Preparation of nitrogen-doped porous carbon via adsorption-doping for highly efficient energy storage

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HIGHLIGHTS
- The adsorption-doping route is proposed to fabricate heteroatom-doped carbons.
- Gelatin is employed as adsorbate serving as nitrogen source.
- Carbon-based electrode exhibits specific capacitance up to 362 F g\(^{-1}\) at 1 A g\(^{-1}\).
- Symmetric supercapacitor delivers an energy density of 9.13 W h kg\(^{-1}\).

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ABSTRACT
Namely “Adsorption-doping Strategy”, a general doping route by absorbing nitrogen-containing organic substances onto organic porous adsorbent materials is proposed for the synthesis of nitrogen-doped porous carbon. The three steps of this strategy can be described as adsorption, pre-carbonization and activation. Herein, nitrogen-doped porous carbon derived from commercial macroporous adsorption resin and gelatin as adsorbent and adsorbate, respectively, exhibits excellent electrochemical capacitive performance. The nitrogen-contained porous carbon delivers a significantly improved specific capacitance as high as 362 F g\(^{-1}\) at a current density of 1.0 A g\(^{-1}\), considerably larger than the capacitance of carbon electrodes that from the direct mixture of dried gelatin (271 F g\(^{-1}\)) and macroporous adsorption resin (251 F g\(^{-1}\)) at the same current loading. The synergistic effect of high specific surface area, well-balanced pore size distribution, low resistance and appropriate content of nitrogen and oxygen functionalities with a reasonable distribution in the carbon walls attribute to the high capacitance.

1. Introduction
Owing to multi-faceted merits such as high specific surface area, hierarchical porous size distribution, low-cost, environmental friendliness, physical, chemical and mechanical stability, porous carbon has been widely employed in electrochemical energy storage, water remediation, catalysis, and gas capture [1–4]. In terms of electrochemical energy storage, porous carbons have been demonstrated a great potential when being applied as electrode materials for double electric-layer capacitors (EDLCs) [2,5–7], which is a type of supercapacitors based on the energy storage mechanism of pure electrostatic interaction between the surface of electrodes and ions or molecules in the electrolyte [5,7,8]. EDLCs possess longer cyclic stability and higher power density compared to other electrochemical energy storage devices, e.g., pseudo-capacitors, another type of supercapacitors with the mechanism of fast reversible surface redox of electrodes, and rechargeable batteries [8,9]. Unfortunately, the lower energy density of EDLCs is hampering the widespread applications [8,9]. According to the quantitative equation of energy density (E): \(E = 0.5C_pV^2\), given a fixed operation voltage (V), a higher specific capacitance (\(C_p\)) produces a higher E. Therefore,
carbon-based electrode materials with high specific surface area, well-balanced porous size distribution, high conductivity and good wettability are essential to improve the performance of EDLCs [10]. Meanwhile, low-cost precursors and cost-effective synthesis processes are in an urgent call to transform EDLCs from a lab-based model to well-balanced porous size distribution, high conductivity and good wettability, and also by providing Faradaic pseudo-capacitance effects [22–27]. For heteroatom-doped porous carbons, beside of self-doping from nitrogen-containing precursors (i.e. the biomass) [19,21,25–27], ammonia activation nitrification has been regarded as a prevalent doping strategy. The latter can be simply described as processing carbon materials in ammonia atmosphere at high temperature [28]. The drawback is that ammonia scrubbing system inevitably elevates the cost, safety risk and complexity of entire processes. Therefore, it is of great urgency to find an environmental friendly, facile and efficient doping strategy in order to acquire excellent cost-effective heteroatom-doped porous carbons.

Since a long time, macroporous adsorption resins (MARs) have been recognized as excellent absorbent material with positive features such as hydrophilicity, high specific surface area, selective adsorption and desorption, acidic and alkaline stability, high mechanical strength, low-cost and environmental friendliness [29–33]. Commercial MARs often serve as the stationary phase in column chromatography for separation and purification of natural bioactive substances, e.g., polysaccharide [29], and peptides or proteins [30–33], etc., from biological crude extracts. Gelatin is a transparent non-crystalline mixture derived from irreversibly partial hydrolyzation of collagen from skin, bones, and connective tissues of animals [34]. As an abundant and sustainable resource, it has been widely used in imaging, food, pharmaceutical and manufacturing industries. Gelatin is also expected to be an economical and efficient carbon and/or nitrogen source in synthesis of N-doped porous carbons for sensing, supercapacitors and batteries [20,22,34].

Herein we report a new, facile and environment friendly strategy, named as “Adsorption-doping Approach”, to synthesize N-doped porous carbons. The new strategy is based on doping nitrogen-containing organics onto skeletons of organic porous adsorbent materials (OPAMs) by physical absorption. The workflow for the formation of N-doped porous carbon (in our case, NCGM) has been described in Fig. 1. As-obtained NCGM was tested as electrodes in supercapacitors, achieving a specific capacitance of 362 and 308 F g\(^{-1}\) at current densities of 1.0 and 5.0 A g\(^{-1}\), respectively (three-electrode test in 6.0 M KOH aqueous electrolyte). A capacitance of 266 F g\(^{-1}\) at a current loading of 1.0 A g\(^{-1}\) with a high energy density up to 9.13 Wh kg\(^{-1}\) were also obtained in a symmetrical two-electrode measurement. Suggestively, we believe that as a general strategy, it could also be applied to other types of OPAMs and heteroatom-containing organic absorbates to prepare other heteroatom-doped porous carbons.

2. Experimental section

2.1. Materials synthesis

Commercial MAR was purchased from Shandong Lukang Record Pharmaceuticals. Detailed physical properties of the MAR were summarized in Table S1. Gelatin was purchased from Sinopharm Chemical Reagent. The fresh MAR had been soaked for 0.5–2 h in deionized water before using. Other reagents in analytical grade were used as-received without further purification. Deionized water was used throughout the experiments.

NCGM sample was prepared via three steps including 1) gelatin (G) adsorption on MAR; 2) pre-carbonization of dried composite (G@MAR) precursor and 3) activation. Typically, 1.5 g gelatin was added into 40 mL deionized water (70 °C) along with moderate agitation until completely dissolved. When cooled down to room temperature, fresh MAR (7.5 g, pre-soaking in water for 1 h) was added into the gelatin solution. Moderate stirring for 60 min and then standing for 60 min, the wet compound was obtained after the filtration. The mixture has been dried at 70 °C overnight, and followed by pyrolysis at 500 °C for 60 min.

Fig. 1. Schematic illustration to prepare nitrogen-doped porous carbon based on adsorption-doping approach. i) Constructing N-containing precursor by physical adsorption. ii) Carbonization to result in pyrolytic char, and iii) activation to yield N-doped porous carbon.
with a heating rate of 4 °C min⁻¹ under N₂ atmosphere. The as-obtained residue was thoroughly washed with 0.5 M HCl solution and deionized water until neutral pH and then dried at 70 °C to harvest the pyrolytic char. Then the char was mixed with KOH (weight KOH/weight char = 3:1) and activated at 750 °C for 60 min, protected by N₂ under a heating rate of 4 °C min⁻¹. Finally, the solid was washed with 0.5 M HCl, deionized water and ethanol in turn and dried at 70 °C, namely NGGM.

Porous carbon derived from MAR (CMR), gelatin (CR), and direct mixture of solid state mixed of dried gelatin and MAR (CMGM) were also prepared via carbonization and chemical activation, respectively, similar to the above process.

2.2. Materials characterization

Thermal gravimetric analysis was performed via TGA/SDTAS851 (Mettler Toledo). Heating rate was 10 °C min⁻¹ from 30 to 800 °C under N₂ atmosphere. Fourier Transform Infrared spectroscopy analysis was performed on a Nicolet 6700 spectrometer (Thermo Fisher Scientific). Raman spectra measurement was carried out on a Renishaw in Via 2000 Raman spectrometer with Ar laser wavelength of 532 nm. X-ray diffraction was taken on a SmartLab (Rigaku) intelligent XRD system and structure. X-ray photoelectron spectroscopy was recorded on a K-Alpha spectrometer (Thermo Fisher Scientific) with Al Kα (1486.6 eV) as the X-ray source. The fitted analyses were performed on the XPSPEAK41 software. N₂ adsorption isotherm was measured at 77 K on an ASAP 2460 analyzer (Micromeritics). The specific surface area was calculated based on the Brunauer-Emmett-Teller and Langmuir models from the adsorption data in the linear range of relative pressure (P/P₀) 0.05–0.30. Pore size distribution was analyzed based on Horvath-Kawazoe model in case of microporosity and Barrett-Joyner-Halenda model in case of mesoporosity.

2.3. Electrochemical measurements

Electrochemical characterizations were carried out on a Shanghai Chenhua electrochemical workstation (CHI760D) at room temperature in 6.0 M KOH aqueous electrolyte. To prepare working electrodes, a viscous homogeneous slurry containing active materials, acetylene black and polytetrafluoroethylene in mass ratio of 85: 10: 5 were pressed onto a nickel foam current collector and then dried at 100 °C in a vacuum oven. Loading quantity of active materials on each current collector was 3.0 mg. In three-electrode tests, the load current collector, saturated calomel electrode and platinum plate were used as the working, reference and counter electrodes, respectively. Cyclic voltammetry curves were obtained in the working potential range of −1.1 and −0.1 V, by varying the scan rate from 5 to 100 mV s⁻¹. Galvanostatic charge–discharge profiles were collected in the same potential window at current densities ranging from 0.5 to 30 A g⁻¹. Electrochemical impedance spectroscopy was measured in a frequency range of 0.01 Hz–100 kHz at open circuit voltage with alternate current amplitude of 5 mV. In two-electrode tests, the preparation of two same electrodes were symmetrically assembled with a non-woven fabric as separator. The test potential window was 0–1.0 V.

The discharge gravimetric capacitance C_m (F g⁻¹) for a single electrode was calculated from galvanostatic charge–discharge profiles with the following equations:

\[ C_m = \frac{I \Delta t}{P} \]  
(Three – electrode test)

\[ C_m = \frac{2I \Delta t}{3P} \]  
(Two – symmetric – electrode test)

where I represented the discharge current density (A g⁻¹) based on the mass of active material within a single electrode. ΔV (V) referred the potential window exclusive of IR drop (V) within the discharge time Δt (s) \([21,22]\).

The energy density (E, W h kg⁻¹) and power density (P, W kg⁻¹) were calculated according to:

\[ E = \frac{1}{8} C_m \Delta V^2 \frac{1}{3.6} \]
\[ P = \frac{E \times 3600}{\Delta t} \]

where C_m represents the capacitance and Δt (s) is the discharge time referring to the voltage interval of the above two-symmetric-electrode test \([10,20,21]\).

3. Results and discussion

3.1. Adsorption-doping approach for nitrogen-doped porous carbon fabrication

Gelatin is a transparent, non-crystalline mixture of inorganic salts, amino acids, peptides and water-soluble proteins \([34]\). The composite precursor containing MAR and nitrogen-containing organic dopant G could be first fabricated based on physical adsorption in solution \([29]\). As a result, gelatin can be distributed on the pore surfaces and inner channels of MAR via non-covalent interactions, e. g., hydrogen bond and van der Waals force \([29–33]\). Afterwards, carbon skeleton derived from MAR was achieved with in-situ nitrogen doping with homogeneous distribution after carbonization of the dried composite. Finally, well-developed pore structures on carbon walls were introduced through activation process. As shown in Fig. 1, in our study, the MAR
3.2. Structural characterizations

Water-soluble gelatin was first dissolved in 70 °C deionized water and then was adsorbed in the porous structure of MAR at room temperature. Thermogravimetric analyses for dried precursors were then performed, as shown in Fig. 2. There were two decomposing intervals centered on 319 °C and 452 °C for the G@MAR composite, corresponding to the maximum decomposition rate of dried gelatin and MAR, respectively.

SEM revealed that the pyrolytic char was composed of micron- or submicron-scale 3D block assemblies after the carbonization of G@MAR (Fig. S1a). After activation, along with further narrowing of the sheets, lots of porous were formed simultaneously, as shown in Fig. 3a and b. The porous structure would provide sufficient storage space for the access of electrolyte ions. TEM analyses (Fig. 3c) not only confirmed the morphology of NCGM, but also implied that the major form of the char was amorphous (Fig. 3d and the inset graph of selected area electron diffraction). The SEM, TEM and HR-TEM records of other samples were shown in Figs. S2–S4. Notably, when using the similar processes for treating the direct mixture of dried gelatin and MAR, the microstructure of the resulting carbon partly remained intact spherical morphology with “meteorite crater”-like surface, even after chemical etching (Fig. S2a).

The XRD patterns (Fig. 4a) showed no obvious diffraction peak, indicative of the almost completely amorphous state of all products. Raman spectra (Fig. 4b) showed that all samples exhibited two absorbed peaks located at 1340 cm⁻¹ and 1590 cm⁻¹, which were corresponded to the D-band and G-band, respectively. D-band originates from the structure disorder of sp³ carbon atoms and G-band represents the graphite in-plane stretching vibrations (sp² carbon) [19, 27, 28]. All samples showed stronger intensities of D-band than G-band, suggesting low graphitization along with a higher extent of defects and disordered structures. The observed amorphous structural features of products from XRD pattern and Raman spectra were consistent with the results of HRTEM. The surface functional groups of the as-synthesized samples were identified by FT-IR spectroscopy (Fig. S5). The broad signals centered on 1080 cm⁻¹ was assigned to C–O stretching vibration. Peaks located at 1380 cm⁻¹ and 1630 cm⁻¹ corresponded to bending vibration of C–H, vibration of carbonyl group (C=O) and/or stretching vibration of C=C in aromatic ring, respectively. The intense bands centered upon 3440 cm⁻¹ was the result of O–H stretching vibration in carboxyl hydroxyl group (HO–C=O) and/or chemisorbed water on the sample surface [35–37, 38]. Peaks at 2850 cm⁻¹ and 2920 cm⁻¹ could be classified as –CH₂ symmetric stretching and −CH₂ anti-symmetric stretching, respectively [36, 38].

XPS analysis was conducted to determine chemical states of specified elements. Quantitative analysis information has been summarized in Table S2. Take NCGM for example, three peaks protruded from the survey spectrum (Fig. 4c), centering at 284.5, 399.9 and 532.2 eV prompted gelatin to cover on the pore surfaces and inner channels of MAR more evenly. The saturated adsorption microspheres fully broke into fragmented blocks in the following measurements. HRTEM records indicate the amorphous feature of CMG (Fig. S2d), CMR (Fig. S3d), and CG (Fig. S4d) samples.

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corresponded to C 1s (~93.66 at. %), N 1s (~1.85 at. %) and O 1s (~4.49 at. %), respectively. Detailed line shape analysis was performed by core level fitting. Three individual component peaks (Fig. 4 d) corresponding to \(sp^2\) hybridized C–C (284.5 eV), C–O (286.4 eV), and O–C–O (288.5 eV) could be extracted from the high-resolution (HR) C 1s spectrum [22, 39]. The HR N 1s spectrum shown in Fig. 4 e revealed the co-existence of three types of nitrogen-based groups including pyridinic N (N-6 at 398.2 eV, 28.3 at. %), pyrrolic N (N-5 at 399.9 eV, 46.8 at. %), and quaternary N (N-Q, 401.0 eV, 24.9 at. %) [21, 22, 40]. Generally, the pseudo-capacitive can be triggered on negatively charged pyridinic N and pyrrolic N. The positively charged graphitic N helps the electron transfer, and then improves the electronic conductivity of carbon materials [22, 23, 26, 27]. Deconvolution of the HR O 1s core-level fitting (Fig. 4 f) also provided three peaks at 533.3 eV, 532.2 eV and 531.3 eV, which corresponded to functionalities of O–C–O, O–C–O and C–O, respectively [19, 21, 39]. Oxygen arose from the incomplete release of the oxy-organics and potential oxygen adsorption on the surface of sample [27], and the nitrogen was derived from gelatin [20, 22, 34]. The co-existence of O and N functionalities not only enhanced the wettability and electrical conductivity of electrodes, but provided additional pseudo-capacitance for the EDLC as well [26, 27].

N\(_2\) sorption isotherms analyses were employed for investigating the pore distribution. Quantitative results have been summarized in Table 1. As shown in Fig. 4 g, all samples showed type-I sorption isotherms and nearly saturated at a low relative pressure \((p/p_0)\) below ~0.15, which indicated the abundance of micropores [21, 41]. Among these four samples, desorption branch of NCGM and CMGM with \((p/p_0)\) larger than ~0.45 demonstrated the presence of a slight type-H4 hysteresis loop (type-IV isotherm), indicating additional mesopores in the two samples [10]. Generally, taking NCGM as an example, distribution of microporosity (Fig. 4 h) calculated by Horvath-Kawazoe model revealed that pore sizes were mainly centered on 0.9 nm and 1.6 nm. Barrett-Joyner-Halenda method was applied to analyze the mesopores diameter distributions, Fig. 4 i illustrated that a sharp maximum peak located at ~3.7 nm, however, the contribution ratio of mesoporous for total volume and specific surface area was small. The NCGM held the largest \(S_{\text{BET}}\) of 1346 m\(^2\) g\(^{-1}\) with a total pore volume \((V_{\text{total}})\) of 0.60 cm\(^3\) g\(^{-1}\), and over 90% contribution of the volume was originated from the micropores. The CMGM had \(S_{\text{BET}}\) as low as 671 m\(^2\) g\(^{-1}\) with the total volume of 0.33 cm\(^3\) g\(^{-1}\). The CMGM and NCGM were obtained via same processes including carbonization and chemical activation. The difference of specific surface area between them was mainly related to the precursor. Previous reports have shown that, generally, a significant difference in \(S_{\text{BET}}\) of the powders with the
similar size of crystallites often deal with the different packing mode of these crystallites [41]. Since close packing of the crystallites could prevent the gas from the penetration into the bulk of the sample, only a fraction of its surface was available for the adsorption in this case. Therefore, the \( S_{\text{BET}} \) of this sample measured by the \( N_2 \) adsorption was reduced proportionally. In other words, the difference in the carbon particle packing mode in NCGM and CMGM could be related to the different spatial distribution of gelatin in the corresponding precursors before the carbonization. Therefore, it demonstrated that different mixing strategies not only seriously influenced the micro-topography, but also caused huge difference in pore structures. It is also a powerful proof of the effectiveness of “adsorption doping strategy” put forward in this work. It has been reported that high specific surface area could provide sufficient active electrode-electrolyte interface to form electric double layers [21]. Therefore, it is believed that the NCGM is highly desirable for supercapacitors.

3.3. Electrochemical performances

A three-electrode test in 6.0 M KOH aqueous solution was first introduced to evaluate electrochemical capacitance performances of as-synthesized samples. Take NCGM-based electrode as an example, Fig. 5a showed the quasi-rectangular cyclic voltammetry curve without obvious redox humps of NCGM-electrode at scan rate of 5 mV s\(^{-1}\) from 1.1 to 0.1 V, reflecting the capacitive behavior during the charge-discharge process. The reason was that the electrolyte ions had enough time to

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penetrate into the pores. In other words, the utilization ratio of basic pores was relatively high at a low scan rate. While the scan rate was elevated from 10 to 100 mV s\(^{-1}\), the rectangle gradually distorted (Fig. 5b), which was the result of the decreased available concentration of ions on the electrode/electrolyte interface. Further interpretation could be described as electrolyte ions diffusion mass transfer rate was relatively slow, leading to the quantity of electrolyte ions on the interface not able to be timely supplemented to match the quantity of ions that electrode needed at large current densities or high scan rate. Therefore, this would induce electrode polarization effect and then gradually become to the limiting step. At the current loadings from 1.0 to 30 A g\(^{-1}\), all galvanostatic charge-discharge profiles with approximate isosceles triangle shape were shown in Fig. 5c and d, illustrating the typical charge-discharge processes of nitrogen-doped carbon based electrodes. However, the fact is that the IR-drop is increasing with the increased current density due to the existence of internal resistance. Cycling life test at the current density of 8.0 A g\(^{-1}\) exhibited that the capacitance still remained 92.9% of the initial capacitance after 5000 cycles (Fig. 5f), suggesting a good electrochemical cycling stability.

Comparatively, NCGM-based electrode possessed the highest capacitive energy storage capacity, which could be concluded from the largest area loop among the cyclic voltammetry curves (Fig. 6a). NCGM-based electrode harvested specific capacitance as high as 362, 331 and 318 F g\(^{-1}\) at current densities of 1.0, 2.0 and 4.0 A g\(^{-1}\) (Fig. 5e), respectively, higher than the specific capacitance of carbon electrode materials from graphene, graphene oxide, templated carbon and bio-based activated porous carbons under similar test conditions in previous reports, and detailed quantitative comparisons have been listed in Table S4. The CG, CMR and CMGM electrodes respectively obtained the specific capacitance of 316, 271 and 251 F g\(^{-1}\) at 1.0 A g\(^{-1}\) current loading. By increasing the current density to 10 A g\(^{-1}\), specific capacitance of NCGM, CG, CMR and CMGM correspondingly retained about 303, 272, 216 and 196 F g\(^{-1}\) (Fig. 6d). Notably, even at the current density of 30 A g\(^{-1}\), NCGM, CG, CMR and CMGM still account for 77.6% (281 F g\(^{-1}\)), 81.6% (258 F g\(^{-1}\)), 79.3% (215 F g\(^{-1}\)) and 72.9% (183 F g\(^{-1}\)) of the initial specific capacitance at the 1.0 A g\(^{-1}\) respectively, indicating good rate capabilities. Detailed curves and profiles for CG-, CMR- and CMGM-based electrodes have been shown in Fig. S6–S8.

Nyquist plot (shown in Fig. 6e) was measured over the frequency ranging from 0.01 Hz to 100 kHz. All the samples exhibited the characteristic segment of circles at high-frequency, which consisted of charge transfer resistance (R\(_{ct}\)) and electrolyte resistance (R\(_{s}\)). In Warburg impedance (W) segment at mid-frequency, the 45° inclined lines reflected resistance of electrolyte ions diffusion/transport into these active materials [19,21,40]. Quasi-vertical lines in low-frequency indicated the capacitive behaviors, especially for NCGM. The value of R\(_{ct}\) and R\(_{s}\) could be quantified calculation from the semi-circle segment that right intercept of the same segment and the left intersection with the horizontal real axis (Z\(_{\text{real}}\)), respectively (Fig. 6e right panel). The NCGM electrode exhibited the smallest R\(_{ct}\) (~0.96 Ohm), R\(_{s}\) (~0.98 Ohm) and the CMGM electrode delivered the biggest resistances of ~1.35 Ohm and ~1.23 Ohm, respectively. It is well known that the lower resistance, the better electrochemical performance more likely to be achieved. In Bode plot (Fig. 6f), the characteristic frequency f\(_{0}\) at ~45° phase angle corresponds to the time constant t\(_{0}\) (~1/f\(_{0}\)). The time constant of NCGM, CG, CMR and CMGM were 0.83 s, 1.04 s, 0.89 s and 1.02 s, respectively. A much shorter time constant means that the rate of fast ion/charge transport is higher [10,21].

To further investigate the performance of NCGM material, the symmetric two-electrode test was carried out in the same electrolyte. The device exhibited typical rectangular cyclic voltammetry curves at different scan rates, indicating the capacitive feature (Fig. 7a). Symmetrical, linear galvanostatic charge-discharge profiles at various current densities were shown in Fig. 7b, suggesting the highly reversible charge-discharge process. A specific capacitance of 269 F g\(^{-1}\) was calculated at the current density of 1.0 A g\(^{-1}\), and a good satisfying retention rate could be demonstrated, retaining of 197 F g\(^{-1}\) (74.2%) and 188 F g\(^{-1}\) (71.1%) relative to 266 F g\(^{-1}\) at current loadings of 10 and 20 A g\(^{-1}\), respectively (Fig. 7c). Fig. 7d showed Ragone plot of NCGM electrode corresponding to the relationship between the energy density

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Fig. 7. Two-symmetric-electrode electrochemical performances. (a) Cyclic voltammetry curves, (c) galvanostatic charge-discharge profiles, (c) specific capacitance at different current densities, and (d) Ragone plot.
and the power density. One single electrode of the symmetric device delivered a maximum energy density of 9.13 Wh kg\(^{-1}\) with the power density of 254 Wh kg\(^{-1}\). The performance was better than that of any existing state-of-the-art EDLCs based on commercial porous activated carbon (4–6 Wh kg\(^{-1}\)) [11,21]. The energy density was also outstanding among various carbon materials based electrodes for supercapacitors under similar test conditions [14,19,21,22,42–45], as shown in Fig. 7d.

4. Conclusions

As a summary, a novel and simple strategy, namely adsorption-doping approach, based on the nitrogen-containing organics adsorption on OPAM was developed to prepare nitrogen-containing carbon precursor, yielding nitrogen-doped porous carbon by chemical activation. In the present study, gelatin was firstly absorbed on MAR, and then an in situ nitrogen-doped intermediate was obtained by carbonization. Finally, hierarchical porous structures were produced by chemical activation. The obtained NCGM-based electrodes showed better capacitive energy storage performance compared with porous carbons directly from MAR, gelatin and the mixture of dried gelatin and MAR powder. Electrochemical measurements showed that NCGM delivered the specific capacitance as high as 362 and 284 F g\(^{-1}\) at current densities of 1.0 and 30 A g\(^{-1}\), respectively, indicating good rate-capability. Specific capacitance remained ~92.9% after 5000 cycles at the current density of 8.0 A g\(^{-1}\), suggesting excellent stability. Symmetric-electrode tests revealed a specific capacitance of 266 F g\(^{-1}\) and a high energy density of 9.13 Wh kg\(^{-1}\). The present study demonstrated that the NCGM based on the adsorption of gelatin on MAR was a promising carbon electrode material for high-performance supercapacitors.

More importantly, the entire procedure of adsorption-doping approach showed advantages of facile, environmental friendly and cost-effective processes, compared to traditional doping methods. For example, the liquid-phase physical adsorption can distribute dopants more evenly into OPAM inner channels. Neither toxic chemicals nor additional exhaust gas treatment was needed. Further works could be focused on extending the present adsorption-doping approach to other types of matrix and heteroatom-containing organics to create various high-performance electrode materials for supercapacitors.

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Appendix A. Supplementary data

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References


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