

Porous B/N-doped Carbons

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Introduction

The structural advantages of porous carbons coupled with their unique chemistry together has lead to their use in a variety of applications including gas separation, water purification and catalyst supports as well as important new areas in electrochemistry (e.g. electrodes for supercapacitors and fuel cells).^[1] Recent reports have shown that heteroatom doped carbons can act as inexpensive metal-free catalysts in the oxygen reduction reaction.^[2] The introduction of dopants into the carbon structure is known to enhance performance of double-layer electrode in supercapacitor applications due to the pseudo-capacitive effect.^[3] The combination of B and N dopants generates both acidic and basic heteroatoms in the graphitic structure, producing a strong pseudo-capacitive effect due to reversible chemical surface reactions. The demand for these promising properties of comparatively cheap carbon materials explains the high research activity in this area.

Recently our group has shown that by using cyano-containing ionic liquids (e.g. 3MBP-dca) as precursors is an advantageous new method to produce this kind of functional materials via the hard template approach.^[4] The obtained materials, showing a very high nitrogen content of about 10%, are even more conductive than graphite, making them interesting especially - but not only - for electrochemical applications. In this work the use boron containing ionic liquids (B-ILs) as direct precursors for the synthesis of B/N containing carbon materials is presented. The complete miscibility of ionic liquids opens the possibility to vary precisely the B/N content in the final product by adjusting the educt ratio. The ease to infiltrate for instance silica templates due to the liquid state at room temperature and the strong interaction with inorganic surfaces let the liquid salts be perfect precursors. Another advantage, also in terms of safety, is the negligible vapour pressure.^[4] The synthesized materials are characterized with ICP-AES, X-ray Photoelectron Spectroscopy, TEM, WAXS and Solid-state NMR. Using hard templates (e.g. silica nanoparticles) porosity may be introduced enhancing the application potential of these exciting carbon materials.

Experimental

3MBP-dca was acquired from Merck with a purity of >98% and used without further treatment. Ionic liquid precursors were simply poured into ceramic crucibles and heated over 1 h to the target temperature under constant N₂ flow in a

Nabertherm N//H Chamber Oven (e.g. 1000 °C). Ludox ® solutions were used as hard templates. 1 mL of the solution was vigorously stirred in 1 mL ionic liquid until a gel was formed. The gel was transferred to the crucible and heated as described before. Silica was removed using in NH₄HF₂ (aq) (c= 4 mol l⁻¹) chemical etching. TEM images were obtained using a Zeiss EM 912 Ω instrument. Nitrogen sorption measurements were accomplished after degassing samples at 150 °C under vacuum on a Quantachrome Quadrasorp SI porosimeter. WAXS patterns were measured on a Bruker D8 Advance instrument using Cu-K_α-radiation. XPS measurements were carried out at a Thermo Scientific K-Alpha ESCA instrument equipped with aluminium K_α1,2 monochromatized radiation. ¹¹B MAS NMR spectra were recorded at 11.75 T on a Bruker Advance500 wide-bore spectrometer operating at 128.28 MHz, using a Bruker 4 mm probe and a spinning frequency of 14 kHz.

Results and Discussion

Product analysis via ICP-AES measurements of the black and shiny powder revealed a boron content of 12 %wt. As for the product of the cyano-containing ionic liquid 3MBP-dca reported previously^[4] a layered graphite-like material was obtained (Fig. 1). The similarity of the products is also found in the broadened WAXS peaks typical for graphitic or isostructural *h*-BN like material.

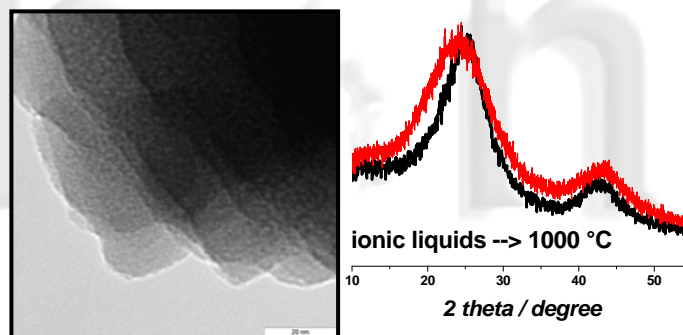


Fig. 1: TEM picture of B-IL-1000°C and WAXS comparison of 3MBP-dca-1000°C (black) and B-IL-1000°C (red).

X-ray Photoelectron Spectroscopy (XPS) was used to evaluate the surface elemental composition of the material (Table 1) and the chemical environment of boron (Fig. 2). The well known oxophilicity of boron often leads to complete oxidation of boron containing material. For comparison two samples of B-IL-1000°C, one prepared under N₂ and the other under a normal atmosphere were investigated by XPS using argon sputtering. The higher boron content compared to ICP-AES results can be explained by lower boron content at the surface. Table 1 already shows that the product is rather a BCN(O) material though not saying anything about its chemical nature.

Table 1. Elemental composition of B-IL products from XPS measurement after sputtering with Ar.

sample	B	N	C	O
B-IL-1000°C- N ₂	21,9	18,9	43,1	16,1
B-IL-1000°C- O ₂	27,8	5,1	33,2	33,9

High resolution XPS spectra reveal a dramatic shift from 191 eV to 194 eV in the maxima of the B 1s peaks due to oxidation of boron by heating under atmospheric conditions (Fig. 2). The signal for B-IL-1000 °C-O₂ can be understood as the sum of two peaks related to partly oxidized and oxidized sites at 192.35 eV ([O]-BN) and 194.50 eV (BO). The XPS signal of B-IL-1000 °C-N₂ however is generated by partly oxidized species at 192.56 eV ([O]-BN) and BN₃ species at 190.91 eV.

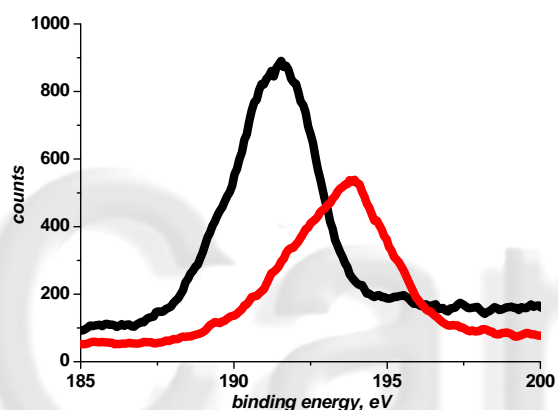


Fig. 2: Comparison of high resolution XPS of the B 1s photoelectron envelope for B-IL-1000 °C-N₂ (black) and B-IL-1000 °C-O₂ (red).

These results show that BN sites are already structurally integrated into the graphitic carbon structure. To further prove this, solid-state ¹¹B MAS NMR (Fig. 3) was used to give more information about the chemical state of B as second-order quadrupolar broadening occurs for trigonally coordinated but not for tetragonal boron.^[5] The relatively sharp peak at $\delta = 0$ ppm relates to BO₄ sites, while the broad shoulder at values > 10 ppm contains with increasing chemical shifts trigonal coordination sites like BO₃, BCN₂ and BN₃.^[6] Also there should partly oxidized moieties contribute, which usually occur at edge sites.

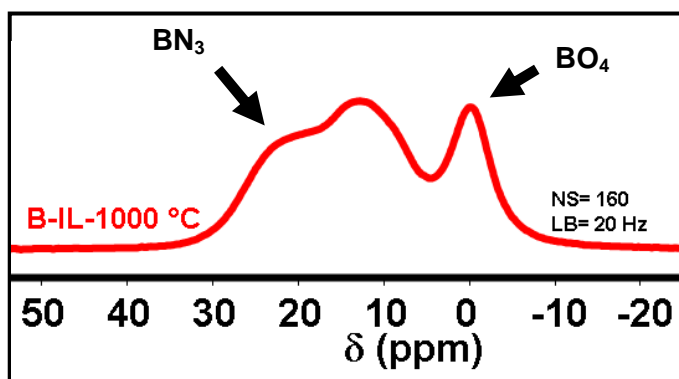


Fig. 3: ¹¹B MAS NMR spectrum of B-IL-1000 °C

Conclusions

Via the use of boron-containing ionic liquids as direct precursors, it is possible to produce carbon materials with structurally integrated planar BN sites. As the structure possesses high oxygen content making it more precisely a mixed BNC(O) material, investigations at higher synthesis temperatures are currently ongoing. WAXS and TEM results indicate the similarity between N doped carbons synthesized from cyano-containing ionic liquids and these new products. The complete miscibility of ionic liquids opens the possibility to vary precisely the B/N content in the final product by adjusting the educt ratio while maintaining advantageous properties for hard templating technique. Using a 1:1 mixture of the aforementioned ionic liquids and Ludox ® solution a mesoporous BCN(O) product with 984 m² g⁻¹ was synthesized. Further investigations are currently proceeding in the promising carbon research area.

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References

References (9 pt) should follow the style of the journal *Carbon*; examples for various types of references are given below.

References

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