



View Article Online

View Journal

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: H. Peng, X. Dai, K. Sun, X. Xie, F. Wang, G. Ma and Z. Lei, *New J. Chem.*, 2019, DOI: 10.1039/C9NJ02509J.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/njc

8 9

10

11 12

13

14

96

લી 7

7413/2019 1 1.6102/2019 1

. ⊋1

Agendaryourgenergy with the second se

38

<u>3</u>9

18<mark>14</mark>0

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

Journal Name

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/



Hui Peng,^{‡*a} Xiuwen Dai,^{‡a} Kanjun Sun,^b Xuan Xie,^a Fei Wang,^a Guofu Ma,^{*a} and Ziqiang Lei^a

To achieve the high energy density of supercapacitor and maintain their intrinsic high power density, it usually extend the operating voltage by assembling high specific capacitance electrode materials into an asymmetric supercapacitor (ASC) device. Herein, an ASC is assembled based on three-dimensional (3D) interconnected porous carbon framework (PRPC-1K) as negative electrode and 3D sphere-like nickel nitride (Ni₃N) nanosheets as positive electrode in aqueous KOH electrolyte. The PRPC-1K is prepared by a simple activation process with biomass poplar root as carbon precursor, and the Ni₃N nanosheets are successfully synthesized via a simple low temperature hydrothermal and further urea-assisted nitridation process. In virtue of their unique structures and high capacitive performance, the Ni₃N//PRPC-1K ASC assembled based on these two materials achieved a high energy density of 30.9 Wh kg⁻¹ at a high power density of 412 W kg⁻¹, and acceptable electrochemical cycling stability with 81% retention after 5000 cycles.

1. Introduction

Supercapacitors, because of its superior power density, long lifetime and short charging time, have attracted widely attention as one of the most promising devices for electrical energy storage.^[1,2] However, it has been recently discovered that the supercapacitors have serious deficiencies of low energy density (E) and high cost. According to the equation of $E = 1/2 \text{ CV}^2$, the device capacitance (C) and operating voltage (V) are the determinants of high energy density in supercapacitors. The device capacitance of a supercapacitor mainly depends on the inherent properties of electrode materials, including special micromorphology (e.g., 2D nanosheets and 3D network), good electronic conductivity, high cycle stabilities, and existence of multiple redox status and so on. In addition, designing the aqueous asymmetric supercapacitor (ASC) is an effective way for extending the operating voltage, since it could utilize the working potential of two different electrodes in the same aqueous electrolytes.^[2-4] ASC is usually assembled based on carbon-based capacitive-type (high power output) negative

^aKey Laboratory of Eco-Environment-Related Polymer Materials of Ministry of Education, Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China.

^bCollege of Chemistry and Environmental Science, Lanzhou City University, Lanzhou 730070, China.

- DOI: 10.1039/x0xx00000x
- 59 60

materials and faradaic-type (high energy output) positive materials, thus the high power density and high energy density of the device can be realized simultaneously.

Carbon materials, ranging from activated carbon,^[5,6] carbon nanotubes,^[7] carbon aerogel,^[8] graphene,^[9,10] and biomass derived porous carbons,[11-16] have attracted the attention of researchers due to their high specific surface area, high electronic conductivity, good chemical stability and long cycling life.[17-19] Among those carbon materials, biomass derived porous carbons are the most potential candidates for supercapacitor electrode materials on account of their easy preparation, renewability, low cost and eco-friendliness.^[1,5,9] To fabricate the biomass-based carbon materials with a developed porous structure and large specific surface area, the activators such as KOH, ZnCl₂, etc., are usually employed because they can generally create abundant mesopore structures in biomass carbon materials.^[11] Especially, the 3D interconnected porous carbon framework can provide continuous conductive network for electron transport and a fully interconnected hierarchical porosity for ion transport.^[20] This inspires us to study the 3D interconnected porous carbon nanomaterials made from biomass-based carbon precursor with regular pore structure naturally as advanced electrode materials for energy storage applications. We expect that the poplar root with abundant porous structure naturally from carbon framework structures will likely reveal some interesting features and properties.

Recently, transition metal nitrides have attracted increasing attention and are more and more widely for used as lithium ion battery and supercapacitor electrodes on account of their low



Corresponding authors: penghui@nwnu.edu.cn (H. Peng), magf@nwnu.edu.cn (G. Ma).

[‡]These authors contributed equally to this work. They should thus be considered co-first authors.

ARTICLE

cost, superior energy densities and corrosion resistance.^[21-24] However, the specific capacitance of most metal nitrides is relatively small due to the high electrical resistance, and volume changes caused by corresponding reactions.^[25] Nickel compounds are widely studied in faradaic-type materials because of their high theoretical capacity, low cost, and reversible redox reaction. Similarly, nickel nitride has also been developed as electrode materials for supercapacitors. For instance, Yu et al. reported the tiny Ni₃N nanoparticles firmly fastened to graphene sheets and used as electrodes in supercapacitors, which had high specific capacitance of 2087.5 F g⁻¹ at 1 A g^{-1.[26]} Prasad et al. prepared the 3D nanorhombus Ni₃N thin films and used in supercapacitor electrodes, which the specific capacitance is 285 F g⁻¹ at a scan rate of 10 mV s⁻ ^{1.[27]} We should note that the synthesis of nickel nitride materials generally contains complicated steps and strenuous.

To achieve the high energy density of supercapacitor and maintain their intrinsic high power density, here, a novel asymmetric supercapacitor is designed by utilizing 3D interconnected framework of porous carbon (PRPC-1K) as negative electrodes and 3D sphere-like nickel nitride (Ni₃N) nanosheets as positive electrodes. The 3D sphere-like Ni₃N nanosheets was synthesized via simple hydrothermal and subsequent nitriding Ni precursors (Ni(OH)₂·0.75H₂O) method, and the PRPC-1K was obtained by a KOH activation method from poplar root as carbon precursor. The assembled asymmetric supercapacitor (Ni₃N//PRPC-1K) achieved a high energy density and electrochemical stabilities. These findings imply that Ni₃N//PRPC-1K ACS may be promising for the future use in the energy storage systems.

2. Experimental section

2.1. Materials

Poplar roots (the poplar grown in Gansu province of China), Nickel (II) chloride hexahydrate (NiCl₂·6H₂O), urea and potassium hydroxide (KOH) are purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All the chemical reagents were in analytical grade and without further purification before used.

2.2 Synthesis of 3D poplar roots-based interconnected porous carbon framework

Briefly, the poplar roots were thoroughly washed with distilled water several times and dried in an oven at 60 °C. The cleaned poplar roots were first pre-carbonized at 500 °C for 2 h at heating rate of 5 °C min⁻¹ in a continuous slowly flowing N₂ atmosphere. Then, the obtained carbon materials were mixed with KOH in different proportions (ratio of KOH/carbon precursor = 1 and 2) in 30 mL distilled water and followed by evaporation step at 60 °C until the formation of solid precursor mixture. Then, the mixture was activated and carbonized at 800 °C for 2 h at heating rate of 5 °C min⁻¹ in a continuous slowly flowing N₂ atmosphere. The resulting mixture product was washed with 2 M HCl solution to remove the inorganic salts and then thoroughly washed with distilled water until the

filtrate became neutrality. Finally, the obtained vicarbon was dried in a vacuum oven at 60 °C for 12 hP. The resulting varbon materials prepared at weight ratio of KOH/carbon precursor of 1 and 2 were named as PRPC-1K and PRPC-2K, respectively.

For comparison purpose, the carbon precursor without mixing KOH was directly carbonized at 800 °C for 2 h at heating rate of 5 °C min⁻¹, and the obtained carbon material is labeled as PRPC.

2.3 Synthesis of 3D sphere -like Ni₃N nanosheets

The Ni₃N nanosheets are successfully synthesized via a simple low temperature hydrothermal and further urea-assisted nitridation process. In a typical synthesis, NiCl₂·6H₂O (0.0285 g, 1.2 mmol) and urea (0.0720 g, 1.5 mmol) were dissolved in distilled water (80 mL). After sonication for at least 30 minutes, the solution was transferred to Teflon-lined stainless steel autoclave (100 mL) and heated to 150 °C for 3 hours in an oven and then cooled it down to room temperature. The nickel compound precursor (Ni(OH)₂·0.75H₂O) was washed with water, ethanol for several times and dried in an oven at 60 °C for 12 h.

To prepare 3D sphere-like Ni₃N nanosheets, the above asprepared Ni(OH)₂·0.75H₂O (100 mg) and urea (2.0 g) were put at two separate porcelain boat and placed into the tube furnace with urea at the upstream side of the furnace. After that, the sample was heated to 350 °C with a heating rate of 2 °C min⁻¹ and then stayed at this temperature for 3 h under static N₂ atmosphere. Finally, the furnace was cooled to room temperature naturally to obtain the Ni₃N material. For comparison purposes, the NiO was synthesized in the same way as that for Ni₃N except without urea and under the air condition.

3. Results and discussion

3.1 The structure of the negative electrode and its electrochemical performance.

Poplar is a very ordinary plant that grows in many parts of the world, the poplar roots (PRs) possess an abundant 3D porous structure naturally. However, those PRs usually have no commercial value and will cause the environment pressure. In order to make the PRs have high added value, here, 3D interconnected PRs-based porous carbon (PRPC-1K) was prepared by pyrolysis of PRs using KOH as activating agent.

Fig. 1a illustrates the preparation procedure for PRPC-1K. Briefly, the low-cost and abundant natural poplar roots were cut into pieces and pre-carbonized under a nitrogen atmosphere. Then, the obtained pre-carbonized carbon materials were mixed with KOH and further activated and carbonized at 800 °C for 2 h under a nitrogen atmosphere to prepare the 3D hierarchical PRPC-1K with numerous nanopores. Fig. 1b shows the SEM images of PRPC direct carbonized without KOH activation step, where the cross-linked 3D honeycomb porous morphology is clearly observed. Moreover, it can be seen that multistage macroporous and hole channels (30-60 mm) are surrounded by numerous small hole channels (5-10 mm), indicating the coexist of numerous macroporous and mesopores structure in

3

4

5

6

7

8

9

10

11

12

13

14

%¦6 ?ी7

21

.22 1923

<u>-</u> 24

දු0

A36 137

38

39

÷<u>∄</u>0

42 43

> 44 45

> 46

47

48

49 50

51

52

53

54

55

56

57

58

59 60

Journal Name

PRPC. Fig. 1c and 1d show the SEM images of PRPC-1K and PRPC-2K, respectively, showing that the unique honeycomb porous structure of poplar roots is still retained after activation by different levels of KOH. Fig. 1e and 1f show the crosssectional view and magnified top-view SEM image of PRPC-1K, respectively. From the cross-sectional view, we can observe that the channels are aligned straight through from top to bottom and have many mesopores on them. From the magnified top-view SEM image, we can see the pore structure around the macroporous more clearly. TEM image (Fig. 1g) of the PRPC-1K further confirms its amorphous feature. It is suggesting that many mesopores and macropores were created during the carbonization process.



Fig. 1 (a) Scheme of the scalable preparation for PRPC-1K; SEM images of the (b) PRPC; (c) PRPC-1K; (d) PRPC-2K; (e) cross-sectional view of PRPC-1K; (f) top-view SEM images of PRPC-1K; (g) TEM image of the PRPC-1K.

Nitrogen adsorption-desorption isotherms of PRPC, PRPC-1K and PRPC-2K illustrate the variety of porosity by KOH activation, the results are shown in **Fig. 2a**. All of the samples exhibit the type IV isotherm, showing they have a significant amount of mesopores. It can be seen that the adsorbed volume of PRPC-1K and PRPC-2K are remarkable larger than that of PRPC material, indicating carbonized poplar roots by KOH activation can improve porosity of carbon. In addition, the PRPC-1K has unambiguous hysteresis loop at the relative

pressure of 0.1-0.9 P/P₀, suggesting the presence inf abundant mesoporous and macroporous structure?.01719e10aetanee028PPT surface area and pore structure parameters of the as-prepared PRPC, PRPC-1K, and PRPC-2K samples are shown in Table S1. The specific surface area of the PRPC, PRPC-1K and PRPC-2K materials measured by the Brunauer-Emmett-Teller (BET) method are 17.8, 710.7 and 268.7 m² g⁻¹, respectively. However, the specific surface area and pore volume of PRPC-2K are lower than that of PRPC-1K when increase the weight ratio of KOH/carbon precursor from 1 to 2, which may be due to the collapse of pores caused by the excessive activation.^[1,13] Fig. 2b shows the corresponding pore size distributions of PRPC, PRPC-1K and PRPC-2K samples. It is found that the pore size of PRPC, PRPC-1K and PRPC-2K is mainly centered in the range of 2-10 nm, indicating the existence of superior mesoporous structures. The PRPC-1K possesses the high specific surface area and pore volume, which is expected to display outstanding electrochemical performance as a supercapacitor electrode material.

The XRD patterns of PRPC, PRPC-1K and PRPC-2K samples are shown in Fig. 2c. All samples exhibit two typical peaks, corresponding to diffractions of (002) and (100), respectively, indicating typically graphite carbon with an amorphous structure. The (002) diffraction peak of PRPC-1K and PRPC-2K samples are slightly larger than that of PRPC, which may be due to the enhanced graphitic structures in the samples during the activation process.^[1] The Raman spectra of the PRPC, PRPC-1K and PRPC-2K samples were further evaluated their graphite carbon structure (Fig. 2d). All the samples have the typical D-band (about 1350 cm⁻¹) and G-band (about 1610 cm⁻¹) peaks, indicating typically graphite carbon structure.



Fig. 2 (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution curves of PRPC; PRPC-1K and PRPC-2K samples; (c) XRD patterns and (d) Raman spectra of PRPC, PRPC-1K and PRPC-2K samples.

The electrochemical performance of the PRPC, PRPC-1K and PRPC-2K electrodes was firstly studied in a three-electrode system using 2 M KOH aqueous electrolyte. **Fig. 3a** shows the typical cyclic voltammetry (CV) curves of all samples obtained

ARTICLE

Journal Name

1 2 3 4 5 6 7 8 9 10 11 12 13 14 ₩6 લેં7 7413/2019.1 0 0 0 . ⊋1 Notkingkam Trant Knikersky 6 8 2 9 5 5 8 6 736 1717 1717 38 <u>3</u>9 18<mark>14</mark>0 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

ARTICLE

at 50 mV s⁻¹. The CV curves of PRPC-1K and PRPC-2K electrodes show quasi-rectangular shapes, indicating that the rapid electrochemical response and typical and typical electrochemical double layer energy storage characteristics. By comparison, the CV curve of PRPC exhibits a small and irregular triangular shape, indicating low charge response caused by the electrolyte ions difficult to diffuse into the electrode material and thus lead to an ion sieving effect.^[28] PRPC-1K shows the largest electrochemical CV area among the electrodes, meaning it has the maximum specific capacitance.



Fig. 3 (a) CV curves of PRPC, PRPC-1K, andPRPC-2K at 50 mV s⁻¹; (b) GCD curves at 1 A g⁻¹; (c) GCD rate performance PRPC, PRPC-1K, and PRPC-2K; (d) CV curves of PRPC-1K at various sweep rates; (e) GCD curves of PRPC-1K at various current densities; (f) cyclic stability of PRPC-1K at 1 A g⁻¹ for 10,000 cycles.

Fig. 3b shows the galvanostatic charge-discharge (GCD) curves of the PRPC, PRPC-1K and PRPC-2K electrodes at a current density of 0.5 A g⁻¹. Similarly, PRPC-1K shows the longest charge-discharge time with the maximum specific capacitance among the electrodes. Fig. 3c shows the specific capacitance of all the electrodes at various current densities. Specifically, the specific capacitance of PRPC-1K is 170 F g⁻¹ at 0.5 A g⁻¹, which is larger than that of PRPC (96 F g⁻¹) and PRPC-2K (155 F g⁻¹). Moreover, PRPC-1K exhibits high capacitance retention of 68% even at 20 A g⁻¹, which value is also higher than that of PRPC and PRPC-2K. The high specific capacitance of PRPC-1K is results from the hierarchical pore structure with high specific surface area and large mesopore volume matching with the aqueous electrolyte ions.^[29-31] Fig. 3d shows the typical CV curves of PRPC-1K at various scan rates. Fig. 3e shows the charge-discharge profiles of PRPC-1K at different current densities. The cycling performance of PRPC-1K based on a

three-electrode cell is shown in Fig. 3f. The PRPC $_{\rm VIK}$ electrode shows a good capacitance retention $\delta P^{0}89\%03$ after $P^{0}9\%03$ consecutive charge-discharge cycles, indicating that the PRPC-1K electrode has a high electrochemical stability.

3.2 The structure of the positive electrode and its electrochemical performance.

The 3D nickel nitride (Ni₃N) nanosheets were synthesized via a simply hydrothermal reaction and subsequent urea assists nitridation process.



Fig. 4 (a, b) SEM image of Ni₃N nanosheets; (c) TEM image of Ni₃N nanosheets; (d) HRTEM image of the Ni₃N nanosheets.

The mechanism of annealing reaction follows the equations (1 and 2) below:

 $CO(NH_2)_2 \rightarrow NH_3\uparrow + HCNO \text{ (Above 160 °C)}$ (1)

 $6Ni(OH)_2 + 4NH_3 \rightarrow 2Ni_3N + 12H_2O + N_2$ (2)

The SEM image of the Ni precursor (Fig. S1a) is presented 3D sphere-like morphology with intertwined nanosheet subunits. Similarly, the Ni₃N (Fig. 4a-b) and NiO (Fig. S1b) are also showed uniform 3D sphere-like morphology composed of intertwined nanosheets, indicating that the original morphology of nickel precursor was not destroyed by nitridation and oxidation process. The TEM image further confirmed the 3D sphere-like structure of the Ni₃N (Fig. 4c). The lattice spacings were measured to be 0.23 nm corresponding to the (100) planes of the hexagonal Ni₃N (JCPDS Card No. 89-7096) (Fig.4d). The selected-area electron diffraction (SAED) pattern revealed that the Ni₃N is a polycrystal structure with c-axis crystalline orientation (Fig. 4d).

The characterization of crystallographic structure and phase purity of the samples were analyzed by X-ray powder diffraction (XRD) measurement. As shown in Fig. S2a, the diffraction peaks can be well assigned to (Ni(OH)₂·0.75H₂O) (JCPDS No. 38-0715), and Fig. S2b exhibits the counterpart sample of NiO (JCPDS No. 44-1159). As shown in **Fig. 5a**, the diffraction peaks can be mainly assigned to the hexagonal phase of Ni₃N (JCPDS No. 89-7096), which major diffraction peaks at 38.9°, 41.9°, 44.4°, 58.5°, 70.6°, and 78.4° can be

Chemistry Accepted ew Journal

3

4

5

6

7

8

9

10

11

12

13

14

₩6

લી 7

. ⊋1

Mappage Margaret 0

736 1717 1717

38

<u>3</u>9

18<mark>14</mark>0

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60

Journal Name

indexed to the (100), (002), (101), (102), (110), and (103) planes of the Ni₃N phases. Meanwhile, other diffraction peaks at 37.2° and 62.9° are ascribe to the corresponding (101) and (104) planes of the NiO phases (JCPDS No. 44-1159). The above results prove that the material is mainly contain the Ni₃N and some NiO. Element mapping (Fig. S3a) and Energy dispersive spectroscopy (EDS, Fig. S3b) were conducted to analyze the elemental distribution of sample. As shown in Fig. S3b, the signals of Ni and N have been detected with a Ni:N ratio of 3.7, which is higher than the theoretical value of Ni₃N. This deviation may result from the presence of some NiO.



X-ray photoelectron spectroscopy (XPS) was carried out to confirm the existence of this Ni₃N composition. Elements of Ni, O, C, N can be found in the XPS survey spectrum (Fig. 5b). As shown in Fig. 5c, the peaks at 852.6 and 872.3 eV in spectrum of Ni₃N nanosheets are attributed to monovalent Ni $2p^{3/2}$ and Ni $2p^{1/2}$, respectively.^[21,32] The two bands at 860.4 and 879.5 eV are ascribed to the satellite peaks of Ni $2p^{3/2}$ and Ni $2p^{1/2}$, respectively.^[32] The N 1s peak 400.8 eV can be also ascribed to the formation of Ni₃N (Fig. 5d).^[33,35] In addition to these peaks, the peaks at 855.7 and 878.3eV are assigned to NiO, which is generated due to the surface oxidation of Ni₃N in the air.^[32,34,35]

Similarly, the electrochemical performance of the Ni₃N electrode was also first estimated in a three-electrode system with 2 M KOH electrolyte. **Fig. 6a** shows the typical CV curves of Ni₃N at various scan rates in the potential window from -0.1 to 0.65 V. The Ni₃N electrode shows a pair of redox peaks at various scan rates, manifesting it has typical Faradaic behavior. Fig. 6b shows the GCD curves of the Ni₃N electrode at various current densities. All discharge curves are almost symmetrical to the corresponding charge curves, suggesting excellent electrochemical reversible behavior of the electrode material. Fig. 6c shows the typical CV curves of NiO and Ni₃N electrodes are show a pair of redox peaks. However, the electrochemical active area of Ni₃N electrode is larger than that

ARTICLE

of NiO electrode, indicating Ni₃N electrode has a larger specific capacity than NiO electrode. Fig. 6d^D shews³³ the^N specifie capacitance of NiO and Ni₃N electrodes at various current densities. The Ni₃N electrode exhibits a high specific capacity of 92.7 mAh g⁻¹ at a current density of 1 A g⁻¹, which is larger than that of NiO (23.8 mAh g⁻¹ at 1 A g⁻¹). Fig. S4a shows the Nyquist plots of Ni₃N and NiO. Apparently, the Ni₃N possesses the steeper slope of the curves and the smaller diameter of semicircle; it means that Ni₃N has the reduced ion diffusion resistance. As presented in Fig. S4b, the capacity retention of Ni₃N is 80% after charging/discharging cycling for 1500 cycles.



Fig. 6 (a) CV curves of Ni₃N at various scan rates; (b) GCD curves of Ni₃N at various current densities; (c) CV curves of Ni₃N and NiO at 10 mV s⁻¹; (d) GCD rate performance Ni₃N and NiO.

3.3 Electrochemical properties of the as-fabricated asymmetric supercapacitor

In this work, an asymmetric supercapacitors (ASC) have constructed by utilizing the nickel nitride (Ni₃N) nanosheets as the positive electrodes and 3D interconnected framework of porous carbon (PRPC-1K) as negative electrodes. **Fig. 7a** illustrates the conceptual design of Ni₃N//PRPC-1K ASC. Fig. 7b shows the CV curves of Ni₃N (-0.10 to 0.65 V) and PRPC-1K (-1 to 0 V) electrodes with their corresponding voltage windows at a scan rate of 10 mV s⁻¹ for comparison.

According to their CV curves, the potential window of the as-assembled Ni₃N//PRPC-1K ASC can be extended to 1.65 V as the sum of the potential ranges of the positive and negative electrodes. Fig. 7c shows the CV curves of the ASC at various scan rates with one pairs of redox peaks, indicating typical reversible Faradaic behavior. In addition, the almost symmetric GCD curves (Fig. 7d) indicate the ASC has a high coulombic efficiency and electrochemical reversibility. Fig. 7e shows the Ragone plot (energy density vs power density) of the Ni₃N//PRPC-1K ASC device, which value was calculated based on GCD data (Fig. 7d). It is shows that the Ni₃N//PRPC-1K ASC achieved a high energy density of 30.9 Wh kg⁻¹ at a high

Journal Name

ARTICLE

1 2

3

4

5

6

7

8

9

10

power density of 412 W kg⁻¹ and still remains energy density of 15.4 Wh kg⁻¹ at high power density of 4173.7 W kg⁻¹. Furthermore, the maximum energy density of Ni₃N//PRPC-1K ASC is remarkable higher than most symmetrical supercapacitors such as FTMAC-4//FTMAC-4 (18.14 Wh kg-¹) ,^[1] N,S-PCNs1-1//N,S-PCNs1-1 (21.0 Wh kg⁻¹),^[7] BDHSC-1//BDHSC-1 (20 Wh kg⁻¹),^[30] and even higher than that of the previously reported some ASC (Table S2), such as PCNS@VNNP//NiO (16 Wh kg-1),[36] Ni(OH)2 //N-CNS/VNNPs (29.5 Wh kg⁻¹).^[37] Ni/VN//N_{1-x}V_xO₂ (23.3 Wh kg⁻¹) ¹),^[38] Co(OH)₂//VN (22 Wh kg⁻¹),^[39] Ni-Co oxide//AC (12 Wh kg⁻¹).^[40] Electrochemical impedance spectroscopy (EIS) analysis of the Ni₃N//PRPC-1K ASC was shown in Fig. S5, There is apparent semicircle in the high-frequency range and a sloping line in the low-frequency region in the EIS spectrogram, representing low bulk resistance (R_s=1.94), low charge transfer resistance (R_{ct}=1.48) and significant capacitance behavior, respectively. The sloping curve is greater than 45° in low frequency region indicates the ideal capacitive behavior of the device. As presented in Fig. 7f, there is a high capacitance retention of 81% achieved after а long-term charging/discharging cycling for 5000 cycles, showing that the Ni₃N//PRPC-1K ASC displays excellent cycling stability.



Fig. 7 (a) Graphically illustration of the design concept of Ni₃N//PRPC-1K ASC; (b) Comparative CV curves of Ni₃N nanosheets and PRPC-1K, tested in a three-electrode system in 2 M KOH electrolyte at 10 mV s⁻¹; (c) CV curves of Ni₃N//PRPC-1K ASC at different scan rates; (d) GCD curves of Ni₃N//PRPC-1K ASC at different current densities; (e) Ragone plots related to energy and power densities of the Ni₃N//PRPC-1K ASC; (f) Cycling stability of the Ni₃N//PRPC-1K ASC.

4. Conclusions

In summary, 3D interconnected framework of porous carbon (PRPC-1K) with unique honeycomb porous structure and high specific surface area was successfully synthesized by a simple activation process with biomass poplar root as carbon precursor, which is further used as negative electrode material for supercapacitor that exhibits high specific capacitance of 170 F g^{-1} at 0.5 A g^{-1} . In addition, the uniform 3D sphere-like Ni₃N composed of intertwined nanosheets units was prepared via a simple low temperature hydrothermal and further urea-assisted nitridation process, which further used as positive electrode material for supercapacitor that exhibits high specific capacity of 92.7 mAh g⁻¹ at 1 A g⁻¹. In virtue of their unique structures and high capacitive performance, the Ni₃N//PRPC-1K ASC assembled based on these two materials achieved a high energy density of 30.9 Wh kg⁻¹ at a high power density of 412 W kg⁻¹, and acceptable electrochemical cycling stability 81% retention after 5000 cycles. Such hybridized ACS presented here aims at lowing fabricating cost and high specific capacitance materials for practical applications. These findings imply that Ni₃N//PRPC-1K ACS may be promising for the future use in the energy storage systems.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We gratefully acknowledge the National Science Foundation of China (21664012, 21703173, 51863019), the program for Changjiang Scholars and Innovative Research Team in University (IRT15R56), Basic Scientific Research Innovation Team Project of Gansu Province (1606RJIA324), University Scientific Research Innovation Team of Gansu Province (2017C-04).

Notes and references

- X. Tian, H. Ma, Z. Li, S. Yan, L. Ma and F. Yu, J. Power Sources, 2017, 359, 88-96.
- 2 H. Peng, G. Ma, K.Sun, Z. Zhang, J. Li and X. Zhou, J. Power Sources, 2015, 297, 351-358.
- 3 W. He, C. Wang, H. Li, X. Deng, X. Xu, and T. Zhai, *Adv. Energy Mater.*, 2017, **21**, 1-11.
- 4 S. Li, C. Yu, J. Yang, C. Zhao, M. Zhang and H. Huang, *Energy Environ. Sci.*, 2017, **10**, 1958-1965.
- 5 Y. Li, G. Wang, T. Wei, Z. Fan and P.Yan, *Nano Energy*, 2016, **19**, 165-175.
- 6 J. Wang, L. Shen, B. Ding, P. Nie, H. Deng and H. Dou, *RSC. Adv.*, 2014, **4**, 7538-7544.
- 7 J. Kalupson, D. Ma, R. Rajagopalan and K. Adu, J. Mater. Chem., 2014, 118,2943-2952.
- 8 N. Liu, J. Shen and D. Liu, *Micropor Mesopor. Mat.*, 2013, **167**, 176-181.
- 9 Q. Chen, X. Li, X. Zang, Y. Cao, Y. He and P. Li, RSC. Adv., 2014, 68, 36253-36256.
- 10 Z. Xing, B. Wang, W. Gao, C. Pan, JK. Halsted and ES. Chong et al., *Nano Energy*, 2015, **11**, 600-610.

3

4

5

6

7

8

9

10

11

12

13

14

₩6

લી 7

38

<u>3</u>9

18<mark>1</mark>3

42

43

44

45

46

47

48

49

50

51

52

53

Journal Name

View Article Online DOI: 10.1039/C9NJ02509J

Energy Environ. Sci., 2017, 10, 538-545.
12 Y. Huang, J. He, Y. Luan, Y. Jiang, S. Guo and X Zhang, et al., RSC. Adv., 2017, 7, 10385-10390.

11 C. Chen, Y. Zhang, Y. Li, J. Dai, J. Song and Y, Yao et al.,

- 13 N. Guo, M. Li, Y. Wang, X. Sun, F. Wang and R. Yang, *ACS Appl. Mater. Interfaces*, 2016, **8**, 33626-33634.
- 14 Y. Q. Zhao, M. Lu, P. Y. Tao, Y. J. Zhang, X. T. Gong and Z. Yang, et al., *J. Power Sources*, 2016, **307**, 391-400.
- 15 C. Wang, D. Wu, H. Wang, Z. Gao, F. Xu and K. Jiang, J. Mater. Chem. A, 2018, 6, 1244-1254.
- 16 B. Liu, Y. Liu, H. Chen, M. Yang and H. Li, J. Power Sources, 2017, 341, 309-317.
- 17 K. Wang, N. Zhao, S. Lei, R. Yan, X. Tian and J Wang, et al., *Electrochim. Acta*, 2015, 166, 1-11.
- 18 T. Cai, W. Xing, Z. Liu, J. Zeng, Q. Xue and S. Qiao, et al., Carbon, 2015, 86, 235-244.
- 19 X. He, H. Zhang, X. Li, N. Xiao and J. Qiu, *J. Mater. Chem. A*, 2014, **2**, 19633-19640.
- 20 N. Padmanathan, H. Shao and K. Razeeb, ACS Appl. Mater. Interfaces, 2018, 10, 8599-8607.
- 21 K. Xu, P. Chen, X. Li, Y. Tong, H. Ding and X Wu, et *al.*, *J. Am. Chem. Soc.*, 2015, **137**, 4119-4125.
- 22 Andreas Leineweber, Herbert Jacobs and A. Hull§ S, *Inorg. Chem.*, 2001, **40**, 5818-5822.
- 23 M. Chen, J. Qi, D. Guo, H. Lei, W. Zhang and R. Cao, *Chem Commun (Camb).*, 2017, **53**, 9566-9569.
- 24 K. Wang, X. She, S. Chen, H. Liu, D. Li and Y Wang, et al., *J. Mater. Chem. A*, 2018, **6**, 5560-5565.
- 25 M. S. Balogun, W. Qiu and W. Wang, et al., *J. Mater. Chem. A*, 2015, **3**, 1364-1387.
- 26 Y. Yu, W. Gao, Z. Shen, Q. Zheng, H. Wu and X. Wang, et al., *J. Mater. Chem. A*, 2015, **3**, 16633-16641.
- 27 S. Prasad, G. Durai and D Devaraj, et al., *RSC Adv.*, 2018, **8**, 8828-8835.
- 28 P. Hui, G. Ma and K. Sun, et al., *Electrochim. Acta*, 2016, **190**, 862-871.
- 29 H. Feng, H. Hu, H. Dong, Y. Xiao, Y. Cai and B. Lei, et al., J. Power Sources, 2016, 302, 164-173.
- 30 W. Tian, Q. Gao, Y. Tan, K. Yang, L. Zhu and C. Yang, et al., *J. Mater. Chem. A*, 2015, **3**, 5656-5664.
- 31 J. Wang, M. Oschatz, T. Biemelt, L. Borchardt, I Senkovska and M. R. Lohe, et al., *J. Mater. Chem.*, 2012, **22**, 23893-23899.
- 32 S. Nandi, S. K Singh, D. Mullangi, R. Illathvalappil, L. George and C. P. Vinod, et al., *Adv. Energy Mater.*, 2016, 6, 1-11.
- 33 J. Balamurugan, T. Nguyen, and V Aravindan, *Adv. Funct. Mater.*, 2018, **28**, 1804663.
- 34 M. S. Balogun, Y. Zeng, W. Qiu, Y. Luo, A. Onasanya and T. K. Olaniyi, et al., *J. Mater. Chem. A*, 2016, 4, 9844-9849.
- 35 M. Gao, L. Chen, Z. Zhang, X. Sun and S. Zhang, J. Mater. Chem. A, 2018, 6, 833-846.
- 36 Y. Liu, L. Liu, L. Kong, L. Kang and F. Ran, *Electrochim. Acta*, 2016, **211**, 469-477.
- 37 Y. Tan, Y. Liu, Z. Tang, Z. Wang, L. Kong and L Kang, et al., *Sci Rep*, 2018, **8**, 2915.
- 38 C. Ji, J. Bi, S. Wang, X. Zhang and S. Yang, *J. Mater. Chem. A*, 2016, **4**, 2158-2168
- 39 .R. Wang, X. Yan, J. Lang, Z. Zheng and P. Zhang, *J. Mater. Chem. A*, 2014, **2**, 12724-12732.
- 40 C. Tang, Z. Tang and H. Gong, J. Electrochem. Soc., 2012, 159, A651-A662.

Table of contents entry



This journal is C The Royal Society of Chemistry 20xx