

Supporting Information

**Single-step synthesis of highly porous nitrogen-doped carbon by solid-gas
mechanochemical treatment as an oxygen reduction electrocatalyst**

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Preparation of N-PC(HT) by heat treatment

First, 100 mg of CB (TOKABLACK#3845, Tokai Carbon) and 4 mL of 50 wt% cyanamide solution (Sigma-Aldrich), which was used as a nitrogen source, were dispersed by ultrasonication for 30 min in 100 mL of distilled water. The mixture was evaporated to dryness, and subsequently heated at 550 °C under flowing N₂ for 4 h to initiate the thermal condensation of cyanamide to polymeric carbon nitride (C₃N₄). Further heat treatment at 900 °C for 4 h to undergo C₃N₄ decomposition generated N-PC(HT).

Material characterization

The XRD patterns were recorded using an X-ray diffractometer (Smartlab, Rigaku) with Cu K α radiation. The interlayer distance, d_{002} , was calculated using Bragg's equation:

$$d_{002} = \lambda / 2 \sin \theta \quad (1)$$

where λ is the wavelength of the Cu K α radiation (0.154 nm), and θ is the angle at the position of the peak maximum.¹ The carbon crystallite sizes along the a-axis, L_a , and c-axis, L_c , based on 100 and 002 diffraction peaks, respectively, were calculated using Scherrer's equation:

$$L = k \lambda / \beta \cos \theta \quad (2)$$

where L is the crystallite size, k is the foam factor (1.84 for L_a , 0.9 for L_c), and β is the full width at half maximum.^{1,2} L_a and L_c correspond to the layer diameter and stacking height of the carbon crystallite, respectively. XPS (Axis Ultra, Kratos Analytical) was performed using a monochromatic Al $K\alpha$ source. The sample powders for the XPS experiments were pressed into an In plate. The surface atomic concentrations were analyzed on the basis of the peak areas in the spectra and the relative standard factor for each element. SEM (Regulus8230, Hitachi High-Technologies) was used to observe the samples. Nitrogen gas sorption isotherms were obtained using a surface area and pore size distribution analyzer (BELSORP-max, Nihon BEL). The surface area, micropore volume, and total pore volume were calculated from the Brunauer–Emmett–Teller equation in the partial pressure range of 0.05–0.20, the intercepts of the t -plots, and the adsorbed amount at a partial pressure of 0.98, respectively.³ The pore size distribution was obtained on the basis of the Barrett-Joyner-Halenda model.⁴

Electrochemical characterization

Electrochemical measurements were performed using an RDE. All water used was first purified using Direct-Q UV3 (Millipore). To obtain homogeneous sample inks, 10 mg of the catalyst sample was dispersed in 0.95 mL of 2-propanol solvent (Wako Pure Chemical) with 0.05 mL of a 5.0 wt% Nafion solution (Sigma-Aldrich) by ultrasonication

(42 kHz) for more than 30 min. Eight μL of the suspension (10 mg mL^{-1}) was deposited on an RDE with a diameter of 5 mm and dried at 60°C . RDE measurements were performed using a potentiostat (HZ-7000, Hokuto Denko). Before the linear sweep voltammetry measurements, 50 cycles of cyclic voltammetry were performed by scanning the potential between 0.2 and -0.6 V vs. Hg/HgO at a scan rate of 50 mV s^{-1} in N_2 -saturated electrolyte to clean the surface of the samples. After O_2 bubbling for more than 30 min, linear sweep voltammetry was performed at 25°C with a scan rate of 5 mV s^{-1} in O_2 -saturated electrolyte. The kinetic current density, i_k , was calculated from the mass-transport correction of the RDE by

$$i_k = i \times i_l / (i_l - i) \quad (3)$$

where i is the measured current density and i_l is the diffusion-limiting current density.⁵

The apparent electron transfer number per oxygen molecule, n , was calculated on the basis of the Koutecky-Levich equation:

$$i^{-1} = i_k^{-1} + i_l^{-1} = i_k^{-1} + B^{-1} \omega^{-1/2}, B = 0.201 n F C_0 D_0^{2/3} \nu^{-1/6} \quad (4)$$

where ω is the rotation speed in rpm, F is the Faraday constant (96485 C mol^{-1}), C_0 is the O_2 concentration ($8.7 \times 10^{-7} \text{ mol mL}^{-1}$), D_0 is the diffusion coefficient ($1.53 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), and ν is the kinematic viscosity ($0.01073 \text{ cm}^2 \text{ s}^{-1}$).⁶

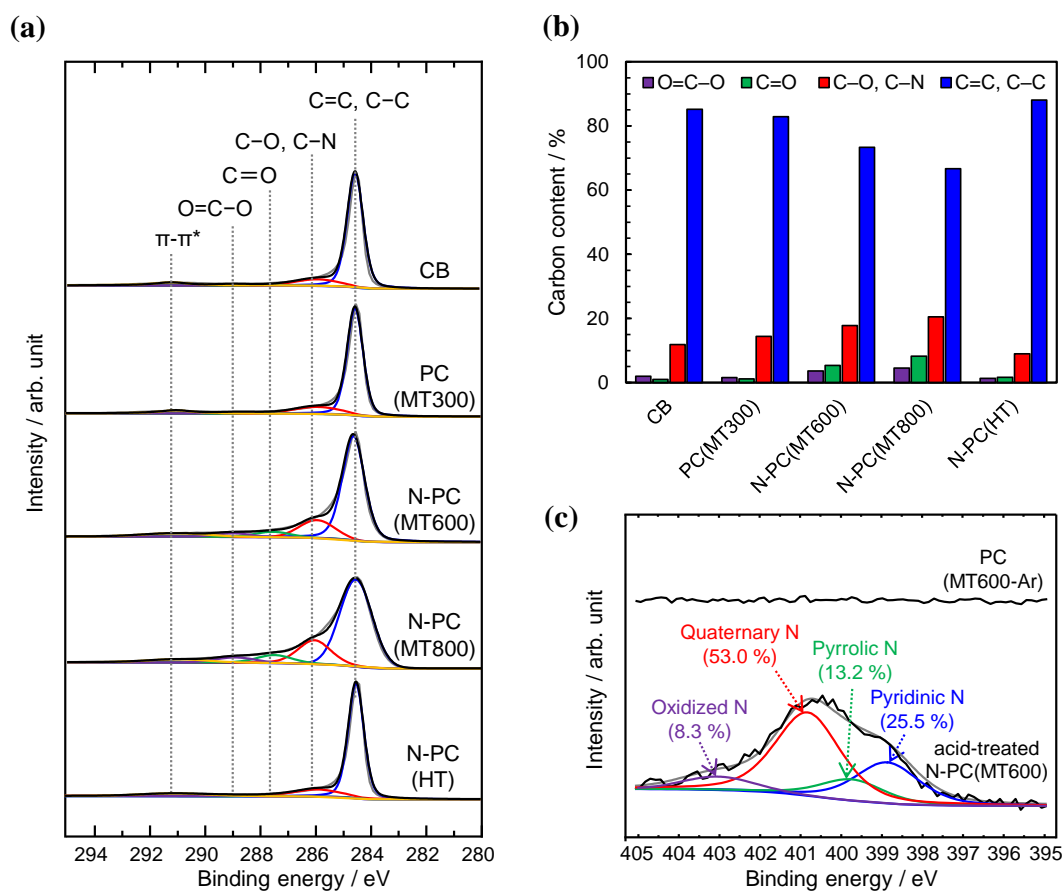


Figure S1. (a) C 1s XPS spectra and (b) the ratio for CB, PC(MT300), N-PC(MT600), N-PC(MT800), and N-PC(HT). (c) N 1s XPS spectra of PC(MT-600-Ar) and acid-treated N-PC(MT600).

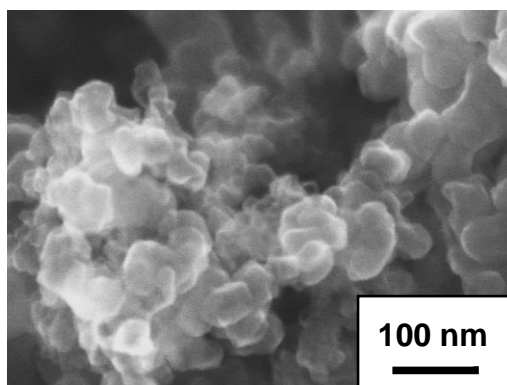


Figure S2. SEM image of CB.

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