room temperature, the sample was washed with water and ethanol for several times and then dried in vacuum 24h.

1.2 Preparation of Fe_2Ni MIL 88 supported on Ti/NiFe LDH

The Fe_2Ni MIL 88 was prepared using a method which was reported by previous literature.[2] In a typical synthesis, 0.362 g of Iron(III) chloride hexahydrate, 0.192 g of Nickel(II) nitrate hexahydrate and 0.332 g of 1,4-benzenedicarboxylic acid (H_2BDC) were dissolved in 20 ml of dimethylformamide under stirring for 30 min. Then, 4 ml of 0.4 mol L^{-1} NaOH solution was added with continuous stirring for 15 min. After that, the mixture was transferred into a 50 mL Teflon-hydrothermal kettle and a Ti/NiFe LDH was immersed into above solution. The Teflon-hydrothermal kettle was transferred to vacuum drying oven and maintained at 100 ºC for 10 h. After the system was cooled to room temperature，the sample was washed with water and ethanol for several times and then dried in vacuum 24 h.

1.3 Preparation of NiFe/NC@Al_2O_3

The as-prepared Fe_2Ni MIL 88 supported on NiFe LDH/Ti were put into atomic layer deposition system (ALD, BeneqTFS200) for Al_2O_3 layers deposition. Aluminum trimethide (TMA) and H_2O were precursors, and high purity nitrogen was used as the carrier gas. The growth rate was 0.09 nm per cycle at 85 °C and thickness of Al_2O_3 layers was controlled by adjusting the cycle numbers. The cycle number are 112, 333, 556 to from the thickness of 10 nm ,30 nm,50 nm Al_2O_3 layers, respectively. After that, the samples were transferred to tube furnace, argon gas as protective gas and 600 ℃ keep 2 h, the heating rate is 5 ℃ per minute. In this work, the catalysts with thickness of 10 nm, 30 nm, 50 nm Al_2O_3 layers are written as NiFe/NC@Al_2O_3-1, NiFe/NC@Al_2O_3-2, NiFe/NC@Al_2O_3-3, respectively. The NiFe/NC was prepared at the same condition, and just without Al_2O_3 atomic layer deposition.

1.4 Preparation of NiFe alloy@Al_2O_3

In a typical synthesis, 0.3g of $Ni(CH_3COO)_2 \cdot 4H_2O$ and 0.441g of $Na_3C_6H_5O_7 \cdot 2H_2O$ were dissolved in 40 ml deionized water under stirring for 10 min to form mixture A. 0.264g $K_4Fe(CN)_6 \cdot 3H_2O$ was dissolved in 60 ml deionized water under stirring for 10 min to form solution B. Then, solution B added to Mixture A and stirring 3 min. After that, the mixture was transferred into a 200 mL beaker and a NiFe LDH/Ti mesh was immersed into above solution. The beaker was transferred to vacuum drying oven and maintained at 80 ºC for 24 h. After the system was cooled to room temperature, the sample was washed with water and ethanol for several times and then dried in vacuum 24h. The procedure of atomic layer deposition as same as NiFe/NC@Al_2O_3, and the thickness of Al_2O_3 is 30 nm. After that, the sample was transferred to tube furnace, argon gas as protective gas and 600 ℃ keep 2 h, the heating rate is 5 ℃ per minute.

1.5 Physicochemical Characterizations

The X-ray diffraction (XRD) results were recorded with D8 Rigaku 9000. Raman spectra were recorded with LabRAM HR Evolution at excitation laser wavelength of 532 nm. JSM7610F (JEOL Ltd., Tokyo, Japan) scanning electron microscope (SEM) and a Thermo Fischer Talos F200x transmission electron microscope (TEM) were used to characterize the morphology and structure of catalysts. X-ray Photoelectron Spectroscopy (XPS, Thermo fisher Scientific K-Alpha$^+$) was carried out to explore the surface chemical composition and oxidation state of catalysts. The dioxygen yield was measured by gas chromatography (GC) analysis (FULI GC 9790II) purchased from Zhejiang FULI Analytical Instrument (Co., Ltd., Zhengjiang, China).

1.6 Electrochemical measurements

All electrochemical measurements were performed in a standard three-electrode system (CHI 760D, CH Instrument) at room temperature, using graphite rod as a counter electrode and Hg/HgO as a reference electrode. The catalyst on Ti mesh was directly used as working electrode. 1 M KOH was served as electrolyte. The potential readings were reported with respected to RHE according to $E_{RHE} = E_{Hg/HgO} + 0.0592 \times pH + 0.098$. Linear sweep voltammetry (LSV) were performed at scan rate 5 mV s^{-1} and without IR-correct. The scan rates were from 40 mV s^{-1} to 120.0 mV s^{-1} for CV and the voltage range is 0.925-1.025 V. The electrochemically active surface areas (ECSA) were measured by the capacitive current associated with double-layer charging from the scan-rate dependence of CV. The linear fitting of the charging current density differences ($\Delta j = (ja - jc)/2$ at a potential of 0.975 V (vs. RHE) against the scan rate was done. The slope is the double-layer capacitance C_{dl}, which is used to represent ECSA. The ISTEP-Multi-Current steps was used to record the stability of catalysts. Electrochemical impedance spectroscopy (EIS) test was carried out at a polarization potential of 1.55 V vs. RHE and frequency range of $0.1\text{-}10^5$ Hz with an amplitude of 10 mV, recorded by a Princeton electrochemical workstation (Veras STAT 3-400).

2. Supporting Figure

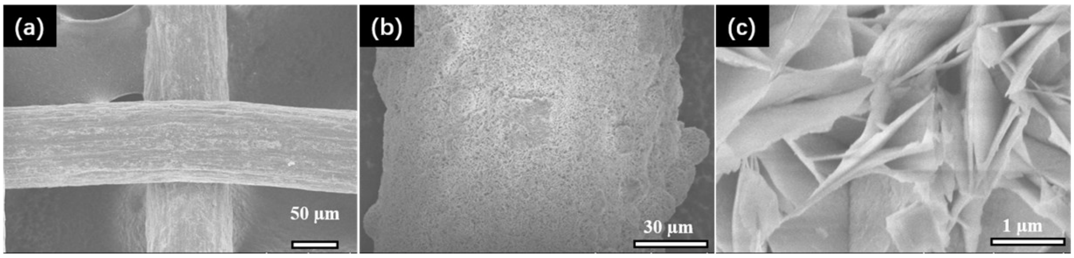

Figure S1. (a) SEM image of bare titanium foil. (b-c) SEM images of Ti/NiFe LDH at different scale bar.

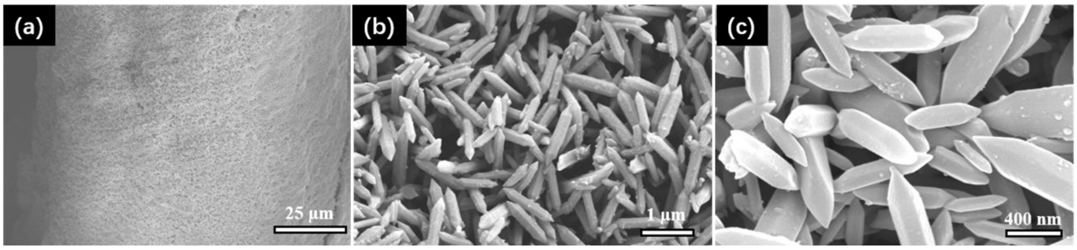

Figure S2. (a-c) SEM images of Fe_2Ni MIL 88 on Ti/NiFe LDH.

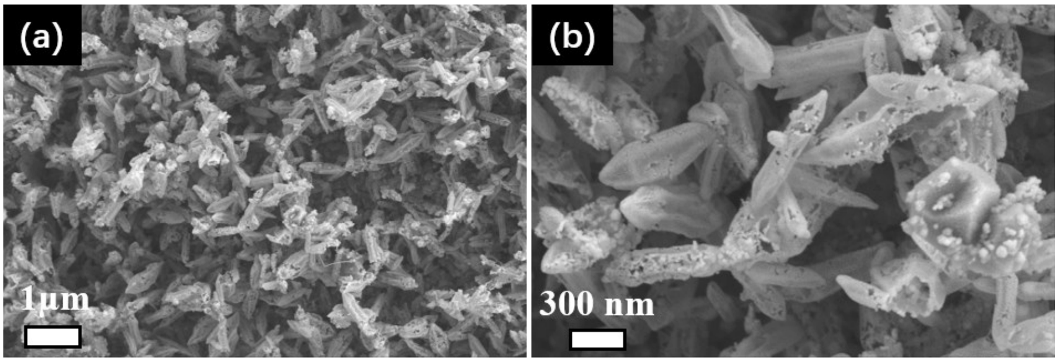

Figure S3. (a, b) SEM images of NiFe/NC@Al_2O_3-2 after Al_2O_3 layer was removed.

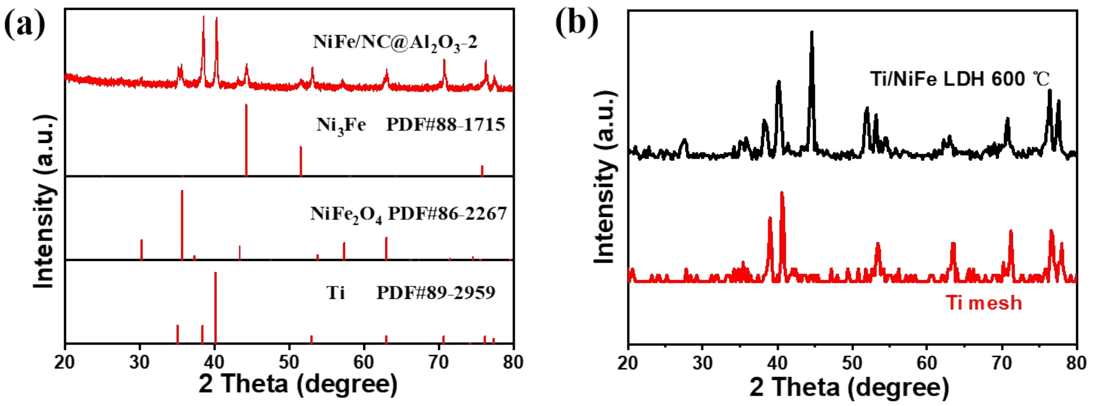

Figure S4. (a) The XRD pattern of NiFe/NC@Al_2O_3-2. (b) The XRD pattern of Ti mesh and Ti/NiFe-LDH 600 °C.

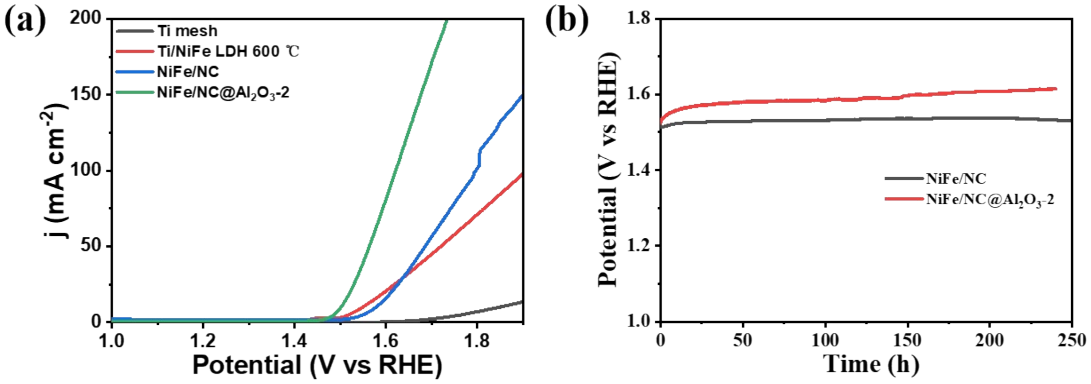

Figure S5. (a) Without IR-corrected LSV curves of Ti mesh, Ti/NiFe LDH, NiFe/NC and NiFe/NC@Al_2O_3-2 toward OER in 1M KOH. (b) Chronopotentiometric curves of NiFe/NC and NiFe/NC@Al_2O_3-2 in a 1 M KOH electrolyte at 10 mA cm^{-2}.

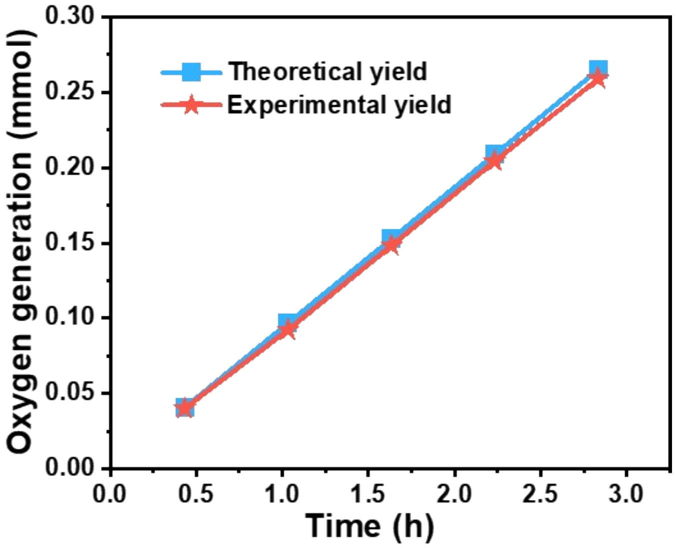

Figure S6. Coulombic efficiency of the theoretically calculated and experimentally measured O_2 gas versus different reaction time.

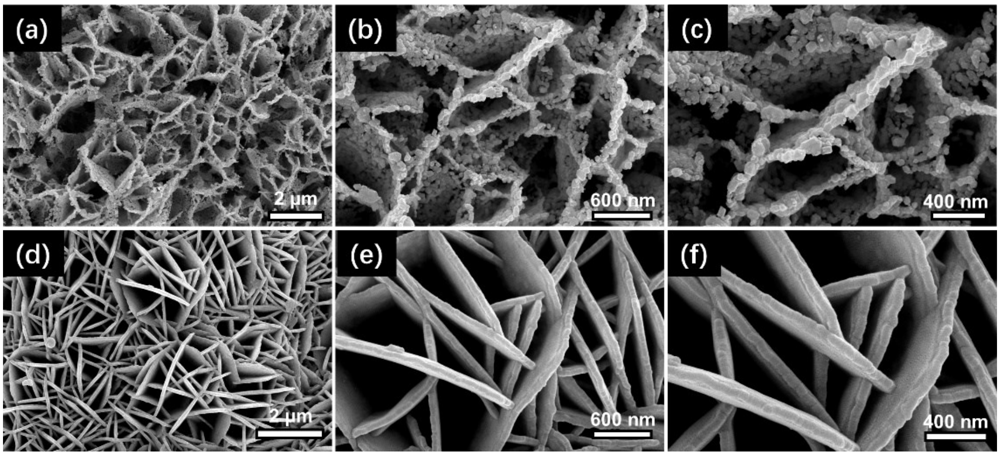

Figure S7. (a-c) The SEM images of NiFe LDH after 600 ℃ pyrolysis at different scale bar. (d-f) The SEM images of NiFe LDH/Al2O3 after 600 ℃ pyrolysis at different scale bar.

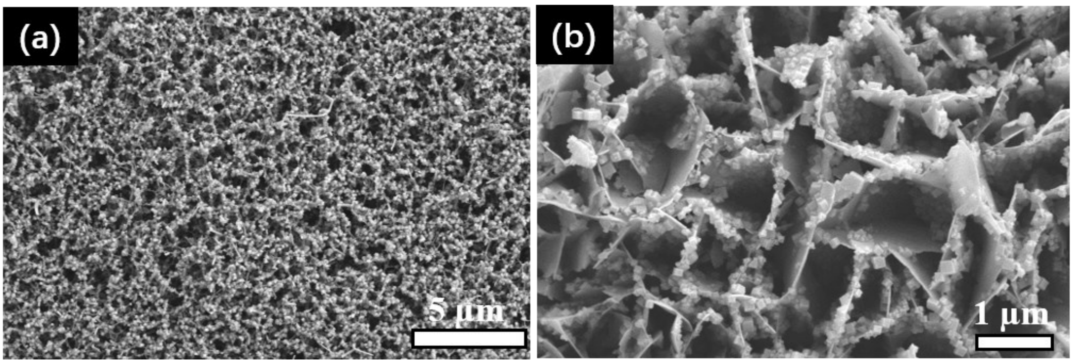

Figure S8. (a-b) SEM images of Ti/NiFe LDH/NiFe PBA@Al_2O_3 at different scale bar.

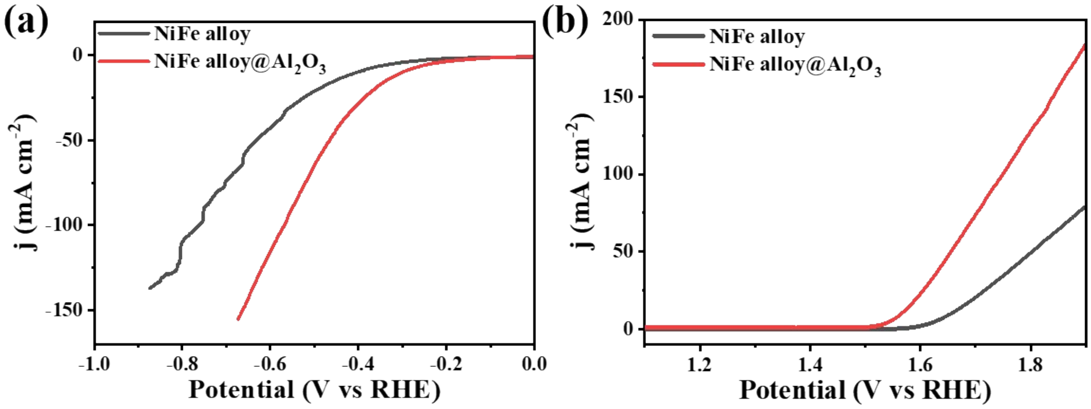

Figure S9. (a) Without IR-corrected LSV curves of NiFe alloy and NiFe alloy@Al_2O_3 for hydrogen evolution reaction in1M KOH. (b) Without IR-corrected LSV curves of NiFe alloy and NiFe alloy@Al_2O_3 for oxygen evolution reaction in1M KOH.

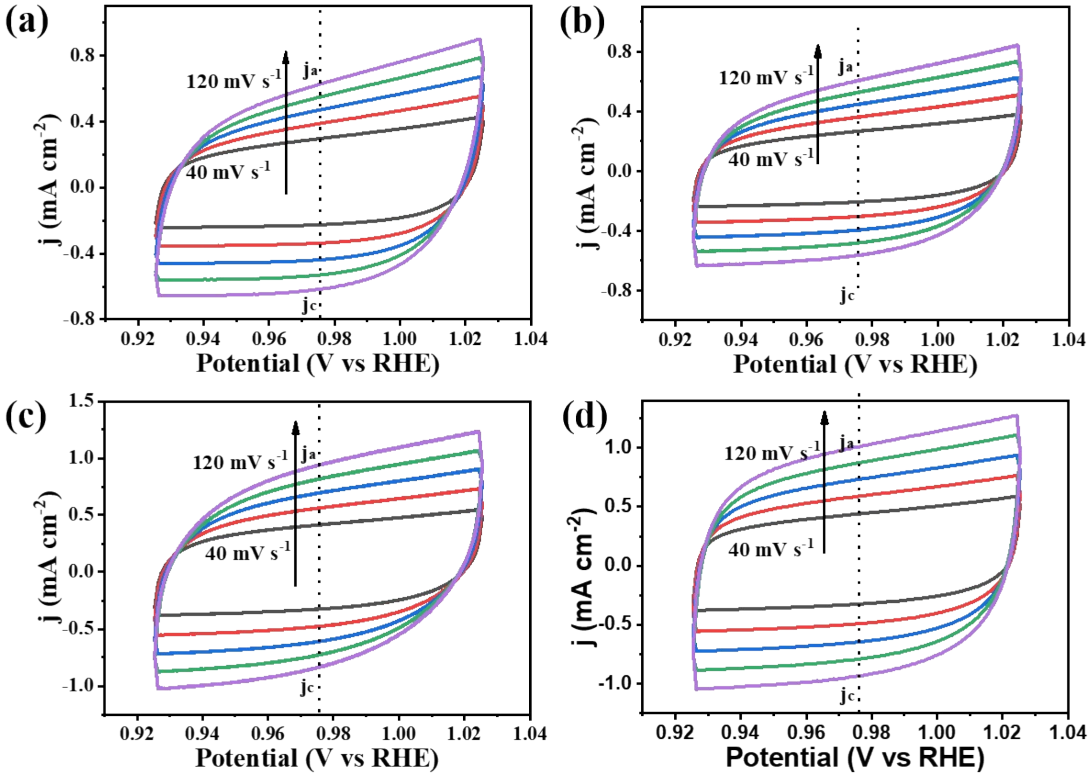

Figure S10. Cyclic voltammetry of (a) NiFe/NC (b) NiFe/NC@Al_2O_3-1 (c) NiFe/NC@Al_2O_3-2 (d) NiFe/NC@Al_2O_3-3 at different scan rate.

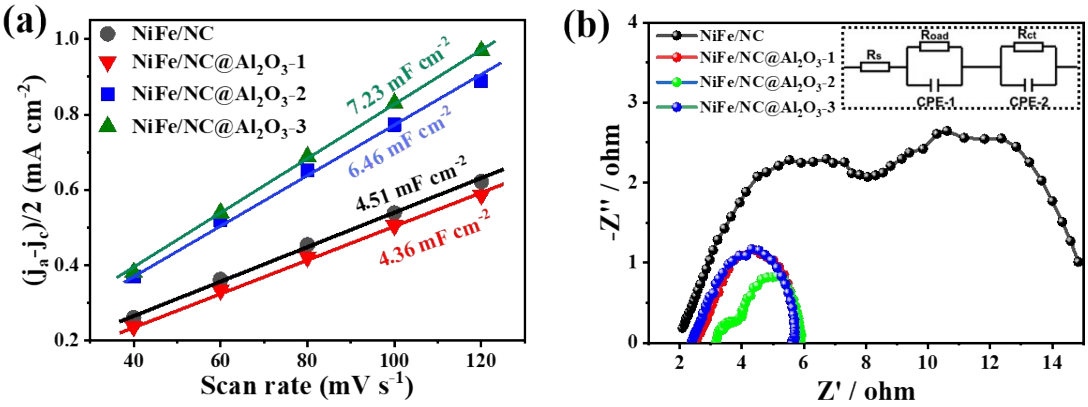

Figure S11. (a) Capacitive currents as a function of the scan rate to give the double-layer capacitance (C_{dl}) and (b) Electrochemical impedance spectra of different catalysts.

Reference

1. J. Zhang, J. Liu, L. Xi, Y. Yu, N. Chen, S. Sun, W. Wang, K. M. Lange and B. Zhang, Single-atom Au/NiFe layered double hydroxide electrocatalyst: probing the origin of activity for oxygen evolution reaction, *J. Am. Chem. Soc.*, 2018, **140**, 3876-3879.

2. G. Huang, F. Zhang, L. Zhang, X. Du, J. Wang and L. Wang, Hierarchical $NiFe_2O_4/Fe_2O_3$ nanotubes derived from metal organic frameworks for superior lithium ion battery anodes, *J. Mater. Chem. A*, 2014, **2**, 8048-8053.