Nontemplating Porous Carbon Material from Polyphosphamide Resin for Supercapacitors

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HIGHLIGHTS
A cross-linking polyphosphamide resin with defined N and P structure is synthesized
A PCM prepared from the special resin exhibited high supercapacitor performance
The pore formation mechanism of the PCM was investigated

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Nontemplating Porous Carbon Material from Polyphosphamide Resin for Supercapacitors

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SUMMARY
The nontemplating preparation of porous carbon materials by using specially designed polymer precursors for supercapacitor is attracting considerable research attention because of the more controllable frame structure and easier processes than templating methods. Herein, a deliberately designed cross-linking polyphosphamide resin with defined N and P structure is synthesized and then carbonized to obtain porous carbon material. The as-obtained porous carbon material has a specific surface area of 2,620 m² g⁻¹, high porosity of 1.49 cm³ g⁻¹, and well-distributed micro/mesoporous carbon structure. Different from activation by post-added NH₄H₂PO₄, the confined N and P in the polymer frame are confirmed to play an important role in pore structure development by forming in situ highly dispersed NH₄H₂PO₄ during carbonization. When evaluated as the electrode material for supercapacitors, the polyphosphamide-resin-based porous carbon material demonstrates excellent capacitance (440 F g⁻¹ under 0.5 A g⁻¹) and high stability (retention of 93% over 10,000 cycles).

INTRODUCTION
With the depletion of conventional energy resources, green and sustainable energy conversion and storage technologies are attracting more and more attention. Among various energy storage devices, supercapacitors have their advantages of high charge-discharge rate, long cycle life, high energy conversion efficiency, etc. (Wang et al., 2012). According to the energy storage mechanisms, supercapacitors can be categorized into electrical double-layer capacitors (EDLCs) and pseudocapacitors (Salanne et al., 2016). EDLCs store energy through ion adsorption-desorption at the electrode-electrolyte interfaces. The typical materials for EDLCs always have high specific surface area (SSA), such as porous carbon (Yao et al., 2018), carbon nanotube (Yu et al., 2014), and graphene (Strauss et al., 2018). Pseudocapacitors store energy by reversible faradaic reactions of the electrode materials, such as Ni(OH)₂ (Su et al., 2014), MnO₂ (Wang et al., 2015), and V₂O₅ (Wang et al., 2018a). Up to now, EDLCs still hold the dominant market position owing to their low cost and high reliability.

Porous carbon materials (PCMs) are widely used as electrode materials in supercapacitors, especially EDLCs, owing to their stable physical and chemical properties, large SSA, controllable pore structure, high electronic conductivity, and low cost (Liu et al., 2017; Simon and Gogotsi, 2008; Zhai et al., 2011; Zhang and Zhao, 2009). The capacitance of PCM-based supercapacitors is mainly determined by the SSA and pore structure of PCMs, providing ion storage interface and facilitating the ion transportation, respectively (Chmiola et al., 2006a; Pandolfo and Hollenkamp, 2006). Therefore much research has been devoted to optimize the pore structure by preparing ordered and hierarchical (micropores and mesopores) PCMs on the premise of remaining large SSA to enhance the EDLC capacity (Kondrat et al., 2012; Largeot et al., 2008; Qie et al., 2013; Tran and Kalra, 2013). Although metal-organic frameworks (Hu et al., 2010) and metal carbides (Chmiola et al., 2006b) have been used to prepare pore-controllable PCMs, organic polymers are promising precursors because they can be handily designed and synthesized with specific structures and composition; these features are important to obtain PCMs with the desired pore structure (Dutta et al., 2014; Wei et al., 2013; Xu et al., 2013; Zhong et al., 2012).

Polymerization of monomers for preparing organic polymers provides the possibility of tuning the final structures, during which monomers may be restricted to the specific space for in situ polymerization or self-assembly. For instance, Böttger-Hiller et al. used spherical SiO₂ particles as hard templates to allow in situ monomer polymerization and prepared hollow carbon spheres with porous shell by carbonization and washing of the templates (Böttger-Hiller et al., 2013). Using surfactants or block copolymers as soft
templatizing can direct the polymerization of monomers, and after drying and carbonization, PCMs can be obtained (Chuenchom et al., 2012). For instance, block copolymers, such as Pluronic F-127 (EO106PO70EO106), are commonly used as structure-directing agents for the self-assembly of monomers (Hasegawa et al., 2016; Wang et al., 2018b; Xiong et al., 2017). Liang et al. reported that, by changing the mixture of F127, phloroglucinol, and formaldehyde and the processing conditions, different forms of fibers, sheets, films, and monoliths can be readily synthesized (Liang and Dai, 2006). Estevez et al. reported a dual-templatizing and post-activation strategy to prepare hierarchical porous carbon (Estevez et al., 2013). Combined ice-template and colloidal silica followed by physical activation was applied to generate interconnected macro-, meso-, and microporosity. However, most of the templates are rather expensive and nonrenewable, which limits their application.

In recent years, several studies focused on developing new methods from direct carbonization of special polymers without using any template (Hu et al., 2012; Zhang et al., 2013; Zhu et al., 2015). Porous structure can be formed by regulating the cross-linking style of the polymer or inserting specific elements into the framework. For instance, Puthusseri et al. reported a nontemplatizing method to synthesize interconnected microporous carbon material by direct pyrolysis of poly (acrylamide-co-acrylic acid) potassium salt without any additional activation. During the pyrolysis, the potassium in the polymer reacted with the carbon to form K2CO3, which creates pores in the carbon framework (Puthusseri et al., 2014). Sevilla et al. reported similar results by using potassium citrate as the precursor (Sevilla and Fuertes, 2014). Apart from K2CO3, chemical compounds, such as KOH, NH3, and NH4H2PO4, were also helpful in the formation of porous carbon (Krüner et al., 2018; Li et al., 2010; Wang and Kaskel, 2012; Zhou et al., 2015).

In this study, we proposed a nontemplatizing method to prepare PCM with high capacitance. We first designed and synthesized a hyper-cross-linked N, P-rich polymer containing the P–N groups, denoted as polyphosphamide resin (PAR). Hyper-cross-linked N, P-rich polymer with hierarchical framework can not only facilitate the formation of well-defined pore structure but also increase the SSA by activation of the formed N, P species (such as NH3 and NH4H2PO4). Afterward, the PAR was pyrolyzed and post-activated to prepare PCMs. The properties of PAR and the as-prepared PCM were characterized by Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), Raman spectrum, scanning electron microscopy (SEM), etc. The electrochemical capacitance performance of the as-obtained PCMs was evaluated both in the three-electrode and two-electrode systems. The role of N, P in improving the PCM performance was also investigated.

RESULTS
Preparation of Polyphosphamide Resin
PAR was prepared according to our previous work (Zeng et al., 2011). The synthetic route of the PAR is shown in Scheme 1.

In the synthesis of PAR, N–P bonds were formed to link the phosphoryl trichloride and hexane-1,6-diamine. Phosphoryl trichloride acted as a center to connect three molecules of hexane-1,6-diamine, and the other head of hexane-1,6-diamine was bonded to another phosphoryl trichloride. Thus, a branch-like network grew. Therefore the O=P–(N–C)3 structures were well-dispersed as nodes in the PAR network, as shown in Figure 1.
The FTIR spectrum of PAR is shown in Figure 2A. The broad band at 3,422 cm \(^{-1}\) indicated the existence of N–H. The doublet peaks occurring at 2,930 and 2,858 cm \(^{-1}\) were ascribed to the symmetric and asymmetric stretchings of alkyl C–H. The band at 1,640 cm \(^{-1}\) was the stretching of P=O. The peaks at 1,546 and 1,463 cm \(^{-1}\) were the deformation vibration of N–H and bending vibration of C–H, respectively. The peaks at 1,267 and 1,096 cm \(^{-1}\) were attributed to the symmetric and asymmetric stretching vibrations of C–N. Notably, the peak at 982 cm \(^{-1}\) indicated the presence of N–P. Furthermore, the XPS spectra shown in Figure S2 demonstrated the existence of N–P bonds. All these peaks found in the FTIR spectrum and XPS spectra suggested that the phosphoramide structure of the resin was formed, consistent with the initial design.

The thermal degradation behavior of PAR is shown in Figure 2B. Two major degradation peaks are shown in the differential thermal analysis curve (red line). One is from \(\sim 381^\circ\text{C}\) to \(495^\circ\text{C}\), with 18.6% loss of the total weight attributed to the decomposition of the P–N, C–N, and P=O groups. The other is from \(\sim 495^\circ\text{C}\) to \(779^\circ\text{C}\), with 52.1% loss of the total weight due to polymer carbonization (e.g., the cleavage of C–H and C–C bonds) to form the carbon framework.

**Physicochemical Properties of PCMs**

Based on the thermogravimetric analysis (TGA), the PAR was pyrolyzed under an Ar atmosphere to prepare PCM\textsubscript{PAR}. The morphology and structure of PCM\textsubscript{PAR} were first examined by SEM and transmission electron microscopy (TEM). The SEM image shows that PCM\textsubscript{PAR} has rough surface with multiple micropores (Figure 3A). The TEM image exhibits large number of micropores in the inner structure of the material (Figures
indicating that it is a porous material. The porous nature of PCM_{PAR} can enhance the performance of supercapacitor (Hou et al., 2015; Huang et al., 2016; Tian et al., 2015). N\textsubscript{2} adsorption-desorption method was used to analyze the SSA and pore texture of the PCMs. In Figure 3C, compared with PCM_{PFR}, PCM_{PAR} and PCM_{PFR+NP} exhibit a significant increase in volume when P/P\textsubscript{0} increases from 0 to 0.3. This phenomenon suggests that the curves are between types I and IV (IUPAC classification), which is attributed to the presence of certain mesopores in the materials (Tao et al., 2006). The result can also be proved by pore size distributions (Figure 3D), which indicates that all the PCMs possess a certain fraction of mesopores (>2 nm). The figure clearly shows that the micropores of PCMs concentrated at 1–3 nm along with a small proportion at approximately 0.5 nm. Notably, the proportion of mesopores showed an order of PCM_{PAR}>PCM_{PFR+NP}>PCM_{PFR}. The Brunauer–Emmett–Teller (BET) SSAs of PCM_{PAR}, PCM_{PFR}, and PCM_{PFR+NP} were 2,620, 2,233, and 3,062 m\textsuperscript{2} g\textsuperscript{-1}, respectively. The SSA, pore volume, and average pore size of the PCMs are summarized in Table 1.

Influence of the Precursor on the Formation of PCMs

To reveal the roles of nitrogen and phosphorus in the formation of special pore structure of PCM_{PAR}, PFR was selected as a common precursor to fabricate PCM_{PFR}, which contains no nitrogen and phosphorus. The transformation of N and P during the entire process was investigated to explore their effect on the formation of PCMs. The change of P content during the porous carbon preparation is shown in Figure 4A. Briefly, 13.2 wt % P in original PAR concentrated to 18.8 wt % in PAR-char after pre-carbonization and further decreased to 0 wt % after activation (Table 1). This result can also be proved by the XPS result (Figures 4C and 4D). The high-resolution XPS spectra of N 1s were fitted and presented in Figure 4E. The peak at 401.0 eV of PCM_{PAR} and PCM_{PFR+NP} can be ascribed to the binding energy of graphitic-N, whereas the peak at 399.3, 401.0, and 401.9 eV of PCM_{PFR} can be fitted to pyrrolic-N, graphitic-N (eV), and oxidized-N, respectively (Sun et al., 2018). The content of the doped-N of all PCMs are around or below 1 atom % (1.14 atom % for PCM_{PAR}, 1.09 atom % for PCM_{PFR}, and 0.60 atom % for PCM_{PFR+NP}). Therefore we concluded that the low content of doped N has little influence on the capacitance performance, which is similar to the effect of phosphorus. X-ray diffraction (XRD) results showed that after PAR pre-carbonization, the nitrogen and phosphorus were transformed to NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4} in PAR-char. NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4} may act as an activating agent to create pores.

PCM_{PAR} had fine textural properties with high nitrogen uptakes and a BET surface area of 2,620 m\textsuperscript{2} g\textsuperscript{-1}, which was higher than that of PCM_{PFR} (2,233 m\textsuperscript{2} g\textsuperscript{-1}). Moreover, PCM_{PAR} had more mesopores than PCM_{PFR}, as proven by the pore size distribution and the average pore diameters (2.3 nm of PCM_{PAR} and 2.1 nm of PCM_{PFR}). To verify the importance of chemically bonded N and P in PAR, equal weight of NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4} was added in PFR-char for the following activation (PFR-char:NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4}:KOH = 0.59:0.41:4). The results showed that the introduction of NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4} to the PFR can significantly improve the micropore formation. Thus the pore volume (1.68 cm\textsuperscript{3} g\textsuperscript{-1}) and SSA (3,062 m\textsuperscript{2} g\textsuperscript{-1}) of PCM_{PFR+NP} increased, which was 1.37 times higher than that of PCM_{PFR} and 1.17 times higher than that of PCM_{PAR}. Therefore both external and in situ NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4} acted as an activating agent to create pores (Li et al., 2010; Xu et al., 2017). However, the in situ NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4} may be helpful in forming mesopores than externally added NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4}. It can be clearly found that PCM_{PAR} has a higher proportion of mesopores/micropores than PCM_{PFR+NP} (Figure 4D). This condition may affect the capacitance performance of PCM.
There are no sharp peaks in the XRD pattern of PCMPAR, PCMPFR, and PCMPFR+NP, indicating the amorphous state of carbon in PCMs (Figure S4). Raman spectra of the PCMs are shown in Figure S5. Two characteristic peaks at 1,340 and 1,580 cm$^{-1}$ are assigned to the defect-induced band (D) and graphitic band (G), respectively (Wang et al., 2018c). The disorder degree of the PCMs can be generally described by the intensity ratio between the D and G bands (I_D/I_G). The I_D/I_G of PCMPAR, PCMPFR, and PCMPFR+NP were 0.90, 0.98, and 0.92, respectively. The slightly lower I_D/I_G of PCMPAR indicated that it had lower disorder degree and higher degree of graphitization, which was beneficial to improve the electric conductivity.

**Explanation of the Effect of N and P**

The role of N, P in the formation of porous carbon was proposed (Figure 5). In pre-carbonization, N–P and C–N bonds decomposed, and part of the N, P combined with H to form NH$_3$ and PH$_3$. The others combined with H and O and transformed to NH$_4$H$_2$PO$_4$. The polymer framework was partially carbonized to form a

![Figure 3. Characterization of the PCMs](image)

(A) SEM image of PCMPAR (scale bar, 100 nm). (B) TEM image of PCMPAR (scale bar, 100 nm). (C) N$_2$ adsorption and desorption isotherms of PCMPAR, PCMPFR, and PCMPFR+NP. (D) Pore size distributions of PCMPAR, PCMPFR, and PCMPFR+NP.

| Sample Code | $S_{BET}$ (m$^2$ g$^{-1}$) | $V_p$ (cm$^3$ g$^{-1}$) | Pore Size (nm) | Elemental Analysis | XPS Analysis |
|-------------|--------------------------|------------------------|---------------|-------------------|--------------|
|             |                          |                        |               | N (wt %) | P (wt %) | N (at%) | P (at%) |
| PCMPAR      | 2,620                    | 1.49                   | 2.3           | 1.07    | 0       | 1.14    | 0.08    |
| PCMPFR      | 2,233                    | 1.19                   | 2.1           | 0.80    | 0       | 1.09    | 0       |
| PCMPFR+NP   | 3,062                    | 1.68                   | 2.2           | 0.27    | 0       | 0.60    | 0.16    |

*Pore volume determined at P/P$_0$ = 0.99.

![Table 1. Textural and Chemical Properties of PCMPAR, PCMPFR, and PCMPFR+NP](image)
NH₄H₂PO₄-decorated raw char. During the activation process, KOH could firstly react with the NH₄H₂PO₄ as follows: NH₄H₂PO₄ +3 KOH = NH₃ + K₃PO₄ + 3H₂O. To confirm this hypothesis, we conducted Thermogravimetric Analysis and Fourier Transform infrared spectroscopy (TG-FTIR) characterizations of PAR samples. The pre-carbonized PAR (PAR-char) and the KOH-added sample (PAR-char + KOH) were first analyzed with a TG analyzer, and the released gaseous products were online analyzed by an FTIR spectrometer. TG-differential thermal gravity (DTG) results show that PAR-char + KOH has a significant weight loss in the range of 100°C – 400°C, which is rather different from PAR-char (>600°C). Given that PAR-char was already pre-carbonized at 500°C and exhibited no apparent weight loss (Figure S6), the weight loss of PAR-char + KOH should be caused by the reactions between NH₄H₂PO₄ in PAR-char and KOH during carbonization and released gaseous products. Furthermore, FTIR results show that H₂O, NH₃, and CO₂ were the main gaseous products of PAR-char + KOH, whereas little H₂O and NH₃ were released from PAR-char (Figures S5–S6 and S7), demonstrating that the reaction of NH₄H₂PO₄ in PAR-char and KOH occurred. Therefore the NH₄H₂PO₄ in PAR-char is not easy to decompose below 500°C, but can react with KOH during the heating process. In addition, the main gaseous products (H₂O, NH₃ and CO₂) as well as K₃PO₄ and the excess KOH can all act as activating agents to improve the porosity of
carbon substrate. Besides, the pre-carbonized PAR was just physically mixed with KOH powder, thus the NH$_4$H$_2$PO$_4$ embedded in carbon was partially in contact with KOH. Importantly, the special N–P structure of PAR formed highly dispersed NH$_4$H$_2$PO$_4$ and thus resulted in the development of well-distributed micro/mesopores, which is beneficial to improve the capacitance performance (Li et al., 2014; Zheng et al., 2015).

**Figure 5. Mechanism of the Formation of Micro/Mesopores**

(A) Scheme for PCM$_{PAR}$ synthesis from PAR, and the possible roles played by N and P during the formation of micro/mesopores.

(B) 3D infrared spectrum of gaseous compounds released during pyrolysis of PAR-char + KOH.

(C) 3D infrared spectrum of gaseous compounds released during pyrolysis of PAR-char.

(D) FTIR spectra of pyrolysis products of PAR-char + KOH at selected temperatures.

(E) FTIR spectra of pyrolysis products of PAR-char at selected temperatures.
Electrochemical Performance of the PCMs

The electrochemical performance of the PCMs was investigated with CV and GCD measurements. The cyclic voltammetry (CV) curves and galvanostatical charge–discharge (GCD) profiles of PCMs are shown in Figure S8. The CV curves of PCMPAR under wide scan rates from 5 mV s\(^{-1}\) to 100 mV s\(^{-1}\) showed a similarly rectangular and symmetric shape (Figure S8A). Importantly, the CV curves of PCMPAR still maintained a rectangular shape even at a sweep rate of 100 mV s\(^{-1}\) and an inapparent reduction in the CV area. This phenomenon indicated that PCMPAR has a fine ion transporting and accessible surface area. The PCMPFR and PCMPFR+NP had similar CV shapes with PCMPAR but suffered an area distortion at a high scan rate and a prominent area reduction with the increase in scan rate. This condition indicated a poor capacitance performance of PCMPFR and PCMPFR+NP at high charge-discharge rate. Instead of the typical rectangular shape, a region of reversible pseudofaradaic reaction can be observed at about 0.5 V in the CV curves. In addition, the approximate triangular charge-discharge profiles and their slightly nonlinear characteristic exhibited the primary EDLC performance and additional pseudocapacitance performance (Figure S8B). The pseudocapacitance can be attributed to the high oxygen content (7%–8%) of the PCMs (Table S1) (Guo et al., 2014; Liu et al., 2018; Tang et al., 2017).

CV curves of the PCMs at scan rate of 50 mV s\(^{-1}\) show that the specific capacitance has an order of PCMPAR>PCMPFR+NP>PCMPFR (Figure 6A). The result can also be proved by the GCD profiles under current density of 5 A g\(^{-1}\) (Figure 6B). The GCD measurements were performed under different current densities to assess specific capacitance (Figure 6C). The PCMPAR showed a high specific capacitance of 440 F g\(^{-1}\) under a current density of 0.5 A g\(^{-1}\) and still maintained at 278 F g\(^{-1}\) at a high current density of 20 A g\(^{-1}\). This PCM material shows a competitive performance among carbon-based supercapacitor electrodes (Table S2). As a comparison, the specific capacitances of PCMPFR and PCMPFR+NP are also listed in Figure 6C. PCMPFR had the lowest specific capacitance (348 F g\(^{-1}\) at 0.5 A g\(^{-1}\) and 150 F g\(^{-1}\)
at 20 A g\(^{-1}\)) attributed to the lowest SSA (2,233 m\(^2\) g\(^{-1}\)) because the specific capacitance of EDLC mainly depended on the SSA and porosity characteristics of electrode materials. PCM\(_{\text{FR+NP}}\) (3,062 m\(^2\) g\(^{-1}\)) had larger SSA than PCM\(_{\text{PAR}}\) (2,620 m\(^2\) g\(^{-1}\)), but the specific capacitance of PCM\(_{\text{FR+NP}}\) was not higher than that of PCM\(_{\text{PAR}}\) under overall current densities. When the current density was below 1 A g\(^{-1}\), PCM\(_{\text{FR+NP}}\) exhibited higher specific capacitance than PCM\(_{\text{PAR}}\). However, when the current density was above 1 A g\(^{-1}\), PCM\(_{\text{PAR}}\) showed high specific capacitance. At low charge-discharge rate, ions from the electrolyte had enough time to accumulate on the electrode surface. Therefore, SSA dominated the capacitance performance. Meanwhile, at high charge-discharge rate, ions cannot be delivered to the surface in time owing to the limitation of the pore structure. This phenomenon indicated that SSA was not finely utilized. As a result, the pore characteristics and the accessible surface area determined the specific capacitance at high charge-discharge rate. Researchers found hierarchical porous microstructures, namely, proper macroporous, mesoporous, and microporous distributions, which are favorable for the diffusion of electrolyte ions, thus leading to a high-rate electrochemical capacitance (Li et al., 2013; Zhang et al., 2016; Zheng et al., 2010). The pore size distribution showed that PCM\(_{\text{PAR}}\) has more mesopores than PCM\(_{\text{FR}}\) and PCM\(_{\text{FR+NP}}\) (Figure 2D). With the increase of the proportion of mesopores, PCM\(_{\text{PAR}}\) can provide a sufficient electrode-electrolyte interface for the accumulation of ions. Thus capacitance performance was improved.

Electrochemical impedance spectroscopy (EIS) was performed to further understand the ion or charge transport of the PCMs. As shown in Figure 6D, in the low-frequency region, the PCMs showed almost vertical curves, wherein PCM\(_{\text{PAR}}\) had the highest slope. This phenomenon indicated the nearly ideal EDLC behavior and the small equivalent diffusion resistance. In the high-frequency region (inset in Figure 6D), the intercept on the real axis presented low values (<0.4 Ω). This finding corresponded to low equivalent series resistances and indicated the excellent conductivity of the PCMs in aqueous electrolyte system. From the low- to high-frequency region, the low interfacial charge transfer resistances calculated from the diameter of the semicircle were 0.09 Ω of PCM\(_{\text{PAR}}\), 0.29 Ω of PCM\(_{\text{FR}}\), and 0.10 Ω of PCM\(_{\text{FR+NP}}\). The EIS results showed that PCM\(_{\text{PAR}}\) had smaller contact resistance among the electrode materials and electrolyte ions, indicating lower charge transfer resistance on the electrode surface. Furthermore, the cycling stability of the PCM\(_{\text{PAR}}\) was evaluated by long-term CV cycling measurement at a scan rate of 50 mV s\(^{-1}\). The result showed that PCM\(_{\text{PAR}}\) has fine capacitance retention of 93% over 10,000 cycles (Figure S9). Besides, PCM\(_{\text{PAR}}\), PCM\(_{\text{FR}}\), and PCM\(_{\text{FR+NP}}\) are all soaked well in water (Figure S10 and Table S3), which has no negative effect when used as electrode materials in aqueous solution. Combining the results of CV, GCD, EIS, and long-term cycling, PCM\(_{\text{PAR}}\) exhibited a favorable performance as supercapacitor electrode.

**DISCUSSION**

Phosphoramidate resin was synthesized, wherein the special N–P structure was chemically bonded as the nodes for linking the monomers into polymers. The N and P in the PAR framework can be transformed to NH\(_4\)H\(_2\)PO\(_4\) during carbonization. The well-distributed NH\(_4\)H\(_2\)PO\(_4\) acts as the in situ activating agent to form micro/mesopores, which has better effect on activation than post-added NH\(_4\)H\(_2\)PO\(_4\). The as-prepared PCM\(_{\text{PAR}}\) has a high SSA of 2,620 m\(^2\) g\(^{-1}\) and pore volume of 1.49 cm\(^3\) g\(^{-1}\) and fine micro/mesoporous structure. Electrochemical tests show that PCM\(_{\text{PAR}}\) has approximately rectangular CV curves and triangular GCD profiles. This finding indicates that PCM\(_{\text{PAR}}\) is a typical EDLC electrode. The PCM\(_{\text{PAR}}\) exhibits a specific capacitance of 440 F g\(^{-1}\) at 0.5 A g\(^{-1}\) and 278 F g\(^{-1}\) at 20 A g\(^{-1}\). The high capacitance retention at high charge-discharge rates signifies that PCM\(_{\text{PAR}}\) has fine micro/mesoporous structure for the transport of electrolyte ions. The results show that PAR is a good candidate to prepare PCMs for supercapacitor due to its unique form of N and P in the framework.
Limitations of Study

Based on the current preparation method of PCMs from PAR involving drastic activation, it is hard to precisely control the pore size. Therefore we would design and synthesize more N, P resins by changing the monomers in future work and adopt the mild activation process. The effect of monomer structures on the characteristics of the PCMs should be investigated to optimize the design and preparation of new PCMs for energy storage, catalysis, environmental remediation, and so on.

METHODS

All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION

Supplemental Information includes Transparent Methods, 10 figures, 3 tables, and 2 data files and can be found with this article online at https://doi.org/10.1016/j.isci.2019.01.016.

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AUTHOR CONTRIBUTIONS

H.J. developed the concept, designed the experiment, analyzed the data, and composed the manuscript. B.-H.C carried out the experiments and wrote the article. R.J. Z. coordinated the project. All authors provided critical discussion of the data and ideas and gave input on the manuscript.

Figure 7. Electrochemical Characterization of the PCM_{PAR} in Two-Electrode System
(A) CV curves of PCM_{PAR} at different scan rates in a two-electrode system.
(B) GCD profiles of PCM_{PAR} under different current densities.
(C) Specific capacitance of PCM_{PAR} calculated by GCD profiles.
(D) Ragone plot of PCM_{PAR}.
DECLARATION OF INTERESTS

The authors declare no competing interests.

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Supplemental Information

Nontemplating Porous Carbon Material from Polyphosphamide Resin for Supercapacitors

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Supporting Information

Nontemplating porous carbon material from polyphosphamide resin for
supercapacitors

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### Table S1. Oxygen content of PCMPAR, PCMPFR, and PCMPFR+NP, Related to Figure 6

| Sample code   | Elemental analysis | XPS analysis |
|---------------|--------------------|--------------|
|               | O (wt%)            | O (at%)      |
| PCMPAR        | 8.20               | 9.84         |
| PCMPFR        | 7.86               | 7.55         |
| PCMPFR+NP     | 7.32               | 9.49         |

### Table S2. Comparison of specific capacitance between the PCMPAR and other carbon materials, Related to Figure 6

| Supercapacitor materials                      | Specific surface area (m² g⁻¹) | Max. capacitance (F g⁻¹) | Scan rate or current density | Electrolyte    | Cycle number | Stability    | Ref.                        |
|----------------------------------------------|--------------------------------|--------------------------|------------------------------|----------------|--------------|--------------|-----------------------------|
| Hierarchical porous carbon                  | 1593                           | 298                      | 1 mV s⁻¹                    | 1 M H₂SO₄      | 5,000        | 96.7%        | (Zhang et al., 2018)        |
| N,PS-codoped hierarchically porous carbon spheres | 1258                           | 274                      | 0.5 A g⁻¹                   | 6 M KOH        | 10,000       | 95%          | (Yan et al., 2018)          |
| Hierarchically porous carbon nanotubes       | 1419                           | 286                      | 0.1 A g⁻¹                   | 6 M KOH        | 10,000       | ~100%        | (Wang et al., 2018a)        |
| N/S-co-doped carbon nanobows                 | 1567                           | 279                      | 0.1 A g⁻¹                   | 6 M KOH        | 50,000       | 90.8%        | (Wang et al., 2018b)        |
| hollow particle-based N-doped carbon nanofibers | 418                            | 307                      | 1.0 A g⁻¹                   | 2 M H₂SO₄      | 10,000       | 98.2%        | (Chen et al., 2017)         |
| Ultrathin porous carbon shell                | 662                            | 251                      | 1.0 A g⁻¹                   | 6 M KOH        | 10,000       | 97%          | (Yang et al., 2017)         |
| N-doped carbon with pillared-layered pores   | 2118                           | 305                      | 0.2 A g⁻¹                   | 6 M NaOH       | 10,000       | 89.1%        | (Tian et al., 2017)         |
| Phosphorus-doped 3D hierarchical porous carbon | 940                            | 367                      | 0.3 A g⁻¹                   | 6 M KOH        | 10,000       | 96.5%        | (Yang et al., 2018)         |
| Hierarchically porous nitrogen-doped carbon  | 2905                           | 302                      | 1.0 A g⁻¹                   | 6 M KOH        | 10,000       | 95%          | (Zou et al., 2018)          |
| Two dimensional holey carbon nanosheets      | 1258                           | 360                      | 1.0 A g⁻¹                   | 6 M KOH        | 10,000       | 97.7%        | (Cai et al., 2018)          |
| P,N,O co-doped polymer-based core-shell carbon sphere | 595                            | 157                      | 0.05 A g⁻¹                  | 1 M H₂SO₄      | 10,000       | 85%          | (Huang et al., 2018)        |
| N,S self-doped porous carbon nanosheets      | 986                            | 280                      | 1.0 A g⁻¹                   | 6 M KOH        | 10,000       | 94.4%        | (Miao et al., 2018)         |
Table S3. Oxygen content of $\text{PCM}_{\text{PAR}}$ and $\text{PCM}_{\text{PFR}}$ before and after 10,000 cycles, Related to Figure 6

|       | original   | after 10,000 cycles |
|-------|------------|---------------------|
| $\text{PCM}_{\text{PAR}}$ | 9.84 at%   | 14.86 at%           |
| $\text{PCM}_{\text{PFR}}$ | 7.55 at%   | 19.09 at%           |

Both the oxygen contents of $\text{PCM}_{\text{PAR}}$ and $\text{PCM}_{\text{PFR}}$ are increased after 10,000 cycles from the results of XPS survey (Table S2), indicating that the surface of the materials is oxidized to different extent.
Figure S1. Photograph of the as-synthesized PAR, Related to Scheme 1
Figure S2. XPS spectra of PAR, Related to Figure 2

(a) XPS survey spectrum of PAR.

(b) XPS N 1s spectrum of PAR.
Figure S3. TEM images of $\text{PCM}_{\text{PAR}}$. Related to Figure 3

(a) A scale bar of 200 nm.

(b) A scale bar of 100 nm.
Figure S4. XRD patterns of $\text{PCM}_{\text{PAR}}$, $\text{PCM}_{\text{PFR}}$, and $\text{PCM}_{\text{PFR+NP}}$, Related to Figure 3

As shown in Fig. S4, no sharp peaks are observed in the XRD pattern, indicative of the amorphous state of carbon in PCMs.
Figure S5. Raman spectra of $\text{PCM}_{\text{PAR}}$, $\text{PCM}_{\text{PFR}}$, and $\text{PCM}_{\text{PFR+NP}}$, Related to Figure 3
Figure S6. TG-DTG curves, Related to Figure 5

(a) PAR-char+KOH.

(b) PAR-char.
Figure S7. H₂O, NH₃, and CO₂ gaseous compounds released from pyrolysis of PAR-char+KOH and PAR-char, Related to Figure 5
Figure S8. Electrochemical characterization of the PCMs, Related to Figure 6

(a) CV curves of PCM$_{\text{PAR}}$ at different scan rates.

(b) GCD profiles of PCM$_{\text{PAR}}$ under different current densities.

(c) CV curves of PCM$_{\text{PFR}}$.

(d) GCD profiles of PCM$_{\text{PFR}}$.

(e) CV curves of PCM$_{\text{PFR+NP}}$.
Figure S9. Cycling stability of the PCMs over 10,000 cycles at a scan rate of 50 mV s\(^{-1}\), Related to Figure 6

The cycling performance of the PCMs was measured with 10,000 cycles. PCM\(_{\text{PAR}}\), PCM\(_{\text{PFR}}\), and PCM\(_{\text{PFR+NP}}\) showed capacitance retention of 93%, 93%, and 97% after 10,000 cycles, respectively.
Figure S10. Photograph of PCM$_{\text{PAR}}$, PCM$_{\text{PFR}}$, and PCM$_{\text{PFR+NP}}$ soaked in water, Related to Figure 6

PCM$_{\text{PAR}}$, PCM$_{\text{PFR}}$, and PCM$_{\text{PFR+NP}}$ are all soaked well in water (Figure S6), which has no negative effect when used as electrode materials in aqueous solution.
Transparent Methods

Materials

The cured phenol-formaldehyde resin (PFR) was purchased from a chemical company in Anhui, China and was then ground and screened through a 100 mesh sieve. All the chemicals used in this experiment were analytically pure and without further purification.

Preparation of polyphosphamide resin

Firstly, 0.045 mol hexane-1,6-diamine and 0.09 mol triethylamine were dissolved in 200 mL dichloromethane and mechanically stirred in a 500 mL three-neck flask. Besides, 0.03 mol phosphoryl trichloride was diluted by 100 mL dichloromethane and transferred to a drip funnel. Then, the solution in the funnel was added dropwise into the flask. Continuous stirring was maintained, and the flask was cooled in an ice-water bath throughout the reaction. After stirring for 8 h, the resultant crude product was filtered and washed thrice with methanol and water successively. Then, the solid was dried in a vacuum oven at 80 °C for 24 h. Finally, the dried PAR was ground and screened through a 100 mesh sieve to collect the particles (Figure S1).

Preparation of PCMs

The PCMs were produced using PAR or PFR as carbon precursors. The synthesis of the PCMs consisted of the following steps: pre-carbonization and chemical activation. In the pre-carbonization, 5 g PAR or PFR powder was heated in an alumina crucible at 500 °C for 1 h in an argon flow at a 5 °C min \(^{-1}\) in a tube furnace.
The pyrolyzed char (denoted as C) was collected for further use.

For the chemical activation, the pyrolyzed char was first ground with powder KOH at a weight ratio of 1:4 (char:KOH). Then, the mixture was heated to 700 °C for 1 h at 5 °C min\(^{-1}\) in a tube furnace. After cooling down, the activated samples were thoroughly washed with 10 wt% HCl solution to remove the inorganic compounds and then washed with deionized water until neutral pH. Finally, the samples were dried in a vacuum oven at 80 °C for 24 h, and the obtained PCMs were denoted as PCM\(_{\text{PAR}}\) and PCM\(_{\text{PFR}}\). To explore the effect of nitrogen and phosphorus in this process, we made a control test that contains NH\(_4\)H\(_2\)PO\(_4\) as extrinsic N and P elements. In addition, the corresponding activation was held at the same heating condition at a weight ratio of 0.59:0.41:4 (PFR–char:NH\(_4\)H\(_2\)PO\(_4\):KOH) according to X-ray diffraction (XRD) result. The obtained porous carbon was denoted as PCM\(_\text{PFR-NP}\).

**Characterization of materials**

The FTIR results were recorded using a VERTEX 70 FTIR (Bruker Co., Germany) spectrometer. Thermogravimetric analysis (TGA) of PAR was performed on a TGA instrument (TGA, Q5000, V3.15, Build 263). Scanning electron microscopy (SEM, Sirion 200, FEI electron optics company, USA) and transmission electron microscopy (TEM, JEOL-2100F, Japan) were applied to visualize the morphology of the PCMs. N\(_2\) adsorption–desorption isotherms were performed at \(-196 \, ^\circ\text{C}\) by using a Micromeritics ASAP 2020 (Micromeritics Gemini apparatus, ASAP 2020 M+C, Micromeritics Co. USA) to access the SSA and pore size distributions. Brunauer–Emmett–Teller (BET) method was used to calculate the SSA.
The pore size distributions were recorded based on density functional theory (DFT) method. The elemental compositions (C, H, N, and O) of the materials were determined by an elemental analyzer (VARIO EL III, Elementar Inc., Germany). The P content of the samples was determined by the molybdate–ascorbic acid method. The solid samples were first digested in concentrated HNO₃/H₂O₂ at 240 °C. The P concentration in the digestion solution was determined by the molybdate–ascorbic acid method on a UV–VIS spectrophotometer (UV-1800PC Spectrophotometer, Mapada Instruments, China). XRD patterns were collected with 2 θ scan range between 10° and 70° by using a X-ray diffractometer with an 18 kW rotating anode (MXPAHF, Japanese Make Co., Japan). XPS was performed using a Thermo VG-Scientific spectrometer (ESCALAB250, UK) with a monochromatized Al Kα radiation (1,486.92 eV). Raman analysis of the samples was carried out in a Laser Raman spectrometer (LabRamHR, HORIBA Jobin Yvon Co., France) with a laser radiation source operating at 514 nm and a power of 25 mW. The thermal characteristic of pre-carbonized PAR (PAR-char) and the KOH added sample (PAR-char+KOH) were analyzed by online TG-FTIR, namely, the gaseous compounds released from the carbonization were analyzed by Pyris 1 TGA (PerkinElmer) combined with FTIR spectrometer.

**Electrochemical measurements**

For the fabrication of working electrodes, 90 wt% PCM powders and 10 wt% of binder (polytetrafluoroethylene in methanol) were dissolved in methanol and ultrasonically dispersed to obtain a slurry. Then, the slurry was loaded on nickel foam.
by coating an effective geometric area of 1×1 cm² and dried at 80 °C for 30 min. The as-prepared electrodes were then pressed under 10 MPa for 30 s and further dried at 80 °C overnight. The mass loading of carbon materials in electrode is 2 mg cm⁻². Electrochemical measurements were performed using a three-electrode system with 6 M KOH as electrolyte. Platinum wire and Hg/HgO electrode were used as the counter electrode and reference electrode, respectively. Cyclic voltammetry (CV), galvanostatical charge–discharge (GCD), and AC electrochemical impedance spectroscopy (EIS) were recorded on a CHI 760E electrochemical workstation (CH Instrument Co., China). CV curves were obtained at scan rates of 5 mV s⁻¹ to 100 mV s⁻¹ within the potential window from −1.0 V to 0 V (vs Hg/HgO). GCD measurements were carried out at current densities of 0.5 A g⁻¹ to 20 A g⁻¹ over a potential range from −1.0 V to 0 V (vs Hg/HgO). The discharge specific capacitance was calculated from the GCD curves by using Eq. 1 (Wang et al., 2012a):

\[ C_m = \frac{I \Delta t}{m \Delta V} \]

(1)

where \( I \) (A) is the discharge current; \( \Delta t \) (s) is the discharge time; \( \Delta V \) (V) is the voltage change after IR drop; \( m \) (g) is the mass of the PCMs in the electrode, and \( C_m \) (F g⁻¹) is the discharge specific capacitance. EIS was measured in a frequency range from 0.01 Hz to 100 kHz.

The electrochemical performance of PCM PAR was also measured in a two-electrode system with two nearly identical (by weight and size) working electrodes by using a glass fiber as separator. The weight of each electrode was ~2 mg loading in 1×1 cm² area. The CV curves and GCD profile data were obtained in 6 M
KOH electrolyte with a CHI 760E electrochemical workstation. The gravimetric specific capacitance \( C_g (\text{F g}^{-1}) \) of a single electrode was calculated from the discharge curve after the IR drop according to Eq. 2 (Qie et al., 2013):

\[
C_g = \frac{4I\Delta t}{m\Delta V}
\]

(2)

where \( I \) (A) is the discharge current; \( \Delta t \) (s) represents the discharge time; \( m \) (g) is the total mass of the active material on the two electrodes; and \( \Delta V \) (V) refers to the voltage change excluding the IR drop during the discharge. The energy density \( E_{\text{cell}} \) (Wh kg\(^{-1}\)) and power density \( P_{\text{cell}} \) (W kg\(^{-1}\)) were also calculated according to Eqs. 3 and 4 (Qie et al., 2013):

\[
E_{\text{cell}} = \frac{C_g \Delta V}{8 \times 3.6},
\]

(3)

\[
P_{\text{cell}} = \frac{E_{\text{cell}}}{t},
\]

(4)

where \( t \) (h) is the discharge time.
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