Nitrogen-doped porous carbon derived from residuary shaddock peel: a promising and sustainable anode for high energy density asymmetric supercapacitors†

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Exploring high-performance negative electrode materials is one of the great challenges in the development of high-energy density asymmetric supercapacitors (ASCs). Herein, a new kind of high-performance nitrogen-doped nanoporous carbon (NPC) electrode with a large surface area and abundant micropores/mesopores was derived from conveniently available fruit waste (shaddock peel) via a facile pyrolysis process. Electrochemical measurements showed that the as-synthesized NPC electrodes possessed a remarkably large capacitance of 321.7 F g\(^{-1}\) with good rate capability and excellent long-term cycling stability. Such excellent electrochemical performance was achieved by shortening the diffusion distance, increasing the electrode–electrolyte contact area and improving the electron conductivity of the NPC electrode arising from its nanoporous architecture and nitrogen doping. As a prototype, an all-solid-state ASC device based on the NPC negative electrode and a MnO\(_2\) positive electrode achieved an ultrahigh energy density of 82.1 W h kg\(^{-1}\) at a power density of 899 W kg\(^{-1}\), which is considerably larger than most reported carbon based supercapacitor devices.

Introduction

Along with increased concern over the power and energy demands for next-generation energy storage devices, supercapacitors (SCs) have attracted a great deal of attention as a priority candidate for future renewable energy storage for hybrid electric vehicles, and other high power applications due to their long life cycle, high specific power density and highly reversible charge storage process. However, the energy density of SCs is still relatively low, which seriously impedes their future applications. In comparison to conventional SCs, constructing asymmetric supercapacitors (ASCs) is regarded as an effective approach to increase the energy density and make full use of the different potential windows of the positive and negative electrodes to increase the cell voltage, resulting in a higher energy density than symmetric supercapacitors (SSCs). However, for one entire cell, the overall capacitance \(C\) is mainly dominated by the smaller one according to the equation (\(C_{\text{tot}} = C_p^{-1} + C_n^{-1}\)). So far, various high performance pseudocapacitive cathode electrode materials have been investigated for ASCs such as transition metal oxides/hydroxides and conducting polymers, but high-performance negative electrodes have been relatively less investigated. Carbon materials, such as graphene, carbon nanotubes and activated carbon, with good electronic conductivity, excellent electrochemical stability and a large surface area have been commonly used as negative electrodes for ASCs. Unfortunately, these conventional carbon materials are not yet satisfactory for use in ASC anodes because their low specific capacitance (<200 F g\(^{-1}\)) severely limits the overall capacitance of the ASCs. Therefore, to meet the demand for high energy density devices, the capacitance of carbon materials must be boosted further. Moreover, most carbon materials are derived from non-renewable petroleum-based chemical products, which introduces a high cost because of the fossil fuel and environmental crisis looming in the near future.

Recently, carbon materials derived from biomass waste such as banana peel, peanut shell, bamboo chopsticks, Typha orientalis, cotton, olive pit, corn cob, etc. have received extensive attention because of their fascinating structures and wide applications in the oxygen reduction reaction, Li-ion batteries, Na-ion batteries and SCs. For example, Fan et al. reported a kind of densely porous graphene-like carbon (PEC) through hydrothermal treatment and subsequent carbonization of fungus. The PGC electrode exhibited a high specific capacitance of 374 F g\(^{-1}\) at a current density of 0.5 A g\(^{-1}\). Cao et al. fabricated micro/mesoporous interconnected...
structures of 3D carbon with high specific surface areas (2475 m² m⁻¹) through carbonization and activation of rice brans. A maximum specific capacitance of 621.6 F g⁻¹ was obtained at a current density of 1 A g⁻¹. Additionally, a recent report has shown that incorporation of heteroatoms could significantly improve the surface hydrophilicity and conductivity of carbon materials resulting in a higher specific capacitance and rate capability. For instance, Cao et al. reported hierarchical porous nitrogen-doped carbon prepared though activation and graphitization of natural silk in N₂ which presented an improved capacitance (242 F g⁻¹ at 0.1 A g⁻¹) and rate performance (213 and 155 F g⁻¹ at a high current density of 1 and 10 A g⁻¹). However, two challenges remain. First, the majority of hierarchically porous carbons derived from natural bio-materials need chemical activation with alkali to create a meso- and macro-porous structure, which is complicated for practical application. Another disadvantage is that when using ammonia/nitrogen gas as the N source it is difficult to achieve uniform nitrogen doping.

In this work, we report a new kind of nitrogen-doped nanoporous carbon (NPC) derived from shaddock peel without a template or pretreatment process as an advanced negative electrode for high energy density ASCs. Shaddock is a kind of commonly eaten fruit in China and Southeast Asian countries. Most shaddock peel is usually treated as a kind of agricultural waste and directly discarded in a garbage dump, which is harmful for the environment when they decay. Actually, the white flocculent layer in shaddock peel consists of many small cellulose fibers and is an ideal carbon precursor to produce natural porous carbon fibers. Moreover, sponge-like shaddock peel has a strong solution absorption capacity toward metallic and organic solutions, which provides an excellent platform for further optimizing its structure and properties. Herein, we developed a template-free and smart strategy to prepare NPC materials with a high surface area and porosity by a facile soaking process in a melamine solution and post-treatment in Ar. Such a unique N-doped porous carbon can deliver a high specific capacity of 321.7 F g⁻¹ at a current density of 1 A g⁻¹ and excellent cycling ability. When used as a negative electrode for ASCs, a high-performance all solid-state MnO₂//NPC-ASC device with a high energy density of 82.1 kW kg⁻¹ was achieved.

Results and discussion

Fig. 1 illustrates the synthetic process for the NPC electrodes. Firstly, the dried shaddock peel was soaked in a saturated melamine solution for 10 min. Scanning electron microscopy (SEM) images (Fig. S1†) reveal that the dried shaddock peel has a continuous 3D fibrous structure with pore sizes ranging from 100 to 200 μm, which favours melamine adsorption. Secondly, to obtain the NPC, the shaddock peel containing melamine was carbonized at 600–900 °C for 4 h (see ESI† for details).

X-ray diffraction (XRD) patterns of the NPC samples carbonized at different temperatures were collected (Fig. 2a). All of these NPC materials possess two broad peaks located at around 26° and 44°, corresponding to the 002 and 100 planes of the typical turbostratic carbon, demonstrating the presence of graphitic carbon. Particularly, the intensity of the peaks increased with an increased annealing temperature indicating that a high temperature is beneficial for graphitization, which is also confirmed by Raman spectra analysis (Fig. 2b). The peaks located at 1350 cm⁻¹ (D band) and 1590 cm⁻¹ (G band) correspond to defects and graphitic carbon, respectively. The intensity ratio of I_D/I_G is summarized in Fig. S2.† The I_D/I_G ratio obviously increases from 0.63 for NPC-600 to 0.88 for NPC-900, showing that the NPC-900 has the best graphitization. Fig. 2c and d shows the representative SEM images of the NPC-700. The 3D scaffold with a folded surface structure was retained after the carbonization process. It is interesting that such a fiber consisted of several hollow tubes with diameters of 2–10 μm, and a continuous porous network was observed at the hollow tube wall, forming a 3D ordered porous structure. The element mappings clearly revealed that the product contained uniform C, N and O elements (Fig. S3†). The SEM images of NPC-600, NPC-800 and NPC-900 show that the morphology has no obvious change with the different carbonization temperatures, and that the plentiful nanosized holes interconnect the neighboring hollow tubes (Fig. S4†).

In order to investigate the detailed microstructure of the samples, TEM and high-resolution TEM (HRTEM) were carried out. Fig. 2e presents the HRTEM of NPC-700, which clearly reveals that the samples are made up of many micropores and channels (white spots in gray areas) with 2D layered structures, which results in a high surface area. The selected area electron diffraction (SAED) pattern of NPC-700 (Fig. 2e inset) demonstrates the formation of graphitized carbon. In addition, the lattice fringes of the carbon layers (Fig. S5†) increased with the carbonization temperature, indicating the formation of graphitic carbon. The HRTEM micrographs also agreed with the XRD and the Raman results.

To further confirm the percentage of N-incorporation and the elemental composition, the samples were examined by XPS. According to the XPS results, C 1s, O 1s and N 1s can be observed in the survey XPS spectra (Fig. S6a†) and no obvious N 1s signal was found in the untreated PC samples, indicating that the NPC samples were indeed N-doped carbons. The high resolution C 1s spectra of the NPC samples can be fitted with four peaks with binding energies at around 284.5, 285.2, 286.4
and 288.6 eV (Fig. S7†), which were attributed to sp² hybridized C–C, C–N, C–O and C=O, respectively.† The N 1s core level of NPC-700 (Fig. S6d†) was further probed by high-resolution scans, with binding energies around 398.1, 399.1 and 401 eV corresponding to pyridine nitrogen (N-6), pyrrolic/pyridone (N-5), and quaternary nitrogen (N-Q), respectively.† The relative surface concentrations of the carbon species obtained by fitting the C 1s and N 1s core level XPS spectra are listed in Table S1.† It can be seen that NPC-600 displays relatively weak sp² C–C peaks with lower intensity, indicating amorphous carbon. After annealing at 800 °C and 900 °C, the amorphous carbon peaks gradually receded but then the sp² peaks display a sharp shape and increased intensity, suggesting a much higher degree of graphitization at increasing pyrolysis temperature. Moreover, it is known that nitrogen doping of porous carbon can enhance the wettability and produce defects in the graphite layer as well as creating additional active sites for charge storage.⁶,¹⁶ and the quaternary nitrogen (N-Q) in the graphene layers could enhance the electronic conductivity of the carbon materials, which is important for SCs. It is interesting to note that quaternary nitrogen (N-Q) was the dominant nitrogen species in all of the NPC samples in spite of the content of N gradually decreasing with increasing carbonization temperature. The XPS results also confirmed that oxygen-containing functional groups exist on the surface of NPC samples. For NPC-700, the O 1s spectrum can be fitted by two peaks located at around 530.9 eV and 532.6 eV (Fig. S8†), which are attributed to C=O quinone type groups, C–OH phenol groups and/or C–O–C ether groups.⁷ The presence of oxygen functional groups could enable participation in faradaic reactions to provide additional pseudocapacitance and the combined effect between nitrogen and oxygen groups was also beneficial for capacitance-enhancement.⁸ Combined with the XPS results, the possible carbon matrices of NPC with the nitrogen and oxygen functionalities are schematically shown in Fig. 2f.

High specific capacitance of the electrode materials is highly related to the surface area and its porosity. The porous structure of NPC samples were investigated by N₂ adsorption–desorption measurements. Type I isotherms with larger slopes at lower relative pressures could be found for all the NPC samples, which indicated the existence of substantial micropores (<2 nm) and mesopores (2–50 nm).⁴–¹⁴ The pore size distribution curves confirmed that the NPC samples had micro–mesoporous structures (Fig. S9b†). In addition, we also found that the pore volume ratio of micropores vs. mesopores and the specific surface depended on the carbonization temperature. The porous properties of these materials are summarized in Table S2,† and it can be seen that the highest surface area (830 m² g⁻¹) and biggest total pore volume (0.426 cm³ g⁻¹) were obtained for NPC-900, which is comparable to the reported nanoporous carbon materials prepared by templating, or physical or chemical activation methods.⁹ In comparison, NPC-700 possesses less surface area but has the highest fraction of mesopores. For an electrochemical double-layer capacitor, a high surface area with abundant micropores is the basic requirement to enable energy storage at the electrode/electrolyte interface. On the other hand, the presence of the mesopores also plays a critical role in ion transport and electrolyte diffusion.

In order to test the capacitive activities of the NPC electrodes, we measured their electrochemical properties in a 6 M KOH aqueous electrolyte in a three-electrode cell with a saturated calomel electrode (SCE) as the reference electrode and a Pt counter-electrode. For comparison, a porous carbon without nitrogen (PC-700) and Ni foam (NF) electrode was also measured. The cyclic voltammetry (CV) curves of the NPC-700,
PC-700 and NF electrodes collected at 20 mV s\(^{-1}\) are shown in Fig. 3a. Compared with the NPC-700 and PC-700 electrodes, the NF electrode shows much lower current density, indicating that NF has a very weak contribution to the electrochemical capacitance of the NPC and PC electrodes. The NPC-700 electrode shows a much higher current density than that of the PC-700 electrode with a similar mass loading (1 mg cm\(^{-2}\)), indicating that the substantial enhancement of capacitance activity was due to the doped heteroatom (N). The rectangular shape of the CV curves of the NPC-700 electrode is characteristic of a double-layer capacitor (Fig. 3b). Significantly, the CV profiles still retain a rectangular shape even when the scan rate increases from 1 to 100 mV s\(^{-1}\) demonstrating its excellent rate capability and capacitive behavior. Furthermore, in comparison to the CV curves of the NPC-600, NPC-800 and NPC-900, the NPC-700 electrode also exhibits a higher current density (Fig. S10†). The electrochemical performance of the NPC electrodes was further studied by galvanostatic charge–discharge (GCD) measurements. Fig. 3c displays the GCD curves of the NPC-700 electrode collected at various current densities. The maximum discharge time (Fig. S11†) and the minimum IR drop (0.006 V, Fig. S12†) of the NPC-700 electrode reveal its optimal capacitance and superior conductivity. Additionally, compared to the un-doped PC-700 electrode, a longer discharge time and more symmetrical GCD curves are observed for the NPC electrodes, indicating the enhanced capacitance and superior coulombic efficiency of the NPC electrodes. The superior conductivity of the NPC electrodes was further confirmed by electrochemical impedance spectroscopy. As shown in the Nyquist plots (Fig. 3d), all the curves of the NPC electrodes show a rapid upward trend in the low-frequency region, indicating a good capacitive behavior. The corresponding equivalent circuit diagram (Fig. 3d inset; R\(_1\): equivalent series resistance, R\(_2\): charge transfer resistance of NPC, R\(_3\): charge transfer resistance of Ni foam, CPE1: double layer capacitance of NPC, CPE2: double layer capacitance of Ni foam, and Z\(_w\): Warburg impedance) indicates that the charge-transfer resistance (Table S4†) of the NPC-700 electrode could be smaller than the other NPC electrodes. Since the NF electrode has only a weak contribution to the capacitance of the NPC electrodes, its influence can be ignored in this work. Fig. 3e compares the specific capacitance and rate performance of the NPC electrodes (for detailed calculations see the ESIF†). As expected, the highest specific capacitance of 321.7 F g\(^{-1}\) was obtained for the NPC-700 electrode at a current density of 1 A g\(^{-1}\) and good rate capability (51.4% of the initial capacitance at 20 A g\(^{-1}\)), which is higher than the previously reported carbon electrodes derived from other biomass wastes (Table S4†) and other carbon nanostructured electrodes, such as 3D hierarchical porous carbon (318.2 F g\(^{-1}\) at 0.5 A g\(^{-1}\)),\(^ {17}\) graphene hydrogel films (196 F g\(^{-1}\) at 0.5 A g\(^{-1}\)),\(^ {19}\) mesoporous graphene nanoballs (206 F g\(^{-1}\) at 5 mV s\(^{-1}\)),\(^ {20}\) and nitrogen-doped porous carbon nanofibers (202 F g\(^{-1}\) at 1 A g\(^{-1}\)).\(^ {21}\) The significantly enhanced electrochemical performance of the NPC-700 electrode is due to the following reasons: (1) the nitrogen doping and fractional graphitization in porous carbon can enhance the electrical conductivity; (2) the abundant micropores in carbon materials provide a high surface area; (3) the mesopores constructs in the carbon materials facilitate electrolyte accessibility to the microporous area and serve as ion-transport pathways enhancing rapid ion transport. The long-term cycling stability of the NPC-700 electrode was evaluated by a CV test at a high scan rate of 200 mV s\(^{-1}\). As shown in Fig. 3f, there is a slow increase during the first initial 5000 cycles which is probably due to the slow activation process of the electroactive material.

![Fig. 3](image-url)
during the charge/discharge process at a high scan rate. After that, there is no capacity decay observed over 20,000 cycles indicating remarkable electrochemical stability. These results convincingly show that the as-prepared NPC-700 electrode is suitable as a high performance negative electrode for ASCs.

To test the practical application of the NPC-700 as a negative electrode for SC devices, a solid-state ASC device using MnO2 and NPC-700 as the positive and negative electrodes was assembled as shown in Fig. 4a (denoted as MnO2//NPC-ASC). MnO2 was used as the positive electrode because of its outstanding capacitive performance, simple synthesis, and wide voltage window compared to Ni and Co based oxides.\(^\text{22}\)

Hence, MnO2 was uniformly grown on Ni foam using an electrodeposition approach (Fig. S13\(^\text{†}\)). A typical Mn 2p spectrum with a peak binding energy separation (12.2 eV) between Mn 2p\(_{3/2}\) and Mn 2p\(_{1/2}\) confirmed the presence of \(\alpha\)-MnO2 (Fig. S14\(^\text{†}\)). To maximize the performance of the MnO2//NPC-ASC device, the charge between the NPC-700 and MnO2 electrodes should be balanced. The mass ratio of NPC-700 to MnO2 was calculated to be about 1.25 : 1 (for details, see the ESI and Fig. S15\(^\text{†}\)).

Fig. 4b shows the CV curves of the optimized MnO2//NPC-ASC device collected in different voltage windows, the stable voltage window of the device can be extended to 1.8 V. Moreover, the as-prepared devices display outstanding flexibility and mechanical properties under severe bending with almost the same electrochemical performance (Fig. 4c). The GCD curves of the MnO2//NPC-ASC device measured at various current densities exhibit relatively symmetric shapes, indicating its superior capacitive behavior (Fig. S16a\(^\text{†}\)). Fig. 4d presents the calculated specific capacitance (based on the total mass of active material) of the MnO2//NPC-ASC device as a function of current densities based on the GCD curves. The maximum specific capacitance (182.5 F g\(^{-1}\)) of the device was achieved at a current density of 1 A g\(^{-1}\). Additionally, a remarkable rate capacitance was also achieved, with 63% of the initial capacitance retained even when the current density increased to 20 A g\(^{-1}\). In order to investigate the long-term cycling stability of the as-assembled MnO2//NPC-ASC device under distortion, GCD studies were performed in normal, bent and fold states. There was no obvious decrease after 2000 cycles under a normal state as shown in Fig. 4e.

After that, the MnO2//NPC-ASC device was continuously tested for a further 2000 cycles in the bent and fold states, respectively. There was only a 6.6% reduction of the initial capacitance after 6000 cycles, and this loss of capacitance was due to the structural breaking of the Ni foam substrate under drastic distortion.

The energy density (\(E\)) and power density (\(P\)) are two important parameters for evaluating the electrochemical performance of SCs. Fig. 5 compares the energy and power densities of the MnO2//NPC-ASC device to some other recently reported carbon based ASCs. Notably, our MnO2//NPC-ASC device shows an average power density of 900 W kg\(^{-1}\) and a remarkable energy density of 82.1 W h kg\(^{-1}\) at a current density of 1 A g\(^{-1}\). This value is comparable to activated carbon (derived from pollen) based SSCs in ionic liquid electrolytes (88 W h kg\(^{-1}\),\(^\text{24}\) and substantially higher than recently reported carbon based ASC devices,\(^\text{26,25}\) such as Ni(OH)\(_2\)/graphene/porous graphene-ASCs (77.8 W h kg\(^{-1}\)), Ni(OH)\(_2\)/CNT//AC-ASCs (50.6 W h kg\(^{-1}\)), CBP/MnO2//a-CBP-ASCs (63 W h kg\(^{-1}\)), and Co–Ni–S//porous graphene-ASCs (60 W h kg\(^{-1}\)). Significantly, the present energy density is also higher than those reported for oxide based ASCs,\(^\text{28}\) such as MnO2/FGS/F2O2/FGS-ASCs (50.7 W h kg\(^{-1}\)).
W h kg\(^{-1}\)) and RGO/MnO\(_2\)/RGO/MoO\(_3\)-ASCs (42.6 W h kg\(^{-1}\)). To demonstrate the practical application of our as-prepared solid-state MnO\(_2\)/NPC-ASC device, we connected the device units in series to power red light-emitting diodes (LED, 3.5 V). These tandem devices (two or three units in series) exhibited an enhanced voltage window with an unchanging discharge time (Fig. 5b). Here, a LED with a red “SCUT” logo can be powered by three tandem devices (the inset in Fig. 5) for more than 1 min after charging for 20 s at a current density of 10 A g\(^{-1}\).

**Conclusions**

In summary, a scalable and smart approach was developed to transform crude biomass waste (shaddock peel) into N-doped porous carbon without a template or pretreatment process for use as a high performance negative electrode for ASC applications. The as-obtained NPC with a high surface area, high hierarchical porosity and high N-doping exhibited a remarkable capacitance of 321.7 F g\(^{-1}\) at a current density of 1 A g\(^{-1}\), as well as excellent long-term cycling stability without obvious decay of capacitance after 20 000 cycles. Additionally, a high-performance ASC device, based on the as-prepared NPC-700 as the negative electrodes and MnO\(_2\) as the positive electrodes, was also prepared. The MnO\(_2\)/NPC-700 ASC device delivered a maximum energy density of 82.1 W h kg\(^{-1}\) at a current density of 1 A g\(^{-1}\), which is much higher than those of most reported carbon-based ASCs and SSCs. Besides the large energy density, the MnO\(_2\)/NPC-700 ASC device also exhibited excellent stability (only 6.6% capacitance loss after 6000 cycles under bending state). This work shows a promising strategy to synthesize porous carbon as a high-performance negative electrode for high energy density ASCs.

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**Notes and references**


