Supporting Information

Top-Down Synthesis of Sequentially Controlled Architectures for the Honeycomb-Layered Na$_3$Ni$_2$BiO$_6$ Towards High-Voltage and Superior Performance Sodium-ion Batteries

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Part I: Experimental details, Calculations & Discussions

S-1: Sample synthesis

S-1-1: Controllable synthesis of diverse architectures via a top-down process

The top precursors with 1D hybrid fiber structure were prepared by the electrospinning technique. Two kinds of hybrid polymer precursors, i.e. the modified and the primary precursors, are prepared. Both kinds of hybrid polymer precursors were the mixtures of the PAN polymer and the inorganic composites.

i) Firstly, two kinds of the inorganic composites, i.e. the primary and the modified inorganic composites, were prepared.

For the preparation of the primary inorganic composite, stoichiometric amount of the NaCH$_3$COO·3H$_2$O, Bi(NO$_3$)$_3$·5H$_2$O and Ni(NO$_3$)$_2$·H$_2$O in 3: 1: 2 molar proportion were dissolved in the diluted nitrate acid. The additional 3% excess NaCH$_3$COO·3H$_2$O was employed to compensate the possible sodium volatilization in high temperature. The mixture was stirred at 80 °C and followed by drying in an oven over to achieve the primary inorganic precursor.

For the preparation of the modified inorganic composite, stoichiometric amount of the NaCH$_3$COO·3H$_2$O, Bi(NO$_3$)$_3$·5H$_2$O and Ni(NO$_3$)$_2$·H$_2$O in 3: 1: 2 molar proportion were dissolved in the diluted nitrate acid. The additional 3% excess NaCH$_3$COO·3H$_2$O was employed to compensate the possible sodium volatilization in high temperature. Then the additional citric acid and nitric acid were separately added to the above solution. The molar ratio of citric acid to the metal ions is about 0.95~1.05. The mixture was
stirred at 80 °C and followed by drying in an oven over to achieve the modified inorganic precursor.

ii) Next, two kinds of the hybrid polymer fibers were prepared. The polyacrylonitrile (PAN, average $M_w=150000$) was dissolved in N, N-dimethylformamide (DMF) at room temperature to form the PAN polymer solution. Then, the inorganic composite, i.e. the primary inorganic or the modified inorganic composites, were separately added to the PAN solution to form two kinds of mixtures. The mass ratio of the PAN polymer to the inorganic component is about 1: 1.55~1.65. The mixtures were stirring under inert atmosphere to form the viscous solutions. Then they were transferred into a syringe connected to a stainless steel needle. A high potential of 12 kV was applied on the needle relative to a flat plate positioned at about 10 cm from the tip of the needle. The flow rate of the mixture was controlled using a syringe pump at 1 mL h⁻¹. After electrospinning, the collected films were peeled off from the collector and the top precursors were achieved.

The hybrid fiber composed of the PAN polymer and primary inorganic composite was denoted as the primary hybrid fiber precursor; while that composed of the PAN polymer and the modified inorganic composite was denoted as the modified hybrid fiber precursor.

iii) Both of the “top” precursors were subjected to high-temperature calcination to fabricate the “down” products. The primary precursor was calcined firstly at 280 °C for 2 hours then at 750 °C for 8 hours at a slow heating rate of 1 °C min⁻¹ to prepare the product III. As the high heating rate of 10 °C min⁻¹ is used, the product IV was obtained. The same calcination process was applied for the modified precursor with two different
heating rates. When the slow heating rate of 1 °C min\(^{-1}\) is used, the product II was obtained. As the high heating rate of 10 °C min\(^{-1}\) is used, the product I was obtained.

S-1-2: Synthesis of solid-state reference sample

The reference sample is prepared by a solid state method. Stoichiometric amount of Na\(_2\)CO\(_3\), NaBiO\(_3\) and NiO were mixed together in 1: 2: 1 molar proportion and finely grounded using a mortar. The additional 3% excess Na\(_2\)CO\(_3\) was employed to compensate the possible sodium volatilization in high temperature. The mixture was calcinated at 700 °C for 8 hours in oxygen atmosphere and then cooled to room temperature. The product was grinded and recalcinated at 750 °C for 12 hours at oxygen atmosphere.

S-1-3: Synthesis of ball-milling reference sample

The solid-state reference sample was ball-milled by a planetary ball mill (QM-1SP04, Nanjing, China). The milling was performed for 20 hours at a rotation speed of 500 rpm. A ball-to-powder ratio of 20:1 was used.

S-2: Materials characterizations

Powder X-ray diffraction (XRD, Bruker D8/Germany) using Cu K\(_\alpha\) radiation was employed to identify the crystalline phase of the material. The experiment was performed by using step mode with a fixed time of 3 s and a step size of 0.02°. The XRD pattern was refined by using the Rietveld method. The morphology was observed with a scanning electron microscope (SEM, HITACHIS-4700) and a transmission electron microscope (TEM, JEOS-2010 PHILIPS). The element distribution of the sample was confirmed by energy dispersive X-ray detector (EDX). Thermogravimetric analysis
(TGA, NETZSCH STA 449C) in flowing oxygen was used to monitor the combustion process of the gel precursor. Nitrogen adsorption-desorption isotherms were measured using a Micromeritics ASAP 2010. Sample preparation included degassing at 523 K for 12 h in a vacuum of 10^-6 Torr. Specific surface area and pore size distribution were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method, respectively.

S-3: Electrochemical measurements

The electrochemical characteristics were measured in coin cells. The prepared products were mixed with carbon black and polyvinylidene fluoride (PVDF) in a weight ratio of 80:10:10. The coin cells were assembled in an argon filled glove box. The Na foil was employed as counter and reference electrode and 1 mol·L^-1 NaClO_4 dissolved in propylene carbonate (PC) was used as electrolyte. Galvanostatic charge/discharge tests were performed in the potential range of 2.0~4.0 V (vs. Na/Na^+) at ambient temperature on a Land battery testing system (Wuhan, China). For the galvanostatic intermittent titration technique (GITT), a constant current of 0.05 C was applied for 10 min and then interrupted to open circuit condition for 60 min. This process was repeated until the cathode potential exceeded the cut-off potential. EIS measurements were conducted using a Zivelab electrochemical workstation, and the applied frequency range is 100k~0.5 mHz.

S-4: Calculation methods

S-4-1: Calculation of the electrochemical parameters

(1) specific capacity (Q)

The specific capacity is calculated based on the galvanostatic charge/discharge curves,

\[ Q = \frac{I \times \Delta t}{m} \]  \hspace{1cm} (1)
Where $Q$ is the specific capacity, $Δt$ is the discharge time, $I$ is the discharge current, $m$ is the mass of the active material in the single electrode.

(2) Cycling retention

The cycling retention is calculated based on the following equation,

$$CR = \frac{Q_{\text{after}}}{Q_{\text{before}}}$$  \hspace{1cm} (2)

Where $CR$ is the capacitance retentions after cycling, $Q_{\text{after}}$ is the capacity of the electrode after cycling, $Q_{\text{before}}$ is the capacity of the electrode before cycling,

S-4-2: Calculation of the sodium diffusion coefficient based on the GITT results

The ion intercalation coefficients of all the samples are investigated based on the GITT measurements. According to the Fick’s second law of diffusion, $D_{Na}$ can be calculated from the following equation:

$$D_{Na} = \frac{4}{\pi} \left( \frac{m_B V_m}{M_B A} \right)^2 \frac{\Delta E_s}{\Delta E_s} \frac{1}{\tau} \left( \frac{\Delta E_s}{\Delta V_i} \right)^2 \left( \tau \ll L^2 / D_{Na} \right) \hspace{1cm} (3)$$

where $D_{Na}$ (cm$^2$s$^{-1}$) is the ion diffusion coefficient; $m_B$, $M_B$, and $V_m$ are the mass, molecular weight and molar volume of the electrode material, respectively; $A$ is the interfacial area between electrode and electrolyte; $\tau$ is duration of the current pulse. As the relationship between $E$ and $\tau^{1/2}$ is linear in this study, the equation (1) can be simplified as following:

$$D_{Na} = \frac{4}{\pi \tau} \left( \frac{m_B V_m}{M_B A} \right)^2 \left( \frac{\Delta E_s}{\Delta E_i} \right)^2 \hspace{1cm} (4)$$
Part II: Supporting Figures

Figure S1 EDX element mapping results of the primary hybrid fiber.

Figure S2 EDX element mapping results of the modified hybrid fiber.

Figure S3 Differential capacity curves of the all the products at 0.5 C rate.
### Part III: Supporting Tables

Table S1 Refinement results of the XRD patterns of product II.

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<th>( R_{wp} ) : 9.76</th>
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<td>( b ) : 9.3285(6)</td>
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<td>( atom )</td>
<td>( site )</td>
<td>( x )</td>
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<td>8j</td>
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<td>O2</td>
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