Supplementary Information

Boron and nitrogen co-doped ordered microporous carbons with high surface area

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Experimental

Sample preparation

The nanopores of zeolite Y were filled with an ionic liquid, 1-ethyl-3-methylimidazolium tetracyanoborate (EMIT), by using the following method. First, ca. 1 g of zeolite was dried under vacuum in a Schlenk flask at 300 °C for 2 h, and let the flask cool down to room temperature. Then, 10 ml of EMIT were introduced in the flask and the sample was stirred under vacuum at room temperature for 15 h. The sample was thoroughly rinsed with 2, 4, 6-trimethylpyridine to remove EMIT existing outside the zeolite particles, and with also with 1, 3, 5-trimethylbenzene to remove 2, 4, 6-trimethylpyridine, and the sample was recovered by filtration. The resulting sample was vacuum dried at 180 °C for 3 h to obtain EMIT-loaded zeolite. The heat treatment and chemical vapor deposition were carried out in a vertical quartz reactor. The zeolite template was removed by washing the composite of carbon/zeolite in 47 wt% HF at room temperature for 6 h.

Characterization

The amount of EMIT or carbon introduced in the pores of zeolite was estimated by thermogravimetric analysis, in which the samples were heat-treated in an air flow up to 800 °C. The porous texture of the samples was analyzed by physical adsorption of N2 at −196 °C. The Brunauer-Emmet-Teller (BET) surface area, \( S_{\text{BET}} \), was calculated by the BET equation from the data in a relative pressure range of ca. 0.01−0.05. The fitting error is within ±1%. The total pore volume, \( V_p \), was obtained from the amount of adsorbed N2 at a relative pressure of 0.975 using the Gurrvitsch rule. The structural order was examined by X-ray diffraction (XRD; XRD-6100, Shimadzu, using Cu-Kα radiation generated at 30 kV and 20 mA) and transmission electronic microscopy (TEM; JEOL JEM-2010 at an acceleration voltage of 200 kV). The surface chemical structure was analyzed by XPS (JEOL JPS-9200, operating at a pressure of 10⁻⁷ Pa with a Mg Kα X-ray source using a power of 300 W). The XPS spectra obtained were calibrated by the C 1s peak position (284.6 eV). The elemental composition of C, H, and N was determined by conventional elemental analysis. Inductively coupled plasma-optical emission spectrometry (ICP-OES) was performed using Thermo Fisher Scientific IRIS Advantage DUO to determine the elemental concentration of boron in BN-ZTC.

Electrochemical measurement

The electrochemical properties of BN-ZTC in an organic electrolyte (1 M Et4NBF4/PC) were examined at 25 °C, using a three-electrode cell. The reference electrode was Ag/AgClO4. An electrode sheet was prepared by mixing the sample with acetylene carbon black (CB, Denka black, Denki Kagaku Kogyo Kabushiki Kaisha) as a conductive additive and poly(tetrafluoroethylene) (PTFE 6-J, Du Pont-Mitsui Fluorochemicals Company, Ltd.) as a binder with the following weight ratio: sample:CB:PTFE = 90:5:5. A piece of 8 mg and 1 cm² was cut out to form a sheet, and it was sandwiched in a platinum mesh (100 mesh; Nilaco Corp.), pressed at ca. 20 MPa for 1 min, and used as a working electrode. A counter electrode was prepared using the same procedure as that for the working electrode, but using an activated carbon fiber (A20 from Osaka Gas Co. Ltd.) instead of the sample, and its amount was 11 mg. These electrodes were transferred to a glovebox, and the cell was assembled by sandwiching a cellulose separator (TF-4850, Tokyo Sangyo Yoshi Co. Ltd.) between the working and counter electrodes. The electrodes were then impregnated with the electrolyte under vacuum for 1 h, and the cell was rested for 24 h before starting the electrochemical measurements. Cyclic voltammetry (CV), and galvanostatic charge/discharge cycling were carried out with a VMP3 potentiostat (Bio-Logic Science Instruments SAS). Capacitance was calculated as a cation-desorption capacitance from a slope of discharge curve in the potential range corresponding to the cation desorption (below open circuit potential).

The activities of carbonized samples for oxygen-reduction reaction (ORR) and hydrogen evolution reaction (HER) were evaluated by the method reported elsewhere. Briefly, the sample was mixed with a conductive additive (Vulcan XC-72R) and Nafion solution (5%) and the mixture was sonicated to form a catalyst ink. The ink was then dropped on a glassy carbon of a rotating disk electrode (RDE; Hokuto Denko), and the ink was carefully dried to form a uniform catalyst layer. The geometric surface area of the electrode was 0.196 cm² (diameter: 5 mm). The amounts of the sample, conductive additive, and Nafion on RDE were 60, 60, and 262 μg, respectively.

An electrochemical measurement system (HZ-3000, Hokuto Denko) and an RDE apparatus (HR-201, Hokuto Denko) equipped with a glass cell were used for the measurements of the current–potential relationships. The glass cell was cleaned by soaking it in a 1:1 mixture of concentrated HNO3 and H2SO4, followed by a thorough rinsing with ultrapure water and finally steam-cleaning. The counter electrode was a strip of carbon cloth (ElectroChem). The reference electrode was a reversible hydrogen electrode (RHE) in a separate container with a fine glass frit. All potentials were referred to the RHE. The current–potential relationships for ORR and HER were obtained in O2 and Ar-saturated 0.1 M HClO4 at 25 °C at 3000 and 3600 rpm, respectively. The scan rate of the potential was fixed at 10 mV s⁻¹. Prior to the measurement, the electrode was repeatedly and alternately polarized at 0.05 and 1.2 V. The potential was finally stepped to 1.2 V and then swept in the negative direction to obtain the current–potential relationship.
Figure S1. XRD patterns of BN-C and ZTCs prepared by the conditions shown as Entry 1-3 in Table S1. For Entry 1-3, the data before zeolite removal are also shown. In the Entry 3 with zeolite, the zeolite structure apparently collapses, indicating the decomposition reaction by active boron species. This is ascribed to the long period (3 h) for a high temperature treatment at 900 °C. By decreasing this period down to 1 h (Entry 1) or 1.5 h (Entry 2), zeolite XRD peaks get to be retained. However, after the zeolite removal, the resulting carbons cannot retain the ordered structure of zeolite. Since the amount of carbon introduced is large enough (Table S1), this can be ascribed to partial decomposition of zeolite by active boron species to the extent that the XRD patterns are not completely diminished. Another possibility is generation of boron oxide species inside zeolite nanochannels without collapse of the zeolite structure. Such non-carbonaceous species could inhibit the formation of a continuous carbon framework. In either of cases, it can be hypothesized that undesired reactions of active boron species cause the failure of zeolite replication into carbon. As demonstrated in this work, these problems have been solved by supplying a protection gas, i.e., high-concentration (20 vol%) acetylene gas, during the thermal decomposition step of EMIT at 350-550 °C.
Table S1. A summary of the preparation conditions, carbon-loading amount in NaY, and the properties of the templated carbons obtained from the EMIT/NaY composite.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Preparation conditions</th>
<th>Carbon loading (wt.%)</th>
<th>BET (m² g⁻¹)</th>
<th>XRD (111) peak</th>
<th>B (wt.%)</th>
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<tr>
<td></td>
<td>CVD From R.T. 1</td>
<td>C₂H₂ ratio (vol%)</td>
<td>TₘCVD (°C - min)</td>
<td>TₘHT - tₘHT (°C - min)</td>
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<td>900 - 60</td>
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<td>500 - 120</td>
<td>900 - 90</td>
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<td>600 - 30</td>
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<td>20</td>
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<td>500 - 45</td>
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<td>20</td>
<td></td>
<td>600 - 120</td>
<td>900 - 60</td>
</tr>
</tbody>
</table>

1 Whether acetylene is supplied from room temperature or not. In the latter case, CVD is performed at a constant temperature.

2 TₘCVD [°C] and tₘCVD [min] are the maximum temperature in the CVD process and residence time at TₘCVD, respectively. After the CVD period, the gas flow was switched to pure N₂, and the temperature was increased to TₘHT [°C] which was kept for tₘHT [min] for a post-treatment.

3 Amount of carbon infiltrated in the zeolite template after the CVD, obtained by thermogravimetric analysis in air atmosphere.

4 BET surface area of the templated carbons obtained from the N₂ adsorption isotherms at –196 °C.

5 Note of the presence of (111) peak at 2θ = 6.2° in the XRD patterns of the templated carbons: ×, △, and ○ represent no peak, very weak, and discernible, respectively.

6 The total boron content of selected samples was obtained by ICP-OES.

7 No data.
Figure S2. TG curve of EMIT/NaY in N₂ atmosphere at a heating rate of 5 °C min⁻¹. It is found that EMIT embedded in NaY decomposes at 350-550 °C.
Figure S3. TEM image of BN-ZTC with selected area electron diffraction (SAED). (a) TEM image showing an overview of a sample grain analyzed by SAED. (b) TEM image showing the selected area used for SAED. (c) SAED image. Two spots correspond to the ordered structure confirmed by the XRD pattern (Fig. 3a), and its $d$-spacing is obtained as 1.4 nm.
Figure S4. \( \text{N}_2 \) adsorption-desorption isotherm (−196 °C) of BN-ZTC.
Figure S5. Nyquist plot of BN-ZTC conducted in 1 M Et$_4$NBF$_4$/PC at 25 °C. The intersection at x-axis (1.36 Ω) is an equivalent series resistance (ESR). We have previously reported that ESR of ZTC and N-ZTC are 1.60 and 1.49 Ω, respectively, by the same experimental setup as that in this work. Therefore, the difference in ESR is owing to electrical resistances of different carbon materials. It is found that the order of conductivity is BN-ZTC > N-ZTC > ZTC. Thus, BN-doping is more effective to enhance the electrical conductivity than N-doping. This result agrees with the literature in which the preferable effect of BN-doping over N-doping or B-doping has been reported. The improved conductivity could contribute to a good rate capability shown in Fig. 4b.

References