Supplementary Information

Anodization driven synthesis of nickel oxalate nanostructures with excellent performance for asymmetric supercapacitors⁺

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Synthesis of NON@NF electrode materials

The nanostructured nickel oxalate material was synthesized by an in-situ electrochemical method (anodization). Commercial nickel foam was degreased by sonicating in acetone, then rinsed with deionized water and dried in air. A two-electrode electrochemical cell with a nickel foil cathode was used to fabricate nanostructured nickel oxalate. Nickel foam was cut into pieces and sealed to ensure the working area was 2 cm×2 cm or 5 cm×5 cm. The nickel foam was used as the anode. Anodization was performed in a 0.3 M oxalic acid aqueous solution at a constant voltage of 50 V and controlled temperature of -5 °C for 10 min, using a DC stabilized power supply (Wenhua, China). After the reaction, the as-obtained samples were rinsed with deionized water and anhydrous alcohol. Thus the NON@NF electrode was prepared through the facile efficient anodization method. It should be

noted that this anodization route could be easily scaled up, which is crucial for practical applications of such electrode materials for supercapacitors.

Microstructural and electrochemical characterization of NON@NF electrode

The microstructure of the as-obtained samples were characterized by X-ray diffraction (XRD, RigakuD/max-rB) with Cu K α radiation, scanning electron microscopy (SEM, LEO 1530 VP) and transmission electron microscopy (TEM, FEI Tecnai G2). Selected-area electron diffraction (SAED) was also performed to document the crystalline nature of the samples. TEM specimens were prepared by ion milling at 5 kV (Gatan ion mill).

Electrochemical measurements including cyclic voltammetry (CV) and galvanostatic charge-discharge of the NON@NF electrode were performed using a potentiostat (CHI660E, Shanghai, Chenhua) in a cell with a three electrode configuration. The bright Pt foil was used as the counter electrode and an Ag/AgCl electrode (in saturated KCl solution) was used as the reference electrode. The electrolyte was a 6 M KOH aqueous solution which was prepared from analytical-grade KOH and pure deionized water (18.25 m Ω ·cm). The stability of the electrode was evaluated through CV measurements at a scan rate of 50 mV s⁻¹. All measurements were performed at room temperature.

Assembly and electrochemical measurements of NON@NF//AC asymmetric supercapacitor

An asymmetric supercapacitor was assembled using the NON@NF as the positive electrode and an activated carbon (AC) electrode as the negative electrode. The cellulose paper was used as the separator. The electrolyte was the 6 M KOH aqueous solution. The AC electrode was prepared as follows. Firstly, AC (TF-B520) was mixed with TIMCAL SUPER C45 conductive carbon black and polyvinlidene fluoride (PVDF), and their mass ratio was 8:1:1. Appropriate N-methyl pyrrolidone (NMP) was added into the mixture as a solvent to make a slurry which was coated

onto a nickel foam (2 cm \times 2 cm or 5 cm \times 5 cm). Finally, the as-prepared electrode was dried at 80 °C for 5 h to remove the solvent.

It is well known that the charge balance between the two electrodes should follow the relationship $q_+ = q_-$ so that to obtain a good electrochemical performance.^{S1} The charge stored by each electrode usually depends on the specific capacitance C (F g⁻¹), the voltage range ΔV (V) and the mass of the electroactive material *m* (g), and the related equation is given as follows:^{S2}

$$q = C \times \Delta V \times m \tag{1}$$

In order to obtain $q_+ = q_-$, the mass balance will be expressed as follows:^{S2}

$$\frac{m_{+}}{m_{-}} = \frac{C_{-} \times \Delta V_{-}}{C_{+} \times \Delta V_{+}}$$
(2)

Where '+' and '-' denote the positive and negative electrode respectively.

To determine the mass ratio of our NON@NF//AC asymmetric supercapacitor, typical CV curves were obtained for the NON@NF electrode and AC electrode at a scan rate of 50 mV s⁻¹ in the 6 M KOH aqueous solution (**Fig. S7**). The specific capacitance of the NON@NF electrode was calculated as 409.5 F g⁻¹. The specific capacitance of the AC electrode was 78.4 F g⁻¹. Based on the specific capacitance values and the potential windows of the two electrodes, the optimal mass ratio of $m_+(nickel oxalate)/m_(AC)$ was determined to ~0.29 in the NON@NF//AC asymmetric supercapacitor.

Electrochemical measurements of the NON@NF//AC asymmetric supercapacitor were also carried out using the CHI 660E potentiostat, including cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS). EIS was performed in a frequency range from 0.01 Hz to 100 kHz with a 5 mV amplitude at open circuit potential. Energy density and power density of the supercapacitor were calculated based on the galvanostatic discharging profiles, based

upon the total mass of both the positive and negative active materials. The cycling performance of the supercapacitor was evaluated using the galvanostatic charge/discharge cycling between 0 and 1.7 V at a current density of 1 A g⁻¹.

Calculation

Through DSC and XRD, we have confirmed that the water of crystallization could be removed from the as-anodized nickel oxalate through annealing in air at 280 °C. We have done a comparative trial on both the as-anodized (with water of crystallization) and as-annealed (without water of crystallization) samples. The overlapped CV curves of the electrodes (as-anodized and as-annealed) are shown in **Fig. S11**. The almost equal capacitance calculated from the CV curves indicates that the water of crystallization has little influence on the electrochemical properties in the aqueous solution. Thus the as-anodized samples were directly used the electrodes without further treatment in our work.

The calculation principle about the mass of active nickel oxalate was mainly based on the phase changes during the course of thermal annealing. According to the TG-DSC results, there are two weight loss steps in the temperature ranges of 180-280 °C and 280-380 °C, corresponding to the loss of crystallization water in nickel oxalate hydrate and the transformation from nickel oxalate to nickel oxide respectively (both have been confirmed by XRD). The weight change during annealing is owing to the phase transformation from NiC₂O₄·2H₂O to NiO. Based upon the phase transformations we could calculate the weight loss during different steps of annealing, which is in accordance with the TG results. And therefore we could also obtain the mass of the nickel oxalate on the nickel foam.

In addition, we prepared tens of anodized nickel foams (2*2 cm²), labeled and weighted respectively. Thus all samples were annealed at 400 °C. Then we weighted the samples again, obtained the weight loss of each sample and averaged them. These results are also well consistent with the TG analysis.

The specific capacitance of the electrode could be calculated from the CV curves

according to the following equation:^{S3}

$$C = \left(\int I \, d \, V\right) / \left(vm\Delta V\right) \tag{4}$$

Where *C* is the specific capacitance (F g⁻¹) based on the mass of the electroactive material (NiC₂O₄), *I* is the response current (A), *V* is the applied potential, ΔV is the potential window (V), *v* is the potential scan rate (mV s⁻¹), and *m* is the mass of the electroactive material on the electrode (g).

The specific capacitance can also be calculated from the galvanostatic charge/discharge profiles by the following formula:^{S4}

$$C = I\Delta t/m\Delta V \tag{5}$$

Where *I* is the discharge current (A) and Δt is the discharge time (s).

The specific capacitance (C), energy density (E) and power density (P) of the NON@NF//AC asymmetric supercapacitor were calculated using the following equations:^{S4}

$$C = I\Delta t/m\Delta V \tag{6}$$

$$E = 0.5C\Delta V^2 \tag{7}$$

$$P = \frac{E}{\Delta t} \tag{8}$$

Where *m* is the total mass of the electroactive materials (NiC₂O₄ and AC) of the supercapacitor.

Supplementary Figures (Fig. S1-S11)

Supplementary Videos (Video S1-S3)



Fig. S1. Low-magnification SEM image of the nickel foam coated with nickel oxalate nanostructures, showing its instinct 3D network.



Fig. S2. SEM images of the anodized nickel foam (NON@NF). Some nickel oxalate blocks gather together to form clusters, there exist channels or cracks between clusters. One cluster is highlighted by solid red circles.



Fig. S3. High-magnification TEM image of the NON@NF electrode, clearly showing that nickel oxalate hydrate in-situ grew on the skeleton surface of nickel foam.



Fig. S4. XRD pattern of the anodized NON@NF electrode.



Fig. S5. Typical CV curves of the NON@NF and nickel foam electrodes at 100 mV s⁻¹ in the 6M KOH solution.



Fig. S6. CV curves of the NON@NF electrode in the 6 M KOH solution at a scan rate of 50 mV s⁻¹.



Fig. S7. SEM images of the NON@NF electrode after CV treatment of 2000 cycles at a scan rate of 50 mV s⁻¹.



Fig. S8. Typical CV curves of the NON@NF and AC electrodes in the 6M KOH solution.



Fig. S9. Ragone plot related to energy and power densities of the NON@NF//AC asymmetric supercapacitor compared with other data reported in the literature [S5-S8].



Fig. S10. Photographs of the NON@NF//AC asymmetric supercapacitor and the devices used in the demonstration experiments. (a) Photograph of the NON@NF (left) and AC (right) electrodes (5 cm×5 cm). (b) Photograph of a NON@NF//AC asymmetric supercapacitor. (c) Photograph of a series of NON@NF//AC asymmetric supercapacitors. (d) Photograph showing the connection between the supercapacitors and the mobile phone where the battery was removed. (e) Photograph of the 'CHINA' LED displayer which is composed of 48 LEDs. (f) Photograph of the 'SDU' LED displayer which is composed of 32 LEDs.



Fig. S11. CV curves of the nickel oxalate and nickel oxalate hydrate electrodes at 50 mV s⁻¹ in the 6M KOH solution.

Supplementary Videos:

Video S1: Video showing that three supercapacitors can power a mobile phone, including its starting up and running for several minutes.

Video S2: Video showing that five supercapacitors in series can light up a 'CHINA' LED displayer.

Video S3: Video showing that four supercapacitors in series can light up a 'SDU' LED displayer.

Supporting References:

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