Accepted Article

Title: N, S, P Co-doped Interconnected Porous Carbon Nanosheets with High Defect Density for Enhanced Supercapacitors and Li-ion Batteries Properties

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemElectroChem 10.1002/celc.201800444

Link to VoR: http://dx.doi.org/10.1002/celc.201800444
N, S, P Co-doped Interconnected Porous Carbon Nanosheets with High Defect Density for Enhanced Supercapacitors and Li-ion Batteries Properties


Abstract: Porous carbon nanosheets with open 2D nanostructure have been considered a desirable and high-efficient energy-storage material. Herein, N, S, P co-doped interconnected porous carbon nanosheets (CPCNs) with high defect density and open 2D ultrathin nanostructure are prepared by using cork-shaped soybean aerogel as carbon sources. A reasonable design for the preparation technology controls the formation of the distinctive and ordered structure of intermediates during the synthetic processes. The as-prepared CPCN materials are made of interconnected nanosheets with a thickness of 4.9 nm and have a maximum N-dopant content of 5.83 at. % and a high specific surface area of 3586 m²g⁻¹. Due to the synergistic effects of the features, the CPCN electrode for supercapacitors has a high capacitance of 427 Fg⁻¹ with a long cycling stability of 97.42% after 10 000 cycles. For LiBs, the CPCN material also exhibits an excellent capacity of 1220 mAhg⁻¹ at 100 mAg⁻¹ with a high rate capability and cycling stability. Moreover, a scenario through using CPCN to enhance the electrochemical performance of nano-inorganic material proves a high scalability in the application for the products.

Introduction

The development of renewable energy and the application of high performance energy-storage devices are real and viable solutions for the energy and environmental problems. Super capacitors (SCs) and lithium-ion batteries (LIBs) have already attracted significant attention as promising energy storage systems. However, some of the distinct disadvantages, including unsatisfactory capacity, weak rate performance and insufficient long cycling stability, limit their further application in electric vehicles, blue energy storage, etc. To solve these issues, the development of high-performance electrode materials under a rational composition design is one of the effective ways. Currently, carbon-based materials, such as carbon aerogels, graphene, carbon nanotubes, carbon nanofibers, and activated carbon, have been widely studied as electrode materials in energy storage devices. Among them, activated carbon has been widely applied in SCs and LiBs because of their wide availability, relatively well-developed porosity and favorable surface area, which are important properties for increasing the capacity of energy storage devices. Besides, it is well known that a remarkable electrochemical performance also requires a high rate capability. The key to achieving a high rate capability is to decrease the transport time of the electrolyte ions in the electrode material. Therefore, porous carbon materials with open 2D nanostructures have received great attention because of the ability of this structure to effectively shorten ion-diffusion pathways and reduce ions diffusion resistance in the thin dimension. Moreover, defect engineering also is a powerful way for promoting the electrochemical performance of the porous carbon nanosheets as electrode materials for SCs and LiBs. The high-density defects within the carbon not only can offer more vacancies and edges to promote capacity by the insertion of ions, but also cause structural change resulting in a higher surface area and abundant ion-channels in favor of the storage and diffusion of electrolyte for SCs and LiBs. Currently, carbon materials with ultrathin 2D nanostructure, such as graphene and its derivatives, are widely produced by chemical vapor deposition, epitaxial growth, template methods, and micromechanical exfoliation. However, even though these are some of the most cost-effective methods of producing ultrathin 2D nanostructured carbon materials, they are not cheaper than the direct pyrolysis of a biomass precursor to large-scale produce porous carbon nanosheets with ultrathin 2D nanostructures. Therefore, the selection of the suitable carbon source with a reasonable technological design is the key factor for obtaining high-yield, low-cost and satisfactory electrode materials.

Soybeans are widely cultivated globally because of their rich nutritional content (i.e., protein, N, P, S) and easy plant growth. It has a very large output of approximate 350 megaton in 2016-2017, and this value will continue to rise year by year. Inevitably, some soybean is long-term stored in the warehouses, resulting in that this aged soybean is unfit for human consumption. Thus, the development of a high value-added application for the aged soybean is necessary. Recently, soybean, soybean shells and soybean roots have been deeply investigated for use in the synthesis of high-performance activated carbon as an electrode material in energy storage devices. It means a high application value of soybean and its derivatives in energy fields. Soybean hydrogel (SBH), a superior value-added soybean product with a unique and uniform structure, is extensively used...
in the biological and medicinal fields\textsuperscript{33}. Its homogeneous and stable structure with a well processing property is the necessary condition for constantly deepening development of soybean to obtain high added-value products. To the best of our knowledge, SBH or its derivates have not been used as precursors in the preparation of high-performance and low-cost carbon nanosheets. In this study, an effective method was designed to prepare the N, S, P co-doped interconnected porous carbon nanosheets (CPCNs) by combining with the techniques of unidirectional freezing, freeze-drying and KOH activation. The as-prepared CPCNs have a unique interconnected ultrathin nanosheet structure with multiple heteroatoms doping, huge surface area and large defect density, and thus exhibited superior electrochemical properties in multiple types of SCs and LIBs. Herein, 100 g soybean flour is able to produce approximate 10.64 g carbon nanosheets easily, which proves to be a highly effective approach to large-scale produce high-performance carbon nanosheets. This work not only establishes a promising electrode material candidate for the application in the high-performance and low-cost storage devices, but also provides a feasible approach to produce high-performance, low-cost and large application potential carbon nanosheets.

**Results and Discussion**

The preparation processes for the CPCNs are illustrated in Supplementary Fig. S1, which provides a stable and repeatable synthesis process of the SBH from the soybean flour. Then, the key technology for the preparation process was explored from SBH to CPCNs (Fig. 1a). Firstly, soybean aerogel (SBA) with an ordered structure was papered from the SBH by unidirectional freezing and freeze-drying techniques, which is formed by the unidirectional growth of ice crystals under the unidirectional freezing process. This structure is composed of numerous interconnected layers and large voids, which is similar to the cross-sectional structure of cork (Supplementary Fig. S2a-b and Fig. S3a). Subsequently, an ordered layered structure on the carbon was built and stabilized by a pre-carbonization of SBA (Supplementary Fig. S3b). Finally, the pre-carbonized sample was activated at 700–900 °C by KOH under an NH\textsubscript{3} atmosphere to produce carbon nanosheets (CPCNs). An exfoliation of the layered structure played a key role in the formation of the carbon nanosheets under the penetration and activation of KOH. Meanwhile, these carbon nanosheets were activated at high temperature by KOH, leading to the variations of the pore structure. Fig. 1b shows a scanning electron microscopy (SEM) image of CPCN-800, which revealed the interconnected nanosheet structure. The corresponding magnified SEM image in Fig. 1c demonstrates that their structure consisted of interleaved carbon nanosheets with abundant wrinkle-like morphologies on the surface. Similar carbon nanosheets were also observed in the SEM images of the CPCN-700 and CPCN-900 samples (Supplementary Fig. S4a-b). Owing to the presence of wrinkle-like structures, large voids formed between stacked nanosheets could act as reservoirs to store electrolyte in favor of the promotion of rate performance\textsuperscript{34}. Besides, the voids also provided the possibility for the preparation of carbon-coated inorganic materials by using CPCNs as carbon shell. Fig. 1d illustrates that the thickness of the carbon nanosheets within CPCN-800 was approximately 4.9 nm by atomic force microscopy (AFM) measurement. This ultrathin 2D structure offered the necessary conditions for rapid infiltration and diffusion of the ions, corresponding to a superior response performance at a higher current density\textsuperscript{35}. Fig. 1e shows a transmission electron microscopy (TEM) image of CPCN-800, which highlights this unique structure composed of interconnected carbon nanosheets. The magnified TEM image (Fig. 1f) further exemplifies the presence of plenty of voids on the carbon nanosheets and between the carbon nanosheets. Abundant mesopores and micropores were observed in the high-resolution TEM image of CPCN-800 (Fig. 1g). The pores were connected with the ultrathin pore wall and even have merged with each other. It provides a large electrode and electrolyte interface, which is available for the storage and fast transfer of ions\textsuperscript{36}. Meanwhile, the energy dispersive spectroscopy (EDX) mapping of CPCN-800 revealed the presence of C, N, O, S, and P atoms (Fig. 1h). X-ray photoelectron spectroscopy (XPS) proved the presence of C, O, N, S, and P elements in the CPCNs in Fig. 2a. Table S1 summarizes the contents of these elements in the CPCN samples and reveals that the total O, N, S, and P contents decreased with increasing carbonization temperature, whereas the C content increased. In general, higher heteroatom contents in carbon
materials produces more structural defects, which is reflected in the expanded half-peak widths of C1s peaks. Interestingly, CPCN-800 shows a similar half-peak width compared to the CPCN-700 even it have a higher carbon content. It might be attributed to the activation effect of KOH, suggesting a high defect density of CPCN-800. The inset of Fig. 2b shows the high-resolution C1s spectrum, which exhibited main peaks at 284.3 eV(C=C) and 284.8 eV(C-C). The weak peaks at 283.3, 285.78, 286.4, 287.6 and 288.9 eV could be distributed to C-P, C=N, C-O/C-S, C-N and C=O groups, respectively. As shown in Fig. 2c, the N1s spectra of the CPCN samples showed four characteristic peaks centered at approximately 398, 400, 401 and 403 eV, corresponding to pyridinic N, pyrrolic N, graphitic N, and oxidized N, respectively. Remarkably, the CPCNs exhibited different shape peaks with N contents of 5.52 at. % in CPCN-700, 5.83 at. % in CPCN-800, and 4.23 at. % in CPCN-900, indicating a change in the nitrogen functional groups configuration. This change is clearly illustrated in Fig. 2d. As increasing of the temperature from 700 °C to 900 °C, the contents of all the nitrogen functional groups except graphitic N gradually decreased during KOH activation in an NH3 atmosphere, which could be ascribed to the different thermal stabilities of these groups. Fig. 2e shows that S mainly existed in the forms C-S=Ox-C (163.8 eV), C-S-C2p3/2 (164.9 eV), and C-S-C2p1/2 (169.1 eV). The high-resolution P2p peak could be fitted by two peaks at 132.9 eV (C-P) and 134.1 eV (P-O) in Fig. 2f. Fig. 2g illustrates the possible locations of N, S and P incorporation in the carbon network. A high N content is expected to improve the electrode materials performance as follows: First, the electronic conductivity of synthesized carbon can be relatively strengthened by doped N because it contributes electrons to the π-conjugated system of carbon. Second, the pyridinic and pyrrolic N configurations are assumed to be the main contributors for pseudocapacitance. In addition, these N doping also create defects in the carbon network that can supply active sites and diffusion channels for ion insertion. Low levels of sulfur (1.13~1.79 at. %) and phosphorus (0.87~1.58 at. %) in carbon structures are also beneficial for enhancing the pseudocapacitance properties and lowering the charge transfer resistance of SCs and LIBs. Because S element is located at the same family (Vla) with the oxygen, S doping plays a similar doping contributions as O for SCs, which is expected to improve the capacitance of carbon materials. Generally, S doping is beneficial to enhance pseudocapacitance properties for LIBs. P element doping causes more structural distortion due to its greater radius compared to the N. It is believed to produce pseudocapacitance and provide more defects for SCs. P doping also can cause the topological defects that is able to improve performance for LIBs. Thus, synthesizes each kind of situation including the dopant contents and their corresponded contributions for SCs and LIBs, N elements might play the most important role in this work.

Raman measurement (Fig. 3a) is a powerful tool to detect the defect density and graphitization degree of carbon materials, which can be fitted by five Gaussian peaks as follows: (1) D1 band (~1350 cm⁻¹) represents the edges of graphene layer. (2) D2 band (~1642 cm⁻¹) represents the supercell graphene layers. (3) D3 band (~1508 cm⁻¹) represents the amorphous carbon. (4) D4 band (~1906 cm⁻¹) represents the heteroatom contents and polyenes. (5) G band (~1608 cm⁻¹) represents the ideal graphitic lattice. The fast-growth D1 content (Fig. 3b) was much higher than G content with the increasing of the temperature, and showing a large D1 content of 47.5%, 50.7% and 54.3% for CPCN-700, CPCN-800 and CPCN-900, respectively. It indicated a large defect density within the CPCNs, which played a major role in the ions storage and fast-diffusion for SCs and LIBs. For T-SBH (SBH after the direct carbonization) and A-SBH (SBH after the direct activation), the D1 values of 38.1% and 47.9% revealed that the formation of defects was mainly attributed to the effect of KOH activation. This effect also resulted to the nearly equal contents of the G band for the different CPCN samples. Besides, the decreased D4 content was caused by reduced heteroatoms (O, S, P, and N). Two broad peaks at approximately 23.8° and 43.8° in CPCNs were identified by the X-ray diffraction (XRD) patterns in Fig. 3c, which were attributed to diffraction of disorder carbon (002) and diffraction of graphitized carbon (101), respectively. It is observed that the (002) peak begin to weak and broad at temperature higher than that at 700 °C. This interesting phenomenon was resulted by the structure variation from the turbostratic stacking layers to the ultrathin and connected layers, which caused to the change of pore structure. The broad (002) peaks of A-SBH and T-SBH suggested that the structure of

Figure 2. (a) Survey XPS spectra of CPCNs. The inset shows the magnified survey spectra from 100 eV to 250 eV. (b) High-resolution C1s spectra of CPCNs. The inset is the chemical compositions of C1s in CPCN-800. (c) High-resolution N1s spectra of CPCNs. (d) The contents of four nitrogen species of CPCNs. (e) High-resolution S2p spectra of CPCN-800. (f) High-resolution P2p spectra of CPCN-800. (g) Possible configurations of nitrogen, sulfur and phosphorus doping in the carbon network.
Figure 3. (a) Raman spectra and (b) the contents of Gaussian peaks of CPCNs. (c) XRD pattern, (d) nitrogen sorption isotherms and (e) pore-size distribution curves of CPCNs.

turbostratic stacking layer was the main part in the carbon microstructure (Fig. S5c). Fig. 3d and Table S2 show the N₂ sorption isotherms and porosity of the CPCNs, respectively. The \( S_{\text{BET}} \) surface area of CPCN-700, CPCN-800 and CPCN-900 were 2141, 3586 and 2612 m²g⁻¹ with high pore volumes of 1.14, 2.27 and 1.82 cm³g⁻¹, respectively. The absorption isotherms of CPCNs were classified as type IV. The obvious type H4 hysteresis loop on both CPCN-800 and CPCN-900 compared to CPCN-700 revealed the formation of more mesopores. The wide pore size distributions of 0.3–4 nm and 0.3–5 nm for CPCN-800 and CPCN-900 in Fig. 3e could prove this point. All the CPCNs exhibited fast absorption processes at a low relative pressure, which corresponds to micropore filling, indicating the presence of the micro/mesoporous structure. The micropore and meso/macropore in the carbon can provide the large surface area to act as electrochemical reaction interface and ion adsorption area, which is in favor of the promotion of electrochemical performances. Among, the micropore plays a leading role in the ion storage. The macro/mesopore within carbon is able to act as ion-diffusion channels and reservoirs to accelerate ion diffusion/transfer and store electrolyte. Table S2 displays the specific surface area of micropore and meso/macropore in the carbon. The highest surface area of the micropore and meso/macropore for CPCN-800 suggested a high capacitance with a good rate property of the CPCN-800 electrode. Additionally, low surface area of the A-SBH and T-SBH with the narrow pore size distributions (Fig. S5d) demonstrate that the superiority of the 2D ultrathin nanostructure in the porosity of materials.

The electrochemical performances of CPCN electrodes for SCs were evaluated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements. Fig. 4a shows that the CV curves of all the samples displayed the typical capacitive behavior (rectangular shape). The presence of humps in CV curves revealed the occurrence of pseudocapacitance supplied by the redox reactions of the doped heteroatoms. Among these materials, CPCN-800 was the most promising candidate electrode due to its largest CV curve area. These curves of the CPCN-800 were further analyzed in Fig. 4b. The CV curves of the CPCN-800 maintained roughly rectangular shape clearly at 100 mVs⁻¹, implying good ion diffusion and high capacitance retention. The GCD curves of the CPCN-800 electrode exhibited nearly symmetrical features with an almost linear slope, indicating a low overall resistance (Fig. 4c).

The CV and GCD curves of CPCN-700 and CPCN-900 are displayed in Supplementary Fig. S6. As shown in Fig. 4d, the highest capacitance of 427 Fg⁻¹ was obtained for CPCN-800 at 0.5 Ag⁻¹, versus the highest values of 330 Fg⁻¹ for CPCN-700 and 352 Fg⁻¹ for CPCN-900. Even at 50 Ag⁻¹, the capacitance of CPCN-800 still was 294 Fg⁻¹, which was much higher than that of the other CPCN samples. By contrast, T-SBH and A-SBH (Fig. S6a–e) exhibited the low capacitance of 254 and 117 Fg⁻¹ at 0.5 Ag⁻¹, which reflected a high contribution of the 2D ultrathin nanostructure for electrochemical energy storage. Supplementary Table S3 shows the supercapacitor properties of previously reported activated carbon materials, and the performance of CPCN-800 as a supercapacitor electrode was higher than the performances of these carbon. This very high capacitance of CPCN-800 could be attributed to the synergistic effects of their superhigh surface area, high heteroatomic contents, large defect density and unique interleaving ultrathin nanosheet structure. Fig. 4e shows the Nyquist plots of the CPCNs. In the low-frequency region, sample CPCN-800 electrode exhibited a nearly vertical line with a large slope, representing a lower ion-diffusion resistance ascribed to their higher surface area and hierarchical porous of this material⁴⁸, ⁴⁹. Short lengths for the Warburg resistance in the middle-frequency region revealed a low resistance for electrolyte ion transfer. Meanwhile, semicircles with small widths were observed in the plots for the CPCN electrodes, revealing a low charge-transfer resistance for these materials. Randles equivalent circuit (inset of Fig. 4e) was used to fit the Nyquist plots (Fig. 4e and Fig. S7f), and the results was displayed in Table S4. The equivalent series resistances (Rs) values of CPCN-700, CPCN-800 and CPCN-900 in the high-frequency region were 0.961, 0.844 and 0.884 Ω, respectively. A low Rs value of CPCN-800 electrode was attributed to the advantageous synergistic effect of the electron conductivity, surface structure and the heteroatoms property. The interconnected structure between the carbon nanosheets plays the role of electron transfer pathways in favour of the promotion of electron conductivity. The high surface area with high heteroatomic contents prompts the CPCN-800 have a good wettability, which can improve the interface contact between the electrode and electrolyte. However, the charge transport resistances (Rct) value of CPCN-800 (0.489 Ω) was lower than CPCN-900 (0.114 Ω), but higher than CPCN-700 (1.018 Ω). The Rct value was highly related to electronic conductivity of the electrode. The characteristics of high degree of graphitization, low micro/mesopores content, high graphitic N proportion and low heteroatomic content for CPCN-900 led it have a higher electronic conductivity, which reflected to the higher Rct value and better rate capability of the CPCN-900. The T-SBH and A-SBH electrodes displayed the weak Rs values of 0.986 and 0.895 Ω with the bad Rct values of 3.01 and 1.468 Ω, respectively. The results further supported that the outstanding structural advantages of 2D ultrathin nanostructure for electrochemical energy storage due to the similar elemental contents of all the samples. Then, GCD measurements were employed to further investigate the long-term cycling stability of the CPCN electrodes. As shown in Fig. 4f, the CPCN-700, CPCN-800 and CPCN-900
Figure 4. (a) Cyclic voltammetry (CV) measurements of CPCNs at a scan rate of 10 mVs$^{-1}$. (b) CV measurements of CPCN-800 at different scan rates from 5 mVs$^{-1}$ to 100 mVs$^{-1}$. (c) Galvanostatic charge-discharge (GCD) curves of CPCN-800 at different current densities from 0.5 Ag$^{-1}$ to 50 Ag$^{-1}$. (d) Specific capacitances of CPCNs. (e) Nyquist plots for CPCNs. A Randles equivalent circuit displayed in the inset of Figure was used to fit the Nyquist spectra. (f) Cyclic stability of CPCNs at 5Ag$^{-1}$ for 10 000 cycles.

Figure 5. (a-c) TEM images of Ni(OH)$_2$&CPCN. (d) HAADF-STEM and corresponding EDX elemental mapping images of Ni(OH)$_2$&CPCN. (e) CV curves of Ni(OH)$_2$&CPCN at different scan rates range from 2 to 40 mVs$^{-1}$. (f) GCD curves of Ni(OH)$_2$&CPCN at different current densities. (g) Specific capacitances of Ni(OH)$_2$&CPCN. (h) GCD curves of Ni(OH)$_2$&CPCN and pure Ni(OH)$_2$ at 1 Ag$^{-1}$. (i) ESI plots of Ni(OH)$_2$&CPCN between 0.01 Hz and 100 KHz. (j) Long cycling performance of Ni(OH)$_2$&CPCN at 10 Ag$^{-1}$. (k) Schematic representation of advantages of Ni(OH)$_2$&CPCN.

Ni(OH)$_2$ to NiOOH and the reverse reduction process. With increased scan rate, both of the oxidation/reduction peaks gradually shifted to more extreme electrical potentials (more positive or more negative), which can be ascribed to the enhanced resistance of internal diffusion. The obvious plateau regions in the GCD curves (Fig. 5f) were caused by the redox reaction and by adsorption-desorption of the electrolyte ions, which were highly consistent with the CV results. Fig. 5g shows the corresponding capacitances of Ni(OH)$_2$&CPCN. These synthesized Ni(OH)$_2$&CPCN sample exhibited a good galvanostatic capacitance of 1891 Fg$^{-1}$ at 1 Ag$^{-1}$ and retained an excellent capacitance of 1285 Fg$^{-1}$ at 40 Ag$^{-1}$. This value was much better than that of a pure Ni(OH)$_2$ electrode, which had a value of 372 Fg$^{-1}$ at 1 A g$^{-1}$ (Fig. 5h). The Nyquist plots of the Ni(OH)$_2$&CPCN showed that the ESR of Ni(OH)$_2$&CPCN was only 0.60 Ω, which was lower than that of the pure CPCN-800 electrode with an ESR of 0.85 Ω (Fig. 4e). This difference might be due to the effect of hydrophilic Ni(OH)$_2$, and it suggests that this composite had a low internal resistance and high degree of charge transfer. Moreover,
the Ni(OH)\textsubscript{2}\&CPCN composite retained a superior capacitance of 89.46\% after 8 000 cycles at 10 Ag\textsuperscript{−1}, as shown in Fig. 5j, better than the performance of pure Ni(OH)\textsubscript{2} with a 45.65\% retention. These results indicated that CPCN material have some great powers to improve the pseudocapacitance and cycling stability of nano-inorganic materials. Fig. 5k illustrates the unique features of high potential CPCN material, as follows: (1) Ultrathin carbon nanosheets with a unique interconnected structure and an ultrahigh surface area offers many sites to cover and immobilize nano-inorganic materials. (2) A continuous and effective contact between the different nanoparticles by using conductive nanosheets as bridges is conducive to improve the rate performance and cycling stability. (3) The large defect density, ultrathin structure, abundant pores and high heteroatomic doping of the CPCN supply a good reaction interface and a low ion-diffusion resistance between the nanoparticles and electrolyte ions. The Li-ion storage performances of CPCNs were evaluated by CV and GCD tests in a half-cell configuration versus Li foil. Fig. 6a and Supplementary Fig. S10 show the GCD curves of the CPCNs at initial 1st-4th cycles. Based on the discharge curves at 100 mAg\textsuperscript{−1}, the CPCN-700, CPCN-800 and CPCN-900 electrodes exhibited high initial discharge capacities of 1644, 2616 and 2101 mAhg\textsuperscript{−1} with initial charge capacities of 1027, 1313, and 1179 mAhg\textsuperscript{−1}, respectively. These high irreversible capacities were ascribed to the formation of the solid-electrolyte-interphase (SEI) layer on the surface area carbon nanosheets\textsuperscript{51}. After the 1st cycle, the CPCN-700, CPCN-800 and CPCN-900 electrodes exhibited reversible discharge capacities of 1032, 1335, 1201 mAhg\textsuperscript{−1}, respectively, and the corresponding capacitance retentions were 62.02\%, 50.19\% and 57.16\%. The inset of Fig. 6a shows typical CV curves of carbon nanosheet electrodes at 0.1 mVs\textsuperscript{−1}. A wide reduction peak (0−2.5 V) was observed in the first cycle for the formation of the SEI layer on the CPCN surface, which was consistent with the GCD curves. The rate capabilities of the CPCN electrodes ranging from 100 mAg\textsuperscript{−1} to 2 000 mAg\textsuperscript{−1} are illustrated in Fig. 6b. During the first 10 cycles at 100 mAg\textsuperscript{−1}, CPCN-800 delivered a stable and reversible capacity of 1220 mAhg\textsuperscript{−1}, which was better than that of CPCN-700 (941 mAhg\textsuperscript{−1}) and CPCN-900 (1 098 mAhg\textsuperscript{−1}). With higher current densities of 200, 500, 1 000, and 2 000 mAg\textsuperscript{−1}, the corresponding capacities of CPCN-800 had stable values of 1 083, 966, 892, and 838 mAhg\textsuperscript{−1}, respectively. When the current density was finally restored to 100 mAg\textsuperscript{−1}, the capacity of CPCN-800 recovered to 1139 mAhg\textsuperscript{−1}, indicating a good tolerance to the fast Li\textsuperscript{+} insertion/extraction process. Even after 350 cycles at 1 000 mAg\textsuperscript{−1}, the CPCN-800 retained an excellent reversible capacity of 924 mAhg\textsuperscript{−1} in Fig. 6c, indicating that the structure of this ultrathin carbon nanosheet have a high stability to tolerate the high-frequency and fast Li\textsuperscript{+} insertion/extraction processes. Remarkably, the coulombic efficiency still approached 100\% after approximately 350 cycles, implying an excellent reversible Li\textsuperscript{+} insertion/extraction performance. The specific capacities of CPCN-800 is illustrated in Supplementary Fig. S11, and the figure shows that the capacity of this material was higher than those of previously reported carbon electrodes for LIBs. These results have once again proved a strong applied value of this large-scale produced carbon nanosheet. Moreover, to evaluate electrochemical performances of the CPCN-800 in practical, full cells were assembled using commercial LiCoO\textsubscript{2} as cathode and CPCN-800 as anode in Fig. S12. It further confirmed a high practical application value of CPCN-800. To summarize, all of the electrochemical measurements proved that the N, S, P codoped CPCN materials are promising candidates for using in energy-storage fields for SCs and LIBs. Their unique features played deciding roles in the energy storage performance. Firstly, interconnected structure of these carbon nanosheets provides effective electron transfer paths to promote the response to ions. The interconnected structure of the carbon nanosheets allowed them to fit close together in assembled devices, which might be beneficial for fully utilizing their high intrinsic specific surface area (3586 m2g\textsuperscript{−1}) and hierarchical porous structure. Secondly, ultrathin carbon nanosheet structure with macroporous voids and mesoporous is favorable for reducing the diffusion resistance of the electrolyte ions by shortening ion-diffusion pathways and storing electrolyte. It is worth mentioning that the high defect density on the carbon nanosheets not only helps to enhance the rate performance and capacitance for SCs, but also plays a main role as gateway in the insertion/extraction processes of lithium ions in favor of the promotion of capacity and rate for LIBs. Furthermore, the high contents of N, S and P within the carbon nanosheets are also beneficial for improving electrochemical performance in SCs and LIBs by contributing pseudocapacitance, enhancing electroconductibility and forming structural defects. These unique characteristic makes the CPCN material have a great application potential not only as high-performance carbonaceous electrode materials, but also as substrate to improve electrochemical performance of nano-inorganic materials for SCs. It proves that this large-scale produced carbon nanosheet have a wide application range and a
high production value, and might be good for further commercialization of the product.

Conclusions

In this work, rationally designed N, S, P codoped porous carbon nanosheets with interconnected ultrathin nanosheet structure and high defect density have been successfully large-scale prepared via the organic integration of the techniques of unidirectional freezing/freeze-drying and KOH activation. To reduce interference from different various SBH, the aged soybean flour was used to manufacture SBH by a simple, repeatable and conventional process. Then, an ordered cork-shaped structure of SBA was built by unidirectional freezing/freeze-drying treatments for SBH. Under the pre-carbonization and KOH activation processes, this ordered structure was stabilized to be layered carbon, and then stripping off nanosheets to form CPCN materials. Beside its unique 3D interconnected structure and high defect density, the high-performance CPCN material obtained at 800 °C (CPCN-800) possessed an ultrahigh BET of 3586 m²g⁻¹, an ultrathin nanosheets structure (4.9 nm) and a high total co-doped contents of N, S, P (8.36 at. %). Based on these beneficial synergistic effects, the as-obtained carbon nanosheets exhibited superior electrochemical properties, including a high capacity, high rate charge/discharge performance and long cycling stability, in SCs and LIBs. Moreover, an enhanced electrochemical performance of nano-inorganic material by using CPCN-800 as substrate proves a high scalability application for these carbon nanosheets. Therefore, this work provides a high-performance and low-cost carbon nanosheets by a large-scale approach that is a promising electrode material candidate for SCs and LIBs.

Experimental Section

Materials. Soybean flour (Glycine max) was prepared from the aged soybean. All of the experiment reagents were purchased from Aladdin Chemistry Co., Ltd. and used directly without further purification.

Preparation of SBH. To reduce interference from different various SBH, a simple, repeatable and conventional process was used to manufacture SBH. Soybean flour (100 g) and 500 mL of deionized water were crushed into a paste by small high-speed grinders. The obtained paste was stirred for 1 h at 50 °C using a magnetic stirrer (200 rpm). The sample was filtered at a high temperature 3 times. The obtained filtrate was placed in a Teflon mold (10×10×5 cm). Subsequently, a H₂PO₄ solution (18.6 mL) as a crosslinking agent was added to this filtrate until the solution pH was 4.5. Finally, a homogeneous SBH was successfully prepared by further thermostetting at 60 °C for 1 h.

Preparation of cork-shaped SBH. The SBH material was completely frozen using a simple unidirectional freezing device. A model of the device and the process are shown in Supplementary Fig. S13. Then, the frozen SBH was freeze-dried for more than 48 h. The SBA material was obtained after removal of the mold. For comparison, another SBH that was directly frozen in a refrigerator (−35 °C) was freeze-dried at the same time.

Preparation of CPCNs. The SBA samples were cut into small pieces and then carbonized primarily at 700 °C for 2 h. The obtained layered carbon mixed with a KOH solution (weight of KOH:weight of sample = 2:1) was pyrolyzed at 700, 800, and 900 °C for 2 h with 3 °C min⁻¹ under NH₃. The resulting products were ground and washed by 1 M HCl and deionized water until the pH was 7. The final samples were collected and dried at 120 °C for 5 h, and they were named CPCN-X (X = 700, 800, 900) based on the temperature of carbonization. Additional details about the preparative cost of CPCN-800 are listed in Supplementary Table S5. For comparison, the direct freeze-dried SBH without unidirectional freezing process also was treated under the same conditions (800 °C), named as A-SBH. The direct carbonized SBH under the same conditions (800 °C) without KOH activation was named as T-SBH.

Preparation of Ni(OH)₂&CPCN. A total of 2 g of Ni(OH)₂+2H₂O and 0.4 g of CPCN-800 were added into deionized water (30 mL) and stirred for 10 min. This solution was placed into a 50 mL Teflon-lined stainless-steel autoclave and heated at 100 °C for 1 h in an oven. Subsequently, 1.5 g of KOH was dissolved into this solution, which was again heated in the oven at 100 °C for 12 h. The sample was thoroughly washed by ethanol and dried at 90 °C for 24 h. The as-prepared product was denoted Ni(OH)₂&CPCN. The pure Ni(OH)₂ was prepared by a same process without CPCN-800.

Characterization. SEM images were obtained from an FEI Quanta FEG 250 instrument. TEM and high-angle annular dark-field scanning TEM images (HAADF-STEM) were collected on an FEI Tecnai G2 F20 instrument. Atomic force microscopy (AFM, MM8, DI MultiMode®) was used to observe the surface morphology of the sample. The XPS analysis was performed using an X-ray photoelectron spectrometer (ESCALAB 250 XI, Thermo Fisher). An X-ray diffractometer (XRD, Rigaku, D/MAX 2200) was used to collect X-ray diffraction patterns using Cu Kα radiation (40 K, 30 mA) at a scan rate (29) of 4° min⁻¹ in the range 5° to 80°. Nitrogen adsorption-desorption isotherms were used to calculate the specific surface area using the Brunauer-Emmett-Teller method. The pore-size distribution was calculated by the nonlocal density functional theory (NLDFT) method. Raman spectroscopy measurements were performed using a Renishaw Via laser micro-Raman system at an excitation wavelength of 633 nm.

Electrochemical Measurements.

The electrochemical performances of the CPCNs in a supercapacitor were studied in 6 molL⁻¹ KOH using a three-electrode cell. Hg/HgO and Pt were used as reference and counter electrodes, respectively. Meanwhile, CPCN-800 electrode was also tested in a two-electrode system (KOH as electrolyte). Electrode materials were prepared in ethyl alcohol by mixing the CPCNs powders, Super P and PVDF (80:15:5 by weight). The obtained slurry was made into a thin film and then dried at 120 °C for 24 h (~2 mg cm⁻², ~50 µm thick, Supplementary Fig. S14). Unlike the electrode materials prepared from the CPCNs, the slurry obtained from the Ni(OH)₂&CPCN composite was coated on clean nickel foam. This sample was dried at 80 °C for 24 h and pressed for 10 s at 15 MPa (~2 mg cm⁻²). The CV, GCD and EIS measurements using these electrode materials were performed on a CHI660E electrochemical workstation (25 °C).

The capacitances in the three-electrode system (KOH as electrolyte) were calculated according to equation (1) as follows:

\[ C = \frac{1}{\Delta V} \frac{m}{x}\Delta V \]
The specific capacitance of the single electrode in the symmetrical supercapacitor system were calculated according to equation (2) as follows:

$$C = \frac{FkM}{m \times \Delta V}$$

(2)

where $C$ (F g$^{-1}$), $\Delta V$ (V), $I$ (A), $\Delta t$ (s), and $m$ (g) are the specific capacitance, the voltage window, the discharge current, the discharge time, and the weight of the active material in the single electrode, respectively.

To prepare electrodes for use in LIBs, the CPCNs, Super P and PVDF (80:15:5 by weight) in N-methyl-2-pyrrolidone were dispersed under vigorous stirring to form a homogeneous slurry. Subsequently, the obtained slurry was coated on Cu foil and then dried at 120 °C for 12 h in a vacuum oven (1.8–2 mg cm$^{-2}$). This as-prepared Cu foil was cut into a water with a radius of 6 mm. The half cells (CR2016 type cells) were assembled with pure lithium metal foil (counter electrode) and a PP microfiber filter film (Celgard2500, 25 μm) (separator) in an Ar-filled glove box using a solution of 1 M LiPF$_6$ (ethylene carbonate:dimethyl carbonate=1:1 by weight) as electrolyte. The GCD experiments were conducted over a potential range of 3.0–0.01 V on the Land Battery Test System (LAND CT2001A). The CV experiments were performed using the CHI66E electrochemical workstation at scan rates of 0.1 mV s$^{-1}$. For the full cells, the commercial LiCoO$_2$ as cathode (LiCoO$_2$: Super P: PVDF=70:25:5 by weight) and CPCN-800 as anode was assembled and evaluated between 2.50–4.20V. Commercial LiCoO$_2$ cathode was also assembled into a cell using pure lithium metal foil as counter electrode. The electrochemical performance of this half-cell was tested between 2.75–4.20V.

Acknowledgements

The work was financially supported by Scientific Research Foundation of Zhejiang A&F University (Grant No. 2014FR077) and Key Laboratory of Bio-based Material Science & Technology (Northeast Forestry University), Ministry of Education, SWZCL2016-3.

Keywords: Carbon nanosheets • Biomass • Supercapacitors • Li-ion Batteries

A large-scale and low-cost approach was explored to prepare N, S, P co-doped interconnected porous carbon nanosheets with high defect density and open 2D ultrathin nanostructure that can provide high capacity and rate performance with excellent cycling stability for SCs and LIBs.
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