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Octrooi Centrum
Nederland

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2036091

12 A OCTROOIAANVRAAG

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Aanvraagnummer: 2036091

51

Int. Cl.:
H01M 4/04 (2024.01)

22

Aanvraag ingediend: 21 oktober 2023

62

30

Voorrang:
31 juli 2023 CN 202310951462.0

41

Aanvraag ingeschreven:
10 februari 2025

43

Aanvraag gepubliceerd:
11 februari 2025

71

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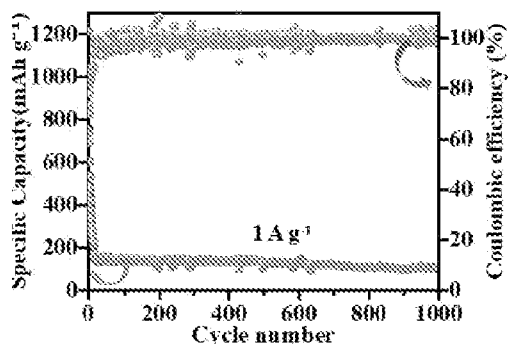
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Self-standing Nitrogen-doped Hollow Biochar Bi/SnO₂@N-HCFs Composite Material, Preparation Method and Application Thereof

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A self-standing nitrogen-doped (N-doped) hollow biochar Bi/SnO₂@N-HCFs composite material, and a preparation method and an application are provided in the present application, belonging to the technical field of energy storage materials for sodium-ion batteries. Firstly, willow catkin fibres are collected and cleaned with deionized water and ethanol for several times and dried. Then, the dried willow catkin fibres are soaked in a precursor solution composed of Sn source and Bi source, then taken out to be placed into a tube furnace, followed by carbonization under N₂ atmosphere, then the self-standing N-doped hollow biochar Bi/SnO₂@N-HCFs composite material is obtained. The willow catkin fibres used as carrier of active substances are abundant with wide range of sources, achieving the objective of recycling waste, and the hollow structure and nano-sized active substances effectively alleviate the volumetric expansion caused by sodium ions during charging and discharging, thus improving the cycle stability of sodium-ion batteries.



Self-standing Nitrogen-doped Hollow Biochar Bi/SnO₂@N-HCFs Composite Material, Preparation Method and Application Thereof

TECHNICAL FIELD

5 The present application belongs to the technical field of sodium-ion battery energy storage materials, and particularly relates to a self-standing nitrogen-doped hollow biochar Bi/SnO₂@N-HCFs composite material, a preparation method and an application thereof.

BACKGROUND

10 Willow catkins flying all around the sky not only cause respiratory diseases, water sources pollution, sewer blockage, but also prone to cause fires. It is therefore a focus of many researchers to deal with willow catkins scientifically and effectively so as to turn waste into resources. Studies have found that willow catkins are small in fibre diameter, with a high degree of hollowness, and also rich in a variety of functional groups, thus enabling the adsorption of a
15 variety of metal ions, and the hollow willow catkin fibres (HCFs) activated by pyrolysis carbonization are applied in the fields of adsorption and catalysis. In recent years, the cost of lithium batteries has risen sharply as a result of lithium resources shortage, making increasing researchers to turn their attention to sodium-ion batteries, which are more abundant in reserves. However, sodium-ion batteries suffer from a number of problems in practical applications, such
20 as the rapid capacity degradation in cyclic application and the low Coulombic efficiency, among other shortcomings. With a view of overcoming the above defects, the researchers identified that the hollow porous structure has the ability not only to effectively alleviate the volumetric expansion caused by the charging and discharging process, but also to enable the electrolyte to fully moisten the active material and accelerate the embedding and detachment of sodium ions,
25 thus improving the electrochemical performance of the sodium-ion batteries.

In this context, various alloy-type materials (e.g., P, Si, Sb, Sn, and Bi) have been studied, and double-based alloy materials (Sn and Bi) are well studied among others for many advantages such as higher capacity, suitable low potential and abundant reserves, etc. Nevertheless, double-based alloy-type materials still prone to enormous volumetric expansion
30 during charging and discharging, resulting in electrode crushing and fracture, which reduces the cycling stability and restricts the development of sodium-ion batteries.

SUMMARY

To achieve the above objectives, the present application discloses a self-standing nitrogen-
35 doped (N-doped) hollow biochar Bi/SnO₂@N-HCFs composite material, and a preparation method and application thereof, so as to solve the problems that the existing double-based alloy materials are prone to volumetric expansion during charging and discharging and poor cycling stability.

In order to achieve the above objectives, the present application adopts the following technical schemes:

the present application discloses a preparation method of a self-standing N-doped hollow biochar Bi/SnO₂@N-HCFs composite material, including following steps:

1) weighing a bismuth source and a tin source, followed by dissolving in a solution consisting of ethanol and ethylene glycol to obtain a mixed solution; then soaking willow catkin fibres in the mixed solution; and

2) oven-drying the willow catkin fibres soaked in step 1) and carbonizing under a N₂ atmosphere to obtain a composite material of the self-standing N-doped hollow biochar

Bi/SnO₂@N-HCFs.

Optionally, in the step 1), the bismuth source is Bi(NO₃)₃•5H₂O, and the tin source is SnCl₄•5H₂O.

Optionally, a volume ratio of ethanol to ethylene glycol is (1 - 4) : 1.

Optionally, before the step 1), the willow catkin fibres are washed and dried.

Optionally, in the step 1), a molar ratio of the bismuth source to the tin source is 1: (1 - 2).

Optionally, in the step 1), a soaking duration is 12 - 24 hours (h).

Optionally, in step 2), oven-drying conditions are: drying at 60 - 100 degrees Celsius (°C) for 12 - 24 h.

Optionally, in the step 2), carbonizing conditions are: heating to 500 - 900°C at a rate of 2-5 °C/min under the N₂ atmosphere.

The present application also discloses a self-standing N-doped hollow biochar Bi/SnO₂@N-HCFs composite material prepared by the preparation method.

The present application also discloses an application of the self-standing N-doped hollow biochar Bi/SnO₂@N-HCFs composite material in preparing sodium-ion batteries.

Compared with the prior art, the present application has the following beneficial effects:

in the self-standing N-doped hollow biochar Bi/SnO₂@N-HCFs composite material and the preparation method provided by the present application, the willow catkin fibres are used as a substrate to prepare Bi/SnO₂@N-HCFs composite material after being soaked in the mixed solution composed of the Bi source and the Sn source and after being calcined; in the preparation method, the adopted carbon source of willow catkin fibres has a wide range of sources, which achieves not only the purpose of resourceful utilization of waste, but also ensures environmental protection and safety, and the hollow carbon fibre structure formed by activation effectively promotes the contact area between the electrolyte and the active substance, alleviates the volumetric expansion of sodium ions caused by the process of charging and discharging, accelerates the chemical reaction in this process, and enhances the cyclic stability of the sodium-ion batteries; the preparation method conforms to the strategy of green and sustainable development, and enjoys a promising prospect for application; the process of soaking and calcination enables the substantially nanosizing of Bi and SnO₂ and

alleviates the volumetric expansion of the materials during the charging and discharging process, and makes Bi and SnO₂ uniformly distributed and prevents agglomeration through the loading of willow catkin fibres, thus allowing the acceleration of the sodium ions transport and further improving the electrochemical reaction between the active substances and the electrolyte; the hollow porous structure and excellent electrical conductivity of carbonized willow catkin carbon fibres are utilized to mitigate the volumetric expansion and conductivity of SnO₂, while the doping of Bi elements can effectively increase the specific capacity of sodium-ion batteries, thus enhancing the electrochemical performance of sodium-ion batteries; in the preparation method of the self-standing N-doped hollow biochar Bi/SnO₂@N-HCFs composite material, the traditional coating process is removed by the self-standing structure, creating favourable conditions for large-scale preparation, and enabling the mitigation of the volumetric expansion and conductivity of SnO₂ by utilizing the hollow and porous structure of the carbonized willow catkin carbon fibres and the excellent electrical conductivity; meanwhile, the specific capacity of sodium-ion batteries is effectively increased by the doping of the Bi element, thus enhancing the electrochemical performance of the sodium-ion batteries.

BRIEF DESCRIPTION OF THE FIGURES

Fig. 1 shows a schematic diagram of volumetric changes in willow catkin fibres before and after undergoing the heating and carbonization treatment, where a is before the heating and carbonization treatment and b is after the heating and carbonization treatment.

Fig. 2 shows an X-ray Diffraction (XRD) diagram and a picture of a self-standing electrode sheet of the N-doped hollow biochar Bi/SnO₂@N-HCFs composite material, where a is the XRD diagram and b is the picture of a tailored self-standing electrode sheet for direct use as anode materials in sodium-ion batteries.

Fig. 3 shows a scanning electron microscope (SEM) image of the N-doped hollow biochar Bi/SnO₂@N-HCFs composite material at different scales, with a being 5 micrometres (μm) and b being 3 μm.

Fig. 4 illustrates an elemental distribution of the N-doped hollow biochar Bi/SnO₂@N-HCFs composite material, where a is an original diagram of energy dispersive spectrometer (EDS) plane-scanning, and b, c, d, e, and f are the elements of Bi, O, C, N, and Sn, respectively.

Fig. 5 is a diagram illustrating electrochemical performance of the N-doped hollow biochar Bi/SnO₂@N-HCFs composite material at a current density of 1 ampere/g (A/g).

DESCRIPTION OF THE INVENTION

In order to enable those skilled in the art to understand the features and effects of the present application, the following is a general description and definition of the terms and phrases mentioned in the specification and the claims. Unless otherwise specified, all technical and

scientific words used in this specification are the ordinary meanings understood by those skilled in the art. In case of conflict, the definitions in this specification shall prevail.

The theories or mechanisms described and disclosed herein, whether right or wrong, should not limit the scope of the present application in any way, that is, the contents of the present application can be implemented without being limited by any particular theory or mechanism.

In this specification, all characteristics defined in the form of numerical range or percentage range, such as numerical value, quantity, content and concentration, are only for simplicity and convenience. Accordingly, the description of numerical range or percentage range shall be deemed to have covered and specifically disclosed all possible sub-ranges and individual values within the range (including integers and fractions).

In this specification, unless otherwise specified, the words "containing", "including", "comprising", "having" or similar words cover the meanings of "consisting of" and "mainly consisting of". For example, "A contains a" covers the meanings of "A contains a and others" and "A only contains a".

In this document, all possible combinations of individual technical features in individual implementations or embodiments are not described for the sake of brevity of description. Therefore, as long as there is no contradiction in the combination of these technical features, each technical feature in each implementation or embodiment may be combined in any combination, and all possible combinations should be considered to be within the scope of the present specification.

The present application provides a preparation method of a preparation method of a self-standing N-doped hollow biochar Bi/SnO₂@N-HCFs composite material, including the following steps:

firstly, collected willow catkin fibres are cleaned by deionized water and ethanol for several times and dried in an oven at 60 - 100 degrees Celsius (°C) for 12 - 24 hours (h); then Bi(NO₃)₃•5H₂O and SnCl₄•5H₂O are weighed and dissolved in a mixed solution composed of ethanol and ethylene glycol, where a molar ratio of Bi(NO₃)₃•5H₂O and SnCl₄•5H₂O is 1 : (1 - 2), and a volume ratio of ethanol and ethylene glycol is (1 - 4) : 1; then the oven-dried willow catkin fibres are soaked in the mixed solution for 12 - 24 h, where a ratio of the dosage of willow catkin fibre to the dosage of the mixed solution is (0.3 - 0.6) g: (30 - 100) ml; the willow catkin fibres are then taken out and dried again in the oven at 60 - 100°C for 12 - 24 h and placed in a tube furnace, followed by heating to 500 - 900°C at 2 - 5 °C/min under N₂ atmosphere and a N₂ flow rate of 40 - 60 standard cubic centimetres per minute (SCCM), and carbonized for 2 h, then the self-standing N-doped hollow biochar Bi/SnO₂@N-HCFs composite material is obtained after the furnace is cooled to a room temperature.

The present application is further described below in connection with specific embodiments. It should be understood that these embodiments are intended only to illustrate the invention and not to limit the scope of the present application. It is also to be understood that after reading what

is taught herein, various alterations or modifications may be made to the invention by those skilled in the art, and that these equivalent forms likewise fall within the scope limited by the claims appended to this application.

The following embodiments adopt apparatus and equipment that are conventional in the art.

5 The experimental methods in the following embodiments, for which no specific conditions are indicated, are generally in accordance with conventional conditions, or in accordance with conditions recommended by the manufacturer. Various raw materials used in the following embodiments, unless otherwise indicated, are commercially available products with specifications conventionally adopted in the art. In the specification of the present application as well as in the
10 following embodiments, where not otherwise indicated, % denotes a percentage by weight, part signifies a weight portion, and ratio stands for a weight ratio.

Embodiment 1

In the present embodiment, the preparation method of the self-standing N-doped hollow
15 biochar Bi/SnO₂@N-HCFs composite material includes the following steps:

Firstly, the collected willow catkin fibres are cleaned by deionized water and ethanol for several times and dried in the oven at 60°C for 18 h; then 0.98 g Bi(NO₃)₃•5H₂O and 0.7 g SnCl₄•5H₂O are weighed and dissolved in the mixed solution composed of ethanol and ethylene glycol, where the ethanol and ethylene glycol are both 20 ml; 0.3 g of the oven-dried willow catkin
20 fibres is soaked in 30 ml of the above mentioned mixed solution for 12 h, and then taken out and dried again in the oven at 60°C for 12 h and placed in the tube furnace, followed by heating to 600°C at 3 °C/min under N₂ atmosphere and a N₂ flow rate of 50 SCCM, and carbonized for 2 h, then the self-standing N-doped hollow biochar Bi/SnO₂@N-HCFs composite material is obtained after the furnace is cooled to the room temperature.

25 With reference to Fig. 1, the volume of willow catkin fibres shrinks after high temperature carbonization, which is mainly caused by the volatilization of part of the organic matter and moisture by high temperature.

As shown in a of Fig. 2, the diffraction peaks are sharp and free of heterogeneous peaks, indicating that this sample has a good crystallinity and purity, and b in Fig. 2 shows that the tailored
30 self-standing electrode sheet can be directly used as an anode material for sodium-ion batteries.

The Fig. 3 shows scanning electron microscope (SEM) images of the composite material, and a hollow tubular structure of the willow catkin fibre is clearly observed.

The Fig. 4 illustrates an elemental distribution of the N-doped hollow biochar Bi/SnO₂@N-HCFs composite material, and all elements are observed to be evenly distributed on the surface
35 of willow catkin fibre.

The prepared self-standing N-doped hollow biochar Bi/SnO₂@N-HCFs composite material is used as a negative electrode and metal sodium is used as a counter electrode, with electrolyte being 1 mole (M) NaPF₆ ethylene glycol dimethyl ether (DME) solution, and diaphragm being a

celgard2400 membrane; the sequence of assembling the battery is negative shell, sodium sheet, diaphragm, negative sheet, gasket, spring sheet and positive shell, and a button battery is assembled in a glove box filled with inert atmosphere (water oxygen value < 0.1 ppm); the assembled button battery is subjected to charge-discharge cycle test, with results as shown in Fig. 5; the charge-discharge cutoff voltage is 0.01 - 2.6 Volts (V), and the charge-discharge current is 1 A/g, suggesting that the sample prepared this time not only has a good specific capacity and cycling stability at a high current of 1 A, but also features a self-standing structure (b in Fig. 2) that eliminates the traditional coating process and enables favourable conditions for large-scale preparation.

Embodiment 2

The preparation method of the self-standing N-doped hollow biochar Bi/SnO₂@N-HCFs composite material includes the following steps:

firstly, the collected willow catkin fibres are cleaned by deionized water and ethanol for several times and dried in the oven at 60°C for 12 h; then 0.48 g Bi(NO₃)₃•5H₂O and 0.35 g SnCl₄•5H₂O are weighed and dissolved in the mixed solution composed of ethanol and ethylene glycol, where the ethanol and ethylene glycol are both 15 ml; 0.3 g of the oven-dried willow catkin fibres is soaked in 30 ml of the above mentioned mixed solution for 12 h, and then taken out and dried again in the oven at 100°C for 12 h and placed in the tube furnace, followed by heating to 500°C at 2 °C/min under N₂ atmosphere and a N₂ flow rate of 40 SCCM, and carbonized for 2 h, then the self-standing N-doped hollow biochar Bi/SnO₂@N-HCFs composite material is obtained after the furnace is cooled to the room temperature.

Embodiment 3

The preparation method of the self-standing N-doped hollow biochar Bi/SnO₂@N-HCFs composite material includes the following steps:

firstly, the collected willow catkin fibres are cleaned by deionized water and ethanol for several times and dried in the oven at 70°C for 12 h; then 1.45 g Bi(NO₃)₃•5H₂O and 1.4 g SnCl₄•5H₂O are weighed and dissolved in the mixed solution composed of ethanol and ethylene glycol, where the ethanol is 40 ml and the ethylene glycol is 20 ml; 0.5 g of the oven-dried willow catkin fibres is soaked in 40 ml of the above mentioned mixed solution for 15 h, and then taken out and dried again in the oven at 60°C for 15 h and placed in the tube furnace, followed by heating to 700°C at 5 °C/min under N₂ atmosphere and a N₂ flow rate of 50 SCCM, and carbonized for 2 h, then the self-standing N-doped hollow biochar Bi/SnO₂@N-HCFs composite material is obtained after the furnace is cooled to the room temperature.

Embodiment 4

The preparation method of the self-standing N-doped hollow biochar Bi/SnO₂@N-HCFs composite material includes the following steps:

5 firstly, the collected willow catkin fibres are cleaned by deionized water and ethanol for several times and dried in the oven at 100°C for 12 h; then 1.45 g Bi(NO₃)₃•5H₂O and 2.1 g SnCl₄•5H₂O are weighed and dissolved in the mixed solution composed of ethanol and ethylene glycol, where the ethanol is 60 ml and the ethylene glycol is 20 ml; 0.5 g of the oven-dried willow catkin fibres is soaked in 70 ml of the above mentioned mixed solution for 24 h, and then taken out and dried again in the oven at 80°C for 24 h and placed in the tube furnace, followed by
10 heating to 800°C at 5 °C/min under N₂ atmosphere and a N₂ flow rate of 60 SCCM, and carbonized for 2 h, then the self-standing N-doped hollow biochar Bi/SnO₂@N-HCFs composite material is obtained after the furnace is cooled to the room temperature.

Embodiment 5

15 The preparation method of the self-standing N-doped hollow biochar Bi/SnO₂@N-HCFs composite material includes the following steps:

firstly, the collected willow catkin fibres are cleaned by deionized water and ethanol for several times and dried in the oven at 60°C for 24 h; then 1.94 g Bi(NO₃)₃•5H₂O and 2.8 g SnCl₄•5H₂O are weighed and dissolved in the mixed solution composed of ethanol and ethylene
20 glycol, where the ethanol is 80 ml and the ethylene glycol is 20 ml; 0.5 g of the oven-dried willow catkin fibres is soaked in 100 ml of the above mentioned mixed solution for 20 h, and then taken out and dried again in the oven at 70°C for 16 h and placed in the tube furnace, followed by heating to 900°C at 5 °C/min under N₂ atmosphere and a N₂ flow rate of 50 SCCM, and carbonized for 2 h, then the self-standing N-doped hollow biochar Bi/SnO₂@N-HCFs composite material is
25 obtained after the furnace is cooled to the room temperature.

Embodiment 6

The preparation method of the self-standing N-doped hollow biochar Bi/SnO₂@N-HCFs composite material includes the following steps:

30 firstly, the collected willow catkin fibres are cleaned by deionized water and ethanol for several times and dried in the oven at 80°C for 20 h; then 0.97 g Bi(NO₃)₃•5H₂O and 1.4 g SnCl₄•5H₂O are weighed and dissolved in the mixed solution composed of ethanol and ethylene glycol, where the ethanol is 40 ml and the ethylene glycol is 20 ml; 0.5 g of the oven-dried willow catkin fibres is soaked in 50 ml of the above mentioned mixed solution for 18 h, and then taken
35 out and dried again in the oven at 60°C for 20 h and placed in the tube furnace, followed by heating to 600°C at 3 °C/min under N₂ atmosphere and a N₂ flow rate of 50 SCCM, and carbonized for 2 h, then the self-standing N-doped hollow biochar Bi/SnO₂@N-HCFs composite material is obtained after the furnace is cooled to the room temperature.

The above content is only to illustrate the technical ideas of the present application, which should not be used to limit the scope of protection of the present application, and any changes made on the basis of the technical schemes in accordance with the technical ideas put forward in the present application shall fall within the scope of protection as defined in the claims of the

5 present application.

CONCLUSIES

1. Een werkwijze voor het bereiden van een op zichzelf staand hol composietmateriaal van met stikstof gedoteerde biologische houtskool van Bi/SnO₂@N-holle wilgenkatjesvezels (HCFs), welke werkwijze de volgende stappen omvat:
 - a) het wegen van bismut-uitgangsmateriaal en tin-uitgangsmateriaal, gevolgd door het in een oplossing van ethanol en ethyleenglycol oplossen ter verkrijging van een gemengde oplossing; vervolgens het weken van wilgenkatjesvezels in de gemengde oplossing; en
 - b) het in een oven drogen van de in stap 1) geweeekte wilgenkatjesvezels en carboniseren in een N₂-atmosfeer om een composietmateriaal te verkrijgen van het op zichzelf staande holle composietmateriaal van met stikstof gedoteerde biologische houtskool van Bi/SnO₂@N-HCFs.
2. De werkwijze voor het bereiden van een op zichzelf staand hol composietmateriaal van met stikstof gedoteerde biologische houtskool van Bi/SnO₂@N-HCFs volgens conclusie 1, waarbij in stap 1) het bismut-uitgangsmateriaal Bi(NO₃)₃·5H₂O is, en het tin-uitgangsmateriaal SnCl₄·5H₂O is.
3. De werkwijze voor het bereiden van een op zichzelf staand hol composietmateriaal van met stikstof gedoteerde biologische houtskool van Bi/SnO₂@N-HCFs volgens conclusie 1, waarbij de volumeverhouding van ethanol tot ethyleenglycol (1 - 4) : 1 bedraagt.
4. De werkwijze voor het bereiden van een op zichzelf staand hol composietmateriaal van met stikstof gedoteerde biologische houtskool van Bi/SnO₂@N-HCFs volgens willekeurig welke van de conclusies 1 - 3, waarbij de wilgenkatjesvezels voorafgaand aan stap 1) worden gewassen en gedroogd.
5. De werkwijze voor het bereiden van een op zichzelf staand hol composietmateriaal van met stikstof gedoteerde biologische houtskool van Bi/SnO₂@N-HCFs volgens willekeurig welke van de conclusies 1 - 3, waarbij in stap 1) de molaire verhouding van het bismut-uitgangsmateriaal tot het tin-uitgangsmateriaal 1: (1 - 2) bedraagt.
6. De werkwijze voor het bereiden van een op zichzelf staand hol composietmateriaal van met stikstof gedoteerde biologische houtskool van Bi/SnO₂@N-HCFs volgens willekeurig welke van de conclusies 1 - 3, waarbij de inweekduur in stap 1) van 12 - 24 uur bedraagt.
7. De werkwijze voor het bereiden van een op zichzelf staand hol composietmateriaal van met stikstof gedoteerde biologische houtskool van Bi/SnO₂@N-HCFs volgens willekeurig welke

van de conclusies 1 - 3, waarbij de droogomstandigheden in de oven in stap 2) zijn: gedurende 12 - 24 uur drogen bij 60 - 100°C.

- 5 8. De werkwijze voor het bereiden van een op zichzelf staand hol composietmateriaal van met stikstof gedoteerde biologische houtskool van Bi/SnO₂@N-HCFs volgens willekeurig welke van de conclusies 1 - 3, waarbij carbonisatie-omstandigheden in stap 2) zijn: onder N₂ atmosfeer verhitten tot 500 - 900°C bij een snelheid van 2 - 5°C/min.
- 10 9. Een op zichzelf staand hol composietmateriaal van met stikstof gedoteerde biologische houtskool van Bi/SnO₂@N-HCFs dat is bereid door de werkwijze volgens willekeurige welke van conclusies 1 - 8.
- 15 10. Een toepassing van het op zichzelf staande holle composietmateriaal van met stikstof gedoteerde biologische houtskool van Bi/SnO₂@N-HCFs volgens conclusie 9 bij het vervaardigen van natrium-ion batterijen.

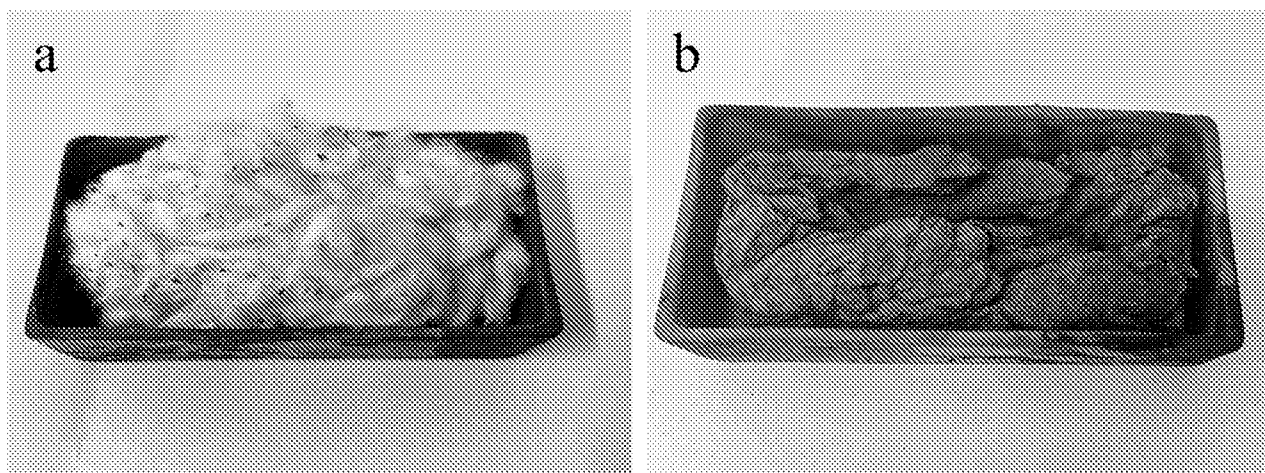


Fig. 1

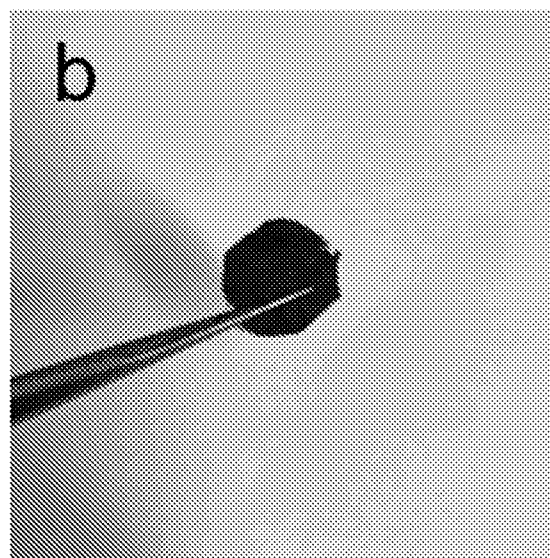
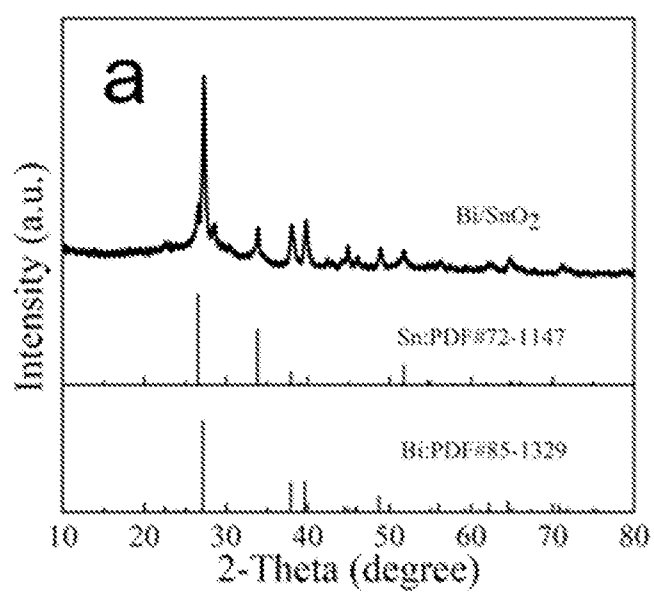


Fig. 2

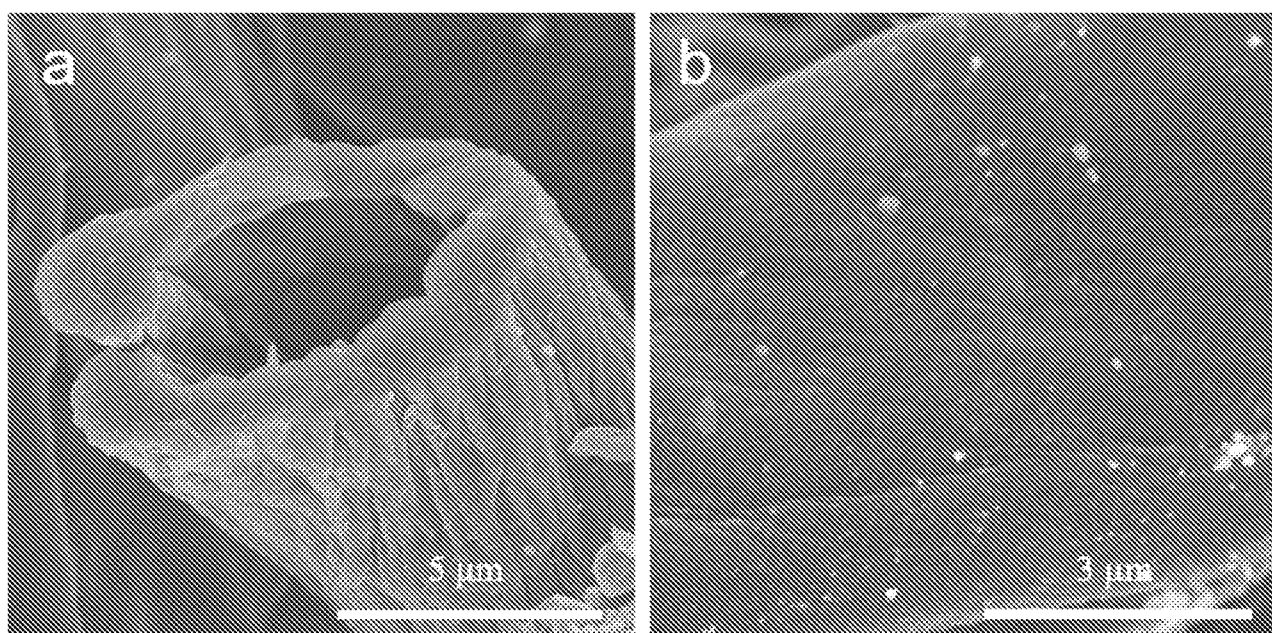


Fig. 3

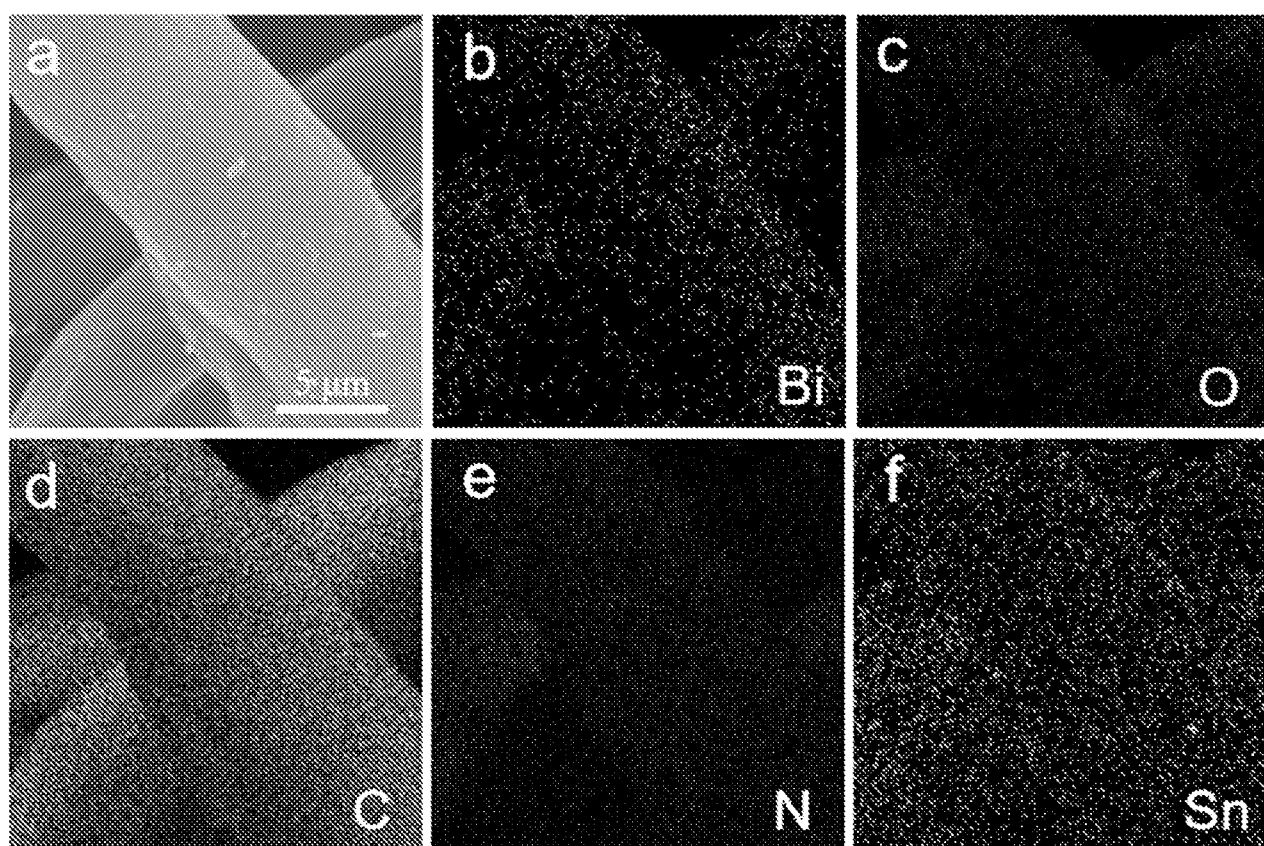


Fig. 4

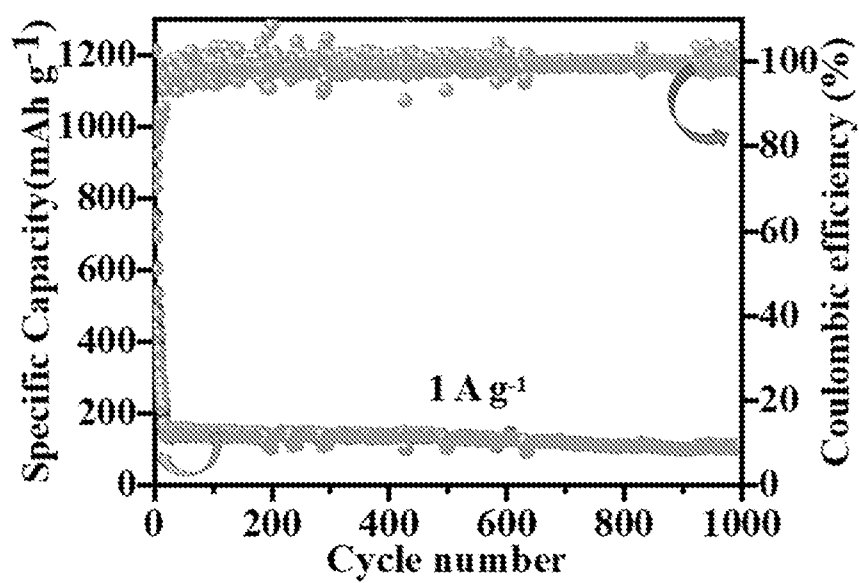


Fig. 5