

Template-free assembling Ni nanoparticles to 3D hierarchical structure for superior performance supercapacitor

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Experimental Section

Material synthesis

Synthesis of the nanoflake arrays of Ni(OH)₂·0.75H₂O on Ni foams

All chemicals used in this work were analytical reagent grade and commercially available, and used without further purification. The arrays of Ni(OH)₂·0.75H₂O nanoflakes were grown on Ni foams by facile hydrothermal methods according to the previous reported work[19, 20]. Firstly, aqueous solution composed of 0.03 M Ni(NO₃)₂, 0.15 M urea and 0.06 M NH₄F were prepared under magnetic stirring. Then, Ni foam substrates were vertically immersed in those solutions after chemically cleaned with acetone, methanol, and deionized water. The resulting two solutions with Ni foams were then sealed in Teflon-lined stainless steel autoclaves, and maintained at 120 °C for 6 h, followed by rinsing the nickel foams with deionized water and dried at 60 °C for 12 h. Powder products in the solution were collected by centrifugation.

Synthesis of the Ni nanoparticle nanoflake arrays (NFAs) on Ni foams

The as-grown hydroxide precursors both on the nickel foams and powders from the solution were treated with a non-contact Al-reduction process to obtain the Ni nanoparticle flake arrays, as well

as the corresponding powders, according to the previous work of our group[21]. **Figure 1** illustrates non-contact Al-reduction process. Specifically, the as-grown samples (nickel hydroxide nanoflake arrays and powder) and aluminum powder were separately placed in a two zone tube furnace, and then the tube was evacuated to a base pressure ~ 4 Pa, then the aluminum was heated at 850 °C and samples were heated at 350 °C, for 90 min. For comparison, the same hydroxide precursors were also reduced by H_2/Ar (1 : 9) at 260 °C for 90 min to obtain the irregular Ni particles on Ni foam and irregular Ni particle powder.

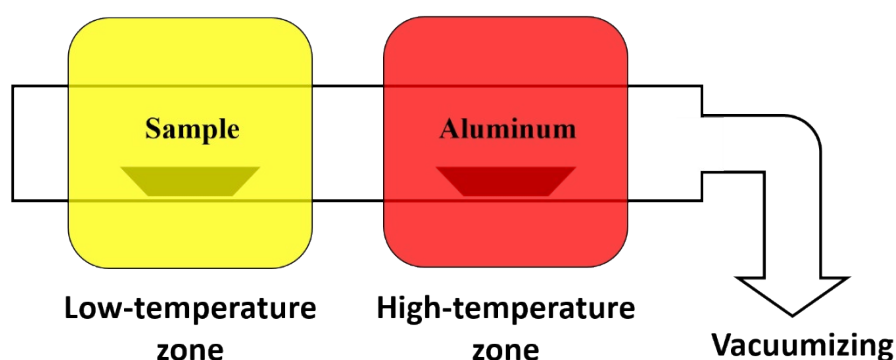


Figure 1. Schematic of the fabrication of NFAs by the non-contact Al-reduction process.

Synthesis of the NiO nanoflake arrays (NOFAs) on Ni foams

The nanoflake arrays of $Ni(OH)_2 \cdot 0.75H_2O$ on Ni foams were annealed in Ar atmosphere at 350 °C for 2h to obtain the nanoflake arrays of NiO. Similarly, the powder of $Ni(OH)_2 \cdot 0.75H_2O$ was also treated by the same annealing process to obtain the NiO nanoflake powder.

Material Characterization

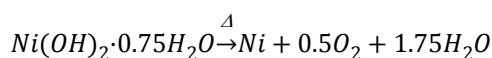
The samples were characterized by powder X-ray diffraction (XRD) using a Bruck D2 X-ray diffractometer with nickel filtered Cu $K\alpha$ radiation ($k = 1.5418 \text{ \AA}$) at a scanning rate of $0.1^\circ \cdot \text{min}^{-1}$ in the 2θ range of 20° – 80° . The sizes and morphologies, the microstructures, and the chemical composition of the samples were characterized by field-emission scanning electron microscopy (FE-SEM, JSM-6330F), transmission electron microscopy (TEM, JEM2010-HR) and X-ray photoelectron

spectroscopy (XPS, ESCALab250). Nitrogen sorption isotherms were measured using a Micromeritics ASAP 2020 analyzer at $-196\text{ }^{\circ}\text{C}$. The weight of the nickel nanoflake powder used in the measurement was 100–200 mg. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area (S_{BET}) using the adsorption data at $p/p_0 = 0.06\text{--}0.30$.

Electrochemical measurements

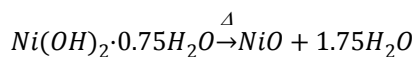
The electrochemical properties of the samples were investigated with cyclic voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance tests in a conventional three-electrode cell employing a CHI 660E electrochemical workstation (Chenhua, Shanghai). 2 M KOH solution was used as the electrolyte and a saturated calomel electrode (SCE) was used as the reference electrode and a Pt wire as the counter electrode. The Nyquist plots were recorded at a frequency range of 0.01 Hz –100 kHz at an amplitude of 5 mV versus the open circuit potential.

The special capacity of the NFA was calculated based on the loading mass of the nickel, which is estimated from the mass loss before and after annealing, according to the reaction equation:



The average loading density of NFA electrodes was calculated about 5 mg for the 3 cm^2 tested geometrical surface area.

Similarly, The special capacity of the NOFA was calculated based on the loading mass of the nickel oxide, which is estimated from the mass loss before and after annealing, according to the reaction equation:



The average loading density of NiO of Air-NiO and Ar-NiO electrodes was calculated about 6 mg for the 3 cm^2 tested geometrical surface area.

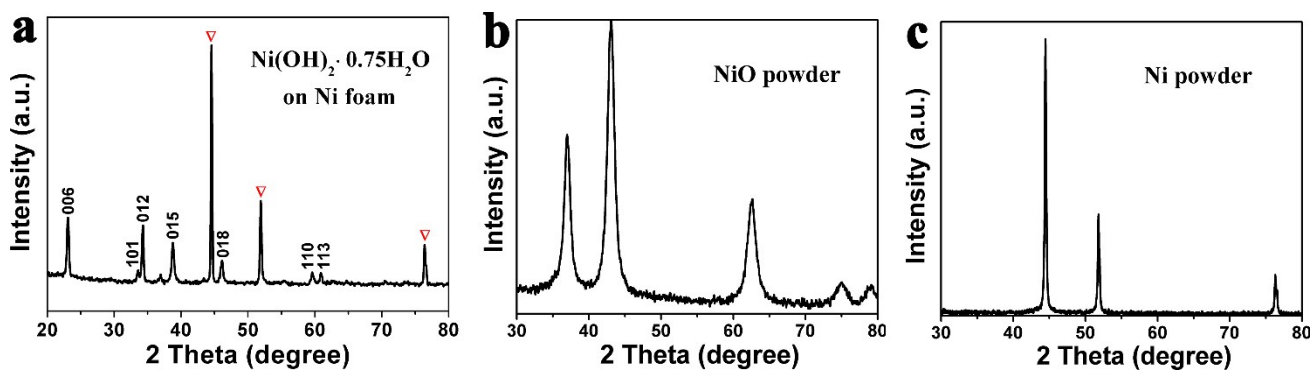


Figure S1. XRD patterns of (a) nanoflake array of $\text{Ni(OH)}_2 \cdot 0.75\text{H}_2\text{O}$ on Ni foam, (b) NiO nanoflake powder obtained from Ar-annealing process and (c) irregular Ni particle powder obtained from H_2/Ar reduction process.

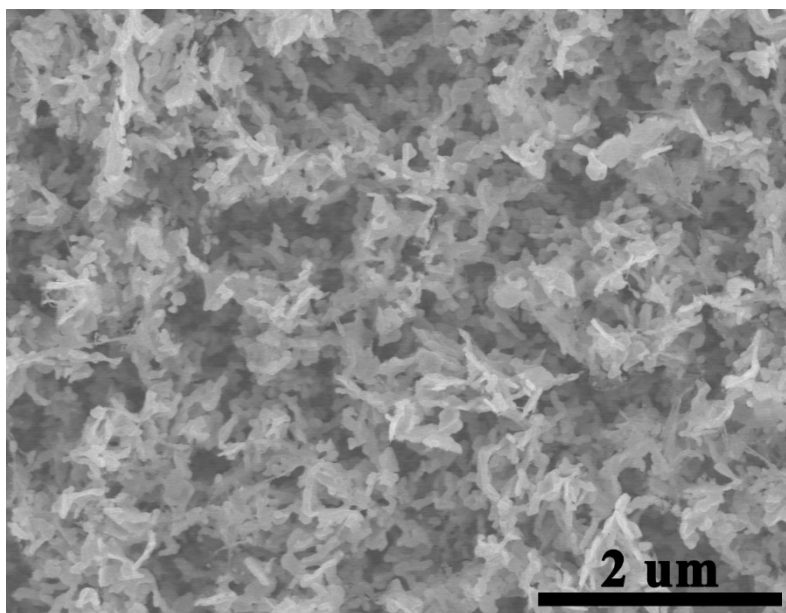


Figure S2. SEM image of irregular Ni particles on Ni foam derived from the $\text{Ni(OH)}_2 \cdot 0.75\text{H}_2\text{O}$ precursor treated by H_2/Ar reduction.

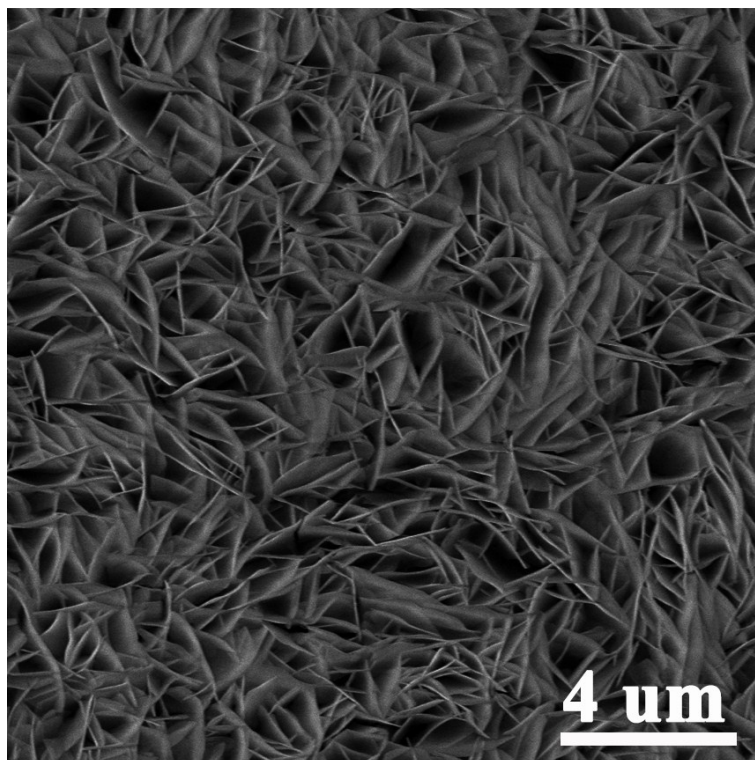


Figure S3. SEM image of NiO nanoflake array on Ni foam

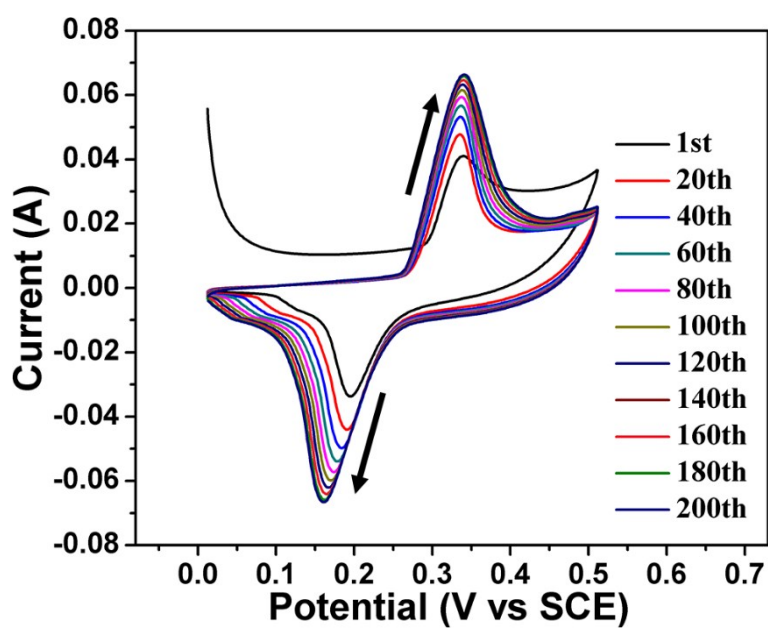


Figure S4. Cyclic voltammetry of the nickel nanoflake array in 2 M KOH for 200 cycles, in order to activate this electrode before the supercapacitor performance measurements. It can be seen that the redox peak currents were gradually increase, until reaching to nearly steady values after 200 cycles

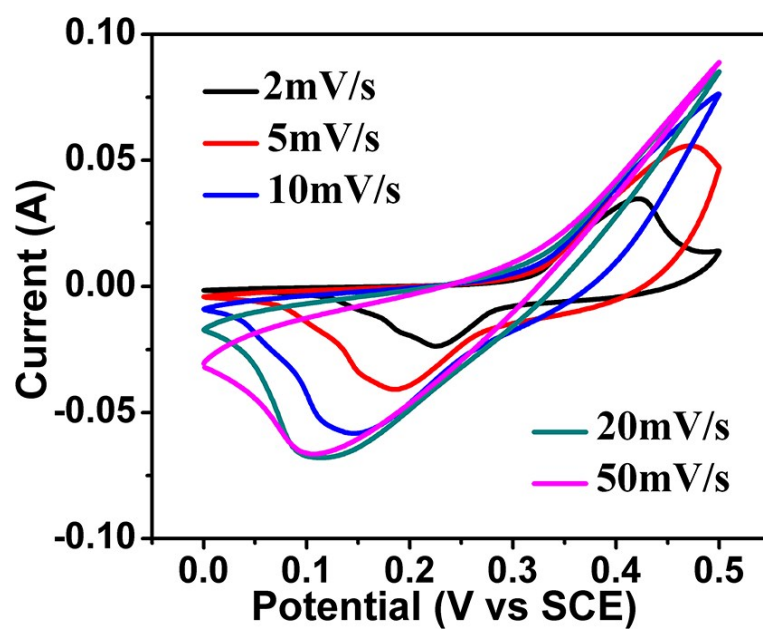


Figure S5. Cyclic voltammetry curves of the NiO nanoflake array at a series of scan rate from 5 mV s⁻¹ to 10 mV s⁻¹ and to 20 mV s⁻¹.