Mesoporous carbons (MCs) are currently attracting significant attention due to their high specific surface area, unique porous architecture, low density, high conductivity, thermal stability, and chemical inertness. The incorporation of heteroatoms such as nitrogen and sulfur into MCs may impart new catalytic active sites and structural irregularities to the sp2-hybridized carbon lattice, providing a high functionality. For example, the present nitrogen species in MCs was reported to improve the conductivity, basicity, and oxidation stability of MCs through the conjugation between the nitrogen lone-pair and the π-system of the carbon lattice. Consequently, the nitrogen-doped mesoporous carbon materials (NMCs) have potential applications in various areas especially involving catalysis, adsorption, and energy storage/conversion (fuel cells, supercapacitors and lithium batteries).

In general, MCs are prepared by either an in-situ carbonization of heteroatom-containing precursors with the sophisticated nanocasting method or a post-treatment of the as-synthesized MCs, wherein the heteroatom-containing precursors with the sophisticated nanocasting method are much more feasible to control the incorporated heteroatom content and makes the doped heteroatom more homogeneously distribute throughout the material, compared to the latter that requires additional complex and time-consuming steps. However, the precursors for MCs synthesis currently available are very limited, since most of the organic precursors are completely evaporated or decomposed during high-temperature carbonization. For example, NMCs can be synthesized by carbonization of N-containing polymers such as polyacronitrile, polyaniline polypyridine and etc., which are difficult to handle due to their complicated synthesis and limited solubility.

Recently, we have demonstrated that small-molecule protic salts could be successfully utilized as new versatile carbon precursors for carbon materials with tunable structure and properties depending on the precursor species, such as high nitrogen content, high conductivity even over graphite, or large surface area. Compared to the traditional precursors such as polymers, the protic salts are very easy to synthesize, low cost, widely available, and suitable for mass production. However, most of the highly porous carbons obtained from protic salts possess a low N content and are microporous. The poor N-doping structure and absence of mesopores undoubtedly hinder their potential applications. In contrast, protic salts-derived carbons having high N contents appear more attractive, while their very low surface area or nonporous structure strongly limits the amount of accessible surface area for fully utilizing the doped N heteroatoms. In order to address this issue, sophisticated hard templating method was used in this work to fabricate advanced MCs via the strong interactions between a protic salt ([Phen][2HSO4]) and inorganic surfaces (SBA-15). The obtained carbon (CMK-3P) exhibits not only high nitrogen (6.0 at%) and sulfur (0.61 at%) contents, and large surface area (1030 m² g⁻¹) and pore volume (2.403 cm³ g⁻¹), but also better electrocatalytic activity for oxygen reduction reaction (ORR) than CMK-3S obtained from the same silica template but using sucrose as precursors.

Materials preparation.—1,10-phenanthroline 1,1-dihydrogen bisulfate ([Phen][2HSO4], see inset in Fig. 1) was prepared as described previously. For synthesis of CMK-3P, [Phen][2HSO4] (1.0 g) was mixed with aqueous dispersion (1.0 g SBA-15 and 1.5 mL H2O) under sonication until the complete dissolution of the protic salt, and then the mixture was vacuum dried. The obtained composite was subjected to carbonization at a heating rate of 10°C min⁻¹ from room temperature to 900°C and held for 2 h under argon atmosphere. After cooling down, the resulting silica/carbon composite was etched with 10 wt% HF solution to remove the silica template. After drying overnight at 100°C and then grinding at room temperature, CMK-3P was obtained as a black powder. Likewise, CMK-3S was prepared using sucrose as precursor, for which H2SO4 has to be replaced with H3PO4.

Figure 1. Schematic illustration for the synthesis of N, S-codoped mesoporous carbon (CMK-3P) from protic salt [Phen][2HSO4].

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added and additional polymerization and pre-carbonization steps at low temperature are required.9

Characterization.—Powder X-ray diffraction (XRD) patterns were collected by using a Rigaku RINT-2000 diffractometer with CuKa (\(\lambda = 0.154 \text{ nm}\)) radiation. The diffractograms were recorded in the 20 range between 10 and 90° with a 20 step size of 0.02 at a scanning speed of 10° min\(^{-1}\). Nitrogen sorption isotherms were recorded by using a BELSORP-mini II (BEL Japan, Inc.) sorption analyzer at -196°C (77 K), after the samples were purged with flowing \(\text{N}_2\) at 250°C for 3 h. The specific surface area (\(S_{ BET}\)) was calculated by using the Brunauer-Emmett-Teller (BET) method. The total pore volume (\(V_{total}\)) was determined from the uptake of \(\text{N}_2\) at a relative pressure (\(p/p_0\)) of 0.99, and the pore-size distribution was assessed by the Barrett-Joyner-Halenda (BJH) method. The chemical state, composition, and valence band spectra were analyzed by using PHI Quantera SXM X-ray photoelectron spectroscopy (XPS) with a base pressure of 6.7 × 10\(^{-9}\) Pa with AlK\(_\alpha\) (1486.6 eV) as the X-ray source and pass energies of 280.00 eV (survey scan) and 55.00 eV (high-resolution scan). High-resolution transmission electron microscopy (HRTEM) was performed with a JEOL JEM-2100F field-emission source transmission electron microscope operating at 200 kV. The composition analysis was conducted on a field-emission scanning electron microscope (JSM-7001F, JEOL Ltd.) with an energy-dispersive spectrometry (EDS) accessory (EDAX, USA). Elemental analysis for nitrogen content was performed with a Vario-EL III CHN elemental analyzer.

Oxygen reduction reaction.—All electrochemical measurements were performed in a three-electrode electrochemical cell by using a CHI701E electrochemical workstation (CH Instruments, USA) at room temperature. An Ag/AgCl electrode (3.0 M NaCl) and a Pt coil electrode were used as the reference and counter electrodes, respectively. A graphite-rod electrode was also used to exclude Pt contamination from the counter electrode during oxygen reduction. To prepare the working electrode, the carbon catalyst (i.e., CMK-3P or CMK-3S, 2 mg) was dispersed in a mixture of deionized water (0.75 mL), ethanol (0.20 mL) and Nafion (50 μL, 5 wt%), and the mixture was sonicated for at least 30 min to form a homogeneous ink. An aliquot (8 μL) of the ink was then dropped onto the surface of a prefabricated glassy carbon (GC) electrode (4 mm) and dried naturally. For comparison, an electrode comprising commercial 20 wt% Pt/C catalyst (Sigma-Aldrich) was also prepared and assessed under the same conditions. Cyclic voltammetry (CV) experiments were conducted in \(\text{N}_2\)- or \(\text{O}_2\)-saturated 0.1 M KOH solution at a scanning rate of 100 mV s\(^{-1}\). Linear sweep voltammograms (LSV) were recorded by using the rotating disk electrode (RDE) technique at a scanning rate of 10 mV s\(^{-1}\). For rotating ring disk electrode (RRDE) experiments, an electrode with a glassy carbon disk (4 mm diameter) and a Pt ring (5 mm inner diameter and 7 mm outer diameter) was used as the working electrode with the same catalyst loading as the RDE measurements. The ring potential was held constant at 0.5 V vs. the reference electrode. The electron transfer numbers (n) and the peroxide yields (Y [%]) were calculated by the following equations respectively:

\[
n = 4 \times \frac{I_d}{I_d + I_r/N} \quad [1]
\]

\[
Y = 200 \times \frac{I_r/N}{I_d/N + I_r} \quad [2]
\]

where \(I_d\) and \(I_r\) are the disk and ring currents respectively, and N (0.44) is the ring collection efficiency.

Results and Discussion

Figure 2 shows the transmission electron micrograph (TEM) images of CMK-3P and CMK-3S, both confirming the 2D hexagonal mesoporous structure. Unlike the highly ordered and large area-dimensional arrays of carbon nanorods observed for most typical CMK-3S (e.g. in Fig. 2c and 2d for CMK-3S)\(^{9,10}\), the partially-ordered arrays composed of several to tens of hexagonally arranged cylindrical rods were observed in CMK-3P (Fig. 2a), with lateral size ranging from tens to hundreds of nanometers. Most of the nanorod arrays in CMK-3P are curved and intertwined with each other, forming inter-aggregate void space. High resolution TEM image (Fig. 2b) indicates that these arrays have an average diameter of about 4 nm and mesopore size of about 3.5 nm. The relatively less ordered structure of CMK-3P compared to CMK-3S could be contributed to the different kinds of precursors. Compared with the full coverage of the precursor on the inner surface of SBA-15, the absence of prepolymerization step for the protic salt may lead to partial infiltration of it into the channel-interconnecting micropores. Furthermore, the rapid evolution of gaseous molecules during decomposition of [Phen][2HSO\(_4\)] may break the thin interconnecting rods.\(^{7,8}\)

Figure 3a depicts the small-angle powder XRD patterns of CMK-3S and CMK-3P. Clearly, CMK-3S exhibits three well-resolved diffraction peaks, which can be indexed to the (100), (110) and (200) planes of the 2D hexagonal space group (p6mm), in good agreement with the reported CMK-3.\(^{9}\) Interestingly, CMK-3P shows a weak diffraction intensity for low-angle (100) compared to CMK-3S, and nearly featureless XRD patterns for high-angle (110) and (200). Considering the equal contrast in density between the walls and the open pores for both CMK-3S and CMK-3P, the result could be interpreted as a severe loss of structural order, as observed in TEM. Wide-angle XRD (Fig. 3b) of CMK-3P shows a (002) diffraction peak centered at 24.6° along with clearly observable (100) reflection characteristic for graphitic structures. The calculated interlayer distance (\(d_{(002)}\)) of 0.361 nm is a little larger than that of graphite (0.335 nm).\(^{11}\) In contrast, CMK-3S displays a low angle-shifted and wider (002) diffraction peak centered at 21.8°, indicating that CMK-3S consists of very small amounts of stacked crystalline graphite phase relative to CMK-3P. This result is not unexpected, because sucrose was generally viewed as a non-graphitic precursor,\(^{12}\) while [Phen][2HSO\(_4\)] was a potential candidate that results in partially graphitized carbon.\(^{7,8}\)

The pore structure of CMK-3P and CMK-3S together with SBA-15 was measured by N\(_2\) sorption isotherms. As shown in Fig. 3c, SBA-15 exhibits a type-IV curve with a well-defined H1 hysteresis loop according to the IUPAC classification.\(^{13}\) The nearly vertical capillary condensation occurring at a narrow range of relative pressure (\(p/p_0 = 0.65 \sim 0.75\)) indicates the presence of well-ordered hexagonal mesopores, corresponding to a quite narrow pore-size distribution (PSD) centered at 8.1 nm (Fig. 3d). In contrast to the silica template, both CMK-3P

![Figure 2. TEM images of CMK-3P (a, b) and CMK-3S (c, d).](image-url)
and CMK-3S display a hysteresis loop at low relative pressure and small pore diameters centered at 3.7 nm. More interestingly, different from CMK-3S, CMK-3P shows a significant capillary condensation at high relative pressure ($p/p_0 > 0.9$), indicating the presence of large mesopores and even macropores. Correspondingly, PSD of CMK-3P extends to even 100 nm (inset in Fig. 3d). This result could be ascribed to inter-nanorod voids in CMK-3P, as observed in TEM. The large mesopores and macropores contribute greatly to the pore volume ($V_{\text{tot}}$) as compared to the specific surface area ($S_{\text{BET}}$), since $V_{\text{tot}}$ is primarily related to the large pores, with minor contribution from micropores and small mesopores. Hence, although CMK-3P possesses a $S_{\text{BET}}$ only slightly higher than that of CMK-3S (1030 vs. 949 m$^2$ g$^{-1}$), the $V_{\text{tot}}$ of CMK-3P is nearly two-folds of that of CMK-3S (2.403 vs. 1.170 cm$^3$ g$^{-1}$), as summarized in Table I.

Surface chemical states of the CMK-3P were investigated by the X-ray photoelectron spectroscopy (XPS). As clearly seen in Fig. 4a, the survey spectrum of CMK-3P shows three additional signals, i.e., N1s, S2s and S2p, compared to that of CMK-3S, suggesting that the direct carbonization from a single protic salt indeed provides a facile route to prepare N and S bi-functional carbon for potential application.14–18 The N content measured by XPS is 6.0 at%, close to the value determined by elemental analysis (5.3 wt%). The N1s spectrum can be resolved into four components, as shown in Fig. 4b. The small peaks at 398.2 and 399.4 eV correspond to pyridinic and pyrrolic N atoms respectively. These two refer to the N atoms located in a $\pi$-conjugated system and contribute to the $\pi$ system with one or two p-electrons. The peak at 400.8 eV corresponds to graphitic N (or named as quaternary N), which refers to the N atoms replacing the C atoms in the graphene layers.19 Fig. 4b reveals the dominant role of graphitic N, thus the N heteroatoms are mainly doped into the graphene lattice in the form of graphitic N. The peak at high binding energy could be ascribed to oxidized nitrogen species (403.1 eV), which is sometimes observed in N-doped carbons.20 The S2p spectrum could be resolved into well-defined four peaks at binding energies of 163.8, 165.0, 167.8 and 170.0 eV, as shown in Fig. 4c. The former two peaks correspond to the S2p3/2 and S2p1/2 of thiophene-S, while the two weak peaks at high binding energy should be originated from oxidized sulfur species, such as sulfonate and sulfate groups.18 Furthermore, the energy-dispersive X-ray spectroscopy (EDX) mapping of the elements in the CMK-3P exhibits the concordance of N, C and S signals, as shown in Fig. 4d, indicating the uniform distribution of heteroatom elements through the in situ carbonization process.

Due to additional N and S-codoping as well as the more developed porosity, CMK-3P exhibits a better electrocatalytic activity than CMK-3S toward ORR. As shown in Fig. 5a, despite the capacitive background typically observed on high-surface-area carbons,21–23 a characteristic oxygen reduction peak appeared at -0.203 V (vs. Ag/AgCl) in the O$_2$ saturated electrolyte, while no any significant

### Table I. N and S contents and porosity of carbons derived from different precursors.

| Sample  | N (wt%) | N (at%) | S (at%) | $S_{\text{BET}}$ (m$^2$ g$^{-1}$) | $V_{\text{tot}}$ (cm$^3$ g$^{-1}$) | Pore size (nm) |
|---------|---------|---------|---------|-----------------|-----------------|---------------|
| CMK-3P  | 5.3     | 6.0     | 0.61    | 1030            | 2.403           | 3.7           |
| CMK-3S  | -       | -       | -       | 949             | 1.170           | 3.7           |
| SBA-15  | -       | -       | -       | 844             | 1.322           | 8.1           |

N: N content determined by elemental analysis (wt%) and XPS (at%) respectively. S: S content. $S_{\text{BET}}$: Specific surface area. $V_{\text{tot}}$: Total pore volume. Pore size: Average pore size.
Figure 4. (a) Survey XPS spectra of CMK-3P and CMK-3S. (b, c) High resolution N1s and S2p XPS spectra CMK-3P. (d) EDS mapping images of C, N and S of CMK-3P.

Figure 5. (a) Cyclic voltammograms (100 mV s\(^{-1}\)). (b) linear sweep voltammetry curves (1600 rpm, 10 mV s\(^{-1}\)). (c) electron-transfer number (n) and (d) peroxide yield (H\(_2\)O\(_2\)% of bare GC, CMK-3S, CMK-3P and the commercial 20 wt% Pt/C in O\(_2\)-saturated 0.1 M KOH solution at a scan rate of 100 mV s\(^{-1}\).
response was observed in the N₂ saturated medium, indicating the effective electrochemical reduction of oxygen on CMK-3P. CMK-3S was also tested under the same conditions for comparison, which resulted in a peak at low potential (-0.242 V vs. Ag/AgCl) and thus a less electrocatalytic activity than CMK-3P. The ORR performance of each sample was also evaluated by using linear sweep on rotating disk electrode (RDE) at 1600 rpm, as presented in Fig. 5b. CMK-3P displays an onset potential of -0.122 V, which is much higher than CMK-3S (-0.160 V) and still lower than the commercial Pt/C catalyst (-0.070 V). Furthermore, the limiting current of the CMK-3P electrode is also much higher than that of CMK-3S electrode over the whole potential range, and even higher than that of Pt/C electrode at negative potential of < -0.9 V. Electron-transfer number (n) and peroxide yield (H₂O₂%) were calculated using Eqn. 1 and 2 respectively, as presented in Fig. 5c and 5d. The number n of CMK-3P (> 3.0) is clearly greater than that of CMK-3S over the entire potential range, indicating that the ORR proceeds mainly via a four-electron (O₂ to OH⁻) reduction pathway. Meanwhile, H₂O₂% of CMK-3P (< 43%) is also significantly lower than that of CMK-3S. These results undoubtedly confirm the enhanced ORR electrocatalytic performance of CMK-3P relative to CMK-3S.

Summary

In summary, mesoporous carbon CMK-3P containing high nitrogen (6.0 at%) and sulfur (0.61 at%) contents was easily prepared through a direct carbonization of low-cost protic salt [Phen][2HSO₄] using pristine SBA-15 as template, without prepolymerization or activation process. In comparison with the highly ordered and large area-hexagonal arrays of nanorods observed for most typical CMK-3 (e.g. CMK-3S derived from sucrose precursor), CMK-3P consists of the curved and intertwined nanorods with lateral size ranging from tens to hundreds of nanometers. As a result, in addition to the templated mesopores centered at 3.7 nm, large mesopores and even macropores come into being as well as high specific surface area (1030 m² g⁻¹) and large pore volume (2.403 cm³ g⁻¹) in CMK-3P. CMK-3P was also applied as a metal-free catalyst for ORR, resulting in significantly higher performance than CMK-3S.

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