A novel adenine-based metal organic framework derived nitrogen-doped nanoporous carbon for flexible solid-state supercapacitor

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In this article, we have synthesized a series of nitrogen-doped nanoporous carbon (NPC) from metal organic framework of UiO-66 with different ratios of adenine and 1,4-benzendicarboxylate (H₂BDC) coated on carbon nanotube film (CNTF) to obtain a flexible porous electrode (NPC/CNTF). It is worth noting that the introduction of adenine at different ratios did not change the structure of UiO-66. We also investigated the effect of carbonization temperature from 800 to 1000°C on the electrochemical properties of the NPC. The ratio (H₂BDC:adenine) 9:1 and the NPC carbonized at 900°C (denoted as NPC-1-900) exhibits better electrochemical properties. The results show that NPC-1-900/CNTF electrode exhibits an exceptional areal capacitance of 121.5 mF cm⁻² compared to that of PC-900/CNTF electrode (22.8 mF cm⁻²) at 5 mV s⁻¹ in a three-electrode system, indicating that the incorporation of nitrogen is beneficial to the electrochemical properties of nanoporous carbon. A symmetric flexible solid-state supercapacitor of NPC-1-900/CNTF has also been assembled and tested. Electrochemical data show that the device exhibited superior areal capacitance (43.2 mF cm⁻²) at the scan rate of 5 mV s⁻¹; the volumetric energy density is 57.3 µWh cm⁻³ and the volumetric power density is 2.4 mW cm⁻³ at the current density of 0.5 mA cm⁻² based on poly(vinyl alcohol)/H₃PO₄ gel electrolyte. For practical application, we have also studied the
bending tests of the device, which show that the device exhibits outstanding mechanical stability under different bending angles. Furthermore, the flexible device shows excellent cyclic stability, which can retain 91.5% of the initial capacitance after 2000 cycles.

1. Introduction

During the last few decades, due to the increasingly serious energy shortages and environmental pollution, development of high-efficiency and environmentally friendly energy storage devices with high power output and long life cycles has attracted attention [1,2]. Compared with other energy storage devices, supercapacitors (SCs) have higher power density, excellent cycle stability and high charge–discharge efficiency [3–5]. Especially, with the increasing demand for wearable and foldable electronic products, flexible solid-state supercapacitors (SSCs) have increasingly evolved to meet the large proliferation of consumer electronics [6,7]. However, there are still some drawbacks, such as low energy density and high cost, which limits their practical applications [8]. To circumvent these shortcomings, it is necessary to develop new electrode materials in order to enhance efficiency and practicability [9–11].

Owing to the excellent physical and chemical stability, low cost and available, high specific surface area and good conductivity, porous carbon (PC) materials, such as activated carbon [12], nanoporous carbon [13], carbon nanotubes [14] and graphene [15], are widely used as electrode materials in SCs [16]. Wang et al. showed enhanced electrochemical properties through the synthesis of all-carbon layer-by-layer motif architectures by introducing two-dimensional ordered mesoporous carbons within the interlayer space of two-dimensional nanomaterials [17]. However, pure carbon materials exhibit poor hydrophilicity, which reduced the electrochemical performance of electrode materials [18]. In terms of enhancing the hydrophilicity of PC materials, nitrogen-doped porous carbons (NPC) are considered the most promising because the doped N atoms can provide a pair of electrons, which modify hydrophilicity and wettability of PC materials. Moreover, the doped N atoms can enhance the conductivity and capacitance of PC materials [19,20]. NPC materials have been prepared through a variety of methods, such as pyrolysis of organic precursors and carbonization of nitrogen-containing precursors [21–24]. However, the synthesis methods mentioned above are complex, expensive and the pore size distribution of carbon materials is disordered. It is well known that electrochemical performances of carbon materials are generally decided by their electrical conductivity, pore structures and specific surface area [25]. So, it is necessary to develop new methods and new materials, which can yield carbon materials with high surface area and uniform pore structures.

Lately, metal organic frameworks (MOFs) have been used for electrode materials of SCs due to their tremendous surface area, permanent porosity and controllable structures [26–28]. The surface area of MOFs ranges from 1000 to 10 000 m² g⁻¹, and pore size can be modified as large as 9.8 nm [26]. However, owing to the low conductivity of pristine MOFs, their application is limited in the electrochemical field. Recently, literature reports a large number of methods to improve their electrochemical capability. For example, Saraf et al. designed a novel Cu-MOF/rGO hybrid as supercapacitor electrode material and electrochemical nitrite sensor [29]. It is worth noting that MOFs are outstanding precursors and templates for the preparation of PC materials with high porosity, particularly for hierarchical nanostructures [30,31]. Compared with traditional method, MOF-derived PC materials show some distinct advantages in terms of simple preparation and precise control over porous structure. Up to now, there are lots of research developments on the preparation of MOF-derived PC materials for supercapacitor application [30–32]. For the first time, Xu et al. demonstrated the application of MOF-5 as a sacrificial template for synthesis of porous carbons; the surface area of porous carbon is 2872 m² g⁻¹ and the specific capacitance is 258 F g⁻¹ at the current density of 5 mV s⁻¹ [33]. Moreover, due to the abundant nitrogen in the organic ligands, NPC materials can be easily synthesized through direct pyrolysis of nitrogen-containing MOFs. Nune et al. used IRMOF-3 as self-sacrificial template to prepare NPC materials; comparing with the nitrogen-free PC materials (the specific capacitance is 24 F g⁻¹), the surface area of NPC is 553 m² g⁻¹, and the specific capacitance is 239 F g⁻¹ at 5 mV s⁻¹ [34], which indicated the importance of N-doping in carbon materials.

In general, NPC materials are prepared through pyrolysis of nitrogen-containing MOFs, such as zeolitic imidazolate frameworks [35,36]. It is necessary to introduce nitrogen source for MOFs without nitrogen. In this work, we provide a new method for preparing NPC materials, in which we added nitrogen ligand (adene) to UiO-66 by adjusting the content of 1,4-benzendicarboxylate (H₂BDC)
and adenine and then prepared NPC at different calcination temperature. It is worth noting that the introduction of adenine at different ratios did not change the structure of UiO-66. The ratio (H$_2$BDC : adenine) 9:1 and the NPC carbonized at 900°C (denoted as NPC-1-900) exhibits better electrochemical properties. The NPC-1-900/carbon nanotube film (CNTF) electrode material shows a maximum areal capacitance of 121.5 mF cm$^{-2}$ which is higher than that of PC-900/CNTF electrode (22.8 mF cm$^{-2}$) at 5 mV s$^{-1}$ with a three-electrode system, indicating that the N-doping improves the capacitive performance of porous carbon. Compared with counterparts [25], the performance of NPC-1-900/CNTF electrode material is excellent. For the needs of practical application, a symmetric flexible SSC has also been assembled and tested.

2. Experimental methods

2.1. Materials

The chemical reagents used in the experiments were as follows. CNTF (Hengqiu Tech. Inc., Suzhou), zirconium chloride (ZrCl$_4$, 99.5%), 1,4-benzendicarboxylate (H$_2$BDC, 98%), adenine (C$_5$H$_5$N$_5$, 98%), the reagents mentioned above being purchased from Energy Chemical. N$_2$N-dimethylformamide (HCON(CH$_3$)$_2$, DMF, 99.8%), ethanol (CH$_3$CH$_2$OH, 99.7%), methanol (CH$_3$OH, 99.5%), sulfuric acid (H$_2$SO$_4$, 95.0–98.0%), phosphoric acid (H$_3$PO$_4$, 85%) and acetic acid glacial (CH$_3$COOH, 99.5%) were purchased from Tianjin Chemical Works. Other reagents were poly(vinyl alcohol) (PVA-124, MW 105000, 99%, hydrolysed), 1-methyl-2-pyrrolidinone (NMP, 99.0%, Aladdin), poly(vinylidenefluoride) (PVDF, Sigma-Aldrich). Prior to use, the CNTF was ultrasonically cleaned in ethanol and deionized water successively. Deionized water was used throughout all the experiments. All the reagents and materials were of analytical grades and were used as received without further purification.

2.2. Synthesis of UiO-66 and adenine-UiO-66

UiO-66 was prepared by mixing ZrCl$_4$ (0.7 g, 3 mmol) and H$_2$BDC (0.5 g, 3 mmol) in 10 ml DMF under vigorous stirring for about 30 min at room temperature; 0.5 ml CH$_3$COOH was then added with stirring. The obtained mixture was sealed and heated at 120°C for 24 h. After cooling naturally, the as-synthesized solid was rinsed by DMF and centrifuged three times, and then the product was purified with anhydrous methanol to exchange the guest DMF molecules for 3 days. After that, the UiO-66 was activated at 110°C for 24 h.

A series of adenine-UiO-66 with different content of adenine were prepared by adjusting the mole ratio of H$_2$BDC and adenine (9 : 1, 8 : 2, 7 : 3, 6 : 4, 5 : 5), using the same procedure as in the preparation of UiO-66. Correspondingly, the as-prepared samples are denoted as U-X, where X is the different mole ratio of H$_2$BDC and adenine, such as 1–5.

2.3. Synthesis of N-doped porous carbon

After excluding air by flowing Ar gas for 3 h, the as-synthesized UiO-66 and U-X were heated at 500°C for 3 h at a heating rate of 5°C min$^{-1}$ under an Ar flow. The products were further carbonized at different temperature (800–1000°C) for 5 h and then immersed into 20% HF aqueous solution to yield the carbon materials. After washing with deionized water several times and drying overnight at 80°C, a series of PC and NPC-X were obtained. Correspondingly, the as-prepared samples are referred to as PC-(800, 900, 1000) and NPC-X-(800, 900, 1000).

2.4. Fabrication of PC/CNTF and NPC-X/CNTF electrodes

The fabrication of PC/CNTF and NPC-X/CNTF electrode materials was carried out as follows: the slurry of 80 wt % active material (PC or NPC-X) and 20 wt % PVDF binder in NMP was coated on CNTF. The mass of the active material coated on the film was about 1 mg for each electrode. The CNTF with 1 mg active materials was dried at 80°C for 12 h as the working electrode. The CNTF used for electrochemical measurement was conductive on one side, and the other side was non-conductive with insulating tape, 1.0 cm × 0.5 cm conductive areas as the substrate.
2.5. Fabrication of flexible symmetric solid-state supercapacitor device

The preparation of polymer-gelled electrolyte was described in our previous work [37]. For the fabrication of the device, two identical pieces of NPC-1-900/CNTF electrode with an area of $1.0 \times 0.5 \text{ cm}^2$ were placed in parallel and PVA/H$_3$PO$_4$ was used as the polymer-gelled electrolyte. The average thickness of the electrolyte separator is about 0.3 mm in the device and it acts as both the electrolyte and the ion-porous separator. The assembled device is placed at room temperature for 2 h, so that the electrolyte could completely penetrate the electrode.

2.6. Morphological and structural characterizations

Thermogravimetric analysis (Setaram Labsys Evo) was conducted up to 1000°C at a heating rate of $5^\circ \text{C min}^{-1}$ under nitrogen atmosphere to evaluate the thermal behaviour of the samples. The morphologies of the samples were observed by using a JEOL-JSM-6701 field-emission scanning microscope (SEM) operating at an accelerating voltage of 10 kV and an FEI Tecnai G2 F20S-Twin transmission electron microscope (TEM) using an accelerating voltage of 200 kV. Powder X-ray diffraction (PXRD) measurements were recorded with a Rigaku Ultima IV diffractometer using Cu Kα radiation and graphite monochromator ($\lambda = 1.54056 \text{ Å}$) at 40 kV voltage and 40 mA current at the scan speed of $5^\circ \text{ min}^{-1}$ with a step size of 0.02°. The N$_2$ adsorption–desorption isotherms were obtained with a Quantachrome Autosorb iQ instrument; a liquid nitrogen bath (77 K) and ultra-high purity grade nitrogen and helium were used for the nitrogen adsorption experiment. All samples were degassed under vacuum at 393 K for 6 h before test. For calculation of the apparent surface areas, the multipoint Brunauer–Emmett–Teller (BET) method was applied using the adsorption branches of the N$_2$ isotherms and the pore size distribution was analysed by density functional theory (DFT) and Barrett Joyner Halenda. X-ray photoelectron spectroscopy (XPS) was conducted with a PHI-5702 instrument. The atomic content of nitrogen was measured by Varion EL CUBE elemental analyser. Before measurements, all the samples were evacuated and activated at 120°C for 24 h under vacuum to remove any residual solvent.

2.7. Electrochemical properties measurements

Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge/discharge (GCD) of CNTF, PC/CNTF and NPC-X/CNTF electrodes were evaluated from an electrochemical workstation SI 1287 and SI 1260 (Solairton, England) using a three-electrode cell in 1 M H$_2$SO$_4$ electrolyte, with silver chloride electrode and Pt sheet as the reference electrode and counter electrode, respectively. The performance of the assembled device was tested by CV, GCD and EIS in a two-electrode configuration. The EIS data were studied in a frequency range of 10–100 mHz at an open circuit potential of 5 mV. The GCD test of all electrode materials and device was conducted at varying current density with the cutoff voltage of 0 and 1.0 V. All tests were carried out at room temperature. The calculation of the capacitance ($C$), power density ($P$) and energy density ($E$) was carried out as described in our previous paper [37].

3. Results and discussion

3.1. The characterization of the electrode material

3.1.1. Thermogravimetric analysis

In order to analyse the thermal stability of as-synthesized UiO-66 and U-1, thermogravimetric analysis was conducted and shown in electronic supplementary material, figure S1. From the electronic supplementary material, figure S1, we can see that the curves of UiO-66 and U-1 were very similar indicating that the incorporation of adenine did not change the stability of UiO-66. At the beginning, the physically adsorbed H$_2$O, guest H$_2$O and DMF solvent molecules of the UiO-66 and U-1 were removed by heating from 30°C to 200°C. On further heating, a weight loss between 500°C and 600°C may be ascribed to the collapse of the structure, which was similar to the previous reported researches [38]. It is worth noting that the weight loss of UiO-66 and U-1 was 60 and 55 wt%, respectively, which might be ascribed to changes in the chemical environment due to the introduction of the adenine.
3.1.2. Powder X-ray diffraction

PXRD has been carried out to analyse the composition of all samples. As shown in the electronic supplementary material, figure S2, in comparison with the simulated PXRD pattern of UiO-66 [39], the as-synthesized UiO-66 and U-X showed a similar structure, which indicated that the introduction of adenine did not change the structure of UiO-66. The reason for this phenomenon may be that the adenine occupied the void spaces of UiO-66. As seen from figure 1a, b, two obvious broad peaks in all samples are observed at around 25° and 44°, which are corresponding to the (002) and (100) planes of graphitic carbon, respectively [40,41].

3.1.3. Nitrogen adsorption measurements

The surface area and porosity of samples were investigated by nitrogen adsorption/desorption measurement. The results of UiO-66 and U-1 are shown in the electronic supplementary material, figure S3. It is worth noting that the BET specific surface area of U-1 is 1375 m² g⁻¹ (electronic supplementary
material, figure S3C), which is larger than that of UiO-66 (1193 m² g⁻¹) (electronic supplementary material, figure S3A). Both UiO-66 and N-U-1 exhibited a type I isotherm. Moreover, the pore size distribution calculated by DFT model from the nitrogen desorption isotherm is shown in the electronic supplementary material, figure S3B,D. The average pore diameter of UiO-66 and N-U-1 is 0.785 nm, which is in the range of the values reported in [42]. The nitrogen adsorption/desorption isotherms of PC-900 and NPC-1-900 are shown in figure 2. Both PC-900 and NPC-1-900 exhibited a type IV isotherm. It is evident from figure 2 that the specific surface area of NPC-1-900 (973 m² g⁻¹) is larger than that of PC-900 (200 m² g⁻¹). The average pore diameter of U-1 is 3.514 nm, which is smaller than that of PC-900 (3.702 nm). The high specific surface area of NPC-1-900 may be due to the introduction of adenine molecules in the pores of UiO-66. Moreover, porous carbon with mesoporous structure is beneficial to improve the performance of SCs.

3.1.4. Morphology characterization

The morphology and microstructure of all the samples were observed by SEM and TEM. Electronic supplementary material, figure S4A and figure S4B show the SEM images of UiO-66 and U-1, respectively. Both UiO-66 and U-1 were of cubic shape. It was further proved that the structure of UiO-66 did not change after the introduction of adenine molecules. The SEM images of PC-900 and NPC-1-900 are shown in figure 3a,b; it can be observed that these particles have good uniformity after calcination. The obtained porous carbon still maintained the structure of UiO-66. Moreover, SEM images revealed that the surface of porous carbon samples became rough after carbonization and HF washing. The TEM images of PC-900 (figure 3c) and NPC-1-900 (figure 3d) show that the amorphous carbon possessed lots of pores over the entire particle surface.

3.1.5. X-ray photoelectron spectroscopy and elemental analysis

It is necessary to clarify whether the nitrogen is introduced into the porous carbon surface by XPS. XPS of PC-900 (figure 4a-a) revealed two binding peaks at 533.08 eV and 286.08 eV, which were assigned to O1s and C1s, respectively. In comparison with the curves of PC-900, the NPC-1-900 (figure 4a-b) shows

Figure 3. SEM images of PC-900 (a) and NPC-1-900 (b). TEM images of PC-900 (c) and NPC-1-900 (d).
another binding peak at 401.08 eV, which was assigned to N1 s. It shows that the NPC was successfully prepared by the introduction of adenine molecules. Moreover, the chemical state of the nitrogen on the surface of NPC-1-900 was further studied by the high-resolution N1 s region XPS analysis. From the XPS spectra of NPC-1-900 corresponding to N1 s transition in figure 4b, the signals of pyridinic-N (N1, 398.2 ± 0.2 eV), pyrrolic/pyridine-N (N2, 399.8 ± 0.2 eV), graphitic-N (N3, 401.6 ± 0.2 eV) and terminal N-O (N4, 404.06 ± 0.2 eV) bonding are shown by means of XPS deconvolution [43–45]. The result further confirmed the nitrogen doping of the porous carbon. The nitrogen atomic content of NPC-1-900 is 2.61% by elemental analysis. This indicated that we successfully obtained NPC by carbonized adenine-based MOF.

3.2. Electrochemical properties

The areal capacitance of electrode materials is of greatest importance, especially in flexible and wearable electronics applications [6,46]. The effects of different ratio (H2BDC: adenine) and calcination temperature on the properties of electrode materials are shown in figure 5a,b. As can be seen from figure 5a,b, NPC-1-900/CNTF electrode shows a larger areal capacitance than other electrodes at 50 mV s−1. In order to further investigate the performance of the samples, the CV curves of PC-900/CNTF (figure 5c and electronic supplementary material, figure S5A) and NPC-1-900/CNTF (figure 5e and electronic supplementary material, figure S5B) electrode materials were carried out at different scan rates from 5 to 500 mV s−1. As shown in figure 5c (electronic supplementary material, figure SSA) and figure 5e (electronic supplementary material, figure SSB), the CV curves show quasi-rectangular shapes from 5 to 500 mV s−1, which indicate a good rate behaviour. The plots of areal capacitance versus CV scan rates for PC-900/CNTF (figure 5d) and NPC-1-900/CNTF (figure 5f) show that the NPC-1-900/CNTF electrode displays an areal capacitance of 121.5 mF cm−2 while it is 22.8 mF cm−2 for PC-900/CNTF at 5 mV s−1. The electrochemical impedance diagrams of all samples are shown in figure 5g,h. Figure 5g shows the Nyquist plots of PC-900 (a) and NPC-X-900 (b–f) (X: 5, 4, 3, 2, 1, respectively) and figure 5h shows is the Nyquist plots of NPC-1 (f–h, 900°C, 800°C, 1000°C, respectively). The data show that the NPC-1-900/CNTF electrode exhibits a lower charge transfer resistance than other electrodes, which verify the better electronic properties of NPC-1-900/CNTF. On the other hand, the GCD curves of PC-900/CNTF and NPC-1-900/CNTF electrodes were obtained at various current densities from 0.5 to 5.0 mA cm−2 in figure 6a,c, respectively. We can see that the GCD curves of both PC-900/CNTF and NPC-1-900/CNTF electrodes exhibit typical symmetric triangular shape, which indicated the electric double layer energy storage mode and an excellent fast charge–discharge performance. However, the performance of NPC-1-900/CNTF electrode is obviously better than that of PC-900/CNTF electrode. Based on the GCD curves of PC-900/CNTF and NPC-1-900/CNTF electrodes at the current density of 0.5 mA cm−2, the areal capacitance was 29.1 mF cm−2 and 134 mF cm−2, respectively. It is worth noting that the internal resistance loss (iR drop) observed from the discharge curve is small even at high current density, indicating a low internal resistance of the NPC-1-900/CNTF electrode material. Figure 6b,d shows the plots of the areal capacitance versus current density for the PC-900/CNTF and NPC-1-900/CNTF electrodes. The highest areal capacitance of 134 mF cm−2 for NPC-1-900/CNTF electrode can be obtained at a current density of 0.5 mA cm−2 with good retention of 77.8% of the initial capacitance.
Figure 5. CV behaviours of CNTF, PC-900/CNTF and NPC-X-900 with different ratio (1, 4-benzendicarboxylate: adenine) (a) and NPC-1 at different calcination temperature (b) of CNTF (a), PC-900/CNTF (b), NPC-5-900/CNTF (c), NPC-4-900/CNTF (d), NPC-3-900/CNTF (e), NPC-2-900/CNTF (f), NPC-1-900/CNTF (g), NPC-1-800/CNTF (h), NPC-1-1000/CNTF (i) at scan rate of 50 mV s$^{-1}$.CV behaviours of PC-900/CNTF (c) and NPC-1-900/CNTF (e) at scan rate of 5–200 mV s$^{-1}$ (from bottom to top is 5, 10, 30, 50, 80, 100 and 200 mV s$^{-1}$). Areal capacitance relationship of PC-900/CNTF (d) and NPC-1-900/CNTF (f) at different CV scan rates. Nyquist electrochemical impedance spectra (g,h) of PC-900/CNTF (a), NPC-5-900/CNTF (b), NPC-4-900/CNTF (c), NPC-3-900/CNTF (d), NPC-2-900/CNTF (e), NPC-1-900/CNTF (f), NPC-1-800/CNTF (g), NPC-1-1000/CNTF (h).
Figure 6. GCD curves of the PC-900/CNTF (a) and NPC-1-900/CNTF (c) electrodes at different GCD current densities (a 0.5, b 0.8, c 1, d 2 and e 5 mA cm$^{-2}$). Areal capacitance relationship of the PC-900/CNTF (b) and NPC-1-900/CNTF (d) electrodes with different current densities.

Figure 7. CV curves of the NPC-1-900/CNTF flexible SSC device at different scan rates of 5–200 mV s$^{-1}$ (a) (from bottom to top is 5, 10, 30, 50, 80, 100 and 200 mV s$^{-1}$). Relationship of the areal capacitance with different CV scan rates (b). GCD curves (c) of NPC-1-900/CNTF flexible SSC device at different GCD current densities (a 0.5, b 0.8, c 1.0, d 2.0 and e 5.0 mA cm$^{-2}$). Relationship of the areal capacitance with different current densities (d). Ragone plot of the volumetric energy and power density of device (e). Nyquist electrochemical impedance spectra of device (f) (inset is the EIS in high-frequency region).

as the current density increases from 0.5 to 5 mA cm$^{-2}$, while the highest areal capacitance obtained for PC-900/CNTF is 29.1 mF cm$^{-2}$ with the retention of 69.1% at the same condition.

In order to further explore the electrochemical property of NPC-1-900/CNTF electrode, a symmetrical flexible SSC was subsequently assembled and tested in two-electrode system, with gel electrolytes as both electrolyte and ion-porous separator for solid-state SCs. The CV curves, GCD and EIS tests were
Figure 8. CV curves of NPC-1-900/CNTF flexible SSC device bent with different angles at 50 mV s$^{-1}$ (a); areal capacitance of device with different angles (b); cycling performance of NPC-1-900/CNTF flexible SSC device measured at 80 mV s$^{-1}$ for 2000 cycles (c); optical images of device bent with different angles (d).

measured at a voltage window (0–1.0 V). As shown in figure 7a and electronic supplementary material, figure S6, the CV curves of the NPC-1-900/CNTF device show excellent quasi-rectangular shapes from 5 to 500 mV s$^{-1}$, which indicate that the device has excellent capacitive behaviour. Figure 7b shows the plots of the areal capacitance versus CV scan rates for the NPC-1-900/CNTF device. When the scan rate increases from 5 to 500 mV s$^{-1}$, the areal capacitance still keeps about 40% of the initial values. Moreover, the quasi-triangular-shaped GCD curves at different current densities are shown in figure 7c. The plot of the areal capacitance versus different current densities for the NPC-1-900/CNTF device is shown in figure 7d. The NPC-1-900/CNTF based device can exhibit a high capacitance of 43.2 mF cm$^{-2}$ at 0.5 mA cm$^{-2}$ and still maintain 18 mF cm$^{-2}$ at a high current density of 5 mA cm$^{-2}$, which indicate that the device has fast charge–discharge performance. The areal capacitance value of NPC-1-900/CNTF device calculated from the CV curves is the same as calculated from the GCD curves.

Figure 7e shows the volumetric power versus volumetric energy Ragone plot, which is used to assess the electrochemical properties of the NPC-1-900/CNTF device. The NPC-1-900/CNTF device exhibits a volumetric energy density of 57.3 µWh cm$^{-3}$ at a power density of 2.4 mW cm$^{-3}$. The Nyquist plots of the device are shown in figure 7f; it is obvious from figure 7f that the device has small overall internal resistance.

Nowadays, flexible SSCs have become more and more important because they are flexible, twistable and wearable. To explore the flexible degree of the device, the bending test was conducted under different angles of 0°, 60°, 90° and 145° through CV method at the scan rate of 50 mV s$^{-1}$. The results (figure 8a,b,d) show that the device is highly folded. Another important factor in practical application is the cycling life. As shown in figure 8c and electronic supplementary material, figure S7, we can see that the device retains 91.5% and 89.5% of the initial capacitance after 2000 cycles under different angles of 0° and 145°, which indicate that the device possesses an excellent cycling stability and flexibility.

4. Conclusion

In summary, we have synthesized a series of NPC from UiO-66 with different ratios of adenine. What is more, the introduction of adenine at different ratios did not change the structure of UiO-66. It was found that when the mole ratio of H$_2$BDC and adenine was 9:1, the carbonization temperature was 900°C, NPC-1-900 electrode possesses a higher surface area and excellent capacitive performance. The NPC-1-900 electrode with a specific areal capacitance of 128 mF cm$^{-2}$ at 5 mV s$^{-1}$ is superior to the PC-900-CNTF electrode (22.8 mF cm$^{-2}$) with a three-electrode system, indicating that the N-doping improves the capacitive performance of porous carbon. The assembled optimum flexible SSC shows superior areal capacitance 43.2 mF cm$^{-2}$ at the scan rate of 5 mV s$^{-1}$ using PVA/H$_3$PO$_4$ gel electrolyte. The flexible device shows excellent foldability and cycling stability, which can retain 91.5% of the initial capacitance after 2000 cycles. The present finding provides us a new method to prepare NPC with the use of MOF materials.
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