J|A|C|S
COMMUNICATIONS

Facile Ionothermal Synthesis of Microporous and Mesoporous Carbons from Task Specific Ionic Liquids

Je Seung Lee,[†] Xiqing Wang,[†] Huimin Luo,[‡] Gary A. Baker,[†] and Sheng Dai*,[†]

Chemical Sciences Division and Nuclear Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Received January 28, 2009; E-mail: dais@ornl.gov

Carbonaceous materials are ubiquitous in various technological and energy-related applications, including separations, catalysis, and energy storage/conversion because of their unique physicochemical properties.[1−8] Traditional synthesis methods involve the carbonization of low-vapor pressure polymeric precursors derived from either synthetic (e.g., polyacrylonitrile (PAN), phenolic resins)[6] or natural sources such as pitch and shell nuts. These polymeric species possess low vapor pressures so that cross-linking reactions can proceed with concomitant char formation and without vaporization of the corresponding precursor units. Nonpolymeric carbon sources are rarely used to form carbon because of their uncontrolled vaporization during high-temperature pyrolysis.[9] One key drawback associated with the use of polymeric precursors, however, lies in the difficulty of generating carbon nanocomposites as well as in the formation of quality carbon coatings. Although nonpolymeric molecular species can be used to generate carbonaceous materials under high pressures, in addition to the experimental complexity and safety concerns, carbon yields are typically very low. In this communication, we describe a novel strategy for synthesizing porous carbons via simple one-step thermolysis of suitable task-specific ionic liquid (TSIL)[10] precursors. Keys to the success of our approach lie in the negligible volatility and molecular tunability associated with these highly promising TSIL carbon precursors.

Ionic liquids (ILs) are defined as semiorganic salts that exist in the liquid state below 100 °C.[10,11] Initially developed as molten electrolytes for battery applications, already ILs have impacted many disciplines beyond their initial conception, including electrochemistry,[12] separations,[13] chemical synthesis,[10,11] and advanced materials.[14] The basic structural attribute of ILs is their ionicity, which gives rise to strong Coulombic interactions between the constituent ions in these unique solvents, a feature responsible for the essentially null vapor pressure associated with the vast majority of known ILs. This intrinsic nonvolatility suggests favorable conditions for an intriguing carbonization process based on well-behaved cross-linking reactions of monomeric TSIL precursor units with minimal loss of reactant.

The key structural prerequisite of char-forming polymeric precursors is the presence of certain functional groups that can undergo cross-linking reactions under pyrolysis conditions. Among the most widely used polymeric carbon precursors are the PANs.[1] The nitrile group and nonvolatility of these polymeric carbon precursors are the two factors in determining their high carbon yields under charring conditions. By appending nitrile functionality onto imidazolium backbones, we sought to develop TSIL-based carbon precursors as intriguing fluid alternatives to existing ones. We note that although the suitability of nitrile-functionalized ILs as solvents for catalysis has been well demonstrated previously by Dyson and co-workers,[15] their use in materials design and synthesis remains unexplored.

Chart 1. Two Representative Dialkylimidazolium TSIL Cations Bearing One and Two Acetonitrile Groups, Respectively

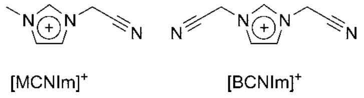

Chart 1 provides the chemical structures of two such nitrile-functionalized cations prepared for this purpose: 1-cyanomethyl-3-methylimidazolium ([MCNIm]$^+$) and 1,3-bis(cyanomethyl)imidazolium ([BCNIm]$^+$). Nitrile-functionalized TSILs were synthesized following literature procedures.[15,16] Final products appeared as nearly colorless, free-flowing liquids or low-melting solids and were dried in vacuo at 80 °C overnight prior to use. Carbonization of ILs was carried out by introducing 0.5 g of a particular IL into an alumina crucible placed within a quartz tube furnace. Under N_2 carrier gas flow (100 mL min^{-1}), the temperature was controllably ramped at a rate of 10 °C min^{-1} to a final temperature of 800 °C, where carbonization ensued for 1 h.

Figure 1 provides thermal gravimetric analysis (TGA) curves measured for three selected nitrile-functionalized TSILs alongside that for the conventional IL 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [BMIm][Tf_2N] (Chart S1 in the Supporting Information, SI). Evident from the TGA profiles is the fact that, for a given cation, the thermal stability of this class of ILs depends strongly on the nature of the anion. Whereas no carbon yield was achieved for the attempted carbonization of [BMIm][Tf_2N], as could be expected,[17] significant yields were observed for all nitrile-functionalized TSILs. As can be seen from the entries in Table 1, the carbonization yields achieved approach the corresponding theoretical values in all cases. Although the halide-based dinitrile TSIL, [BCNIm]Cl gave a very high carbonization yield

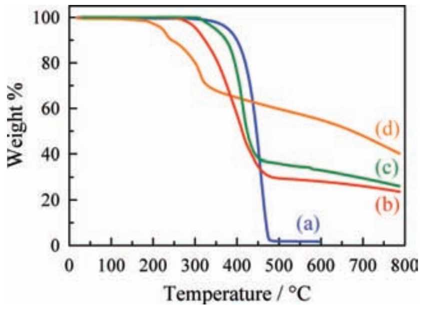

Figure 1. Scanning thermogravimetric profiles of (a) [BMIm][Tf_2N], (b) [BCNIm][Tf_2N], (c) [BCNIm][beti], and (d) [BCNIm]Cl.

[†] Chemical Sciences Division.
[‡] Nuclear Science and Technology Division.

10.1021/ja900686d CCC: $40.75

Table 1. Characteristics of Porous Carbons Prepared from TSILs[a]

IL[b]	carbonization yield/%	S_{BET}/m^2 g^{-1}
[BCNIm]Cl	53.0 (46.0)[c]	15.5
[BCNIm][Tf_2N]	22.8 (25.3)	640.4
[BCNIm][beti]	23.0 (25.1)	662.7
[MCNIm]Cl	42.0 (45.7)	4.6
[MCNIm][Tf_2N]	16.8 (23.9)	780.6

[a] Conditions: 800 °C under N_2(g); heating rate = 10 °C min^{-1}; dwell time = 1 h. [b] For a complete listing of ILs studied, refer to Table S1 in the SI. [c] Values of %C for each precursor IL are provided parenthetically.

of 53%, the resulting carbon was essentially nonporous (surface area, S_{BET}, of only 15.5 m^2 g^{-1}). Carbon yields for the same cation paired to the fluorinated anions [Tf_2N]$^-$ and [beti]$^-$ were equivalent within experimental uncertainty and, most importantly, yielded vastly higher S_{BET} values near 650 m^2 g^{-1}.

The BET N_2 adsorption−desorption isotherms for carbons derived from various ILs at 800 °C are given in Figure 2.

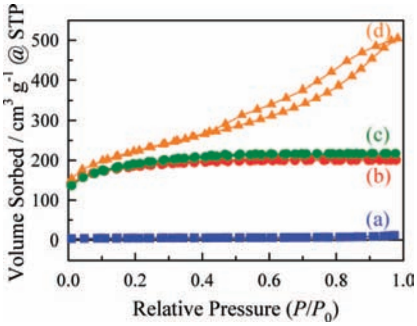

Figure 2. Nitrogen sorption isotherms of (a) [BCNIm]Cl, (b) [BCNIm][Tf_2N], (c) [BCNIm][beti], and (d) [MCNIm][Tf_2N].

Interestingly, the anion structures of these char-forming TSILs also have a profound influence on the ultimate surface area. Carbonaceous materials derived from bulky anions feature high surface areas, suggesting a templating role for the anion during micropore generation. For instance, simply replacing [Tf_2N]$^-$ with chloride for a fixed cation results in complete loss of porosity. The cation structure also impacts the textural properties of the resulting carbon. While [MCNIm][Tf_2N] showed a typical IV-type isotherm with an associated H2 type hysteresis loop indicating the presence of significant mesoporosity, carbons derived from [BCNIm][Tf_2N] were strictly microporous. In any event, the generation of mesoporosity with no requirement for a templating phase is remarkable and should be of wide interest.

The formation of our carbon materials likely proceeds at lower temperatures (<400 °C) via the formation of dynamic amorphous polytriazine networks, reminiscent of reaction mechanisms put forth by Kuhn et al.[18] to account for the formation of porous polymer frameworks assembled from dicyanoaryl groups within a pressurized molten $ZnCl_2$ system. We suggest that irreversible carbonization reaction pathways are activated in parallel with the nitrile cyclotrimerization at higher temperatures (>400 °C). The main decomposition pathway is thought to involve C−C bond formation with consecutive H_2 evolution. XPS results for carbon derived from [BCNIm][Tf_2N] (Figure S2) also reveal nitrogen contents near 2−3%, indicating that significant N functionality is lost during carbonization. However, the residual N content, which can be traced to the involvement of imidazolium building blocks, suggests potential utility for these porous carbons in CO_2 sequestration, for example. Other prospective applications for these new carbon precursors may include conformal carbon coatings and carbon composite fabrication. Indeed, early results demonstrate that our nitrile-pendant TSILs can be used to uniformly coat carbon onto various surfaces (Figure S4).

To summarize, we have described a simple, convenient, and catalyst-free approach for synthesizing high surface area N-doped porous carbons based on open vessel polymerization and thermolysis of TSIL precursors carrying char-forming nitrile functionality on the cation. The structural morphology (porosity and surface area) of the resulting carbon is strongly dependent on the nature of the cation/anion pairing within the TSIL. Notably, a mesoporous carbon was successfully synthesized by direct carbonization of a TSIL precursor which acted as a self-porogen in the absence of either solvent or template species. This novel strategy can be extended to incorporate other carbon-producing functionalities as well as more structurally diverse ions and highlights several exciting opportunities in functional carbon composites. These possibilities as well as reaction mechanisms form the subject of current investigation in our laboratories.

Acknowledgment. This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

Supporting Information Available: Chart S1; Table S1; Figures S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Liang, C. D.; Li, Z. J.; Dai, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 3696.
(2) Yantasee, W.; Lin, Y. H.; Fryxell, G. E.; Alford, K. L.; Busche, B. J.; Johnson, C. D. *Ind. Eng. Chem. Res.* **2004**, *43*, 2759.
(3) Joo, S. H.; Choi, S. J.; Oh, I.; Kwak, J.; Liu, Z.; Terasaki, O.; Ryoo, R. *Nature* **2001**, *412*, 169.
(4) Lee, J.; Yoon, S.; Hyeon, T.; Oh, S. M.; Kim, K. B. *Chem. Commun.* **1999**, 2177.
(5) Wan, Y.; Shi, Y. F.; Zhao, D. Y. *Chem. Mater.* **2008**, *20*, 932.
(6) Lu, A. H.; Kiefer, A.; Schmidt, W.; Schuth, F. *Chem. Mater.* **2004**, *16*, 100.
(7) Kim, T. W.; Chung, P. W.; Slowing, I. I.; Tsunoda, M.; Yeung, E. S.; Lin, V. S. Y. *Nano Lett.* **2008**, *8*, 3724.
(8) Li, Z. J.; Jaroniec, M. *Anal. Chem.* **2004**, *76*, 5479.
(9) Pol, S. V.; Pol, V. G.; Kessler, V. G.; Seisenbaeva, G. A.; Sung, M.; Asai, S.; Gedanken, A. *J. Phys. Chem. B* **2004**, *108*, 6322.
(10) Davis, J. H. *Chem. Lett.* **2004**, *33*, 1072.
(11) (a) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3773. (b) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667.
(12) (a) MacFarlane, D. R.; Forsyth, M.; Howlett, P. C.; Pringle, J. M.; Sun, J.; Annat, G.; Neil, W.; Izgorodina, E. I. *Acc. Chem. Res.* **2007**, *40*, 1165. (b) Nakamoto, H.; Watanabe, M. *Chem. Commun.* **2007**, 2539. (c) Ohno, H. *Electrochem. Acta* **2001**, *46*, 1407.
(13) (a) Han, X.; Armstrong, D. W. *Acc. Chem. Res.* **2007**, *40*, 1079. (b) Dai, S.; Ju, Y. H.; Barnes, C. E. *J. Chem. Soc., Dalton Trans.* **1999**, 1201. (c) Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. *Chem. Commun.* **1998**, 1765. (d) Blanchard, L. A.; Hancu, D.; Beckman, E. J.; Brennecke, J. F. *Nature* **1999**, *399*, 28.
(14) (a) Dai, S.; Ju, Y. H.; Gao, H. J.; Lin, J. S.; Pennycook, S. J.; Barnes, C. E. *Chem. Commun.* **2000**, 243. (b) Taubert, A.; Uhlmann, A.; Hedderich, A.; Kirchhoff, K. *Inorg. Chem.* **2008**, *47*, 10758. (c) Trewyn, B. G.; Whitman, C. M.; Lin, V. S. Y. *Nano Lett.* **2004**, *4*, 2139. (d) Zhou, Y.; Antonietti, M. *Chem. Mater.* **2004**, *16*, 544. (e) Tesfai, A.; El-Zahab, B.; Bwambok, D. K.; Baker, G. A.; Fakayode, S. O.; Lowry, M.; Warner, I. M. *Nano Lett.* **2008**, *8*, 897. (f) Kumar, A.; Murugesan, S.; Pushparaj, V.; Xie, J.; Soldano, C.; John, G.; Nalamasu, O.; Ajayan, P. M.; Linhardt, R. J. *Small* **2007**, *3*, 429.
(15) Zhao, D.; Fei, Z.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 15876.
(16) Burrell, A. K.; Del Sesto, R. E.; Baker, S. N.; McCleskey, T. M.; Baker, G. A. *Green Chem.* **2007**, *9*, 449.
(17) Wooster, T. J.; Johanson, K. M.; Fraser, K. J.; MacFarlane, D. R.; Scott, J. L. *Green Chem.* **2006**, *8*, 691.
(18) Kuhn, P.; Forget, A.; Su, D. S.; Thomas, A.; Antonietti, M. *J. Am. Chem. Soc.* **2008**, *130*, 13331.

JA900686D