In suit activation–graphitization strategy to fabricate hierarchical porous graphitic carbon for supercapacitor

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Abstract

In situ activation–graphitization method based on the atomically dispersed K and Fe in organic salts is developed to synthesize hierarchical porous graphitic carbon by directly pyrolysis potassium citrate and iron citrate. Moreover, (NH$_4$)$_2$C$_2$O$_4$ is also employed as both N dopant and porogen to open up internal structure and regulate pore structure. The inside-out activation leads to the homogeneous reaction and interconnected hierarchical porous structure with few dead pores. Accompanied by high $S_{\text{BET}}$, appropriate pore distribution, good conductivity, and N/O functional groups, the sample exhibits high capacitance of 322.6 F g$^{-1}$ at 0.5 A g$^{-1}$, good rate capability, and excellent cycling stability with 101.3% capacitance retention after 10000 cycles. The supercapacitor shows an energy density of 21.3 Wh kg$^{-1}$ at 456.7 W kg$^{-1}$ in 1 M Na$_2$SO$_4$. Easy synthesis, cost-effective, and environmentally benign, the work provides a promising strategy to produce hierarchical porous graphitic carbon applied in energy storage.

Introduction

Energy storage devices play a pivotal role in the development of clean and sustainable energy and they have been widely applied in electric vehicles, solar energy, wind power industry and so on$^{1,2}$. Supercapacitors represent one of the promising energy storage technologies owing to their high power density, fast charge-discharge rate, and long cyclic stability, which are interesting for various clean-energy device systems$^{3,4}$. Porous carbon (PC) materials offer numerous advantages for energy storage and show excellent electrochemical performances in supercapacitors, based on their large specific surface area ($S_{\text{BET}}$), hierarchical porous structure, relatively good conductivity, and excellent chemical and mechanical stability$^{5,6}$. Specifically, large $S_{\text{BET}}$ can provide numerous active sides for charge storage; hierarchical porous structure can simultaneously serve as ion-buffering reservoirs (macropores), act as rapid ion transfer channels (mesopores), and provide abundant locations for ions accumulation (micropores); good conductivity can greatly enhance electron transport kinetics$^7$. However, pore structure and electrical conductivity of carbon materials have a competitive relationship. A highly porous structure usually lead to poor electrical conductivity owing to excessive macropores and mesopores$^8$. In contrast, good electrical conductivity is usually linked with a high graphitization degree, giving rise to undeveloped pore structure and a small $S_{\text{BET}}$, which are unfavorable for ions transport and charge accommodation. On account of this, a rational balance the relationship between pore structure and electrical conductivity is of great significance to maximize the electrochemical performances.

Porous carbon, especially activated carbon, is often prepared by pyrolyzing carbon rich organic materials with activating agents to develop hierarchical porosity and enhance $S_{\text{BET}}^9$. However, the graphitic structure is not desirable after chemical activation. Catalytic graphitization with transition metals as catalyst is an effective way to promote the formation of graphitic structure. Previous researches indicate that the combination of chemical activation and catalytic graphitization is an effective way to simultaneously improve pore structure and graphitization degree. For example, carbon precursors are
treated with two different catalysts, which are used for chemical activation (pore-forming reagents: KOH, ZnCl$_2$, or K$_2$CO$_3$) and catalytic graphitization (metals salts containing Fe, Co, or Ni)$^8$. Chang et al. fabricated hierarchical porous carbon by metal ion pretreatment and a two-step post-activation$^{10}$. The presence of catalyst Co(NO$_3$)$_2$ is able to balance the reduced graphitization caused by activation. Many porous graphitic carbon (PGC) materials can also be synthesized by one-step carbonization with FeCl$_3$ and ZnCl$_2$ as graphitization catalyst and chemical activator, respectively$^{11,12}$. Although more effective, the majority of activating agents, such as KOH, ZnCl$_2$, and H$_3$PO$_4$, are highly corrosive and harmful, which cause serious corrosion of equipment and environmental problems. To this end, it is highly desirable to develop facile and eco-friendly strategy to develop hierarchical porous graphitic carbon (HPGC) with hierarchical porous structure and high graphitization degree.

Recently, carbon materials derived from organic salts (such as potassium citrate, ferric citrate, calcium gluconate) have drawn considerable attention, owing to their merits of low-cost, well-defined molecular, and facile procedures for carbonization and graphitization$^{13-15}$. Besides, organic salts have atomically dispersed metal species, such as K, Na, Ca, Fe, and so on. These dispersed metal species can be used as self-templates, activating agents, or graphitization catalysts. For example, the polymer containing K can be decomposed and produces K$_2$CO$_3$ during carbonization, which creates pores in carbon framework$^{16}$. As for iron species, it can be reduced by carbon to form Fe$_3$C at high temperature, which is an important intermediate product for the formation of graphitic carbon$^{17}$. Potassium citrate and ferric citrate as two different kinds of organic salts contain a decent amount of K and Fe atoms, respectively, which can achieve in-situ activation and in-situ graphitization during carbonization. Thus, taking advantages of organic salts, in suit activation–graphitization can be achieved by using potassium citrate and ferric citrate as carbon precursors. In this case, we also employed (NH$_4$)$_2$C$_2$O$_4$ as pore-forming agent and nitrogen precursor to increase the active surface area and provide additional pseudocapacitance$^{18}$. The fabrication process of carbon materials was described in Fig. 1.

**Results**

**Morphology and structural properties**

The morphology and pore geometry of the prepared carbon materials were observed by SEM images. Both PC-750 (Fig. 2a) and PGC-750 (Fig. 2b) exhibit a bulky monolithic morphology, and large pores are hard to be observed, indicating in-suit activation of potassium citrate mainly produces micropores. The solid block of carbon with few macropores or mesopores is disadvantageous for ions transport and energy storage. Surprisingly, when (NH$_4$)$_2$C$_2$O$_4$ is incorporated during the activation process, the bulk carbon particles are converted into unique, well-defined 3D honeycomb framework constructed by hierarchical porous carbon skeletons (Fig. 2d), showing good pore connectivity. The macropores are evenly distributed in HPGC-750, which originate from the chemically released gas (NH$_3$, CO, CO$_2$) from (NH$_4$)$_2$C$_2$O$_4$ during thermal pyrolysis. The different structures of PGC-750 and HPGC-750 indicate that the
The employment of \((NH_4)_2C_2O_4\) is contributed to the formation of interconnected porous structure. Figs. 2c–2e manifest that carbonization temperature is the key element influence the morphologies of carbon materials. With the increase of temperature, the honeycomb structure of HPGC-7 step-by-step becomes irregular, which caused by the collapse of the carbon skeleton at high temperature\(^{19}\). TEM images also confirm that HPGC-750 has a honeycomb-like porous structure with macropores, mesopores (Fig. 3a) and dense micropores (Fig. 3b). The combination of macropores, mesopores, and micropores can buffer electrolyte to shorten ion diffusion distance and facilitate fast ion transport to the interior surface, benefitting the creation of numerous electrochemical sites.

The \(N_2\) adsorption–desorption isotherm of PC-750 in Fig. 4a displays a type-I isotherm, indicating the existence of a large amount of micropores, which is in accordance with the pore size distribution curves in Fig. 4c. PGC-750 shows a type-II isotherm with an increased adsorption at high relative pressure region \((P/P_0 > 0.9)\), revealing that PGC-750 consists of micropores and macropores. Obviously, when using \((NH_4)_2C_2O_4\) as pore-forming agent, the adsorbed quantity of HPGC-750 dramatically increases and the isotherm can be classified as type-IV isotherm, which is attributed to a large number of mesopores in the sample as verified by pore size distribution curves in Fig. 4c. Mesopore can effectively minimize ion transport resistance and improve the wettability of the material\(^{20}\). Detailed texture properties of the samples are summarized in Table 1. When only potassium citrate used, PC-750 has the lowest \(S_{BET}\) of 1194.0 \(m^2\) \(g^{-1}\) and the smallest total pore volume \((V_{total})\) of 0.42 \(cm^3\) \(g^{-1}\), and the proportion of the micropore surface area \((S_{mic})\) of 994.0 \(m^2\) \(g^{-1}\) is up to 83.2%, further proves that in-suit activation of potassium citrate attributes to the formation of micropores. With the presence of ferric citrate, \(S_{BET}\) and \(V_{total}\) of PGC-750 increase to 1445.0 \(cm^3\) \(g^{-1}\) and 0.82 \(cm^3\) \(g^{-1}\), respectively. The distinct differences in porosity properties suggest that the presence of Fe species offer additional templates to create pores and increase \(S_{BET}\). Significant increase in both \(S_{BET}\) and \(V_{total}\) have been observed in HPGC-750 because the released gas (\(NH_3\), CO, CO\(_2\), and H\(_2\)O) from \((NH_4)_2C_2O_4\), which may act as pore-forming agents to coalesce numerous micropores to form mesopores.\(^{21}\) Carbonization temperature also has a great influence on porous structure (i.e. \(S_{BET}\), pore size distribution, and total pore volume). As seen in Fig. 4b, HPGC-700 and HPGC-750 have the same features about isotherms, but the isotherm of HPGC-800 has obvious changes. The \(S_{BET}\) of HPGC-7 follows the trend of HPGC-700 \((3118.3 \ m^2 \ g^{-1}) > HPGC-750 \ (2973.3 \ m^2 \ g^{-1}) > HPGC-800 \ (2951.1 \ m^2 \ g^{-1})\). The pore size distribution curves in Fig. 4d indicate an enlargement of pore size, especially mesoporous, as the temperature increases. The average pore size enlarges from 2.03 nm (HPGC-700) to 2.99 nm (HPGC-800). These phenomenons are caused by the collapse of carbon skeleton at higher carbonization temperature.

| Table 1 | Porosity properties of as-prepared carbon samples. |
The graphitic structures of the prepared carbon materials were investigated by XRD and Raman. As shown in Fig. 5a, both PC-750 and PGC-750 show a broad diffraction peak ($2\theta \approx 20–30^\circ$), which is the characteristic of amorphous carbon framework. While, PGC-750 has an additional peak at $2\theta = 26.26^\circ$ assigned to the (002) diffraction of graphitic carbon, indicating its partly graphitic structure. Interestingly, with the presence of $(\text{NH}_4)_2\text{C}_2\text{O}_4$, the intensity of (002) diffraction peak of HPGC-750 becomes sharper and stronger, suggesting a higher graphitization degree. Moreover, a higher intensity of peak at the low-angle scattering region indicates a high density of micropores, thus providing more active sites for charge storage. Carbonization temperature is one of the key factors affecting the graphitic structure of carbon materials. As shown in Fig. 5b, high temperature results in an increased intensity of (002) peak, which is related to the development of amorphous structure towards the graphitic structure.

Raman spectra further prove the characteristic of disorder carbon and graphitic carbon (Figs. 5c and 5d). All Raman spectra of samples show the well-known D-band (stemming from the disordered carbon) at around 1375 cm$^{-1}$ and typical G-band (originating from the $sp^2$-hybridized graphitic carbon) at around 1620 cm$^{-1}$. The $I_G/I_D$ value of carbon material can be taken as an index to reflect the graphitic degree. The $I_G/I_D$ values of PC-750, PGC-750, and HPGC-750 are 0.99, 1.00, and 1.02, respectively. In addition, the $I_G/I_D$ value increases from 1.00 (HPGC-700) to 1.02 (HPGC-800) with carbonization temperature increase from 700 to 800 °C, which is in accordance with the XRD patterns. The appropriate coexistence of graphitic and amorphous carbon could enhance electrical conductivity, improve wettability, and increase active surface area, benfitting for capacitance improvement.

The surface compositions of HPGC-750 were investigated by XPS. As shown in Fig. 6a, two pronounced peaks locate at ~284.8 and ~533.3 eV, attributed to carbon (C 1s, 85.10 at%) and oxygen (O 1s, 11.65 at%), respectively. And a weak peak appeared at ~401.7 eV should be attributed to N 1s, and the N content is 3.24 at%, indicating that NH$_3$ gas generated by pyrolysis process of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ subsequently doped into HPGC-750 to bring N into carbon matrix. The high-resolution of C1s spectra can be deconvoluted into four peaks (Fig. 6b), representing $sp^2$-bonded carbon (284.5 eV), $sp^3$-bonded carbon/C–N (285.0 eV), C–O (286.4 eV), and C=O/C=N (288.9 eV). The deconvoluted high-resolution O 1s
XPS spectra (Fig. 6c) exhibit five peaks centered at 530.7, 531.6, 532.7, 533.5, and 534.0 eV, corresponding to pyridone, C=O, C–OH, O–C–O, and O=C–OH, respectively. Four component peaks of nitrogen are found in the XPS spectra of N 1s (Fig. 6d), indicating four different chemical states of nitrogen atoms in carbon network, including pyridinic-N (398.6 eV), pyrrolic-N (399.9 eV), graphitic-N (400.87 eV), and quaternary–N$^+$–O$^-$ (402.47 eV). Among them, pyridinic-N and pyrrolic-N are electroactive and contribute to providing pseudocapacitance, and therefore enhanced capacitance, whereas graphitic-N can facilitate the electron transfer, improving the conductivity of carbon materials.

**Electrochemical measurements**

Due to honeycomb-like hierarchical porous structure, large accessible surface area, and sufficient heteroatoms, HPGC-750 is expected to be an ideal electrode for supercapacitors. Fig. 7a compares the CV curves of PC-750, PGC-750, and HPGC-750 at a current density of 10 mV s$^{-1}$. In the case of HPGC-750, the CV curve displays the largest CV curve area, indicating a higher specific capacitance, evidencing the advantages of 3D honeycomb-like hierarchical porous graphitic carbon. A slight hump is also observed, which is corresponding to the redox reactions of N and O functional groups. A pair of sharp peaks at the edge of −1 and 0 V could be ascribed to limited ion transport and adsorption in some irregular micropores with narrow bottlenecks. HPGC-750 also has the maximum CV curve area among HPGC-T samples (Fig. 7b). Although HPGC-700 possesses the largest $S_{BET}$, the relatively poor graphitization limited electron transfer and charge storage. Fig. 7c shows the CV curves of HPGC-750 at various scan rates from 10 to 100 mV s$^{-1}$. With increasing scan rate, a slight deviation from the rectangular nature of CV plots is associated with limited ions diffusion at higher scan rate.

The GCD curves of HPGC-750 are shown in Fig. 7d. The approximately symmetric triangle shapes of curves at all current densities indicate a predominantly double-layer charge storage mechanism. In Fig. 7e, we compare the specific capacitances of HPGC-750 with PC-750, PGC-750, and HPGC-T. HPGC-750 has the highest capacitance of 322.6 F g$^{-1}$ at 0.5 A g$^{-1}$. Besides, the high capacitance (258.4 F g$^{-1}$) at an ultrahigh current density of 30 A g$^{-1}$ is also obtained, suggesting 80.1% capacitance retention. This outstanding rate capability can be attributed to easy diffusion of ions into pore channels, buffering effect of hierarchical pores, and rapid charge transfer on the conductive network. Fig. 7f shows the cycling stability of HPGC-750 at a scan rate of 100 mV s$^{-1}$ for 10000 cycles. In the initial 1750 cycles, the capacitance maintains at 99.2% of the initial capacitance, and then increases to 101.3% after 2500 cycles. The cycling-induced increase of capacitance is attributed to the penetration of electrolyte ions and in-situ activation of electrode, which provide additional active surface area for charge storage. After 10000 cycles, 101.3% of initial capacitance is kept.

With 3D hierarchical porous texture and localized graphitic structure, CV curves of symmetric supercapacitor HPGC-750//HPGC-750 performed in 6 M KOH show rectangular shape at various scan rates (Fig. 8a). The rectangular nature even at a higher scan rate of 200 mV s$^{-1}$ is related to the presence of mesopores. All the GCD curves in Fig. 8b show regular symmetric triangle, which again confirm the
double-layer formation at the electrode-electrolyte interface. The maximum specific capacitance for a single electrode calculated from GCD curves is 245.1 F g\(^{-1}\) at 0.5 A g\(^{-1}\) and it retains 201.6 F g\(^{-1}\) at 10 A g\(^{-1}\), corresponding to 82.2% capacitance retention.

The symmetric supercapacitor HPGC-750//HPGC-750 was also tested in 1 M Na\(_2\)SO\(_4\), owing to its lower H\(^+\) and OH\(^-\), which allow it providing a larger operating voltage. Fig. 8c shows the CV curves of HPGC-750//HPGC-750 at 40 mV s\(^{-1}\) within different potential windows, and they present well reversible cycle even at a potential window of 0–1.8 V. The rectangle-like CV curves (Fig. 8d) and symmetrical GCD curves (Fig. 8e) within the voltage windows 0–1.8 V further demonstrate excellent rate capability. The Ragone plots in Fig. 8f show that symmetric supercapacitor HPGC-750//HPGC-750 has an excellent energy density 21.25 W h kg\(^{-1}\) at a power density of 456.8 W kg\(^{-1}\) and still retains 14.4 W h kg\(^{-1}\) at a high power density of 39875.6 W kg\(^{-1}\) in 1 M Na\(_2\)SO\(_4\) electrolyte. In 6 M KOH electrolyte, the energy density is 8.5 W h kg\(^{-1}\) at a power density of 253.0 W kg\(^{-1}\). The energy and power values are comparable or even superior to those of the previously reported carbon materials with aqueous electrolytes\(^{27-32}\). This is attributed to the honeycomb-like carbon skeleton benefiting the mass transport and electron transfer through the open pore channels and interconnected carbon network.

Electrochemical impedance spectroscopy was also measured to evaluate the ion and electron transport kinetics in different electrolytes. Fig. 9a shows the Nyquist plots of HPGC-750 supercapacitors in 6 M KOH and 1 M Na\(_2\)SO\(_4\). The vertical nature of curves in the low frequency region indicates nearly ideal capacitive performance. The semicircle in high frequency region is related to charge transfer resistance (\(R_{ct}\)). It is observed that the diameter of the semicircle for KOH is smaller than that for Na\(_2\)SO\(_4\). The value of equivalent series resistance (\(R_s\)) for KOH electrolyte is calculated to be 0.60 \(\Omega\) and it is 2.07 \(\Omega\) for Na\(_2\)SO\(_4\). The smaller \(R_s\) and \(R_{ct}\) for KOH electrolyte than that for Na\(_2\)SO\(_4\) electrolyte could be ascribed to high conductivity, small ions size, and quick ionic mobility of KOH electrolyte\(^{33}\). Fig. 9b shows the Bode phase angle plots. The large phase angles (\(-87.2^\circ\) for KOH and \(-82.5^\circ\) for Na\(_2\)SO\(_4\)) at low frequency indicate mainly electrical double-layer capacitance. The relaxation time constants (\(\tau_0 =1/f\), at the phase angle of \(-45^\circ\)) are 7.8 s for KOH and 3.3 s for Na\(_2\)SO\(_4\) electrolyte. The fast frequency response indicates the fast charge-discharge rate.

**Conclusion**

In summary, hierarchical porous graphitic carbon with interconnected framework has been successfully synthesized by in suit activation–graphitization method through only one-step pyrolysis of potassium citrate, ferric citrate, and (NH\(_4\))\(_2\)C\(_2\)O\(_4\). The obtained HPGC-750 balances the relationship between pore structure and electrical conductivity. It possesses favorable characteristics, such as high \(S_{BET}\) of 2973.3 m\(^2\) g\(^{-1}\), good conductivity, and hierarchical porous structure facilitating ion transportation and accommodation in electrodes. Such unique architecture endows HPGC-750 with excellent electrochemical performances: a high capacitance 322.6 F g\(^{-1}\) at 0.5 A g\(^{-1}\), good rate capability with
258.4 F g$^{-1}$ at 30 A g$^{-1}$, and an outstanding cycle stability (no loss after 10000 cycles). Supercapacitor prepared with HPGC-750 shows a high energy density 21.3 W h kg$^{-1}$ at a high power density of 456.7 W kg$^{-1}$ in 1 M Na$_2$SO$_4$ electrolyte. This study provides a promising strategy to develop hierarchical porous graphitic carbon for high-performance of supercapacitors and other energy researches such as fuel cell, catalysis, and so on.

**Methods**

**Materials**

Iron citrate (FeC$_6$H$_5$O$_7$·5H$_2$O) was provided by Aladdin Industrial Co., Ltd. Potassium citrate tribasic monohydrate (C$_6$H$_5$K$_3$O$_7$·H$_2$O) and diammonium oxalate monohydrate [(NH$_4$)$_2$C$_2$O$_4$·H$_2$O] were purchased from Tianjin Tianli Chemical Reagent Co., Ltd. Potassium hydroxide (KOH), sodium sulfate (Na$_2$SO$_4$) and hydrochloric acid (HCl) were provided by Tianjin Fengchuan Chemical Reagent Technologies Co. Ltd. All the chemical reagents were used as received. Deionized water was used throughout the experiments.

**Preparation of materials**

In a typical synthesis, 3 g potassium citrate tribasic monohydrate, 1.5 g iron citrate, and 8 g diammonium oxalate monohydrate were grinded homogeneously to achieve a sufficient contact. Subsequently, the mixture was carbonized in a N$_2$ atmosphere at high temperatures (700, 750, and 800 °C) for 2 h at a heating rate of 5 °C min$^{-1}$. The calcined products were treated with 3 M HCl solution and then washed with deionized water several times. After dried at 80 °C, the final product HPGC-$T$ was obtained (where $T$ represents carbonization temperature).

For comparison, the sample synthesized by solely pyrolysis potassium citrate at 750 °C was denoted as PC-750. To evaluate the effect of (NH$_4$)$_2$C$_2$O$_4$ on the structure of the resultant carbon materials, synthesis without (NH$_4$)$_2$C$_2$O$_4$ was also performed, and the resultant sample was labeled as PGC-750.

**Materials Characterization**

Scanning electron microscopy (SEM, JSM-6510F) was conducted to investigate and morphologies and structures of the samples. Transmission electron microscopy (TEM) was taken using FEI-G2F20. X-ray diffraction (XRD) patterns were obtained by Miniflex 600 diffractometer. Raman spectra were measured by using a Jobin-Yvon, HR 800 spectrometer. The N$_2$ adsorption–desorption isotherms were obtained by using Micromeritics ASAP 2460 instrument. Surface chemical composition of the sample was investigated by X-ray photoelectron spectroscopy (XPS, ESCALAB 250)$^{34}$.

**Electrochemical Measurement**

The electrochemical performances of samples were evaluated by cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and electrochemical impedance spectroscopy (EIS) through a CHI760e
electrochemical workstation. Active carbon material (2.4 mg, 80 wt%), acetylene black (10 wt%), and polytetrafluoroethylene (10 wt%) were mixed and coated on a nickel foam to prepare a working electrode. In a three-electrode system, Hg/HgO and Pt foil electrodes were used as the reference electrode and the counter electrode, respectively. The electrolyte was 6 M KOH solution.

Declarations

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Competing Interest

No

References

1 Wang, J., Zhang, X., Li, Z., Ma, Y. & Ma, L. Recent progress of biomass-derived carbon materials for supercapacitors. J. Power Sources 451, 227794, doi:10.1016/j.jpowsour.2020.227794 (2020).

2 Zou, L. et al. A Honeycomb-like bulk superstructure of carbon nanosheets for electrocatalysis and energy storage. Angew. Chem. Int. Ed. Engl., doi:10.1002/anie.202004737 (2020).

3 Zhu, Q. et al. A new view of supercapacitors: integrated supercapacitors. Adv. Energy Mater. 9, 1901081, doi:10.1002/aenm.201901081 (2019).

4 Shang, Y., Ma, S., Wei, Y., Yang, H. & Xu, Z. Flower-like ternary metal of Ni-Co-Mn hydroxide combined with carbon nanotube for supercapacitor. Ionics 26, 3609-3619, doi:10.1007/s11581-020-03496-7 (2020).

5 Chen, Z. et al. Excellent electrochemical performance of potassium ion capacitor achieved by a high nitrogen doped activated carbon. J. Electrochem. Soc. 167, 050506, doi:10.1149/1945-7111/ab6a84 (2020).

6 Chen, Y. et al. Preparation of nitrogen and sulfur co-doped graphene aerogel with hierarchical porous structure using ionic liquid precursor for high-performance supercapacitor. Ionics 25, 2781-2789, doi:10.1007/s11581-018-2785-y (2018).

7 Tian, W. et al. Porous carbons: structure-oriented design and versatile applications. Adv. Funct. Mater., 1909265, doi:10.1002/adfm.201909265 (2020).

8 Chen, Q. et al. Biomass-derived porous graphitic carbon materials for energy and environmental applications. J. Mater. Chem. A 8, 5773-5811, doi:10.1039/c9ta11618d (2020).
9 Zhang, Y. et al. Biomass organs control the porosity of their pyrolyzed carbon. *Adv. Funct. Mater.* **27**, 1604687, doi:10.1002/adfm.201604687 (2017).

10 Chang, C. et al. Fabrication of hierarchical porous carbon frameworks from metal-ion-assisted step-activation of biomass for supercapacitors with ultrahigh capacitance. *ACS Sustain. Chem. Eng.* **7**, 10763-10772, doi:10.1021/acssuschemeng.9b01455 (2019).

11 Hou, J., Cao, C., Idrees, F. & Ma, X. Hierarchical porous nitrogen-doped carbon nanosheets derived from silk for ultrahigh-capacity battery anodes and supercapacitors. *ACS Nano* **9**, 2556-2564 (2015).

12 Chang, B. et al. Graphitized hierarchical porous carbon nanospheres: simultaneous activation/graphitization and superior supercapacitance performance. *J. Mater. Chem. A* **3**, 9565-9577, doi:10.1039/c5ta00867k (2015).

13 He, Y. et al. Porous carbon nanosheets: Synthetic strategies and electrochemical energy related applications. *Nano Today* **24**, 103-119, doi:10.1016/j.nantod.2018.12.004 (2019).

14 Xue, D. et al. Template-free, self-doped approach to porous carbon spheres with high N/O contents for high-performance supercapacitors. *ACS Sustain. Chem. Eng.* **7**, 7024-7034, doi:10.1021/acssuschemeng.8b06774 (2019).

15 Sun, X. et al. Activation of graphene aerogel with phosphoric acid for enhanced electrocapacitive performance. *Carbon* **92**, 1-10 (2015).

16 Guan, L. et al. Green and scalable synthesis of porous carbon nanosheet-assembled hierarchical architectures for robust capacitive energy harvesting. *Carbon* **152**, 537-544, doi:10.1016/j.carbon.2019.06.059 (2019).

17 Zhang, X. et al. Porous graphitic carbon microtubes derived from willow catkins as a substrate of MnO2 for supercapacitors. *J. Power Sources* **344**, 176-184, doi:10.1016/j.jpowsour.2017.01.107 (2017).

18 Wang, K., Zhang, Z., Sun, Q., Wang, P. & Li, Y. Durian shell-derived N, O, P-doped activated porous carbon materials and their electrochemical performance in supercapacitor. *J. Mater, Sci.* **55**, 10142-10154, doi:10.1007/s10853-020-04740-1 (2020).

19 Zhang, X. et al. Strategy for preparing porous graphitic carbon for supercapacitor: Balance on porous structure and graphitization degree. *J. Electrochem. Soc.* **165**, A2084-A2092, doi:10.1149/2.0491910jes (2018).

20 Sun, N. et al. Hierarchical porous carbon materials derived from kelp for superior capacitive applications. *ACS Sustain. Chem. Eng.* **7**, 8735-8743, doi:10.1021/acssuschemeng.9b00635 (2019).

21 Chang, B. et al. N-rich porous carbons with a high graphitization degree and multiscale pore network for boosting high-rate supercapacitor with ultrafast charging. *Chem. Eng. J.* **350**, 585-598,
22 Sun, L. et al. From coconut shell to porous graphene-like nanosheets for high-power supercapacitors. *J. Mater. Chem. A* **1**, 6462-6470, doi:10.1039/c3ta10897j (2013).

23 Kumar, A., Das, D., Sarkar, D., Patil, S. & Shukla, A. Supercapacitors with prussian blue derived carbon encapsulated Fe/Fe$_3$C nanocomposites. *J. Electrochem. Soc.* **167**, 060529, doi:10.1149/1945-7111/ab838f (2020).

24 Li, B. et al. Nitrogen doped and hierarchically porous carbons derived from chitosan hydrogel via rapid microwave carbonization for high-performance supercapacitors. *Carbon* **122**, 592-603, doi:10.1016/j.carbon.2017.07.009 (2017).

25 Chen, Z. et al. High-performance supercapacitors based on hierarchically porous graphite particles. *Adv. Energy Mater.* **1**, 551-556, doi:10.1002/aenm.201100114 (2011).

26 Yoon, Y. et al. Anti-solvent derived non-stacked reduced graphene oxide for high performance supercapacitors. *Adv. Mater.* **25**, 4437-4444, doi:10.1002/adma.201301230 (2013).

27 Sun, Y. et al. Biomass-derived porous carbon electrodes for high-performance supercapacitors. *J. Mater. Sci.* **55**, 5166-5176, doi:10.1007/s10853-019-04343-5 (2020).

28 Ma, F. et al. Construction of 3D nanostructure hierarchical porous graphitic carbons by charge-induced self-assembly and nanocrystal-assisted catalytic graphitization for supercapacitors. *Chemical Commun* **52**, 6673-6676, doi:10.1039/c6cc02147f (2016).

29 Qian, W., Zhu, J., Zhang, Y., Wu, X. & Yan, F. Condiment-derived 3D architecture porous carbon for electrochemical supercapacitors. *Small* **11**, 4959-4969, doi:10.1002/smll.201500859 (2015).

30 Wei, T. et al. A one-step moderate-explosion assisted carbonization strategy to sulfur and nitrogen dual-doped porous carbon nanosheets derived from camellia petals for energy storage. *J. Power Sources* **331**, 373-381, doi:10.1016/j.jpowsour.2016.09.053 (2016).

31 Feng, H. et al. Hierarchical structured carbon derived from bagasse wastes: A simple and efficient synthesis route and its improved electrochemical properties for high-performance supercapacitors. *J. Power Sources* **302**, 164-173, doi:10.1016/j.jpowsour.2015.10.063 (2016).

32 Su, X. et al. Three-dimensional porous activated carbon derived from loofah sponge biomass for supercapacitor applications. *Appl. Surf. Sci.* **436**, 327-336, doi:10.1016/j.apsusc.2017.11.249 (2018).

33 Zhang, X. et al. Direct synthesis of porous graphitic carbon sheets grafted on carbon fibers for high-performance supercapacitors. *J. Mater. Chem. A* **7**, 3298-3306, doi:10.1039/c8ta11844b (2019).
34 Zhang, X. et al. Design and structure optimization of 3D porous graphitic carbon nanosheets for high-performance supercapacitor. *Microporous Mesoporous Mater.* **309**, 110580, doi:10.1016/j.micromeso.2020.110580 (2020).

**Figures**

**Figure 1**

Synthetic route to the fabrication of HPGC-T by direct pyrolysis potassium citrate and iron

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Synthetic route to the fabrication of HPGC-T by direct pyrolysis potassium citrate and iron
Figure 2

SEM images of (a) PC-750, (b) PGC-750, (c) HPGC-700, (d) HPGC-750, and (e) HPGC-800
Figure 3

TEM images of HPGC-750 under different magnifications.

Figure 4
(a) N2 adsorption-desorption isotherms and (c) the pore size distribution curves of PC-750, PGC-750, and HPGC-750; (b) N2 adsorption-desorption isotherms and (d) the pore size distribution curves of HPGC-T.

Figure 4

(a) N2 adsorption-desorption isotherms and (c) the pore size distribution curves of PC-750, PGC-750, and HPGC-750; (b) N2 adsorption-desorption isotherms and (d) the pore size distribution curves of HPGC-T.

Figure 5
(a) XRD patterns and (c) Raman spectra of PC-750, PGC-750, and HPGC-750; (b) XRD patterns and (d) Raman spectra of HPGC-T.

Figure 5

(a) XRD patterns and (c) Raman spectra of PC-750, PGC-750, and HPGC-750; (b) XRD patterns and (d) Raman spectra of HPGC-T.
Figure 6

(a) XPS survey of HPGC-750; high resolution XPS spectra of (b) C 1s, (c) O 1s, and (d) N 1s for HPGC-750.

Figure 7
Electrochemical characteristics of a three-electrode system in 6 M KOH: (a) CV curves of PC-750, PGC-750, and HPGC-750 at 10 mV s\(^{-1}\); (b) CV curves of HPGC-T at 10 mV s\(^{-1}\); (c) CV curves of HPGC-750 at various scan rates from 10 to 100 mV s\(^{-1}\); (d) GCD curves of HPGC-750 under various current densities; (e) specific capacitances of all electrodes as a function of current density. (f) cycling stability of HPGC-750 for 10000 cycles measured at 100 mV s\(^{-1}\).

Figure 7

Electrochemical characteristics of a three-electrode system in 6 M KOH: (a) CV curves of PC-750, PGC-750, and HPGC-750 at 10 mV s\(^{-1}\); (b) CV curves of HPGC-T at 10 mV s\(^{-1}\); (c) CV curves of HPGC-750 at various scan rates from 10 to 100 mV s\(^{-1}\); (d) GCD curves of HPGC-750 under various current densities; (e) specific capacitances of all electrodes as a function of current density. (f) cycling stability of HPGC-750 for 10000 cycles measured at 100 mV s\(^{-1}\).
Figure 8

Electrochemical characteristics of HPGC-750 symmetric supercapacitor: (a) CV curves at various scan rates in 6 M KOH; (b) GCD curves at various current densities in 6 M KOH; (c) CV curves tested in different potential windows at 40 mV s\(^{-1}\) in 1 M Na\(_2\)SO\(_4\); (d) CV curves at different scan rates in a potential window of 1.8 V in 1 M Na\(_2\)SO\(_4\); (e) GCD curves at different current densities in 1 M Na\(_2\)SO\(_4\); (f) Ragone plots of HPGC-750//HPGC-750 supercapacitor and performances comparison with other carbon-based symmetric supercapacitor (circle: 6 M KOH electrolyte, and sphere: 1 M Na\(_2\)SO\(_4\) electrolyte).
Electrochemical characteristics of HPGC-750 symmetric supercapacitor: (a) CV curves at various scan rates in 6 M KOH; (b) GCD curves at various current densities in 6 M KOH; (c) CV curves tested in different potential windows at 40 mV s⁻¹ in 1 M Na₂SO₄; (d) CV curves at different scan rates in a potential window of 1.8 V in 1 M Na₂SO₄; (e) GCD curves at different current densities in 1 M Na₂SO₄; (f) Ragone plots of HPGC-750//HPGC-750 supercapacitor and performances comparison with other carbon-based symmetric supercapacitor (circle: 6 M KOH electrolyte, and sphere: 1 M Na₂SO₄ electrolyte).

Figure 9
(a) Nyquist plots and (b) Bode phase angle plots of HPGC-750 symmetric supercapacitors in different electrolytes.

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