Flexible supercapacitors with high power density, flexibility, and durability have shown enormous potential for smart electronics. Here, a continuous graphitic carbon nitride polyhedron assembly for flexible supercapacitor that is prepared by pyrolysis of carbon nanotubes wired zeolitic imidazolate framework-8 (ZIF-8) composites under nitrogen is reported. It exhibits a high specific capacitance of 426 F g$^{-1}$ at current density of 1 A g$^{-1}$ in 1 M H$_2$SO$_4$ and excellent stability over 10 000 cycles. The remarkable performance results from the continuous hierarchical structure with average pore size of 2.5 nm, high nitrogen-doping level (17.82%), and large specific surface area (920 m$^2$ g$^{-1}$). Furthermore, a flexible supercapacitor is developed by constructing the assembly with interpenetrating polymer network electrolyte. Stemming from the synergistic effect of high-performance electrode and highly ion-conductive electrolyte, superior energy density of 59.40 Wh kg$^{-1}$ at 1 A g$^{-1}$ is achieved. The device maintains a stable energy supply under cyclic deformations, showing wide application in flexible and even wearable conditions. The work paves a new way for designing pliable electrode with excellent electronic and mechanic property for long-lived flexible energy storage devices.

1. Introduction

Nowadays, flexible supercapacitors (f-SCs) with merits of lightweight, foldability, long cycling life, and high power density have attracted tremendous research enthusiasm as a promising power source for modern wearable electronic devices, such as smart watches, sports bracelet, and intelligent detective devices.[1–3] However, relatively low energy density (typically 3–10 Wh kg$^{-1}$) of commercially available activated carbon-based supercapacitors (SCs) has seriously restricted their practical applications.[4–6] There is a more and more increasing need to develop novel structural electrodes with high specific capacitance, which is vital for increasing energy density of SCs.[7,8] In addition, the development of excellent mechanical property of electrode has become another crucial task because f-SCs need to guarantee the stable energy output for wearable devices when encountering various human activities.[9,10] To date, although some achievements on f-SCs have been made, flexible electrode films with a perfect combination of the above two important features are still lacking.[11–13]

Some attempts have been made to develop various electrode materials to achieve high energy density for SCs, such as transition metal oxides, conductive polymers, and carbon nanomaterials.[14–18] Among these, carbon nanomaterials, including fullerenes, carbon nanotubes (CNTs), graphene, graphene-based composites, and other derived carbon materials, have become the mainstream electrode materials for their superior electrical conductivity, large specific surface area (SSA), and hierarchical porous structure.[19–27] Moreover, chemical and electronic properties of the carbon hosts can be further enhanced by doping with heteroatoms, such as phosphorus, boron, sulfur, and nitrogen, leading to an enhanced energy storage capacity.[28] Many programmable nanocarbon-based architectures have also been used as the electrodes of flexible or other unconventional supercapacitors, such as fiber supercapacitor, 3D nanotube array-based supercapacitor, and high-temperature supercapacitor.[29–32] Owing to these previous works, carbon electrode-based SCs could be made out with high energy density and good electrochemical cycling stability. However, some defects of these SCs restricted their application in flexible energy devices mainly due to their poor mechanical properties. First of all, discontinuous microstructure of various nanocarbon, such as nanotube, nanosphere, and nanosheet, could lead to poor mechanical property for the reason that bending processes would destroy the microstructure of materials and deteriorate electron/ion diffusion path in the electrode.[13] Second, heterodoping or compositing could improve energy density with the pseudocapacitance, but large amounts of doped heteroatoms or materials would resulted in physical and chemical structure instability and hence the poor mechanical strength of carbon electrodes, which are still not favorable for flexible supercapacitors.[34] By now, little attention has been paid to effective assembly strategy for designing electrode materials with fine integration of high active heteroatoms doping, hierarchical porous structure, and mechanical strength.

ZIF-8 framework, a well-known type of metal-organic frameworks (MOFs), is an ideal precursor to produce nitrogen-doped porous carbons because of its high nitrogen content, large specific surface area, and hierarchical porous structure.[35] According to previous work, ZIF-8 particles exhibited high energy storage capacity in static state, but were seldom applied
to flexible supercapacitors due to poor mechanical flexibility caused by the discontinuous microstructure.\[36\] Here, we first put forward an assembly strategy for designing novel electrodes with a perfect integration of both high energy density and excellent mechanical flexibility. Specifically, we synthesized the CNTs wired ZIF-8 structure through an in situ growth method. Afterward, we fabricated a highly nitrogen-doped continuous graphitic carbon nitride polyhedron (GCNP) by directly pyrolysis of CNTs/ZIF-8 composites. Particularly, CNTs in the assembly not only serve as the binder to improve continuity of materials for ensuring mechanical properties but also act as the channel to enhance electrical conductivity. Moreover, the inherent nitrogen species of ZIF-8 effectively avoided microphase separation between the doping nitrogen and carbon lattice, resulting in a stable chemical structure without any physical structure collapse. The novel structure could be considered as 3D inner-connected graphene-like framework with a high nitrogen-doping content (17.82%), a large specific surface area (920 m\(^2\) g\(^{-1}\)), and an ideal average pore size (2.5 nm), which improves both electron conduction and mass transport during charge–discharge process, and provides extra pseudocapacitance. Logically, this electrode material exhibited high energy storage capacity with a specific capacitance of 426 F g\(^{-1}\) at a current density of 1 A g\(^{-1}\) in 1 m H\(_2\)SO\(_4\) and excellent cycling stability over 10 000 cycles. Furthermore, we fabricated a flexible solid-state supercapacitor based on the GCNP electrode and a highly ion-conductive polyoxyethylene/nitrile butadiene rubber (PEO/NBR) interpenetrating network (IPN) containing an ionic liquid [1-ethyl-3-methylimidazole tetrafluoroborate (EMIBF\(_4\))].


ewbf{2. Results and Discussion}

\textbf{2.1. Preparation and Characterization}

Preparation of the highly nitrogen-doped graphitic carbon nitride polyhedron is briefly illustrated in Figure 1 and a detailed experimental description is presented in the Experimental Section. Typically, CNTs were preprocessed with polyvinylpyrrolidone (PVP) in solution for achieving good dispersion of CNTs and uniform growth of ZIF-8 crystals by reducing surface energy and promoting coordination with zinc ions. Afterward, the CNTs thread ZIF-8 composites were transformed into the highly nitrogen-doped graphitic carbon nitride polyhedron by direct pyrolysis under N\(_2\) atmosphere at 800 °C without adding any nitrogen sources, such as melamine and urea, because ZIF-8 is N-containing MOFs. Within the high-temperature annealing treatment, zinc ions were reduced into metallic zinc and then evaporated away or subsequently washed off by HCl solution from the framework, producing additional numerous pores and ensuring the formation of metal-free carbon materials.\[37\] During this process, ZIF-8 crystals acted as not only carbon source but also nitrogen source because of carbon and nitrogen species in the organic ligand, meaning that the carbonization precursor is inherent in abundant nitrogen species. This specialty guarantees that the doping nitrogen species in carbon framework would be compatible with carbon lattice at nanometer scale without any microphase separation, comparing with the mainstream carbon materials with additional nitrogen species from outside. As a result, the derived graphitic carbon nitride polyhedron was highly nitrogen doped at nanometer scale with excellent structure stability. Within this unique nanostructure, both N-doped porous carbon network and CNTs not only serve as highways for fast electron transport but also inner channels facilitating ion transport at electrode/electrolyte interfaces. Therefore, it is expected that this new kind of nitrogen doped porous nanostructure will boost the electrochemical performance in supercapacitors.

The morphologies of as-synthesized CNTs/ZIF-8 precursor and GCNP materials were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The CNTs/ZIF-8 exhibit a hierarchical structure with ZIF-8 polyhedrons, ≈200 nm size, uniformly growing onto the CNTs surface, as shown in Figure S1 (Supporting Information). The X-ray diffraction (XRD) pattern of the as-prepared CNTs/ZIF-8 is identical to ZIF-8 simulated pattern shown in Figure S2a (Supporting Information), indicating the densely packing of ZIF-8 onto CNTs surface.\[38\] Thermal gravimetric analysis (TGA) result (Figure S2b, Supporting Information) demonstrated that the CNTs/ZIF-8 framework started to decompose at 600 °C and disappeared completely at 900 °C.

Figure 1. Schematic for the synthetic route of highly nitrogen-doped graphitic carbon nitride polyhedron.
Thus, we analyzed the decomposition process of CNTs/ZIF-8 under 700, 800, and 900 °C, respectively. The final products were denoted as GCNP-X (X is the pyrolysis temperature).

According to SEM and TEM images (Figure 2a,b; Figure S3, Supporting Information), GCNP materials retained the original structure of the ZIF-8 crystals without phase separation from CNTs after high-temperature pyrolysis and the surface showed slightly deformation after carbonization and washing with an HCl aqueous solution. Notably, GCNP-900 material shows more exposed CNTs without dense polyhedrons compared with the others (GCNP-700 and GCNP-800). TGA result in Figure S2b (Supporting Information) demonstrated that degradation rate (derivative weight) reached highest when pyrolysis temperature drawing near 900 °C and precursor disappeared completely at 900 °C. The increasing pyrolysis temperature would lead to more exposed CNTs without dense polyhedrons of GCNP. The high-resolution transmission electron microscope (HRTEM) image (Figure 2c) of GCNP-800 clearly shows graphene-like lamellar structure with adjacent interlayer distances of 0.34 nm, which exhibits numerous porosity and ion channels. This result is close to the d-spacing of the (002) crystal plane (0.335 nm) in bulk graphite with slight distortion, which is in agreement with the XRD results vide infra.[38] Also, the selected-area electron diffraction pattern in Figure 2d reveals typical diffraction rings, which is in accordance with results above. From energy dispersive X-ray spectrometry elemental mappings in Figure 2e–g, it can be concluded that large amounts of N atoms are uniformly distributed in GCNP-800 material.

To further verify microstructure of GCNP materials, structure characterizations, such as XRD pattern, Raman spectra, and X-ray photoelectron spectroscopy (XPS), were conducted. The XRD patterns of GCNP materials contrastive with parent precursor are shown in Figure 3a. The broad peak located at 13.1° assigned to in-planar repeating unit of the graphitic structure according to references about graphitic carbon nitride.[39–42] In addition, as it was a broad peak around 13.1°, the characteristic carbon (001) diffraction around 12° could also be contained.[43,44] The other two broad peaks located at 26.14° and 44.16° were assigned to the characteristic carbon (001), (002), and (100) diffractions, respectively, revealing the presence of long-range 2D ordering in the carbon matrices along with some graphitization.[45,46] In addition, impurities like zinc and zinc compounds were not observed. However, these characteristic peaks barely can be observed in the pattern of CNTs/ZIF-8 precursor. It means that although morphology of precursor retains well after annealing process, microstructure inside has changed stealthily. The Raman spectra in Figure 3b further verify the graphitic structure of the samples. The peaks observed at 1349 and 1590 cm\(^{-1}\) are the D (disordered and defective structure) and G (graphitic structure) bands of carbon materials, respectively. The \(I_D/I_G\) band intensity ratio is always used to evaluate the graphitization degree of carbon materials and high graphitization degree always lead to a superior electrical conductivity.[47,48] Obviously, \(I_D/I_G\) band intensity ratio of GCNP decreased with the increasing pyrolysis temperature, testifying a higher graphitization degree (fewer defects and more graphitic crystallites) of the resultants. It will surely improve the electrical conductivity of GCNP, which is beneficial for enhancement of electrochemical performance.

From the XPS spectra in Figure 3c and Figure S6 (Supporting Information), the N 1s signal can be fitted into three sub-peaks, corresponding to pyridinic N (N-6) (398.2 eV), pyrrolic N (N-5) (399.8 eV), and quaternary N (N-Q) (400.8 eV). A schematic illustration of the GCNP chemical structure is derived in Figure 1. Inset of Figure 3c clearly presents the relative contents of three N species in GCNP materials. Based on previous works, N dopants in carbon lattice, especially N-6, can increase electron density and electron donating properties, because it could efficiently change the valence band structure, including the increasing density of \(\pi\) states near Fermi level and reduction
of work function. However, N-5 is unstable under high temperature and easily converted into N-Q, which benefits for increasing graphitization degree and electrical conductivity of carbon materials. As shown in Figure 3c, with the increasing of pyrolysis temperature, N-6 always keeps dominant in N content, ensuring a stable pseudocapacitive effect of electrode materials, while lots of N-5 converted into N-Q. On the other hand, nitrogen content decreased from 25.30% to 10.49% with the temperature increasing from 700 to 900 °C because most nitrogen species escaped away from the precursor under excessively high temperature. Analysis above seems that either GCNP-700 (highest N-doping level) or GCNP-900 (suitable proportion of N species) will be the best choice for electrode material for SCs. However, experimental results in subsequent section indicate that GCNP-800-based electrode shows the best electrochemical performance. This is mainly because both N content and N doping state are critical to pseudocapacitance and it needs a combination of high N content and suitable N doping state to make synergetic effect in increment of pseudocapacitance. In addition, oxygen content in GCNPs, ranging from 5.76% to 7.03% (summarized in Table S2, Supporting Information), also contributed to the pseudocapacitance.

On the other hand, both SSA and pore size of electrodes are crucial to energy storage besides nitrogen doping. For comprehensive comparison, specific surface area, pore size, and corresponding N contents of the materials were summarized in Figure 3d. The exact values were illustrated in Tables S1 and S2 (Supporting Information). Pore characteristics were clearly examined by the N2 adsorption isotherm measurement (Figures S4 and S5, Supporting Information). All the samples exhibited a type-IV sorption isotherm with a hysteresis loop at a relative pressure from 0.4 to 1.0, which is a typical result of capillary condensation in mesopores. The average pore size of GCNP materials mainly varied from 2.5 to 9.56 nm. In accordance with previous research, a pore size of 2–10 nm facilitates rapid ion transport and charge storage because nanopores and interconnections provide more accessible channels for electrolyte penetration. When the pyrolysis temperature increased, N content of GCNP decreased quickly while pore size and SSA showed extremums, respectively. Obviously, temperature of 800 °C is the optimal condition because 700 °C is insufficient for complete carbonization of precursor (high N content and small SSA) and 900 °C is so high that MOF structure would be destroyed during pyrolysis process (low N content and large pore size). Therefore, the GCNP-800 material exhibited the highest specific surface area of 920 m² g⁻¹ with a high nitrogen content of 17.82% and an ideal average pore size of 2.5 nm, which shows a great potential in the application of supercapacitor electrode.

2.2. Electrochemical Performance as an Electrode Material for SCs

The performance of the highly N-doped graphitic carbon nitride polyhedron as an electrode material for SCs was investigated using a standard three-electrode system in 1 m H₂SO₄ aqueous solution (Figure 4a). Figure 4b shows Nyquist plots of the electrode materials in 1 m H₂SO₄ in a frequency range from 10 kHz to 10 mHz. The equivalent series resistances are all below 4 ohm (inset of Figure 4b), showing good conductivity in aqueous solution and plots show almost vertical at low frequencies representing the dominance of electric double layer effect. Notably, it seems unreasonable that contact...
resistance of GCNP-900 is lower than GCNP-800 with the increasing graphitization degree. In fact, 900 °C is an excessive temperature for carbonization, so polyhedron density and material continuity of GCNP-900 is lower than GCNP-800, which led to a lower contact resistance. (Figure 2a; Figure S3b, Supporting Information) To further verify the viewpoint, we measured the electrical conductivity of the electrodes by a multifunction digital four-probe tester and conductivity order of the three electrodes—GCNP-800 (278 S m⁻¹) > GCNP-900 (233 S m⁻¹) > GCNP-700 (161 S m⁻¹)—was in line with contact resistance order above (summarized in Table S1 in the Supporting Information). In cyclic voltammograms (CV) for the three samples (Figure 4c; Figure S7, Supporting Information), the regular rectangular shapes with slight redox peaks at various scan rate demonstrate their excellent capacitive behavior with some Faradaic effect.

In addition, galvanostatic charge–discharge tests in Figure 4d and Figure S8 (Supporting Information) were measured at various current densities in a three-electrode system to further evaluate the performance of N-doped graphitic carbon nitride polyhedron materials. The typical triangular shape confirms good coulombic efficiency of these electrode materials. Among these materials, GCNP-800 exhibited the highest specific capacitance of 426 F g⁻¹ at a current density of 1 A g⁻¹ (Figure 4e) mainly because it inherited structural characteristics from parent precursor with a high N-doping level (17.82%), a large specific surface area (920 m² g⁻¹), and an ideal average pore size (2.5 nm). The excellent capacitive performance could rival some of the best supercapacitor electrodes based on porous carbon materials (summarized in Table S3 in the Supporting Information), showing the potential of GCNP-800 for practical applications in supercapacitor electrodes. To achieve
high capacitive performance, a proper balance should be considered between surface area, pore size distribution, graphitization degree, nitrogen content, and electrical conductivity. The high performance of GCNP-800 material results from the synergistic effect of large specific surface area, high nitrogen content as well as CNTs wired ZIF-8 structure which allows for rapid ion diffusion and easy charge-transfer. Interestingly, the capacitance falling speed of GCNP-700 from 2 to 3 A g\(^{-1}\) was much faster than that at other current densities while that of GCNP-800 was much slower. Incomplete carbonization of precursor in 700 °C resulted in lower graphitization degree, specific surface area, electrical conductivity, and unstable structure. This would lead to a large decay of capacitance at higher current density (2–3 A g\(^{-1}\)) and a lower rate capability. As main structural damage has happened in charge–discharge process at 2–3 A g\(^{-1}\), decline of capacitance at 3–10 A g\(^{-1}\) became much slower. On the contrary, GCNP-800 carbonized more completely (higher graphitization degree, specific surface area, electrical conductivity, and stable structure) and could retain its high capacitance at higher current density and showed a higher rate capability. Moreover, long-time cycling stability of the GCNP-800 electrode was investigated using galvanostatic charge–discharge test at a current density of 2 A g\(^{-1}\). As shown in Figure 4f, specific capacitance value keeps retention of about 90% over 10 000 cycles, indicating an excellent cycling stability of GCNP-800 electrode material. Furthermore, we found that the mass ratio of MOFs/CNTs could be controlled by regulating the growth time of MOFs and studied the relationship between the mass ratio and the performance of the GCNP-800 electrode. As shown in Figure S9a (Supporting Information), MOFs size finally reached ≈200 nm and did not grow larger any more whatever prolonging the growth time and mass ratio reached a saturated value of 1.49 finally. As a result, the capacitance increased with the increasing mass ratio of MOFs/CNTs and reached 426 F g\(^{-1}\) finally, which resulted from the increasing ion capacity of GCNP electrode (Figure S9b, Supporting Information).

2.3. Construction of the GCNP-800-Based Supercapacitor

To further evaluate the performance of GCNP-800-based device, a flexible symmetrical supercapacitor was constructed by laminating two pieces of electrode films with an electrolyte layer. The schematic of the constructed supercapacitor is shown in Figure 5a. In this work, we introduced a new-type electrolyte layer composed of interpenetrating polymer network with EMIBF\(_4\). The ionic liquid EMIBF\(_4\) was selected as an electrolyte for its wide electrochemical window as well as nonvolatility and incombustibility. Interpenetrating polymer network represented an interesting architecture, in which NBR provided mechanical support for the network and PEO acted as a magnet to attract and hold on ionic liquids. Moreover, PEO-NBR IPN is the first time to be used as polymer separator for SCs by now. Figure S10 (Supporting Information) presents the dynamic mechanical analysis of the as-synthesized IPN network and corresponding single polymer of NBR and PEO. Obviously, the IPN has only one major α relaxation occurring at −5 °C, which located between those of the PEO and NBR.

Figure 5. Construction of the GCNP-800 electrode-based supercapacitor. a) Preparation of flexible supercapacitor. b) Stress–strain curves of PEO-NBR IPN and PVA membrane. c) Ionic liquid uptake and ionic conductivity of IPN-EMIBF\(_4\) and PVA-EMIBF\(_4\) electrolyte. d) CV curves of IPN and PVA electrolyte-based SC at a scan rate of 100 mV s\(^{-1}\).
single polymer –42 and 21 °C, respectively. This result reflected that the interpenetrated structure appeared to be homogenous at the dynamic thermomechanical analysis (DMA) scale, which would lead to a phase cocontinuity across the bulk material and provide integral properties with the two single polymers.[57]

As illustrated in Figure 5b, the PEO-NBR IPN separate membrane exhibited higher tensile modulus and break elongation than traditional polyvinyl alcohol (PVA) membrane. The tensile modulus of IPN is 53 MPa with a break elongation of 115%, while those of PVA membrane are 22 MPa and 59%, respectively. This merit makes it possible to prepare high flexible supercapacitor, which is the mainstream direction of SCs research at present. In addition, ionic liquid uptake of IPN achieved as high as 70% comparing with 23% of the PVA membrane, resulting that ionic conductivity of the as-prepared IPN-EMIBF$_4$ electrolyte was almost three times higher than that of the PVA-EMIBF$_4$ electrolyte, as shown in the Figure 5c. As illustrated in Figure 5d, the IPN-based device shows a better energy storage capability than the widely used PVA electrolyte and the PVA-based device cannot fully reflect the pseudocapacitive effect of GCNP-800 electrode because of lacking enough freely mobile ions. Thus, excellent mechanical property and high ionic liquid uptake of the PEO-NBR IPN network make it a promising electrolyte layer for high-performance supercapacitor.

### 2.4. Performance of the GCNP-800-Based Flexible Solid-State Supercapacitor

A Nyquist plot for this supercapacitor is similar to that obtained in the aqueous electrolyte, including a small semicircle (high frequency region), the Warburg diffusion line (middle frequency region), and the capacitive line (low frequency region), as presented in Figure 6a. The equivalent series resistance for supercapacitor built from GCNP-800 material is $10.1 \, \text{ohm}$, showing a good interface contact between electrolyte and electrode as well as excellent ionic conductivity of electrode material due to CNTs and high graphitization degree of polyhedrons. Electrical conductivity of the electrode film was as high as 278 S m$^{-1}$, which was tested by a multifunction digital four-probe tester, further confirming excellent ionic conductivity. In addition, the plot line of low frequency region looks almost vertical to the y-axis, verifying an ideal capacitive behavior of the device. Figure S11 (Supporting Information) shows the galvanostatic charge–discharge curve at a current density of 1 A g$^{-1}$, demonstrating a symmetrical and stable capacitance behavior. In the meantime, Bode plot in Figure S12 (Supporting Information) shows a phase angle of 78.5° at 0.01 Hz for the GCNP-800-based device, indicating ideal capacitive behavior in line with the result above.

Figure 6b shows that specific capacitance achieved 190 F g$^{-1}$ at a current density of 1 A g$^{-1}$ and specific capacitance of the device decreased with the increasing current density. The inset in Figure 6b indicated that the electrode exhibited a good interlayer adhesion with the electrolyte layer. It was found that GCNP-800 exhibited a high specific capacitance while the rate capability of GCNP-800 is not good compared to some other porous carbon materials reported before. We analyzed the consequence and considered that the carbonization degree of CNTs/ZIF-8 precursor was a bit lower than the pure carbon materials, such as graphene and carbon nanotube, which led to a lower rate capability relatively. We would make further study into the phenomenon in our future work, such as balancing the carbonized degree and electrochemical activity of GCNPs. Ragone plot for the GCNP-800-based supercapacitor in Figure 6c shows that the energy density is about 59.40 Wh kg$^{-1}$ at a current density of 1 A g$^{-1}$ which is superior to the commercial devices (mainly 3–10 Wh kg$^{-1}$) and achieved a high-level energy storage capacity of flexible solid-state supercapacitor. Power density and energy density of the as-prepared device were found to be 4.56 kW kg$^{-1}$ and 25.30 Wh kg$^{-1}$, respectively, at a current drain time of 20 s. The as-prepared supercapacitor could power a light-emitting diode (LED), which further proved its practical value (inset in Figure 6c).

As shown in Figure 6d, electrochemical performance of the device did not deteriorate significantly under twisted state. Although some cracks appeared on surface of the device under stretchable state with an elongation of 10%, the specific capacitance still kept 78% of original state, verifying the key role of continuity of the GCNP electrode materials in flexible supercapacitors. From stress–strain curve of GCNP-800 in Figure S13 (Supporting Information), Young’s modulus of the electrode film is 368 MPa with a break elongation of 6.42%, which ensured the robustness and flexibility of the device. To further test flexibility of the device, CV tests were conducted under various bending angles in Figure 6e. A pair of redox peaks was observed in the rectangular-shaped CV curve due to pseudocapacitive effect of nitrogen species in electrode. Furthermore, CV curves under bending state (bending angle of 180°) did not show noticeable changes comparing to that of the flat state, indicating a good foldability of the device. Especially, specific capacitance retained by 94.8% even after 500 bending cycles with a bending angle of 180° (Figure 6f). Additionally, the flexible device (size 75 mm × 25 mm) is so lightweight that can be lifted up even by a tender flower (inset of Figure 6f). The superior flexibility mainly results from the perfect combination of high mechanical property of PEO-NBR IPN network and the continuity of GCNP electrode material. These excellent energy storage performances indicate that the highly nitrogen-doped continuous GCNP electrode along with the highly ion-conductive IPN electrolyte has an enormous application potential in flexible energy devices.

### 2.5. Mechanism of Mass and Charge Transference in a GCNP-Based Electrode

It is well known that carbon materials are hydrophobic and incompatible with ionic liquids. However, excellent wettability was obtained when carbon materials were doped with nitrogen species, especially with high nitrogen content doping into graphitic lattice.[59] Electronegativity of nitrogen atom (3.5) is higher than that of carbon (3.0) and the atomic diameter is smaller, so N-doping method would lead to stronger interactions between carbon structure and mobile ions. The high nitrogen doping level, especially pyridinic N and pyrrolic N, provides the electrode material with large numbers of active sites, which boost the pseudocapacitive effect greatly by redox reactions.[60] On the
one hand, our work reported a highly nitrogen-doped graphitic carbon nitride polyhedron with a nitrogen content of 17.82%, higher than previously reported works. On the other hand, the pyrolysis precursor CNTs/ZIF-8 contains large amounts of nitrogen species by itself, which results in a good compatibility with carbon lattice avoiding the incompatibility of adding nitrogen source outside. Thus, GCNP materials in this work showed a high capacitive performance due to combination of double electrode layer effect with pseudocapacitive behavior.

As illustrated in Figure 7a, the continuous MOFs-derived carbon nitride polyhedron exhibited a unique nanostructure within CNTs wired polyhedron nanoparticle. The polyhedron framework acted as reservoir with numerous inner channels for ion flux inserted into the electrode, while the CNTs serve as highways for fast electron transport replacing the traditional carbon black additive. Figure 7b shows the difference of ion adsorption and transport between traditional solid nanoparticle and void polyhedron framework. For traditional carbon nanosphere materials, ion flux can only be absorbed onto the surface of solid particle and transported though tortuous path, resulting in a poor charge storage capacity. However, the novel GCNP materials in this work could allow ions diffusing into the inner space of the void polyhedron framework and straightforward ion transport through the framework instead of tortuous ion channel, boosting the electrochemical storage capacity greatly.

A simple but reliable model for evaluating the effect of specific surface area and pore size on capacitive performance is developed, which is based on the slit/cylindrical nonlocal density functional theory (NL-DFT) approach. As shown in Figure 7c, a simple model based on the spherical ions and...
cylindrical pore was built by referring previously reported theory and the two diagrams showed difference between full utilization and partial utilization of pore surface area.\textsuperscript{[65]} For ionic liquid electrolyte system, size of ion ($d$) is always equal to the radius of electrolyte ion in absence of solvation effect and pore size ($D$) is the value measured by specific surface area test. Moreover, effective specific surface area (ESSA) is dependent on the fitness between pore size and ion size. Specific surface area and pore size distribution are both vital to ESSA and capacitive performance consequently. The equation of the effective utilization factor ($x$) of surface area is deduced as follows

$$x = \frac{\text{ESSA}}{\text{SSA}} = \frac{n \cdot d}{\pi \cdot (D - d)}$$  \hspace{1cm} (1)

where $n$ is the number of ions inserted into cylindrical pore, $d$ refers to ion diameter, and $D$ represents cylindrical pore size. A formula for estimation of the specific capacitance of carbon-based electrode was obtained from experimental data by previously reported work according to slit/cylindrical NL-DFT approach,\textsuperscript{[65]} citing as follow

$$C \left( \text{F g}^{-1} \right) = 0.142 \times \text{ESSA} \left( \text{m}^2 \text{g}^{-1} \right) - 7.8$$  \hspace{1cm} (2)

In our work, EMIBF$_4$ ($d = 0.75$ nm) was used as electrolyte and GCNP-800 (pore size = 2.5 nm and SSA = 920 m$^2$ g$^{-1}$) was the electrode material for supercapacitor. The effective utilization factor ($x$) was calculated by formula (1) and resultant $x$ was as high as 96%. The extremely high effective utilization factor demonstrates that pore size of GCNP-800 material matches the ion size perfectly. Then, the theoretical specific capacitance was 118 F g$^{-1}$ calculated from formula (2), which is significantly lower than experimental value of 190 F g$^{-1}$. The remarkable gap between theoretical value and experimental value mainly results from the high level of nitrogen doping, which serves as active site for redox process and consequently improves the specific capacitance by 69% relative to the theoretical value. Therefore, on account of the hierarchically porous structure and numerous nitrogen active sites, the GCNP-800-based supercapacitor exhibited a high capacitive performance.

3. Conclusions

In summary, a highly nitrogen-doped continuous graphitic carbon nitride polyhedron has been developed by direct carbonization of CNTs wired ZIF-8 composites under nitrogen atmosphere. These materials retain the continuous polyhedron structure from precursors with a large surface area (920 m$^2$ g$^{-1}$) and high nitrogen content (17.82%). According to theoretical analysis, the hierarchically porous structure with an average pore size of 2.5 nm made the effective utilization ratio of specific surface area reaching 96%. The electrode based on GCNP-800 material exhibited high capacitive performance with a specific capacitance of 426 F g$^{-1}$ in 1 m H$_2$SO$_4$ at a current density of 1 A g$^{-1}$ and good cycling stability over 10 000 cycles, which nearly rivaled some of the best supercapacitor electrodes based on porous carbon materials. A flexible solid-state supercapacitor based on GCNP electrode and PEO/NBR IPN electrolyte achieved a high-level specific energy density of 59.40 Wh kg$^{-1}$ at a current density of 1 A g$^{-1}$, which is qualified for a promising candidate for the next-generation flexible energy devices. In addition, our study presents a novel strategy for fabricating flexible energy devices and a new insight into rational design of electrolyte separator and electrode materials for other electrochemical devices, such as lithium-ion batteries and artificial muscles.

4. Experimental Section

Materials: CNTs were obtained from Nanjing XFNANO Materials Tech Co., Ltd. Zn(NO$_3$)$_2$ and PVP were bought from Sinopharm Chemical Reagent Co., Ltd. PVA, polyvinylidene fluoride (PVDF), and 2-methylimidazole (2-mim) were purchased from Sigma-Aldrich. Ionic liquid of EMIBF$_4$ was obtained from Shanghai Cheng Jie Chemical Co. Ltd. 2,2-Azobisobutyronitrile (AIBN) and dicumyl peroxide (DCP) were obtained from Aladdin Reagent. Poly(ethylene glycol) methacrylate methyl ether and poly(ethylene glycol) dimethacrylate were bought from Shanghai chemical reagent Co., Ltd.

Synthesis of CNTs Wired Zeolite Imidazolate Framework: CNTs were soaked in nitrohydrochloric acid for 12 h and washed with deionized water to remove toxic catalyst impurities. After the pretreatment, CNTs (15 mg) were dispersed in methanol (80 mL) with ultrasonication for 2 h. Then, Zn(NO$_3$)$_2$ (320 mg) and polyvinylpyrrolidone (200 mg) were added into the solution and stirred for 1 h to form solution A. Subsequently, 2-methylimidazole (600 mg) was dissolved in methanol (80 mL) to form a clear solution B that was added dropwise to solution A with agitation stirring. After stirring for 70 min, the reaction was aged at 25 °C without any disturbance for 18 h. Finally, the black precipitate was collected by centrifugation and washed five times with methanol (30 mL) before vacuum drying at 70 °C overnight.

Preparation of the Highly N-Doped Graphitic Carbon Nitride Polyhedron: The highly N-doped graphitic carbon nitride polyhedron was synthesized by direct carbonization of the as-prepared CNTs/ZIF-8 under nitrogen atmosphere at temperatures of 700, 800, and 900 °C, respectively. Typically, CNTs/ZIF-8 was uniformly dispersed in crucible before placing into tube furnace. After exposing to a flow of nitrogen (200 mL min$^{-1}$) at 25 °C for 1 h, the crucible was heated to the setting temperature using...
a heating rate of 10 °C min⁻¹ and kept for next 3 h before cooling down to room temperature. Then, the resulting sample was washed with 2 M HCl aqueous solution to remove Zn component. Finally, the resultant was washed five times with deionized water and ethanol before vacuum drying at 70 °C overnight.

**Synthesis of PEO-NBR IPN/EMIBF₄ Electrolyte Layer**: PEO/NBR IPN films were synthesized by an in situ polymerization according to a modified previously reported method.[8] First, NBR (1.0 g) was dissolved in cyclohexanone (5.0 g) by stirring for 12 h at room temperature. Then, poly(ethylene glycol) methacrylate methyl ether (0.75 g) and poly(ethylene glycol) dimethacrylate (0.25 g) were added to the mixture and stirred for 3 h at room temperature. Subsequently, AIBN (30 mg) and DCP (60 mg) were added to the mixture and stirred for 30 min at room temperature. The mixture was poured into a teflon mould, then kept at 70 °C for 3 h, 100 °C at 1 h, and 160 °C 1 h, successively. Next, PEO-NBR film was obtained after vacuum drying at 80 °C for 24 h. Finally, 70 wt% EMIBF₄ in PEO-NBR was obtained by immersing the film in EMIBF₄ solution at 80 °C for 72 h.

**Synthesis of PVA/EMIBF₄ Electrolyte Layer**: PVA/EMIBF₄ electrolyte membrane was obtained using a simple solution casting method.[9] Typically, 0.5 g PVA was dissolved in 10 mL deionized water with agitation at 80 °C for 2 h to obtain a clear solution. Then, the clear solution was poured into a plastic Petri dish. After vacuum drying at room temperature for 48 h, the freestanding PVA membrane was obtained. Finally, the PVA/EMIBF₄ electrolyte layer was obtained by immersing the membrane into EMIBF₄ solution for at 80 °C for 72 h.

**Fabrication of the Flexible Symmetrical Supercapacitor**: The fabrication method was modified by referring to a previous work.[7] Specifically, a mixture of 120 mg GCNP-800 powder and 20 mg PVdF powder was dispersed in 30 mL of N,N-dimethyl formamide solution for 30 min through horn sonication treatment in an ice water bath. The suspension was cast onto a mould and became a freestanding electrode film (size 150 mm × 100 mm) after drying at 80 °C for 6 h. The solid-state symmetrical supercapacitor was assembled by laminating two pieces of GCNP-800 electrodes with PEO-NBR/EMIBF₄ electrolyte separator through hot pressing method.

**Material Characterization**: All the electrochemical characterizations were recorded by a CHI760D electrochemical work station. SEM and TEM images were recorded by Hitachi S-4800 and FEI Tecnai G2 F20, respectively. Raman spectra were conducted with a LabRAM HR800 from JY Horiba. X-ray photoelectron spectra were obtained using PHI 5000 VersaProbe II instrument. X-ray powder diffraction analysis was measured by Philips X’Pert PRO diffractometer with nickel-filtered Cu Kα radiation. Nitrogen sorption analysis was analyzed by Micromeritics ASAP 2020 instrument using Brunauer–Emmett–Teller method and the pore size distribution plots were evaluated out with a Q800 apparatus (TA Instruments) operating in tension mode. The electrode conductivity was tested by a multifunction digital four-probe tester (ST-2258C). The electrochemical measurements were carried out using a three-electrode system with a 1.0 M sulfuric acid aqueous solution as electrolyte. In a three-electrode cell, the as-prepared GCNP-800 film was characterized as a working electrode with Pt foil as counter electrode and Ag/AgCl electrode as the reference electrode. CV curves were measured in the potential range of 0–0.8 V versus Ag/AgCl by varying the scan rate from 5 to 100 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was performed from 10 mHz to 100 kHz with a voltage amplitude of 10 mV. Galvanostatic charge–discharge impedance spectroscopy (EIS) was performed from 10 mHz to 100 kHz with Ag/AgCl by varying the scan rate from 5 to 100 mV s⁻¹. CV curves were measured in the potential range of 0–0.8 V versus Ag/AgCl electrode and Ag/AgCl electrode as the reference electrode. GCNP-800 film was characterized as a working electrode with Pt foil as counter electrode and Ag/AgCl electrode as the reference electrode.

The energy density and power density were calculated through the following formulas[26]

\[ E_t = \frac{1}{2} C_t (\Delta V)^2 \]  
\[ P_t = \frac{E_t}{t} \]

where \( E_t \) (Wh kg⁻¹) is the specific energy density, \( P_t \) (W kg⁻¹) refers to the specific power density of supercapacitor, \( C_t \) (F g⁻¹) is the specific capacitance of supercapacitor, and \( \Delta V \) (V) represents the operation voltage for discharging with discharging time \( t \) (h).

Ionic liquid uptake of polymer electrolyte was determined by weighing the membranes before and after immersing step and calculated through the following equation

\[ \text{Ionic liquid uptake} (\%) = \frac{w_2 - w_1}{w_1} \times 100\% \]

where \( w_1 \) and \( w_2 \) represent the mass of the membrane before and after the immersing step.

The ionic conductivity of the gel polymer electrolyte is determined from the impedance spectrum. The ionic conductivity \( \sigma \) (S cm⁻¹) of the electrolyte can be calculated by the following equation[9]

\[ \sigma = D/(R_0 \times S) \]

where \( D \) (cm) is the thickness of electrolyte membrane, \( S \) (cm²) is the contact area of the electrolyte with platinum sheet electrode, \( R_0 \) (ohm) represents the series resistance obtained from the EIS curve.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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