Hydrogen-bonding supramolecular protic salt as an “all-in-one” precursor for nitrogen-doped mesoporous carbons for CO₂ adsorption

Shiguo Zhang, Toshihiko Mandai, Kazuhide Ueno, Kaoru Dokko, and Masayoshi Watanabe*

Department of Chemistry and Biotechnology, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan.

E-mail: mwatanab@ynu.ac.jp

Phone & Fax: +81-45-339-3955

Abstract

Traditional methods for preparation of nitrogen-doped mesoporous carbons (NMCs), especially NMCs with high nitrogen content and narrow pore size distribution, typically require tedious, time-consuming procedures involving polymer precursors (or monomers for pre-polymerization), specific templates, and/or nitrogen-containing agents, as well as additional template-removal step by etching. Herein we reported a facile, template-free, and easily scalable route to NMCs by direct carbonization of an easily prepared, low cost, small-molecule protic salt ([pPDA][2HSO₄]), which was obtained by simple neutralization of p-phenylenediamine with two equivalents of sulfuric acid. NMCs with high relative yield, high nitrogen content, large surface area, large mesopore, and narrow pore size distribution were obtained in one step. Intensive analysis revealed that the key to the success of this strategy was the hydrogen-bond-assisted self-assembled structure, as well as the ingenious “all-in-one” role of the precursor during carbonization, wherein both the cationic [pPDA] and anionic [HSO₄] played indispensable and synergetic roles. Further KOH activation of the obtained NMCs resulted in not only ultrahigh surface areas of up to 3573 m²/g, but also significant increases in selective CO₂ uptake over N₂. Especially, one of the activated carbons, NMC-7-6, exhibited a high CO₂ uptake of 3.69 mmol/g at 25 °C and 1 atm, comparable to the best results by N-doped carbons and higher than those of all known zeolitic imidazolate frameworks.

Keywords: Hydrogen bond, carbon dioxide capture, mesoporous carbon, nitrogen doping, precursor, protic salt.

1. Introduction

Nitrogen-doped mesoporous carbon materials (NMCs), especially NMCs with high nitrogen content and narrow pore size distribution, are of great interest because of their unique features such as large surface area, large pore volume, low density, chemical inertness, and high electrical conductivity. The mesoporous structure as well as the narrow pore size distribution allows a high loading of accessible active sites in carbon, and provides efficient diffusion and mass transfer, whereas nitrogen doping may improve the conductivity, basicity, oxidation stability, and catalytic activity.[1-3] These remarkable properties contribute to their excellent performance in diverse areas, including separation, catalysis, adsorption, sensing, and particularly, energy storage and conversion applications such as fuel cells, supercapacitors, and lithium batteries.[4-6] Generally, nitrogen doping can be realized by either in situ pyrolysis of N-containing organic precursors or post-treatment of the as-obtained porous carbon. The former method allows much greater control of the incorporated N, resulting in a homogeneous distribution of N heteroatoms throughout the carbon material.[1] The latter method may result in morphological defects and structural degradation, including collapse and blockage of the porous architecture.[7] In order to introduce mesopores into carbon, an effective and sophisticated templating technique is commonly used, in which porosity is generated by the removal of the hard or soft sacrificial component.[3] The most widely used hard templates involve several tedious steps such as precursor synthesis, template preparation, infiltration of the template with the precursor, cross-linking and carbonization of the precursor, and template removal via acidic or caustic reagents.[8-10] In contrast, the soft templating method is more facile and attractive because the organic sacrificial blocks used are typically removed by in situ thermal decomposition during carbonization.[3, 11-14] Nevertheless, soft templating only proceeds with toxic formaldehyde, sluggish polymerization, specific substrates and film morphologies, and complicated evaporation-induced self-assembly. Both the traditional hard- and soft-templating methods require wasteful amounts of solvents and reagents, and are multi-step and time-consuming.

A simple procedure to prepare NMCs via direct carbonization of N-containing organic precursors is therefore much more feasible and highly attractive, but appears extremely challenging,[15-17] mainly because of the following two issues: First, currently available carbon precursors are very limited because most organic compounds, owing to their low thermal stability, are completely evaporated or decomposed into volatile products during carbonization. Second, even for those precursors that are sufficiently robust to endure harsh carbonization and ensure high carbon yields, mesopores are always unavailable because of the lack of a suitable and stable self-sacrificial structure-directing agent or template.[17] Clearly, identifying the “right” N-containing carbon precursors, which could simultaneously address these two issues, is the key to the successful fabrication of NMCs via a direct, template-free approach. However, up to now there are only very few reports on the direct synthesis of NMCs through polymerization and carbonization of specific microphase-separated block copolymers,[18] aromatic nitriles in the presence of zinc chloride,[16, 19] or nitrile-containing ionic liquids.[17, 20] These methods are very difficult to be conducted and indispensably bear drawbacks such as tedious synthesis of specific ionic liquids or block copolymer precursors, long reaction time, high cost, very broad pore size distribution as well as low N contents. It should be noted that some metal-containing organic salts such as alkali chloroacetate,[21] poly(styrene sulfonic acid-co-maleic acid) salts containing sodium, iron, cobalt, or nickel,[22] ethylenediamine tetraacetic acid disodium magnesium salt,[23] lithium salts of aromatic acids,[24] have also been subjected to direct pyrolysis, while in this case, an additional etching step is still required to remove the temporary template (inorganic salts generated in situ during pyrolysis) and leave behind the nanoporous carbon. In addition, the less developed mesoporous structure as well as the absence of N heteroatom in most of the resulted carbons strongly hindered their large scale applications.

Very recently, we demonstrated that protic ionic liquids (PILs) and protic salts (PSs), formed by simple neutralization of N-containing bases with acids, could be potential carbon precursors that can withstand severe carbonization.[20, 25-27] Carbons with variable properties, such as very high N contents, large surface areas, or high conductivities greater than that of graphite, were easily obtained by direct carbonization of these versatile precursors, thus overcoming the aforementioned first issue for the one-step synthesis of NMCs. Unfortunately, nearly all the as-synthesized PILs/PSs gave rise to only nonporous or microporous carbons due to their failure to satisfy the second issue (lack of a suitable self-template) as mentioned above.

Herein, we report a very straightforward method for one-step, template-free synthesis of NMCs through direct carbonization of a single small-molecule protic salt, p-phenylenediamine bisulfate ([pPDA][2HSO₄]), which can serve simultaneously as carbon and nitrogen source and self-template during carbonization (Fig. 1). The present strategy has several advantages. First, the entire synthetic procedure is quite simple: the protic salt can be easily prepared by simple neutralization and is low-cost; carbonization can be implemented in a single step at ambient pressure. Second, this method is efficient with the potential for high-yields and nearly quantitative transformation. Third, high nitrogen content and uniform nitrogen doping can be achieved via in situ carbonization. Last, the resultant carbons possess large surface area, large mesopores, and narrow pore size distribution. Thus, this method appears to be highly time- and cost-effective, and very easy to scale up. More importantly, NMCs obtained in this work with excellent mesoporosity provide a high KOH/carbon interfacial area for chemical activation and low-resistance diffusion pathways for activation agents. KOH activation of NMCs result in not only greatly enhanced surface areas, but also significantly improved capacity of CO₂ adsorption.

2. Experiment

2.1. Synthesis of protic salts

pPDA in methanol was dropped into 2 equiv. of dilute H_2SO_4 maintained in an ice bath. A precipitate was instantly formed following which the mixture was stirred for 1 h at room temperature. Then, the solvent was removed by using a rotary evaporator and the mixture subsequently heated at 80 °C for 24 h under high vacuum. The obtained protic salt was powdered for direct carbonization. For comparison, the as-synthesized $[\text{pPDA}][2\text{HSO}_4]$ was recrystallized from an aqueous solution of 50% H_2SO_4 .

2.2. Preparation of nitrogen-doped mesoporous carbons (NMCs)

The protic salt was subjected to direct carbonization in a tube furnace under Ar atmosphere (100 mL/min) via heating ramps of 10 °C/min from room temperature to the desired temperature (e.g., 1000 °C) and maintained at this temperature for 2 h. After cooling down, the obtained carbon black materials were powdered for further characterization and application. The obtained carbons are denoted as NMC-x, where x denotes one-hundredth of the carbonization temperature. For example, NMC-10 denotes carbonization at 1000 °C.

2.3. KOH activation of NMCs

A 2:1 mass ratio of NMCs and KOH at a mass ratio of 2/1 was mixed and powdered. The physical mixture was then heated to the desired temperature at the rate of 3 °C/min, and maintained at that temperature for 1 h under an Ar flow (100 mL min⁻¹). The resulting activated carbon was rinsed with 2 M HCl and repeatedly washed with deionized water and methanol. The final activated carbon was obtained by drying at 100 °C overnight. For convenience, the carbons obtained through chemical activation were denoted as NMC-x-y, where x and y denote one-hundredth of the carbonization and activation temperature (in °C), respectively. For example, NMC-7-8 denotes carbonization at 700 °C and subsequent activation at 800 °C.

2.4. Characterizations

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku RINT-2000 diffractometer using $\text{Cu K}\alpha$ ($\lambda = 0.154$ nm) radiation. The diffractograms were recorded in

the 2θ range from 10° to 90° with a 2θ step size of 0.02 and a scanning speed of $10^\circ/\text{min}$. Carbon, nitrogen, and hydrogen (CHN) Elemental analyses were performed on a Vario EL III CHN elemental analyzer. Chemical states, compositions, and valence band spectra were analyzed by PHI Quantera SXM X-ray photoelectron spectroscopy (XPS) with a base pressure of 6.7×10^{-8} Pa, with an Al K α (1486.6 eV) as the X-ray source and a pass energy of 280.00 (survey scan) and 69.00 eV (high-resolution scan). An Ar ion gun was employed to sputter the sample surface. Thermogravimetric (TG) measurements were performed using a thermo-gravimetry/differential thermal analyzer (TG-DTA 6200, Seiko Instruments). The temperature was increased from room temperature to 1000°C at a heating rate of $10^\circ\text{C min}^{-1}$ under a nitrogen flow of 100 mL min^{-1} with open alumina pans. Nitrogen sorption isotherms were recorded on a Belsorp-mini II (BEL Japan, Inc.) sorption analyzer at -196°C (77 K). Prior to the measurement, the sample was purged with flowing nitrogen at 300°C for 3 h. The specific surface area (S_{BET}) was calculated using the Brunauer-Emmett-Teller (BET) method. The total pore volume (V_{tot}) was determined from the amount of nitrogen uptake at a relative pressure (P/P_0) of 0.99. The micropore and mesopore surface areas were determined by t -plot analysis by using the standard adsorption isotherm of the nonporous carbon black. Raman spectra were measured by using a 532-nm laser Raman spectrometer RMP-300 (JASCO, Japan) at room temperature. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) measurements were performed on a JEOL JEM-2100F field emission source transmission electron microscope operated at 200 kV. The electrical conductivities of the carbon powdered samples were measured by a two-probe method according to the established methodology.[26] CO_2 adsorption experiments were recorded on a Belsorp-mini II (BEL Japan, Inc.) sorption analyzer, and the CO_2/N_2 selectivity was calculated based on an established procedure.[28] NMR spectra were recorded on a Bruker DRX-500 spectrometer using a double NMR tube method. Deuterated dimethylsulfoxide (DMSO-d_6) was added as a lock solvent in the outer tube as a lock solvent, and the sample solution was added in the inner tube. The use of a double tube prevented the mixing of the sample and DMSO, which contained trimethylsilane (TMS) as the external standard.

2.5. Single-crystal X-ray diffraction

For single-crystal X-ray diffraction, suitable crystal of [pPDA][2HSO₄] was grown in an aqueous solution of H₂SO₄. The crystal was mounted on a glass pin supported by a small amount of epoxy resin. Crystal evaluations and data collections were performed with a Rigaku Mercury70 diffractometer using graphite monochromated Mo K α radiation at -50°C under a nitrogen gas stream. The structure was solved by direct methods using the SIR92 program.[29] All the nonhydrogen atoms were obtained from the initial solution. Most of the hydrogen atoms were included in their calculated positions. The remaining hydrogen atom position for the atom on the [HSO₄] anion was derived from the corresponding Fourier peak. The structure was refined by full-matrix least-squares SHELXL-97.[30, 31] All the nonhydrogen atoms were refined anisotropically and all the hydrogen atoms were refined by using the riding model. All the calculations were performed using the crystal structure software package.[32]

3. Results and discussion

3.1. Hydrogen-bond-assisted self-assembly of precursor

[pPDA][2HSO₄] was synthesized by the neutralization of *p*-phenylenediamine (pPDA) with two equivalents of sulfuric acid. The immediately obtained precipitate was practically insoluble in most organic solvents and even in water despite the presence of four strongly hydrophilic sites (2NH₃⁺ and 2HSO₄⁻). The precipitate, however, can be dissolved in ca. 50 wt% sulfuric acid, which has been previously used to break the abundant hydrogen-bonding networks of cellulose.[33] The solution containing [pPDA][2HSO₄] was directly subjected to NMR analysis using a double tube method. The ¹H and ¹³C NMR spectra corresponded very well with the stoichiometric structure (Fig. S1), demonstrating that neutralization occurred during synthesis rather than decomposition (oxidation of the amine by sulfuric acid). White crystal-like powders were obtained via recrystallization from the sulfuric acid aqueous solution. Scanning electron microscopy (SEM) images showed that the crystals

were composed of mostly cubic or rectangle microcrystals with truncated corners and edges (Fig. 2D). The crystal structure of [pPDA][2HSO₄] was analyzed by single-crystal X-ray crystallography (Fig. 2A–2C). [pPDA][2HSO₄] crystallized in the $P2_1/n$ monoclinic space group with two molecules in the unit cell and had a calculated density of 1.742 g cm⁻³ (Table S1). The absence of solvent water molecules in the single crystal structure of [pPDA][2HSO₄] emphasized its hydrophobicity. Each cationic [pPDA] was connected by ten [HSO₄] anions (five on each head) via twelve hydrogen bonds (Fig. S2 and S3). On each head, five medium- to strong-strength hydrogen bonds were formed between an amino N–H and the O atoms of the [HSO₄] moiety, with variable hydrogen bond distances and angles between the hydrogen-bond donor and acceptor. Furthermore, [pPDA] was stabilized by two symmetrical weak-strength hydrogen bonds formed between the H on the benzene moiety and O atoms of the [HSO₄] moiety (Table S2). Interestingly, in addition to the hydrogen bonds between [pPDA] and [HSO₄], very strong-strength hydrogen bonds were also formed between neighboring [HSO₄] moieties (Fig. S2 and S3). Among all these hydrogen bonds, three types (1N(1)–H(1B)...O(3), 1N(1)–H(1C)...O(3), and 2O(2)–H(4)...O(1)) were very strong because these interactions were more direct and linear (Table S2). The numerous hydrogen bonds involving the [HSO₄] anions provided a stable three-dimensional (3D) interconnected supramolecular self-assembled network, which resulted in a liquid crystal-like lamellar structure between [pPDA] and [HSO₄], with two torsional adjacent layers (with a dihedral angle of 58.5°) of pPDA separated by a double-layer of anionic [HSO₄] (Fig. 2C). The hydrophilic moieties were mostly located between two hydrophobic layers owing to the dense hydrogen-bonding networks, hampering the penetration of solvent molecules into the bulk material. This hydrogen-bond-assisted supramolecular network has similarities to the structures of metal-organic frameworks (MOF) and 3D covalent organic frameworks (COF), formed by metal-coordination bonds and covalent bonds, respectively.[34, 35] The recrystallized [pPDA][2HSO₄] was further analyzed by powder X-ray diffraction (XRD), and a close match between the experimental result and the XRD pattern calculated from the single-crystal structure (fig. 2E) was observed. The most intense diffraction at lower 2theta values corresponded to the 002

lattice plane, which is nearly vertical in-between the benzene moieties (fig. 2C) and is expected to be essential to the final NMCs (as discussed below).

3.2. Structure of NMCs

Thermogravimetric analysis (TGA) curves of the as-synthesized protic salt and its parent amine are shown in Fig. 3A. Although pPDA completely evaporated below 210 °C, the as-synthesized protic salt clearly produced carbon residue. Indeed, direct carbonization of [pPDA][2HSO₄] gave rise to carbon powder (denoted as NMC-x, where x denotes one hundredth of the carbonization temperature) with a high yield depending on the carbonization temperature (Fig. 3A). The carbon yield at 800 °C was as high as 23.3%, nearly a quantitative transformation of the overall carbon contents (23.7%) in the precursor into the final carbon. The carbon obtained at 1000 °C (NMC-10) was selected as a typical sample for structure analysis. The XRD pattern (fig. 3B) exhibited two diffraction peaks at 25.3 and 43.5°, corresponding to the (002) and (100) diffractions of carbon, respectively, indicating the presence of nanographitic structures commonly observed in pyrolytic carbons.[36] In contrast, sucrose-based CMK-3 exhibits a much lower degree of graphitization, as seen from its broad (002) diffraction peak at a low angle (22.1°).[25] A crude estimate of the lateral size of the partially graphitic domains based on the width of the (100) peak indicated that they do not exceed 2 nm. Likewise, based on the width of the (002) peak, nanographitic domains were composed of no more than four π -stacked nanographene sheets. The Raman spectrum of NMC-10 exhibited typical D and G bands at 1351 and 1582 cm⁻¹, respectively (Fig. 3C). The D band has been related to the edges or disordered carbon, while the G band results from sp²-hybridized graphitic carbon atoms.[37] The comparable intensity of these bands ($I_D/I_G \sim 1$) suggested that the local carbon contained both graphitic and disordered carbon atoms. The inherently high N content in [pPDA][2HSO₄] (9.21%, N/C molar ratio: 0.333) was expected to yield highly N-doped carbon. As detected by elemental analysis (CHN), the NMCs obtained were mainly composed of C and N (Table S3). The N content was above 20 wt% when carbonized below 600 °C and was still 17.77 wt% at 700 °C, as seen in Fig. 3D. Even at

800 °C, the carbon (NMC-8) had a high N content and N/C molar ratio of up to 13.84 wt% and 0.155, respectively. These values, to our knowledge, are **high and at least comparable with** those found in highly N-doped porous carbons that require complex synthetic procedures (13.1 wt% at 600 °C[38]; 14.8 wt% at 600 °C[39]; 7.1 wt% at 700 °C[40]; 11.9 wt% at 800 °C[41]) **and in carbon nitrides**[27, 42]. In addition to C and N, X-ray photoelectron spectroscopy (XPS) analysis revealed the presence of O (~5.0 at%) and S (~1.0 at%), originated from the [HSO₄] anion or physical adsorption (Fig. 3G). The surface N composition of the NMCs was in good agreement with the bulk content (Table S4), suggesting a homogeneous distribution of N in the whole carbon structure. High resolution N 1s XPS (fig. 3G, inset) revealed that the doped N in NMC-10 consisted of pyridinic (398.2 eV) and quaternary-graphitic (400.9 eV) configurations, as well as oxidized species at higher binding energies (>402 eV).^[43] The S 2p peak was resolved into four peaks at ~164.0, 165.1, 167.0, and 168.8 eV. The former two peaks corresponded to the S 2p_{3/2} and S 2p_{1/2} of thiophene-like structures, whereas the weak peaks at higher binding energies were ascribed to oxidized sulfur species.[44].

The successful fabrication of mesopores was visualized via transmission electron microscopy (TEM). As shown in Fig. 3E and 3F, owing to its highly porous texture, NMC-10 is quite translucent, but is nevertheless stable against degradation in the electron beam. Interconnected, disordered wormlike mesopores with an average pore size of ca. 10 nm were uniformly distributed in the carbon architecture. The generation of porosity was further confirmed by N₂ sorption test. NMC-10 exhibits a typical type IV isotherm with a well-defined H2 hysteresis loop (Fig. 3H). The sharp capillary condensation at relatively higher pressures ($p/p_0 = 0.6\text{--}0.9$) indicated the presence of large mesopores with a narrow size range, which was confirmed by the corresponding pore size distribution (PSD). As shown in Fig. 3I, the PSD of NMC-10 derived from both adsorption and desorption branches were even narrower than those formed using homogeneous inorganic templates,[4, 5, 41] with peaks at 9.2 and 7.0 nm, respectively, in agreement with the TEM result. NMC-10 had a large surface area and large pore volume of 688 m²/g and 1.067 cm³/g,

respectively. The mesoporous and microporous surface areas, calculated by *t*-plot analysis (Fig. 3I, inset), were 508 and 180 m²/g, respectively, indicating a high mesoporosity.

3.3. Tailoring the porosity of NMCs

The pore structure appeared initially at 400 °C (Fig. S4). Such a low temperature is beneficial to maintaining a high N content in the porous structure. With increasing the temperature up to 700 °C, the mesoporous surface area was nearly constant (Table S5), while the micropores were developed, presumably from the burn-off of non-carbon elements and release of volatile fragments at the early stage of pyrolysis. However, when carbonizing above 700 °C, the mesoporous surface area greatly increased, while the microporous surface area was constant. The distinct evolution of the micropores and mesopores at different heating stages accounted for the continuous gain of overall surface area with increasing temperature. In addition to the pyrolysis temperature, the heating rate also affected the porous structure. For example, fast carbonization at 1000 °C, i.e., increasing the heating rate from 5 to 20 °C/min, not only resulted in a shorter carbonization time, but also significantly increased the surface area from 556 to 873 m²/g, whereas further increasing the heating rate to 30 °C/min resulted in a depression of the porosity (Table S6). Interestingly, the initial crystal structure of the precursor also had an effect on the porosity of the NMCs. As seen in Fig. 4 and Table S7, the recrystallized protic salt gave rise to a much higher surface area and mesoporosity, larger pore volume, and narrower pore size distribution than that of the non-recrystallized precursor. Furthermore, the molar ratio of amine/acid in the protic salt played an important role in the final porosity of the NMCs. As summarized in Fig. 4 and Table S7, although the 1:1 salt, i.e., [pPDA][SO₄], produced only micropores and a low surface area (387 m²/g), all the other salts (1:1.5, 1:2, and 1:3) resulted in mesoporous carbons. Particularly, [pPDA][2HSO₄] gave the largest pore volume, highest surface area, and mesoporosity. A series of phenylenediamine-based protic salts with variable structures (Fig. S6) were also prepared for direct carbonization. Although all the protic salts yielded porous carbons with variable yields and surface areas, unfortunately, none produced mesopores (Table S7 and Fig. S7), not even those with the same formula but

different substitution positions, i.e., [oPDA][2HSO₄] and [mPDA][2HSO₄]. These results strongly suggest that the textural characteristics of the carbons were primarily determined by the precursor structure and not the aforementioned preparation conditions. Chemical activation of carbon using KOH is promising as it significantly increases the surface area.[45] NMCs obtained in this work with large mesopores and large surface areas were expected to provide low-resistance diffusion pathways for activation agents and a high KOH/carbon interfacial area. Activation of NMC-7 at 600–800 °C resulted in carbons (denoted as NMC-7-6, NMC-7-7, and NMC-7-8, Table 1) with variable surface areas. In particular, NMC-7-8 exhibited an ultra-large surface area of 3573 m²/g, a seven-fold increase of the surface area compared with that of NMC-7. This remarkably high value is among the best results reported for KOH-activated carbons (Table S8) and is even higher than that of MOF-derived carbon (3405 m²/g).[46].

3.4. Mechanism analysis of carbonization and mesopore formation

In order to shed some light on the mesopore formation and carbonization process, the protic salt was analyzed by TG-MS (in situ), while the samples obtained at variable temperatures were fully analyzed by XRD, Raman spectroscopy, elemental analysis, and particularly, high resolution XPS (ex situ). Based on the detailed analysis (see Supporting Information), the successful fabrication of mesoporous carbon was expected to be realized by a hydrogen-bond-assisted self-assembly with subsequent self-oxidative polymerization and carbonization, wherein the unique structure of [pPDA][2HSO₄] was the crucial factor. A possible carbonization mechanism is depicted in Fig. 5, involving several steps: (A) The protonation with high proton transfer energy made [pPDA][2HSO₄] robust enough to undergo severe carbonization in comparison with its volatile parent amine.[26, 47] [pPDA][2HSO₄] contained solely thermally stable benzene groups with a high bonding energy and no aliphatic groups. According to the established precursor-carbon correlations,[25] aromatic moieties are liable to form polycyclic aromatic hydrocarbons during carbonization, mainly through intermolecular or intramolecular fusion with adjacent fragments by dehydrogenation, therefore, the benzene groups may easily get involved in the

carbon architecture through ring condensation,[26] accounting for the obtained high carbon yield. Moreover, partial-protonation gave rise to bisulfate anions ($[\text{HSO}_4]$) and resulted in the formation of a specific hydrogen-bonding self-assembled structure in the resultant protic salt, which facilitated the subsequent oxidative polymerization of pPDA. The 002 lattice plane located vertically across the benzene moieties, as shown in Fig. 2C, was essential to the final mesopore, because the mesoporosity was found to be greatly depressed with a decrease in the 002 diffraction peak intensities (Table S7 and Fig. 4C). Unlike the traditional soft-template method that requires a very slow heating rate (1 °C/min) to preserve the block copolymer-based self-assembled structure for the final mesoporous carbon,[11-13] herein the hydrogen-bond-assisted supramolecular structure of $[\text{pPDA}][2\text{HSO}_4]$ did not require any additional template, was very stable, and could bear fast carbonization with a heating rate of up to 30 °C/min. **(B)** When increasing the temperature to 270 °C, oxidative polymerization of the aromatic diamines occurred. The cationic $[\text{pPDA}]$ acted as a reductant and polymerizable monomer, while the anionic $[\text{HSO}_4]$ acted as an acidic source and self-oxidant. During the polymerization, $[\text{pPDA}]$ was oxidized to a polyaromatic structure, while $[\text{HSO}_4]$ was reduced to $[\text{HSO}_3]$, resulting in a fully oxidized polyaniline structure, wherein nearly all of the nitrogen was protonated. The resultant mesoscopic architecture, however, was still nonporous because the pores were blocked by the anions. **(C)** When the temperature was increased to 400 °C, nearly all of the polyaniline nitrogen was deprotonated due to the simultaneous elimination of SO_2 and H_2O , resulting in the open mesoporous architecture. At the same time, heteroatoms such as S and O began to be trapped in the framework. **(D)** At temperatures above 500 °C, the heteroatom-doped mesoporous carbon structure began to be gradually developed, while micropores were formed through the release of the non-carbon components from the mesoporous walls. Interestingly, the original shape of the precursor was even completely retained after carbonization (Fig. S8), indicating that the carbonization process did not proceed through a distinct liquid phase, and the cross-linking polymerization and decomposition may occur between isolated self-assembled structures.

3.4. Carbon dioxide capture

N-doped porous carbons with weak basic sites were reported to be notable sorbents for efficient CO₂ capture.[48-51] NMC-7, as a typical example, however, exhibited a CO₂ uptake capacity of as low as 1.64 mmol/g at 25 °C and 1 atm despite of its high N content (Fig. 6B). In contrast, the KOH-activated carbon materials showed significant increases in CO₂ uptake, with values of 2.39, 3.24, and 3.69 mmol/g (equivalent to 9.5, 12.5, and 14.0 wt%) for NMC-7-8, NMC-7-7, and NMC-7-6, respectively. In particular, the uptake capacity of NMC-7-6 was higher than those of the known N-doped porous carbon monoliths,[48] N-doped carbons prepared from deep eutectic solvents,[52] and was comparable to the best reported CO₂ uptakes by N-decorated carbons.[28, 53] The CO₂/N₂ selectivity of NMC-7-6 is 31:1 at 25 °C, which is significant for practical applications. In addition, all of the sorption isotherms show reversible adsorption characteristics (Fig. 6B), indicating weak interactions between the CO₂ molecules and the pore walls. Unlike NMC-7, the isotherms of the activated NMCs also indicated that the capacities progressively increased with pressure and had not reached saturation at 1 atm, suggesting improved capacity at high pressures.

In order to investigate the distinct capture behavior between these carbons, the N contents of NMC-7 before and after activation were measured by elemental analysis (CHN) and XPS (Table 1), and the N configuration was also evaluated by XPS (Fig. S9). It's clear that not only the overall N content but also the percentage of pyridinic N greatly decreased after activation, and high activation temperature results in both low N content and low percentage of pyridinic N. Especially for NMC-7-8, very low N content (< 2 at%) with exclusively graphitic N configuration was detected. The graphitic N is known to have a Lewis basicity much weaker than pyridinic N, because the latter is a type of nitrogen located at edge or defect site and contributes only one p-electron to the aromatic π -system while leaving a lone electron pair in the plane, which increases the electron density and electron-donating character of the carbon matrix. Consequently, pyridinic N may lead to an improvement of the adsorption of acidic CO₂ molecules through strong binding interactions such dipole–dipole interactions,[49] acid–base interactions,[54] and hydrogen bonding[55] between CO₂ molecules and nitrogen-modified heterogeneous pore.[48, 56] In addition, a

close inspection of the N_2 sorption isotherms found that KOH-activation destroyed the pristine mesoporous structure of NMC-7 (Fig. 6A). Alternatively, NMC-7-7 ($p/p_0 < 0.15$) and NMC-7-8 ($p/p_0 < 0.3$) with very large surface areas exhibit significant capillary condensation at relatively lower pressures, indicating the presence of a large number of small mesopores, while the absence of such capillary condensation in NMC-7-6 indicates the presence of only micropores despite its relatively small surface area. Recent studies have revealed that the storage capacity of CO_2 of N-doped porous carbon is strongly dependent on the N content as well as the suitable microporous structure.[57] Taking the above discussion together, the remarkably high capacity of NMC-7-6 could be due to the mild activation at a relatively low temperature, which not only generate significantly exclusive microporosity with high adsorption potential but also minimize the loss of nitrogen species and pyridinic N during the activation process.[49-51, 55].

4. Conclusions

In conclusion, we have shown that NMCs with high carbon yield, high N content, large surface area, high mesoporosity, large mesopore, as well as narrow pore size distribution, could be simply obtained through direct carbonization of a very low-cost and easily available protic salt, without any complicated synthesis, template, pre-polymerization, infiltration, or etching. The porous structure of the NMCs can be tuned by changing the preparation conditions such as pyrolysis temperature, heating rate, molar ratio of amine/acid, recrystallization, and KOH activation. The successful fabrication of NMCs was spontaneously realized by hydrogen-bond-assisted self-assembly with subsequent self-oxidative polymerization and carbonization through an ingenious synergistic interaction between cations and anions. During carbonization, [pPDA][2HSO₄] behaved as an “all-in-one” precursor, i.e., carbon and nitrogen source, oxidant and reductant, polymerizable monomer, and self-template. The anionic [HSO₄] not only acted as a self-oxidant to accelerate the polymerization of pPDA, but also functioned as a unique self-template and porogen during carbonization, while the cationic [pPDA] acted as a self-reductive agent and polymerizable monomer, as well as the carbon and nitrogen source. The

straightforward and easily reproducible method presented herein could be the simplest way to fabricate NMCs reported to date, and can be readily scaled up for mass production. The potential applications of the activated NMCs for CO₂ capture have been tested. One of them, i.e., NMC-7-6, exhibited a high CO₂ uptake of 3.69 mmol/g at 25 °C and 1 atm.

Acknowledgements

This work was supported by the Japan Science and Technology Agency (JST) – Advanced Low Carbon Technology Research and Development Program (ALCA) of Japan.

References

- [1] Y.Y. Shao, J.H. Sui, G.P. Yin, Y.Z. Gao, *Appl. Catal., B* 79 (2008) 89-99.
- [2] H.B. Wang, T. Maiyalagan, X. Wang, *ACS Catal.* 2 (2012) 781-794.
- [3] C.D. Liang, Z.J. Li, S. Dai, *Angew. Chem. Int. Ed.* 47 (2008) 3696-3717.
- [4] W. Yang, T.P. Fellingner, M. Antonietti, *J. Am. Chem. Soc.* 133 (2011) 206-209.
- [5] T.P. Fellingner, F. Hasche, P. Strasser, M. Antonietti, *J. Am. Chem. Soc.* 134 (2012) 4072-4075.
- [6] X. Xu, Y. Li, Y.T. Gong, P.F. Zhang, H.R. Li, Y. Wang, *J. Am. Chem. Soc.* 134 (2012) 16987-16990.
- [7] Y. Zheng, Y. Jiao, M. Jaroniec, Y.G. Jin, S.Z. Qiao, *Small* 8 (2012) 3550-3566.
- [8] R. Ryoo, S.H. Joo, S. Jun, *J. Phys. Chem. B* 103 (1999) 7743-7746.
- [9] S.H. Joo, S.J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki, R. Ryoo, *Nature* 412 (2001) 169-172.
- [10] S. Jun, S.H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, O. Terasaki, *J. Am. Chem. Soc.* 122 (2000) 10712-10713.
- [11] C.D. Liang, K.L. Hong, G.A. Guiochon, J.W. Mays, S. Dai, *Angew. Chem. Int. Ed.* 43 (2004) 5785-5789.
- [12] F.Q. Zhang, Y. Meng, D. Gu, Y. Yan, C.Z. Yu, B. Tu, D.Y. Zhao, *J. Am. Chem. Soc.* 127 (2005) 13508-13509.
- [13] S. Tanaka, N. Nishiyama, Y. Egashira, K. Ueyama, *Chem. Commun.* (2005) 2125-2127.
- [14] J. Liu, T. Yang, D.-W. Wang, G.Q.M. Lu, D. Zhao, S.Z. Qiao, *Nat. Commun.* 4 (2013).
- [15] M. Zhong, E.K. Kim, J.P. McGann, S.E. Chun, J.F. Whitacre, M. Jaroniec, K. Matyjaszewski, T. Kowalewski, *J. Am. Chem. Soc.* 134 (2012) 14846-14857.
- [16] P. Kuhn, A. Forget, D.S. Su, A. Thomas, M. Antonietti, *J. Am. Chem. Soc.* 130 (2008) 13333-13337.
- [17] J.S. Lee, X.Q. Wang, H.M. Luo, G.A. Baker, S. Dai, *J. Am. Chem. Soc.* 131 (2009) 4596-4597.
- [18] M. Zhong, E.K. Kim, J.P. McGann, S.-E. Chun, J.F. Whitacre, M. Jaroniec, K. Matyjaszewski, T. Kowalewski, *J. Am. Chem. Soc.* 134 (2012) 14846-14857.
- [19] P. Kuhn, A. Forget, J. Hartmann, A. Thomas, M. Antonietti, *Adv. Mater.* 21 (2009) 897-901.
- [20] S. Zhang, K. Dokko, M. Watanabe, *Mater. Horiz.* (2015) DOI: 10.1039/C1034MH00141A.
- [21] S.E. Skrabalak, K.S. Suslick, *J. Am. Chem. Soc.* 128 (2006) 12642-12643.

- [22] D. Hines, A. Bagreev, T.J. Bandosz, *Langmuir* 20 (2004) 3388-3397.
- [23] B. Xu, H. Duan, M. Chu, G. Cao, Y. Yang, *J. Mater. Chem. A* 1 (2013) 4565-4570.
- [24] K. Kamegawa, M. Kodama, K. Nishikubo, H. Yamada, Y. Adachi, H. Yoshida, *Microporous Mesoporous Mater.* 87 (2005) 118-123.
- [25] S. Zhang, K. Dokko, M. Watanabe, *Chem. Mater.* 26 (2014) 2915-2926.
- [26] S. Zhang, M.S. Miran, A. Ikoma, K. Dokko, M. Watanabe, *J. Am. Chem. Soc.* 136 (2014) 1690-1693.
- [27] S. Zhang, S. Tsuzuki, K. Ueno, K. Dokko, M. Watanabe, *Angew. Chem. Int. Ed.* 54 (2014) 1302-1306.
- [28] A. Aijaz, N. Fujiwara, Q. Xu, *J. Am. Chem. Soc.* 136 (2014) 6790-6793.
- [29] A. Altomare, G. Casciaro, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* 27 (1994) 435.
- [30] G.M. Sheldrick, in: *SHELX97* (Ed.), University of Göttingen: Göttingen, Germany, 1997.
- [31] G.M. Sheldrick, *Acta Crystallogr A* 64 (2008) 112-122.
- [32] C.S. 4.0.; *Crystal Structure Analysis Package*, Rigaku Corporation, Tokyo 196-8666, Japan, 2000-2010.
- [33] Y. Habibi, L.A. Lucia, O.J. Rojas, *Chem. Rev.* 110 (2010) 3479-3500.
- [34] H.C. Zhou, J.R. Long, O.M. Yaghi, *Chem. Rev.* 112 (2012) 673-674.
- [35] X. Feng, X.S. Ding, D.L. Jiang, *Chem. Soc. Rev.* 41 (2012) 6010-6022.
- [36] F. Bonino, S. Brutti, P. Reale, B. Scrosati, L. Gherghel, J. Wu, K. Mullen, *Adv. Mater.* 17 (2005) 743-746.
- [37] X.Y. Ma, M.H. Cao, C.W. Hu, *J. Mater. Chem. A* 1 (2013) 913-918.
- [38] J. Wei, D.D. Zhou, Z.K. Sun, Y.H. Deng, Y.Y. Xia, D.Y. Zhao, *Adv. Funct. Mater.* 23 (2013) 2322-2328.
- [39] S. Feng, W. Li, Q. Shi, Y. Li, J. Chen, Y. Ling, A.M. Asiri, D. Zhao, *Chem. Commun.* 50 (2014) 329-331.
- [40] S. Shanmugam, T. Osaka, *Chem. Commun.* 47 (2011) 4463-4465.
- [41] H.C. Chen, F.G. Sun, J.T. Wang, W.C. Li, W.M. Qiao, L.C. Ling, D.H. Long, *J. Phys. Chem. C* 117 (2013) 8318-8328.
- [42] A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J.-O. Müller, R. Schlögl, J.M. Carlsson, *J. Mater. Chem.* 18 (2008) 4893-4908.
- [43] J.P. Paraknowitsch, A. Thomas, M. Antonietti, *J. Mater. Chem.* 20 (2010) 6746-6758.
- [44] Y. Yan, Y.X. Yin, S. Xin, Y.G. Guo, L.J. Wan, *Chem. Commun.* 48 (2012) 10663-10665.
- [45] J.C. Wang, S. Kaskel, *J. Mater. Chem.* 22 (2012) 23710-23725.
- [46] H.L. Jiang, B. Liu, Y.Q. Lan, K. Kuratani, T. Akita, H. Shioyama, F.Q. Zong, Q. Xu, *J. Am. Chem. Soc.* 133 (2011) 11854-11857.
- [47] M.S. Miran, H. Kinoshita, T. Yasuda, M.A.B.H. Susan, M. Watanabe, *Phys. Chem. Chem. Phys.* 14 (2012) 5178-5186.
- [48] G.P. Hao, W.C. Li, D. Qian, G.H. Wang, W.P. Zhang, T. Zhang, A.Q. Wang, F. Schuth, H.J. Bongard, A.H. Lu, *J. Am. Chem. Soc.* 133 (2011) 11378-11388.
- [49] M. Sevilla, P. Valle-Vigon, A.B. Fuertes, *Adv. Funct. Mater.* 21 (2011) 2781-2787.
- [50] V. Chandra, S.U. Yu, S.H. Kim, Y.S. Yoon, D.Y. Kim, A.H. Kwon, M. Meyyappan, K.S. Kim, *Chem. Commun.* 48 (2012) 735-737.
- [51] M. Nandi, K. Okada, A. Dutta, A. Bhaumik, J. Maruyama, D. Derks, H. Uyama, *Chem. Commun.* 48 (2012) 10283-10285.

- [52] M.C. Gutierrez, D. Carriazo, C.O. Ania, J.B. Parra, M.L. Ferrer, F. del Monte, *Energy Environ. Sci.* 4 (2011) 3535-3544.
- [53] L. Wang, R.T. Yang, *J. Phys. Chem. C* 116 (2011) 1099-1106.
- [54] G.P. Hao, W.C. Li, D. Qian, A.H. Lu, *Adv. Mater.* 22 (2010) 853-857.
- [55] W. Xing, C. Liu, Z.Y. Zhou, L. Zhang, J. Zhou, S.P. Zhuo, Z.F. Yan, H. Gao, G.Q. Wang, S.Z. Qiao, *Energy Environ. Sci.* 5 (2012) 7323-7327.
- [56] X. Zhu, C. Tian, S. Chai, K. Nelson, K.S. Han, E.W. Hagaman, G.M. Veith, S.M. Mahurin, H. Liu, S. Dai, *Adv. Mater.* 25 (2013) 4152-4158.
- [57] L. Liu, Q.-F. Deng, X.-X. Hou, Z.-Y. Yuan, *J. Mater. Chem.* 22 (2012) 15540-15548.

Figures and Tables

Figure 1. Template-free synthesis of NMCs by direct carbonization of [pPDA][2HSO₄].

Figure 2. (A) Thermal ellipsoid model of [pPDA][2HSO₄]. Expanded structures are indicated in the model. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, and isotropic hydrogen atoms are represented by spheres of arbitrary size. The hydrogen atom of the [HSO₄] anion is located at the highest corresponding Fourier peak. Atom colors: C, Gray; O, red; N, blue; S, yellow; H, white. (B) Perspective view of the hydrogen-bonding network of [pPDA][2HSO₄] in the crystal. Gray dashed lines illustrate hydrogen bonds. (C) A $2 \times 2 \times 2$ supercell of [pPDA][2HSO₄] (triangle-coordinated C, black triangle; tetrahedrally coordinated S, yellow tetrahedron; tetrahedrally coordinated N, blue tetrahedron). The red plane indicates the 002 lattice plane. (D) SEM images of [pPDA][2HSO₄]. (E) Comparison of the experimental XRD pattern (red) with the calculated pattern obtained from the single crystal of [pPDA][2HSO₄] (blue).

Figure 3. (A) TGA curves of [pPDA][2HSO₄] and its parent amine, pPDA. The dashed line indicates the theoretical yield calculated based on the overall carbon content in the precursor and the hollow circles indicate the oven yields. (B) XRD pattern and (C) Raman spectrum of NMC-10. (D) Carbonization-temperature dependent specific surface area and N content detected by elemental analysis of samples derived from [pPDA][2HSO₄]. (E, F) TEM images, (G) XPS spectrum, (H) N₂ sorption isotherms, and (i) pore size distributions of NMC-10. The insets in Fig. 3G and 3I show the high-resolution N 1s and S 2p XPS spectra and *t*-plot of NMC-10, respectively.

Figure 4. N₂ sorption isotherms of NMC-10 (A) derived from protic salts of different pPDA/H₂SO₄ molar ratios at a heating rate of 10 °C/min and (B) of [pPDA][2HSO₄] at variable heating rates. N₂ sorption isotherm of each sample was vertically shifted an additional 200 cm³ (STP)g⁻¹ for comparison. (C) The XRD patterns of pPDA-based protic salts of different pPDA/H₂SO₄ molar ratio.

Figure 5. Schematic illustration of the formation mechanism of NMCs (for detailed analysis, see Supporting Information).

Figure 6. (A) N_2 sorption isotherms of NMC-7 before and after KOH activation. (B) CO_2 adsorption–desorption curves of NMC-7 and its KOH-activated carbon materials at 25 °C. The gravimetric uptake represented by the arrows was calculated using the following equation: $\text{wt\%} = \text{mmol g}^{-1} \times 44 \times 0.001 \times 100 / (\text{mmol g}^{-1} \times 44 \times 0.001 + 1)$.

Table 1. Porosity and CO₂ uptake (25 °C and 1 atm) of KOH-activated NMC-7.

Carbon	S _{BET} (m ² g ⁻¹)	N wt% ^a	N at% ^b	CO ₂ (mmol g ⁻¹)
NMC-7-8	3573	1.17	2.0	2.39
NMC-7-7	2741	4.21	4.2	3.24
NMC-7-6	1260	12.67	12.1	3.69
NMC-7	481	17.77	16.8	1.64

^a Nitrogen content (weight percent) determined by elemental analysis. ^b Nitrogen content (atomic percent) determined by high-resolution XPS.

Shiguo Zhang received his PhD degree in 2011, supervised by Prof. Youquan Deng, from the Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences (CAS), and worked as an assistant researcher in the LICP from 2011 to 2012. In April 2012, he joined Prof. Masayoshi Watanabe's group as a postdoctoral worker at Yokohama National University. His research interests include ionic liquids, carbon materials and electrochemical energy conversion and storage.

Toshihiko Mandai received his PhD degree in 2012, supervised by Prof. Keiko Nishikawa, from Chiba University. He was a research fellow at Yokohama National University, working with Prof. Masayoshi Watanabe from 2012 to 2014. He is currently working as a postdoctoral fellow at Chalmers University of Technology (Sweden) with Prof. Patrik Johansson. His research interests include ionic liquids, crystal structure of organic complexes, and battery electrolytes.

Kazuhide Ueno received his PhD degree in 2009, supervised by Prof. M. Watanabe, from Yokohama National University. He was a postdoctoral fellow at Tohoku University, working with Prof. K. Kurihara, in 2009, and at Arizona State University, working with Professor C. A. Angell, from 2009 to 2011. He is currently working as a research fellow at Yokohama National University. His research interests include ionic-liquid-based soft materials and battery electrolytes.

Kaoru Dokko is an associate professor at Yokohama National University. He received his PhD degree from Tohoku University in 2001, under the supervision of Prof. Isamu Uchida. He then did postdoctoral research at Case Western Reserve University with Prof. Daniel A. Scherson and at Tokyo Metropolitan University with Prof. Kiyoshi Kanamura. He joined Yokohama National University in 2008. His current research interests are the physicochemical properties of concentrated electrolytes, nanostructured materials for energy conversion and storage, and electrochemical reaction processes in electrochemical devices.

Masayoshi Watanabe is a professor at Yokohama National University. He received his PhD degree from Waseda University in 1983. After being a visiting scientist with Prof. Royce W. Murray at the University of North Carolina (1988–1990), he joined Yokohama National University in 1992 and was promoted to full professor in 1998. His main research interests are ionic and nano-structured materials for chemical energy conversion and storage using fuel cells, and Li-ion and Li–sulfur batteries. He has published more than 300 original research papers and 150 books and reviews, and he has more than 16 000 citations (H-index: 64).

Nano Energy: RAPID COMMUNICATION

Hydrogen-bonding supramolecular protic salt as an “all-in-one” precursor for nitrogen-doped mesoporous carbons for CO₂ adsorption

Shiguo Zhang, Toshihiko Mandai, Kazuhide Ueno, Kaoru Dokko, and Masayoshi Watanabe*

Base + Acid $\longrightarrow$ Protic salt $\longrightarrow$ Mesoporous carbon