

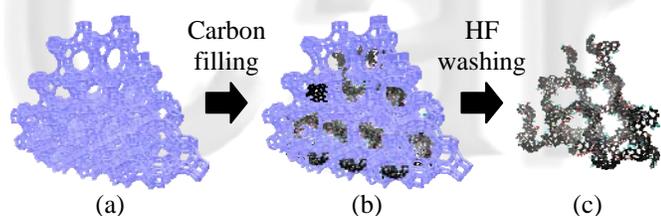
# EFFECT OF HETEROATOM-DOPING ON THE PHYSICAL PROPERTIES OF ZEOLITE-TEMPLATED CARBONS

Hiroyuki Itoi, Hirotomo Nishihara, Peng-Xiang Hou,  
Li-Xiang Li and Takashi Kyotani

Institute of Multidisciplinary Research for  
Advanced Materials, Tohoku University, 2-1-1,  
Katahira, Aobaku, Sendai, 980-8577, Japan

## Introduction

Doping heteroatoms into carbon materials changes the nature of their surface significantly. So far, many research groups have reported positive effects of the heteroatom doping into porous carbons on their performances of the electrochemical capacitance and the hydrogen storage. The detailed mechanisms are, however, still not fully understood, because such doping changes also carbon pore structures that can greatly affect the above performances. Herein, we try to discuss the sole effect of nitrogen (N) and boron (B) dopings by using a model microporous carbon, zeolite-templated carbon (ZTC; its synthesis scheme is shown in Fig. 1). ZTC comprises cross-linked buckybowllike nanographenes forming a three dimensionally ordered framework and, as a result, an ordered array of uniform micropores (Fig. 1c). We introduced heteroatoms into the ZTC framework with its ordered microporous structure intact to discuss the sole effect of each heteroatom doping on the hydrophilicity and the electrochemical capacitance.



**Fig. 1** Synthesis scheme of ZTC: a) zeolite template, b) carbon/zeolite composite, and c) ZTC.

## Experimental

ZTC was prepared by using zeolite Y (Na form,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.6$ ) as a template. Dried zeolite was impregnated with furfuryl alcohol (FA) at room temperature under vacuum. The FA filled in the zeolite channels was polymerized by a heat-treatment at 150 °C for 8 h under  $\text{N}_2$  flow. The resulting composite (referred to as PFA/zeolite) was heated at 5 °C/min under  $\text{N}_2$  flow up to 700 °C. When the temperature reached 700 °C, a chemical vapor deposition (CVD) of propylene (7% in  $\text{N}_2$ ) was accomplished for 2 h to further introduce carbon into the zeolite channels. After the CVD, the obtained carbon/zeolite composite was heat-treated at 900 °C for 3 h under  $\text{N}_2$  flow. Finally, the zeolite template was dissolved away by HF (46 wt% aqueous solution). The liberated carbon is referred to as ZTC.

N-doped ZTC was prepared by an acetonitrile CVD on PFA/zeolite [1]. The PFA/zeolite was heated at 5 °C/min under  $\text{N}_2$  flow up to 850 °C and the acetonitrile CVD (4.2% in  $\text{N}_2$ )

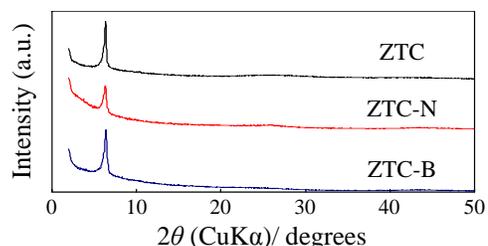
was conducted for 2 h. After the CVD, the resulting carbon/zeolite composite was heat-treated at 900 °C for 1 h under  $\text{N}_2$  flow. The zeolite removal was done in the same manner as the case of ZTC. The N-doped ZTC thus obtained is referred to as ZTC-N.

B-doped ZTC was prepared by a hydroboration on ZTC using borane-dimethylamine complex (DMAB). A dried ZTC was impregnated with DMAB/1,2-dichlorobenzene solution (DMAB 5wt%) at room temperature under vacuum. The resulting mixture was filtrated and washed with mesitylene followed by the drying at room temperature under vacuum for 12 h. The ZTC/DMAB composite thus obtained was heated at 5 °C/min up to 120 °C and kept at this temperature for 2 h under  $\text{N}_2$  flow. In this step, DMAB is decomposed to release highly reactive borane ( $\text{BH}_3$ ) which can react with edge sites of ZTC through the hydroboration. The temperature was then increased to 400 °C and kept for 6 h. The resulting B-doped ZTC is referred to as ZTC-B.

The structure of the ZTCs was analyzed with X-ray diffraction (XRD) and nitrogen physisorption (−196 °C). Chemical forms of the N and B species in ZTC-N and ZTC-B, respectively, were examined with X-ray photoelectron spectroscopy (XPS). The effect of the dopings on the hydrophilicity was evaluated by  $\text{H}_2\text{O}$ -vapor physisorption (25 °C). The doping effect on the electrochemical properties was examined from the electrochemical measurement by using a three-electrode cell in an organic electrolyte solution (1 M  $\text{Et}_4\text{NBF}_4$  in PC) at 25 °C. Each electrode sheet for the working electrode was prepared by mixing ZTC with poly(tetrafluoroethylene) (PTFE) and carbon black (weight ratio was 90:5:5). The counter electrode was prepared by mixing activated carbon fibers (A20, Unitika) with PTFE and carbon black in the same ratio as above. The reference electrode was prepared by immersing an Ag wire into a mixture solution of 0.1M  $\text{AgClO}_4$  and 1M  $\text{Et}_4\text{NBF}_4$ /acetonitrile.

## Results and Discussion

Fig. 2 shows XRD patterns of the three types of ZTCs. All ZTCs have a sharp peak around  $2\theta = 6.3^\circ$ , indicating that a long range ordered structure of the zeolite template was replicated into each type of ZTC. As for the nitrogen adsorption isotherms, all the carbons showed type I isotherms, indicating that all of them are microporous. The surface areas and the pore volumes of ZTCs are listed in Table 1. ZTCs have very high surface areas (2780 to 3680  $\text{m}^2/\text{g}$ ) and large micropore volumes (1.13 to 1.57  $\text{cm}^3/\text{g}$ ).



**Fig. 2** XRD patterns of ZTC, N-doped ZTC (ZTC-N), and B-doped ZTC (ZTC-B).

**Table 1. Surface Areas and Pore Volumes of ZTCs**

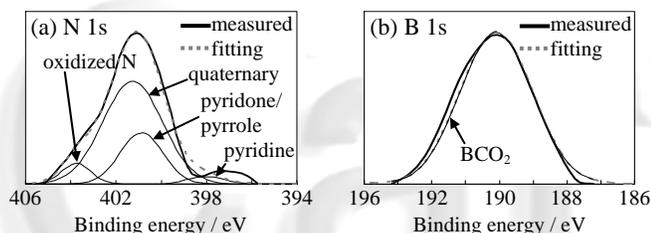
sample	$S_{\text{BET}}^{\text{a}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{total}}^{\text{b}}$ ( $\text{cm}^3/\text{g}$ )	$V_{\text{micro}}^{\text{c}}$ ( $\text{cm}^3/\text{g}$ )
ZTC	3680	1.68	1.57
ZTC-N	2780	1.31	1.13
ZTC-B	3280	1.50	1.32

<sup>a</sup>BET surface area calculated at  $P/P_0 = 0.01-0.05$ .

<sup>b</sup>Total pore volume estimated from the  $\text{N}_2$  adsorption isotherm at  $P/P_0 = 0.96$

<sup>c</sup>Micropore volume calculated by the Dubinin-Radushkevich method.

Fig. 3 shows XPS spectra of the doped ZTCs. From the area ratio of N1s to C1s in ZTC-N, the N/C atomic ratio was estimated to be 0.053. This value is very close to the result obtained by an elemental analysis (0.059). The N1s XPS spectra (Fig. 3a) was divided into four components, pyridine (398.0 eV), pyridone/pyrrole (400.9 eV), quaternary N (401.3 eV), and oxidized N (403.7 eV) [2] and the curve fitting reveals that main functionality in ZTC-N is quaternary N. From the area ratio of B1s to C1s in ZTC-B, the B/C atomic ratio was calculated to be 0.022, and the chemical form of the introduced B is found to be solely  $\text{BCO}_2$  (192.1 eV) [3].

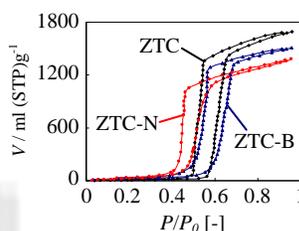


**Fig. 3** XPS spectra of (a) N 1s in ZTC-N and (b) B 1s in ZTC-B. Bold black line indicates a spectrum obtained by XPS, and gray dashed line indicates a sum of the devided peaks.

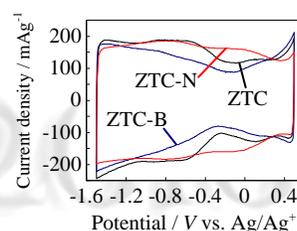
The three types of ZTCs, i.e., pure carbon ZTC, N-doped ZTC (ZTC-N), and B-doped ZTC (ZTC-B), have the same ordered framework structure, but should have different physical properties. We first compared their  $\text{H}_2\text{O}$ -vapor adsorption/desorption isotherms (Fig. 4). ZTC exhibits a rapid uptake of  $\text{H}_2\text{O}$ -vapor around  $P/P_0 = 0.6$  and a large adsorption capability. The uptake pressure of ZTC-N is lower than that of ZTC. This result indicates that ZTC-N has a stronger affinity to  $\text{H}_2\text{O}$  than ZTC. On the other hand, the uptake pressure of ZTC-B is slightly higher than that of ZTC, indicating the higher hydrophobicity of ZTC-B, though B-doping, i.e., the introduction of such polar sites, should have made carbon hydrophilic more or less. This contradictory result may be explained from the presence of larger oxygen functional groups in ZTC than in ZTC-B, since ZTC-B experienced the heat-treatment at  $400^\circ\text{C}$ . The O/C atomic ratios calculated from the results of conventional elemental analysis were as follows; 0.089 (ZTC), 0.082 (ZTC-N), 0.068 (ZTC-B).

Next, we examined the doping effects on the electrochemical properties. Fig. 5 shows the cyclic

voltammograms of ZTCs. ZTC and ZTC-B show butterfly shaped voltammograms in which the current density dropped around the open-circuit voltage ( $-0.2\text{ V}$ ), probably due to the poor electrical conductivity of the ZTC framework without applying voltage [4]. On the other hand, ZTC-N does not show such capacitance drop, indicating its higher electrical conductivity around  $-0.2\text{ V}$ . The capacitances per surface area for ZTCs calculated from the galvanostatic charge/discharge cycling curves at  $50\text{ mA/g}$  are calculated as follows:  $0.050\text{ F/m}^2$  (ZTC),  $0.066\text{ F/m}^2$  (ZTC-N), and  $0.048\text{ F/m}^2$  (ZTC-B). Among all ZTCs, ZTC-N shows highest capacitance per surface area. N-doping thus enhances the capacitance. Meanwhile, the present B-doping, i.e., the introduction of  $\text{BCO}_2$ , do not enhance the capacitance. However, we have recently reported that the doping of  $\text{BC}_3$ ,  $\text{BC}_2\text{O}$ , and  $\text{BCO}_2$  together remarkably increased the capacitance [5]. The present result, therefore, suggests the effectiveness of  $\text{BC}_3$  and/or  $\text{BC}_2\text{O}$  doping on the capacitance enhancement.



**Fig. 4**  $\text{H}_2\text{O}$ -vapor adsorption/desorption isotherms of ZTCs measured at  $25^\circ\text{C}$ .



**Fig. 5** Cyclic voltammograms of ZTCs measured in  $1\text{ M Et}_4\text{NBF}_4/\text{PC}$  at  $25^\circ\text{C}$ .

## Conclusions

Heteroatoms (N and B) were doped into the zeolite-templated carbon (ZTC), with its ordered pore structure intact. N-doping (quaternary N, pyridone/pyrrole, oxidized N, and pyridine) increased the hydrophilicity of ZTC, and in addition, increased electrochemical capacitance. On the other hand, the introduction of  $\text{BCO}_2$  had no effect on the capacitance enhancement.

## References

- [1] Hou PX, Oriksa H, Yamazaki T, Matsuoka K, Tomita A, Setoyama N, et al. Synthesis of nitrogen-containing microporous carbon with a highly ordered structure and effect of nitrogen doping on  $\text{H}_2\text{O}$  adsorption. *Chemistry of Materials*. 2005;17(20):5187-93.
- [2] Raymundo-Pinero E, Cazorla-Amoros D, Linares-Solano A, Find J, Wild U, Schlögl R. Structural characterization of N-containing activated carbon fibers prepared from a low softening point petroleum pitch and a melamine resin. *Carbon*. 2002;40(4):597-608.
- [3] Jacques S, Guette A, Bourrat X, Langlais F, Guimon C, Labrugere C. LPCVD and characterization of boron-containing pyrocarbon materials. *Carbon*. 1996;34(9):1135-43.
- [4] Nishihara H, Itoi H, Kogure T, Hou PX, Touhara H, Okino F, et al. Investigation of the Ion Storage/Transfer Behavior in an Electrical Double-Layer Capacitor by Using Ordered Microporous Carbons as Model Materials. *Chemistry-a European Journal*. 2009;15(21):5355-63.
- [5] Kwon T, Nishihara H, Itoi H, Yang QH, Kyotani T. Enhancement Mechanism of Electrochemical Capacitance in Nitrogen-/Boron-Doped Carbons with Uniform Straight Nanochannels. *Langmuir*. 2009;25(19):11961-8.