Porous Graphitic Carbon Nanosheets Derived from Cornstalk Biomass for Advanced Supercapacitors

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Porous graphitic carbon nanosheets (PGCS) are synthesized by an in situ self-generating template strategy based on the carburized effect of iron with cornstalks. Cornstalks firstly coordinate with [Fe(CN)₆]⁴⁻ ions to form the cornstalk–[Fe(CN)₆]⁴⁻ precursor. After carbonization and removal of the catalyst, PGCS are obtained. Series experiments indicate that PGCS can only be formed when using an iron-based catalyst that can generate a carburized phase during the pyrolytic process. The unique structures of PGCS exhibit excellent capacitive performance. The PGCS-1-1100 sample (synthesized from 0.1 M [Fe(CN)₆]⁴⁻ with a carbonization temperature of 1100 °C), which shows excellent electrochemical capacitance (up to 213 F g⁻¹ at 1 A g⁻¹), cycling stability, and rate performance in 6 M KOH electrolyte. In the two-electrode symmetric supercapacitors, the maximum energy densities that can be achieved are as high as 9.4 and 61.3 Wh kg⁻¹ in aqueous and organic electrolytes, respectively. Moreover, high energy densities of 8.3 and 40.6 Wh kg⁻¹ are achieved at the high power density of 10.5 kW kg⁻¹ in aqueous and organic electrolytes, respectively. This strategy holds great promise for preparing PGCS from natural resources, including cornstalks, as advanced electrodes in supercapacitors.

Introduction

Crop stalks are a type of natural cellulosic biomass, which could be considered as the most valuable and abundant renewable resource on earth.¹,² In China, the annual yield of natural cellulosic biomass exceeds 700 million tons, of which cornstalks account for over 30%.³ As a natural resource, cornstalks contain a rich nutritional and chemical composition, which has attracted special attention to cornstalks in industry, agriculture, and animal husbandry. Accordingly, about 50% of cornstalks have been used to produce feeds and fertilizers, and approximately 30% of cornstalks are used as the fuel and the industrial feedstock for the production of alcohol, hydrogen, and methane.⁴–⁷ However, huge amounts of cornstalks are still left in harvested fields without further utilization, which leads to various environmental problems, and more importantly, results in the waste of renewable resources. Because of the strategy of sustainable development, combined with the original concept of "waste-to-wealth", the potential application of cornstalks in materials science is attracting a large amount of attention.⁸–¹² Therefore, it is very important to convert cornstalks into carbon materials with specific structures because of the rich carbonaceous species that are contained within them. Unfortunately, cornstalks have only been utilized as the feedstock to synthesize activated carbon materials that only have one application, that is, as gas adsorbents.¹⁰ Cornstalks are composed of three main fractions, namely, cellulose, hemicellulose, and lignin, which contain abundant polar hydroxyl and carbonyl groups (see Figure S1).² Such characteristic features enable cornstalks to coordinate with various metal ions, which can be used for the synthesis of carbon materials.¹¹–¹³ These properties enable cornstalks to be an effective feedstock for carbon materials with specific structures for certain fields.

Electrochemical double layer capacitors (EDLCs, also called supercapacitors) that use carbon as the active material, are a class of device for electrical energy storage with high power densities, long lifespans, as well as rapid capture and storage of energy.¹⁴–¹⁸ The energy is stored at the electrolyte/carbon interface by charging of the double-layer capacitance through the reversible ion adsorption on the carbon surface.¹⁹–²¹ Thus, carbon materials with large Brunauer–Emmett–Teller (BET) specific surface areas (S_{BET}) are very important for high-performance EDLCs. However, activated carbon materials with a very high S_{BET} (above 2000 m² g⁻¹) only exhibit a limited improvement in capacitance because ion and electron transport are confined by the low mesoporosity and poor electronic conductivity of the material.²² Many efforts have recently been focused on preparing improved electrode materials with porous structures and good electronic conductivity; porous electrode structures can increase the number of interactions between the electrolyte ions and the electrode by decreasing the ion-transport resistance and diffusion distance, whereas good elec-
Electronic conductivity of electrode can increase electron transport at the electrode.\textsuperscript{[23–27]} Recently, 2D carbon nanomaterials with porous structures have attracted tremendous attention in the area of EDLCs owing to them possessing excellent electronic transportation properties, such as that of graphene.\textsuperscript{[28, 29]} Additionally, we recently discovered that the mesoporous carbon coating on graphene and graphite nanosheets with high $S_{\text{BET}}$ and suitable pore sizes show excellent electrochemical capacitance and cycling stability.\textsuperscript{[30, 31]} The successes have inspired us to synthesize porous graphitic carbon nanosheets (PGCS) as electrodes for EDLCs. To limit environmental pollution and resource scarcity, it is important to develop an economic method for preparing PGCS for EDLCs that are derived from biomass such as cornstalks.

The polar groups (i.e., carboxyl and hydroxyl) in the cellulose, hemicellulose, and lignin from cornstalks have previously been shown to coordinate with various metal ions.\textsuperscript{[11–13]} Our previous study demonstrated that the generation of planar cementite could be beneficial for the formation of 2D-layered carbon nanostructures.\textsuperscript{[32]} Herein, we present a template-free route to synthesize PGCS derived from cornstalks based on the carburized effect of iron. The template-free route means that the catalyst itself acts as the template; this is also referred to as an in situ self-generating template. In the synthesis, the cornstalks are firstly coordinated with $\text{[Fe(CN)}_6\text{]}^{4-}/\text{C}_0$ ions to form a cornstalk–$\text{[Fe(CN)}_6\text{]}^{4-}/\text{C}_0$ composite. After carbonization and removal of the catalyst, PGCS are obtained. To the best of our knowledge, we demonstrate the synthesis of PGCS from natural sources for the first time. Series experiments demonstrate that the selection of a suitable catalyst plays a key role in the formation of PGCS. The unique structure of the resultant PGCS allows for good performance in EDLCs, as illustrated in Scheme 1. Firstly, the highly porous structure is beneficial for electrolyte accessibility and rapid ion diffusion/transport by providing a short ion-diffusion distance. Secondly, the excellent conductivity of the 2D planar nanosheets with graphitic nanostructures are shown to facilitate fast electron transport during electrochemical processes. Finally, independent of the way in which the PGCS are connected, that is, in parallel or in series, the PGCS, which act as mini current collectors, can form an overall conductive network in the electrode. The synthesized PGCS can be used as electrodes for advanced supercapacitors with excellent capacitive performances. Our work demonstrates that cornstalks can be widely utilized as a natural renewable material for applications in materials science, which does not compete with food sources and is widely available as a low-cost feedstock.

**Results and Discussion**

**The structures of PGCS**

To synthesize PGCS, cornstalks were firstly immersed into $\text{K}_4\text{[Fe(CN)}_6\text{]}$ aqueous solutions for 4 h. The cornstalk–$\text{[Fe(CN)}_6\text{]}^{4-}/\text{C}_0$ composite was then obtained through a coordination effect between the cornstalks and $\text{[Fe(CN)}_6\text{]}^{4-}/\text{C}_0$ ions. After carbonization had occurred under argon and the catalyst was removed by using hydrochloric acid, the PGCS were prepared. The sample notation and synthesis conditions are displayed in Table S1. Further insight into the detailed microstructure of the sample was elucidated by using TEM. Figure 1 displays TEM images of PGCS-1-1100, which was synthesized from 0.1 mol $\text{K}_4\text{[Fe(CN)}_6\text{]}$ and carbonized at 1100°C. It was observed that the sample was composed of nanosheets with a mesopore size between 2 and 9 nm, which is a favorable size for applications in the field of supercapacitors. Moreover, the high resolution and high contrast in these images indicate that the PGCS have a layered structure with well-defined graphitic layers. The unique structure of the PGCS allows for good performance in EDLCs, as illustrated in Scheme 1. Firstly, the highly porous structure is beneficial for electrolyte accessibility and rapid ion diffusion/transport by providing a short ion-diffusion distance. Secondly, the excellent conductivity of the 2D planar nanosheets with graphitic nanostructures are shown to facilitate fast electron transport during electrochemical processes. Finally, independent of the way in which the PGCS are connected, that is, in parallel or in series, the PGCS, which act as mini current collectors, can form an overall conductive network in the electrode. The synthesized PGCS can be used as electrodes for advanced supercapacitors with excellent capacitive performances. Our work demonstrates that cornstalks can be widely utilized as a natural renewable material for applications in materials science, which does not compete with food sources and is widely available as a low-cost feedstock.
tion TEM (HRTEM) image shows the distinct lattice distance of graphite (001), which implied the presence of well-graphitized structures beneficial for electron transport. The above analyses indicated that samples containing PGCS were successfully synthesized.

The XRD pattern of PGCS-1-1100 exhibits the (002), (100) and (004) graphite diffraction peaks, see Figure 2a, which indicated that the synthesized sample had good crystallinity; this was consistent with the TEM results. Studies of samples derived from different catalyst concentrations and different carbonization temperatures were also performed for comparison. It was concluded that all samples synthesized by using this strategy presented high crystallinity from the strong characteristic diffraction peaks of graphite. Furthermore, the d-spacing \(d_{002}\), lateral size \(L_a\), and stacking height \(L_c\) were also calculated (Table S2). When the catalyst concentration or the carbonization temperature was increased, the \(d_{002}\) values decreased, whereas the \(L_a\) and \(L_c\) values increased. Crystallite sizes \((L_a\) and \(L_c\)) increase with decreasing \(d_{002}\) because the crystallinity of the samples increase.\[32, 33\] The decrease in \(d_{002}\) with an increase in catalyst concentration and carbonization temperature could be attributed to the development of stacking, which produced a more graphitic structure.\[34\] It was observed that PGCS-1-1100 had a more compact structure, similar to that of a graphite layer \((d_{002}\) for the graphitic structure was 0.335 nm).

To further evaluate the crystallinity of the carbon materials, the samples were characterized by using Raman spectroscopy, the results are shown in Figure 2b. The PGCS-1-1100 sample exhibited the three typical bands, that is, the G band \((1575 \text{ cm}^{-1})\), D band \((1361 \text{ cm}^{-1})\), and 2D band \((2725 \text{ cm}^{-1})\). The G band is characteristic of the vibration of \(sp^2\)-bonded carbon atoms in a 2D hexagonal lattice \((E_{2g} \text{ mode})\). The D band is associated with the vibrations of carbon atoms with dangling bonds for the in-plane terminations of disordered graphite. The second-order 2D band is typical of graphitic carbon.\[35\] The intensity ratio between the G and D bands \((I_G/I_D)\) is proportional to the graphitization degree of carbon materials (Table S3). The PGCS-1-1100 sample demonstrated a high \(I_G/I_D\) value of 1.6, suggesting high crystallinity consistent with the TEM imaging. The high crystallinity could facilitate electron transport during charging–discharging of supercapacitors. Moreover, the samples derived from different catalyst concentrations and different carbonization temperatures were also analyzed for comparison. All of the PGCS samples exhibited narrow D and G bands, and intense 2D bands, symbolic of graphitic carbon with high crystallinity. Additionally, the value for the ratio of \(I_G/I_D\) increased with increasing catalyst concentration and carbonization temperature, which implied that the crystallinity of the resultant PGCS also increased.

The structure of the PGCS samples were further investigated by conducting N\(_2\) sorption isothermal analysis; the results are shown in Figure 3 and the corresponding adsorption parame-

![Figure 2. (a) XRD patterns and (b) Raman spectra for the PGCS samples synthesized under various conditions. The produced carbon materials were labeled according to the catalyst concentration and the carbonization temperature, see the Experimental Section for details.](image)

![Figure 3. (a) N\(_2\) adsorption–desorption isotherms at \(-196 \degree C\) and (b) the corresponding NLDFT PSD curves for the PGCS samples.](image)

The typical type IV isotherms with H3 hysteresis loops indicate the presence of slit-like pores, which are the characteristic of platelet structures.\[36\] It was further demonstrated that the PGCS samples exhibit the structures of planar nanosheets. Moreover, hysteresis loops at \(P/P_0\) values between 0.5 and 0.9 implied that mesopores existed within the samples. These results were confirmed by calculating the pore size distribution (PSD) by using the nonlocal density functional theory (NLDFT) method (inset in Figure 3b), which demonstrated bimodal mesopore sizes of 2.3 and...
9.2 nm, consistent with the above TEM images. The PGCS-1-1100 sample exhibited a $S_{\text{BET}}$ of 540 m$^2$ g$^{-1}$. Moreover, the lowest and highest $S_{\text{BET}}$ values were demonstrated in PGCS-05-1100 and PGCS-1-1000, respectively, which were approximately 326 and 788 m$^2$ g$^{-1}$. It could also be concluded that the $S_{\text{BET}}$ value decreased consistently with increasing catalyst concentration and carbonization temperature. Therefore, the $S_{\text{BET}}$ values decreased with increasing crystallinity in the PGCS samples. It was anticipated that PGCS-1-1100 would exhibit excellent capacitive performance owing to its moderate crystallinity, $S_{\text{BET}}$ value, and pore size. The presented synthetic strategy demonstrated the following advantages: (i) PGCS could be produced from the natural biomass of cornstalks, (ii) PGCS could be synthesized without any additional porogen, in the absence of a template, (iii) it was simple and cost-effective, and (iv) the synthesized PGCS materials exhibited bimodal structures and high crystallinity. The above characteristics enabled the PGCS to be considered for supercapacitor applications.

**Formation mechanism**

2D graphene-like structures are generally formed by using a planar template. For example, the chemical vapor deposition (CVD) method utilizes planar Ni and Cu substrates as templates for the limited growth of graphene.[37, 38] In this study, the PGCS were obtained by carbonizing the cornstalk-[Fe(CN)$_6$]$_4^{-}$ composite and subsequently removing the catalyst. No substrate was adopted during the synthesis. Understanding the formation process of PGCS enables the controllable synthesis of carbon nanostructures that could be tailored for use in different fields.

The type of catalyst used could affect the structure of the resultant carbon materials. To study this effect, FeCl$_3$ solution was used as the catalyst instead of K$_2$[Fe(CN)$_6$] solution (the composite of cornstalk-Fe$^{3+}$ was formed after coordination), followed by carbonization and subsequent hydrochloric acid treatment. Figure S2 displays the TEM images of the as-synthesized GC-FeCl$_3$-1100 sample. It was observed that graphitic carbon nanocapsules could be obtained, but not PGCS. According to previous reports, Fe-, Co-, and Ni-based compounds could be used as the catalysts for the synthesis of graphitic carbon. To study the effect of the catalyst on the morpholo-

<table>
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<tr>
<th>Table 1. Adsorption parameters calculated from $N_2$ adsorption isotherms at $-196^\circ C$.</th>
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<tr>
<td><strong>Samples</strong></td>
</tr>
<tr>
<td>PGCS-05-1100</td>
</tr>
<tr>
<td>PGCS-1-1000</td>
</tr>
<tr>
<td>PGCS-1-1100</td>
</tr>
<tr>
<td>PGCS-1-1200</td>
</tr>
<tr>
<td>PGCS-3-1100</td>
</tr>
<tr>
<td>AC-1100</td>
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$^a$ $S_{\text{BET}}$ calculated from the BET equation. $^b$ $V_1$ is the single-point pore volume from adsorption isotherms. $^c$ $w$ is the mesopore diameter at the maximum of the PSD curves, calculated according to the adsorption branch of the isotherm by using the NLDFT method.

Based on the above analyses, a rational formation process was proposed, as illustrated in Scheme 2. Owing to the presence of cellulose, hemicellulose, and lignin, the cornstalk biomass was able to coordinate with metal ions through many polar groups (i.e., $-\text{OH}$ and $-\text{C-O}$), that is, [Fe(CN)$_6$]$_{n}^{4-}$ ions could coordinate with cornstalks to form a cornstalk-[Fe(CN)$_6$]$_{n}^{4-}$ composite material.[11–13] The [Fe(CN)$_6$]$_{n}^{4-}$-cornstalk composite could be pyrolyzed at a sufficiently high temperature, graphitized, and formed an Fe phase. Some carbon atoms were incorporated into the Fe phase to form dense Fe$_3$C layers. By increasing carbonization temperature, the active carbon atoms in the Fe$_3$C layers could diffuse out to form dense 2D carbon-atom layers (nanosheets) on the surfaces of the formed planar “Fe-template” layers; any excess amount carbon atoms were deposited on the formed nanosheets. During these processes, porous structures were formed through the pyrolysis of groups in the cornstalk-[Fe(CN)$_6$]$_{n}^{4-}$ composite. After the removal of Fe by using hydro-

![Figure 4.

XRD patterns for samples derived from the cornstalk-[Fe(CN)$_6$]$_{n}^{4-}$ composite, synthesized over a carbonization temperature range of 700–1100 °C.](image-url)
chloric acid treatment, PGCS were obtained. In this synthesis, the K₄[Fe(CN)₆] catalyst was favorable to form a dense layer-like “Fe template” that could limit the growth of the carbon atoms along the 2D plane, similar to the planar Cu and Ni substrates commonly used to prepare graphene by using CVD methods.[37, 38]

Electrochemical performances
Good electron transportation and electrolyte penetration are required properties for electrode materials used in EDLCs.[23–27] For the synthesized PGCS, the porous structures were favorable for the accessibility of the electrolyte and rapid ion diffusion/transport. Both the 2D planar carbon nanosheets and the graphitic structures could facilitate the fast transport of electrons. Owing to its unique structure, PGCS were anticipated to exhibit good performance as an electrode material for EDLCs.

The electrochemical performance of PGCS-based electrodes was investigated in 6 m KOH electrolyte by using a three-electrode system. Figure 5 shows the cyclic voltammetry (CV) curves for the PGCS-based electrodes, which were tested at scan rates of 10 and 100 mV s⁻¹. All of the PGCS-based electrodes exhibited a relatively rectangular shape, indicating better ion transport in the PGCS-based electrodes at high charge–discharge rates and ideal capacitive behavior. The sample prepared by directly pyrolyzing cornstalks under argon without any catalyst (denoted as AC-1100) was also studied. Different from the PGCS electrodes, the AC-1100 electrode presented distorted CV curves. This was associated with the low S_BET value of 0.6 m² g⁻¹ for AC-1100 (Figure S5), which implied a nonporous structure that was not favorable for the rapid diffusion of electrolyte ions. Also, the very broad and strong D band suggested an abundance of disordered carbon in AC-1100 (Figure S6),[39] implying poor electronic conductivity that was not beneficial for fast electron transport. Therefore, although the typical quasi-rectangular characteristic was observed in the CV curves, AC-1100 did not exhibit ideal performance because of a low S_BET and poor electronic conductivity.

The galvanostatic charge–discharge curves of electrode materials can be used to accurately determine the specific capacitance of supercapacitors in practical applications, which enable their energy and power densities to be calculated. Figure 6a displays the galvanostatic charge–discharge curves for the PGCS-based and AC-1100 electrodes at a current density of 1 A g⁻¹. All of the obtained galvanostatic charge–discharge curves were highly linear and symmetrical, indicating that the electrodes exhibited excellent electrochemical reversibility and charge–discharge properties.[40] The relationships between the physical properties and the performance of all of the synthesized samples are detailed in Table S3. The highest specific capacitance of 213 F g⁻¹ was demonstrated for the PGCS-1-1100 but without any catalyst is also provided for comparison.

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unique structure of the PGCS in EDLCs. The electrochemical performances of the graphitic carbon nanocapsules structures were also measured. The specific capacitances of the carbon materials that contained graphitic carbon nanocapsules structures (derived from different catalysts) were approximately 53–76 F g$^{-1}$ (see Figure S7 and Table S4 in the Supporting Information), which were lower than the PGCS-based materials. The difference was attributed to the different carbon nanostructures. It was demonstrated that the structures of the PGCS could facilitate the rapid transport of the electrolyte and electrons, leading to the improved electrochemical performance.

Electrochemical impedance spectroscopy (EIS) is an effective method for studying the fundamental behavior of carbon materials in EDLCs. The EIS investigation was performed by using an open-circuit voltage. The radius of the semicircle impedance loop (as shown in Figure 6b) in the high-frequency region could be attributed to resistance associated with the mass transfer/diffusion of ions through the porous structure of carbon material. PGCS-1-1100 exhibited the lowest resistance to electrolyte transport, indicating that PGCS-1-1100 could provide a shortened path for electron transport and electrolyte penetration. The straight line for the PGCS-1-1100 electrode in the low-frequency region was closer to 90° compared to other samples (vertical line for an ideal capacitor), further demonstrating that the PGCS-1-1100 electrode could exhibit excellent performance, which was consistent with the above charge–discharge tests. Notably, compared to AC-1100, all of the PGCS-based electrodes displayed a relatively small semicircle radius for the impedance loops at high-frequency and the straight lines were closer to 90° at low-frequency, implying that the structure of the PGCS was able to facilitate the rapid transport of electrons and electrolyte penetration. The fitting equivalent circuit model obtained by using the coupled nonlinear Schrödinger equation (CNLS) method is shown in Figure 6b. The entire capacitor circuit consisted of $R_s$, $Z_w$, $R_w$, $C$, and $Q$. Herein, $R_s$ refers to the ionic conductivity of the electrolyte and the electronic conductivity of the electrodes and current collectors, which is the sum of the contact resistance and material resistance. $Z_w$ is the Warburg resistance, which is related to ion diffusion/transport in the electrolyte. $R_w$ is the interface resistance of ion adsorption–desorption on the electrode materials. $C$ and $Q$ are related to the capacitor layer that was formed during the charge–discharge process. The fitting results are listed in Table 2. The PGCS-1-1100 electrode exhibit-

![Figure 6. (a) Galvanostatic charge–discharge curves for the PGCS-based and AC-1100 electrodes at a current density of 1 A g$^{-1}$ in 6 M KOH electrolyte, and (b) EIS spectra (presented as Nyquist plots) for the PGCS-based and AC-1100 electrodes in 6 M KOH electrolyte (10 mHz to 100 kHz, AC amplitude: 5 mV), and the corresponding electrical equivalent circuit that used to fit the impedance spectra.](image)

Table 2. The calculated values of $R_s$, $R_w$, $Z_w$, $C$, and $Q$ through CNLS fitting of the experimental impedance spectra based on the proposed equivalent circuit displayed in Figure 6b.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$R_s$ (Ω)</th>
<th>$R_w$ (Ω)</th>
<th>$Z_w$ (Ω)</th>
<th>$C$ (F)</th>
<th>$Q$ (F)</th>
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<tbody>
<tr>
<td>PGCS-05-1100</td>
<td>0.3861</td>
<td>0.5854</td>
<td>0.2708</td>
<td>2.3081</td>
<td>1.3594</td>
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<tr>
<td>PGCS-1-1000</td>
<td>0.3236</td>
<td>0.5663</td>
<td>0.1628</td>
<td>2.6567</td>
<td>1.6081</td>
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<tr>
<td>PGCS-1-1100</td>
<td>0.4319</td>
<td>0.6357</td>
<td>0.3226</td>
<td>1.2207</td>
<td>1.3223</td>
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<tr>
<td>PGCS-1-1200</td>
<td>0.5631</td>
<td>0.7531</td>
<td>0.5716</td>
<td>1.7852</td>
<td>1.2481</td>
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<tr>
<td>PGCS-3-1100</td>
<td>0.5077</td>
<td>0.6875</td>
<td>0.5343</td>
<td>2.567</td>
<td>1.1548</td>
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<tr>
<td>AC-1100</td>
<td>0.6916</td>
<td>0.9106</td>
<td>1.3529</td>
<td>0.8825</td>
<td>0.3205</td>
</tr>
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[a] Calculated by using ZSimWin software.

The capacitance retention with current density is a crucial criterion for estimating the potential application of carbon materials in EDLCs. An ideal EDLC should deliver the same energy at any current density because of extremely fast ion transport, which requires the carbon-based electrode material to exhibit the following features: (i) only large mesopores (> 2 nm) in carbon material, (ii) the diffusion path of electrolyte ions must be reduced to a few nanometers, and (iii) the interactions between the electrolyte ions and the carbon surface are minimal. Therefore, the power characteristics and the capacitance retention should not obviously decrease with the increase of current density. However, the ion “traffic jam” within the micropores of electrode materials and the interaction of the electrolyte with carbon functional groups increases Ohmic resistance. The electrode thickness is generally 10–300 μm, resulting in the capacitance of EDLCs dramatically decreasing at higher current densities. Nevertheless, the samples con-
taining PGCS exhibited good capacitance retention, and the retained capacity of the samples was kept between 70.5% to 81.3% of the initial capacitance as the current density was increased from 1 to 20 A g\(^{-1}\) (Figure 7a). The highest and lowest capacitance retention was observed in the PGCS-1-1100 and PGCS-05-1100 electrodes, respectively. Still, the AC-1100 exhibited the poorest initial capacitance of 36.7% when the current density was increased from 1 to 20 A g\(^{-1}\). Therefore, the PGCS-1-1100 electrode exhibited the best performance owing to its crystallinity, appropriate \(S_{\text{BET}}\) value, and pore size.

The cycling stability of the electrode materials for supercapacitors is crucial for practical applications. Figure 7b shows the cycling lifetime tests over 6000 cycles for the PGCS-1-1100 sample at a current density of 5 A g\(^{-1}\). PGCS-1-1100 exhibited good cycling stability and 98% of its initial capacitance was maintained even after 6000 cycles, as demonstrated by the charge–discharge curves for the last ten cycles (inset of Figure 7b), which was crucial for its consideration in practical applications. Importantly, the cycling efficiency still remained above 99% after 6000 cycles. It was demonstrated that the repetitive charge–discharge cycles did not result in any obvious changes of the structure of PGCS-1-1100, and simultaneous exfoliation of the electrode material (PGCS-1-1100) from the nickel foam current collector did not occur. The large capacity and excellent cycling stability of the synthesized PGCS-1-1100 sample was associated with its unique nanostructure, further indicating its potential application for advanced electrodes in high-performance supercapacitors.

Symmetric capacitors consisting of PGCS-1-1100 with aqueous and organic electrolytes were constructed, respectively. 6 M KOH aqueous solution and 1 M tetraethylammonium tetrafluoroborate in propylene carbonate (NEt\(_4\)BF\(_4\)-PC) were used as the aqueous and organic electrolytes, respectively. As shown in Figure 8a and b, the symmetric triangular galvanostatic charge–discharge curves indicated almost ideal capacitive behaviors with high coulombic efficiency at discharge current densities of 0.5, 1, and 2 A g\(^{-1}\) in both aqueous and organic...
electrolytes. The specific capacitances \( (C_{\text{cell}}) \) for both cells were about 63.5 and 47.3 \( \text{F g}^{-1} \) at the current density of 1 \( \text{A g}^{-1} \) in 6M KOH and 1M \( \text{NEt}_4\text{BF}_4 \)-PC electrolytes, respectively. A higher specific capacitance is generally obtained by using aqueous electrolytes compared to organic electrolytes. Nevertheless, one of the main advantages of EDLCs with organic electrolytes is that it is possible to deliver a higher energy density over a wider voltage window.\(^{[47]}\) Further characterizations were demonstrated in the Ragone plots, as shown in Figure 8c. A specific energy density of up to 9.4 Wh kg\(^{-1} \) could be achieved at extremely low power densities, and 8.3 Wh kg\(^{-1} \) was retained at a power density of 10.5 kW kg\(^{-1} \) in 6M KOH electrolyte. Additionally, a specific energy density of 61.3 Wh kg\(^{-1} \) was delivered at a lower power density in 1M \( \text{NEt}_4\text{BF}_4 \)-PC electrolyte. Moreover, a high specific energy density of 40.6 Wh kg\(^{-1} \) could be retained, even at a higher power density of 10.5 kW kg\(^{-1} \). The performances in both aqueous and organic electrolytes were much greater than that of the previously reported porous carbon-based materials, such as porous graphitic carbon, activated carbon/graphene, and carbon sphere/graphene composites.\(^{[48-50]}\) The good performance of PGCS-1-1100 in both aqueous and organic electrolytes further highlighted its potential in high-performance supercapacitors.

Conclusions

We demonstrate an in situ, self-generating template strategy, for the synthesis of PGCS. The \( S_{\text{BET}} \) and crystallinity of the synthesized PGCS can be tuned by changing the experimental parameters, including the catalyst concentration and carbonization temperature. The nanostructures of the obtained PGCS exhibit excellent energy storage performance as candidates for advanced electrode materials for supercapacitors. Remarkably, the synthesized PGCS-1-1100 material exhibits good capacitive characteristics (higher specific capacitance, improved capacity retention, as well as higher rate capability and cycling stability) in 6M KOH electrolyte. Also, the symmetrical capacitors can deliver high energy and power densities in both aqueous and organic electrolytes. The excellent performance is attributed to the unique structure of the PGCS: (i) the porous structure in the PGCS is favorable for the rapid diffusion of electrolyte ions by providing low-resistant pathways, and (ii) owing to the nature of excellent conductivity, the planar and graphitic structures of the PGCS can facilitate the electron transport. Additionally, the synthetic strategy opens up a new path to synthesize PGCS for applications in energy storage. Most importantly, this study emphasizes the exploration and adoption of the most abundant resource available in nature, that is, cornstalks, in the field of materials science.

Experimental Section

Preparation of PGCS

In a typical synthesis, cornstalks (2.6 g) without further treatment were immersed into \( K_4[\text{Fe(CN)}_6] \) aqueous solution (180 mL, 0.1 M) at 35°C for 4 h. During this process, the cornstalks coordinated with \( [\text{Fe(CN)}_6]^{3-} \) to form a cornstalk-[Fe(CN)]\(^{4+}\) composite. Then, the solid was collected and a pyrolytic procedure was conducted at 1100°C for 2 h with a constant heating rate of 5°C min\(^{-1} \) in an argon atmosphere. Subsequently, the sample was treated with hydrochloric acid (120 mL, 1.0 M) at 85°C for 6 h. Finally, the PGCS were obtained after being washed with water until neutralized and dried in an 80°C oven. The resultant samples were denoted as PGCS-c-T, where c was the concentration of the \( K_4[\text{Fe(CN)}_6] \) solution and T was the carbonization temperature. Therefore, the above synthesized sample was named as PGCS-1-1100. To study the effect of the carbonization temperature on the performance of the resultant PGCS, different carbonization temperatures were used to prepare PGCS-1-1000 (1000°C) and PGCS-1-1200 (1200°C). Samples synthesized from different concentrations of \( K_4[\text{Fe(CN)}_6] \) catalyst were also studied, denoted as PGCS-05-1100 (0.05 M) and PGCS-3-1100 (0.3 M). For comparison, a sample was prepared under the same conditions as that of the PGCS-1-1100 but without any catalyst; this sample was denoted as AC-1100. To study the effect of different metal catalysts on the nanostructure of the resultant carbon materials, the synthesis was performed by replacing \( K_4[\text{Fe(CN)}_6] \) with \( \text{FeCl}_3 \), \( \text{CoCl}_2 \), and \( \text{NiCl}_2 \) (180 mL, 0.1 M in all cases); the cornstalks coordinated with the \( \text{Fe}^{2+} \), \( \text{Co}^{2+} \), and \( \text{Ni}^{2+} \) ions to form cornstalk-\( \text{Fe}^{2+} \), cornstalk-\( \text{Co}^{2+} \), and cornstalk-\( \text{Ni}^{2+} \) composites, respectively. After carbonization at 1100°C and subsequent removal of the catalyst by using hydrochloric acid, the graphitic carbons, denoted as GC-\( \text{FeCl}_3 \)-1100, GC-\( \text{CoCl}_2 \)-1100, and GC-\( \text{NiCl}_2 \)-1100, were obtained. The sample numbers and detailed experimental parameters are displayed in Table S1.

Characterizations

XRD patterns were obtained by using a Rigaku D/max-IIIB diffractometer with CuK \( \alpha \) (\( \lambda = 1.5406 \) Å) radiation. The accelerating voltage and the applied current were 40 kV and 20 mA, respectively. TEM images were obtained with a JEM-2100 electron microscope (JEOL) and an acceleration voltage of 200 kV. Carbon-coated copper grids were used as the sample holders. Raman measurements were performed with a Jobin Yvon HR 800 micro-Raman spectrometer at 457.9 nm. X-ray photoelectron spectroscopy (XPS) studies were performed on a Kratos-AXIS UL TRA DLD with an AlK \( \alpha \) radiation source. The \( N_2 \) adsorption–desorption isotherms of the samples were obtained by using Micromeritics TriStar II. The samples were outgassed for 14 h at 210°C under vacuum before the measurements were obtained. The PSD was calculated by using the NLDFT method.

Electrode preparation and electrochemical measurements

The working electrodes were prepared by mixing the prepared PGCS active materials (75 wt%), carbon black (20 wt%), and polytetrafluoroethylene (PTFE; 5 wt%). The above electrode material mixture (5 mg) was pressed onto a foam nickel electrode. The electrochemical performance was tested by using a three-electrode system in 6M KOH aqueous electrolyte at room temperature. A saturated calomel electrode (SCE) and Pt slice were used as the reference and counter electrodes, respectively. CV curves were obtained by using a BAS100B electrochemical workstation. The constant-current charge-discharge capacitance tests (voltage window: \(-1.1-0.1 \) V) were conducted on a CHI 660D electrochemical workstation. The capacitance was calculated by using the following formula.\(^{[51]}\)
\[ C = \frac{|I|}{(m \Delta V)} \]  

herein \( C \) is the capacitance (F g\(^{-1}\)), \( I \) and \( \Delta t \) are the constant discharge current (A) and the discharge time (s), respectively, and \( m \) and \( \Delta V \) are the mass of active material within the electrode (g) and the potential range (V), respectively. The columbic efficiency was calculated by using the following formula:[44]

\[ \eta = \frac{t_d}{t_c} \]

herein \( t_d \) and \( t_c \) represent the times of charge and discharge, respectively. The two-electrode cells were prepared by using 2025-type coin cells. The aqueous and organic electrolytes used were KOH solution (6 m) and NE\(_2\)BF\(_4\)·PC (1 m), respectively. The symmetric cells were charged and discharged by using a LAND battery tester. The specific capacitance as well as other power and energy densities were calculated based on the total mass of the anode and cathode materials.[44] The energy densities (\( E_{\text{cell}} \)) were calculated by using the following formula:

\[ E_{\text{cell}} = 0.5 C_{\text{cell}} V^2 \]

herein \( C_{\text{cell}} \) and \( V \) are the total cell capacitance and the cell operation potential, respectively. The power density (\( P_{\text{cell}} \)) was calculated according to the following formula:

\[ P_{\text{cell}} = \frac{V^2}{(4\pi ESRm)} \]

herein \( ESR \) is the equivalent series resistance and \( m \) is the total mass of anode and cathode materials.

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