Supporting information

Hierarchical NiO/NiMn-Layered Double Hydroxide Nanosheet Array on Ni Foam for High Performance Supercapacitor

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1. Experimental Section

1.1. Materials preparation and characterizations

All chemicals in the experiments were of analytical grade and used as received without any further purification. If not specified, all solutions were prepared using deionized water that was purified through a Millipore system. Prior to the synthesis, several pieces of nickel foam (NF) $(1cm \times 2cm)$ were cleaned with acetone, 2M HCl solution, deionized water, and absolute ethanol, each in an ultrasound bath for 15 min, to ensure a clean surface.

Powder X-ray diffraction (PXRD) patterns were obtained using by a Bruker D8 advance Xray powder diffractometer using a Cu Kαradiation source (0.15418 nm). The morphology of the as-prepared samples was investigated by Hitachi S-4800 field-emission scanning electron microscope (FE-SEM) with an acceleration voltage of 20 kv, combined with energy dispersive Xray spectroscopy (EDS). The electrochemical tests were performed by an electrochemical analyzer system, CHI660E (Chenhua, Shanghai, China) using a three-electrode cell in 3.0 M KOH aqueous solution.

1.2. Preparation of NiO nanosheets on nickel foam substrate

The NiO nanosheets arrays were prepared by a facile hydrothermal synthesis method. Typically, 5 mmol of Ni(NO₃)₂·6H₂O and 10 mmol hexamethylenetetramine (HMT) were dissolved in 45 ml of deionized water under stirring for several minutes . And then the solution was transferred into a Teflon-lined stainless steel autoclave. A piece of clean nickel foam substrate was immersed into the above solution, with the top side coated with a polytetrafluoroethylene tape to prevent the solution contamination. The autoclave was sealed and maintained at 95°C for 8h. After the reaction, the NiO/NF substrate was washed with deionized water for several times, followed by calcination at 350°C in air for 2h.

1.3. Preparation of NiMn-LDH nanosheets on nickel foam substrate

The NiMn-LDH nanoarrays were prepared by the hydrothermal synthesis method. Typically, 3 mmol of NiCl₂· $6H_2O$, 1 mmol MnCl₂· $4H_2O$, 5mmol NH₄F and 5 mmol HMT were dissolved in 30 ml of deionized water under stirring, and then was transferred into a Teflon-lined stainless steel autoclave. A piece of pretreated nickel foam was immersed into the above solution. The autoclave was sealed and maintained at 90°C for 6 h. The nickel foam were cleaned by centrifuging and washing with distilled water and ethanol, and dried in a vacuum oven at 60°C for 6h.

1.4. Preparation of hierarchical NiO/NiMn-LDH nanosheet arrays

The NiO/NiMn-LDH nanoarrays were prepared by the hydrothermal synthesis method. Typically, 3 mmol of NiCl₂· $6H_2O$, 1 mmol MnCl₂· $4H_2O$ and 5 mmol HMT were dissolved in 30 ml of deionized water under stirring, and then was transferred into a Teflon-lined stainless steel autoclave. A piece of pretreated nickel foam covered with NiO nanosheets was immersed into the above solution. The autoclave was sealed and maintained at 90°C for 6 h, and then cooled naturally. The synthesized samples were cleaned by centrifuging and washing with distilled water and ethanol, and dried in a vacuum oven at 60°C for 6h. For NiO/NiMn-LDH, the mass of the active material on NF was about 3.6 mg/cm² according to the weight difference of NF before and after the hydrothermal reaction. Furthermore, the mass loading of NiMn-LDH was around 1.7 mg/cm², and the mass loading of NiO was around 0.73 mg/cm².

1.5. Preparation of AC electrode

AC electrode was fabricated through a slurry coating technique, in which AC powder, acetylene black and polyvinylidene fluoride (PVDF) were taken in the ratio of 80:10:10 and the slurry was made using N-methyl-2-pyrrolidone (NMP) solvent and then coated on Ni foam.

1.6 Electrochemical measurements

The electrochemical test was performed by an electrochemical analyzer system, using a three-electrode cell in 3M KOH electrolyte. The prepared NiO/NiMn-LDH electrode, a platinum foil and a saturated calomel electrode (SCE) were used as working electrode, counter electrode and reference electrode. The specific capacitance was calculated from the discharge curves as follows: $C = (I \Delta t)/(m \Delta V)$ where C (F/g) is the specific capacitance, I (A) is the discharge current, Δt (s) is the total discharge time, m (g) is the mass of active materials and ΔV (V) is the potential range of discharge.

The electrochemical properties of asymmetric supercapacitor were investigated under a twoelectrode cell configuration with NiO/NiMn-LDH electrode as the positive electrode and AC as the negative electrode in 2 M KOH electrolyte solution. In order to build a supercapacitor , the key point is to balance the charges following the relationship $q^+ = q^-$. The charge (q) stored by the electrodes depend on the specific capacitance (C), the potential range for the charge ang discharge process (ΔE) and the mass of the electrode (m) following the equation: $q=C\times\Delta E\times m$. To get $q^+=q^-$, the mass ratio of can be calculated by the equation: $m_+/m_-=(C_-\times\Delta V_-)/(C_+\times\Delta V_+)$. In our case, the optimal mass ratio between positive and negative electrodes should be $m_{(NiO/NiMn LDH)}/m_{(AC)}=0.43$. The energy density and power density of the asymmetric supercapacitor was calculated by the

$$E = \frac{1/2C\Delta V^2}{2C} P = \frac{3600E}{4E}$$

equations: Δt , where E (Wh kg⁻¹) is the energy density, V (V) is voltage range, P (W kg⁻¹) is the power dengsity, C (F/g) is the specific capacitance, Δt (s) is the total discharge time.



Figure S1. (a) CV curves of NiO electrode grown on Ni foam at different scan rates. (b) GCD curves of NiO electrode at different current densities. (c) The corresponding specific capacitance

of NiO electrode calculated by the GCD curves.



Figure S2. (a) CV curves of NiMn-LDH electrode grown on Ni foam at different scan rates. (b) GCD curves of NiMn-LDH electrode at different current densities. (c) The corresponding specific capacitance of NiMn-LDH electrode calculated by the GCD curves. (d) Electrochemical impedance spectra (EIS) of NiMn-LDH grown on Ni foam in 3M KOH solution.



Figure S3. Comparative EIS curves of the NiO/NiMn-LDH electrode before and after 1000

charge-discharge cycles.



Figure S4. (a) CV curves of AC electrode at different scan rates. (b) GCD curves of AC electrode at different current densities. (c) The corresponding specific capacitance of AC electrode calculated by the GCD curves.



Figure S5. CV curves of ASC in various potential windows at scan rate of 30 mV/s.