

From Metal–Organic Framework to Nitrogen-Decorated Nanoporous Carbons: High CO₂ Uptake and Efficient Catalytic Oxygen Reduction

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S Supporting Information

ABSTRACT: High-surface-area N-decorated nanoporous carbons have been successfully synthesized using the N-rich metal–organic framework ZIF-8 as a template and precursor along with furfuryl alcohol and NH₄OH as the secondary carbon and nitrogen sources, respectively. These carbons exhibited remarkable CO₂ adsorption capacities and CO₂/N₂ and CO₂/CH₄ selectivities. The N-decoration in these carbons resulted in excellent activity for the oxygen reduction reaction. Samples NC900 and NC1000 having moderate N contents, high surface areas, and large numbers of mesopores favored the four-electron reduction pathway, while sample NC800 having a high N content, a moderate surface area, and a large number of micropores favored the two-electron reduction process.

Nanoporous carbons are promising for a variety of applications, such as contamination removal, gas/liquid storage, supercapacitors, and fuel cell systems.^{1–3} Metal–organic framework (MOF)-templated carbons have attracted great attention because of their exceptionally high surface areas and the ability to control their pore textures.⁴ MOFs are a new class of crystalline porous materials having multiple functionalities and containing nanoporous spaces suitable for small molecules to access and participate in “ship-in-bottle” reactions.^{5,6} The main advantage of using a MOF as a template is that the MOF itself works as a precursor and contributes to the formation of high-quality nanoporous carbons.⁴ Since our first work on this subject,^{4m} great progress in MOF-templated porous carbons has been made.

It has been suggested that the incorporation of heteroatoms such as nitrogen into the carbon nanomatrix can enhance the mechanical and energy-storage properties.⁷ These N-decorated carbon materials are thermally/chemically stable and have good regeneration ability. In general, N-decorated porous carbons might be prepared from N-containing precursors via high-temperature pyrolysis, including carbonization of polymer aerogels or ionic liquids, template synthetic procedures, and so on.^{8–11} Traditional inorganic porous materials such as mesoporous silica and zeolites have been successfully used in recent years as excellent templates for preparing mesoporous and microporous N-decorated carbons, respectively, by the nanocasting technique.¹⁰ Each approach has its own advantages for the formation of carbons with controlled pore texture or/and improved surface area, which are of great importance and considered to be the key factors in optimizing the performance in most applications, especially for enhancing their gas storage

capacities. However, MOF-derived high-surface-area N-decorated carbons and their intrinsic properties, including electronic characteristics and surface and local chemical features, have not been explored.^{4b}

Because of the decorated basic N functionalities, these N-decorated carbon frameworks provide active basic centers and therefore could be favorable adsorbents for capturing acidic guest molecules such as CO₂, which is a major greenhouse gas causing global warming.^{9,10} To enhance the CO₂ interaction and storage capacity, one simple approach is to fabricate carbon adsorbents with tunable and optimized pore structures and increased surface areas. Another strategy that has been explored is to increase the alkalinity of the carbon framework via amine grafting.^{1c} However, the postsynthetic incorporation of amine groups not only blocks pores but also suffers from leaching and instability in any subsequent regeneration step. It is therefore desirable to develop permanently N-decorated porous carbon materials via new synthetic strategies for superior and selective CO₂ uptake. Also, the unique electronic interactions between the lone-pair electrons of nitrogen and the π system of graphitic carbon in these N-decorated porous carbons result in electrocatalytic activity for the oxygen reduction reaction (ORR), an important reaction in fuel cell systems, which might bring a breakthrough in avoiding or minimizing the use of precious noble metals such as platinum.¹⁰ Herein we report the use of the N-rich MOF ZIF-8 as a template and precursor to synthesize high-content N-decorated high-surface-area nanoporous carbons that exhibit not only superior CO₂ uptakes with high heats of adsorption due to the presence of basic N sites but also excellent ORR catalytic activities.

Deliberately chosen N-rich ZIF-8,¹² a highly porous zeolite-type MOF, might work as both a precursor and a template. Furfuryl alcohol (FA) and NH₄OH were first introduced into the cavities of activated ZIF-8 by allowing the mixture to stir for 12 h at room temperature. After careful filtration and washing with ethanol, the FA–NH₄OH/ZIF-8 composite was charged into a temperature-programmed furnace under a flow of Ar, heat-treated at 80 °C for 24 h and then at 150 °C for 7 h for FA polymerization, and finally calcined at 600, 700, 800, 900, or 1000 °C for 8 h with subsequent HF washing (except for the 1000 °C sample), affording the N-decorated carbon materials designated as NC600, NC700, NC800, NC900, and NC1000, respectively [see the Supporting Information (SI)].

Powder X-ray diffraction (PXRD) profiles of these N-decorated carbons displayed only two weak broad peaks located

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at around 25 and 44°, which were assigned to the carbon (002) and (101) diffractions, respectively (Figure S1 in the SI). The (101) peak became more intense at elevated temperatures. Transmission electron microscopy (TEM) revealed retention of the ZIF-8 crystal morphology at lower temperatures (up to 800 °C) (Figures S2 and S3), while at 900 and 1000 °C, partially and completely destroyed ZIF-8 morphologies, respectively, with distorted graphite structures and only few oriented multilayer graphene domains were observed (Figures 1, S4, and S5). Their

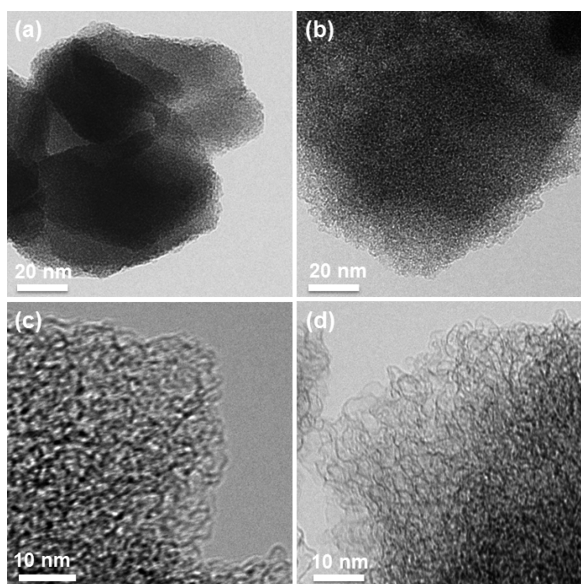


Figure 1. TEM images of (a) NC600, (b) NC700, (c) NC900, and (d) NC1000.

variational textures suggest that the structure of the resultant N-decorated carbon can be tuned reasonably by changing the calcination temperature. X-ray photoelectron spectroscopy (XPS) was used to identify N functional groups decorating the carbon matrix (Figure S6). XPS of the NC samples showed the presence of the C 1s peak at ~285 eV, the N 1s peak at ~398–402 eV, and the O 1s peak at ~531 eV. Careful examination and deconvolution of the N 1s peak of NC600 resulted in a combination of pyridinic (398.4 eV), amidic/pyrrolic (400.1 eV), and quaternary nitrogens (401.4 eV) with a maximum located at 398.5 eV (Figure S7a). The N 1s peak positions shifted from pyridinic/amidic/pyrrolic to more quaternary (i.e., the quaternary nitrogen decoration became more prominent) and the N content decreased at higher temperatures (Figure S7). Elemental analysis showed a decrease in the N content in the carbon framework with increasing the calcination temperature. XPS of an NC800 sample before and after acid washing confirmed the removal of most of the Zn present in the sample (Figure S8). The NC1000 sample had no Zn impurity because the carbonization temperature was higher than the boiling point of Zn metal (Figure S8).^{4m} The existence of oxygen in all of the prepared carbons may arise from the presence of moisture, atmospheric O₂, or oxygen from NH₄OH (see the SI).

N₂ sorption experiments were performed at 77 K to examine the surface areas of the NC samples (Figure 2a), and the results are summarized in Table S1 in the SI. These carbon materials have high Brunauer–Emmett–Teller (BET) surface areas (455–3268 m² g⁻¹) and pore volumes (0.25–2.15 cm³ g⁻¹). All of the samples show type-I isotherms with steep increases at

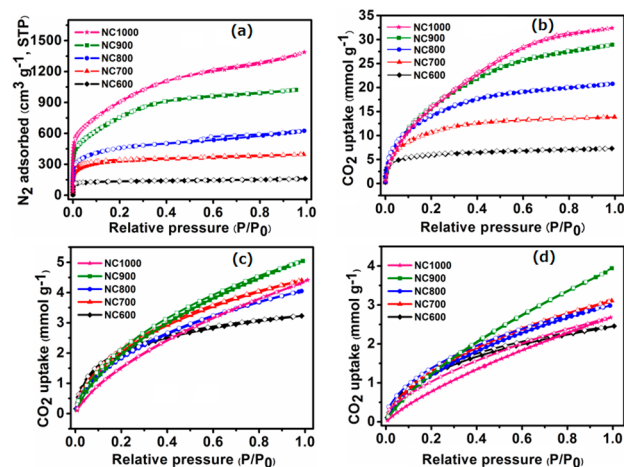


Figure 2. (a) N₂ sorption isotherms at 77 K and (b–d) CO₂ sorption isotherms at (b) 195, (c) 273, and (d) 298 K of NC samples.

low relative pressures (Figure 2a), suggesting that micropores are dominant. The slight hysteresis of the desorption curves and the durative increase of the adsorption capacity before $P/P_0 = 0.4$, especially for the samples prepared at higher temperatures, reveal the presence of meso- and macropores also. Pore size distributions obtained from the adsorption isotherms using nonlocal density functional theory and assuming a cylindrical pore shape confirmed their micro- and mesoporous nature with pore sizes mainly centered at 1–3 nm (Figure S9).

CO₂ uptake isotherms of these N-decorated carbons at 195, 273, and 298 K are shown in Figure 2b–d. NC900, which has a moderate N content (2.7 wt %) but a high surface area and pore volume, exhibited the highest CO₂ uptakes of 5.1 and 3.9 mmol g⁻¹ at 273 and 298 K, respectively, at ambient pressure, which are comparable to the best reported CO₂ uptakes by N-decorated carbons and higher than those of all known zeolitic imidazolate frameworks.^{10c,12} The uptake of 5.1 mmol g⁻¹ at 273 K and 1 atm is very high, comparable to the highest values reported for porous materials.⁹ NC600, which has the highest N content (25.9 wt %) but a much lower surface area, displayed CO₂ uptakes of 3.3 and 2.4 mmol g⁻¹ at 273 and 298 K, respectively. Clearly, both the surface area and N content play important roles in determining the CO₂ adsorption capacity. Also, the very high CO₂ uptakes (up to 32.4 mmol g⁻¹) at 195 K demonstrate the CO₂ storage capacities of these N-decorated porous carbons (Figure 2b).

To clarify the effect of N-decoration on the CO₂ uptake capacity, the CO₂ uptakes were normalized with respect to the surface areas (Figure 3a), which shows the enhancement of CO₂ uptake with increasing N content. The very high CO₂ uptake by NC600 (1.53 mmol g⁻¹ at 0.1 atm and 273 K) confirms the stronger interaction of CO₂ molecules with the more basic N-decorated carbon framework at low pressures. Also, the slight hysteresis in the CO₂ sorption curves for all of these carbon materials reflects the greater affinities for CO₂.^{13a} To determine the strength of the interactions between CO₂ and the carbon materials, the isosteric heats of adsorption (Q_{st}) for all of the N-decorated carbons were calculated from the CO₂ sorption isotherms measured at 273 and 298 K using the Clausius–Clapeyron equation (Figure 3c). The characteristic initial sharp decrease to a plateau observed in these curves is indicative of initial adsorption driven by more active basic N surface sites. The Q_{st} values for CO₂, up to 69 kJ mol⁻¹ at lower coverage and 30 kJ mol⁻¹ at higher coverage, are among the highest reported for

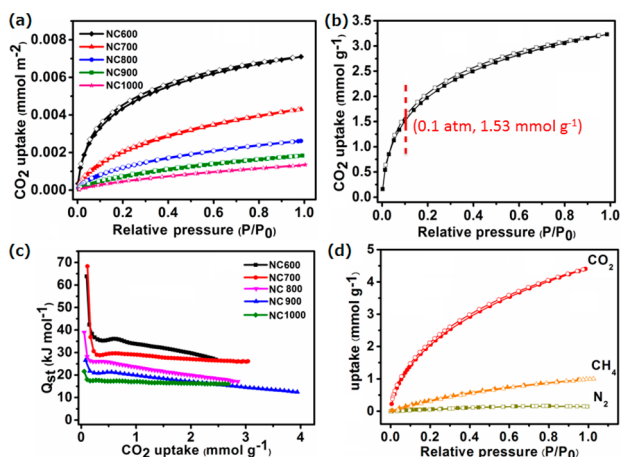


Figure 3. (a) CO_2 uptakes of NC samples at 273 K normalized with respect to the surface areas. (b) CO_2 uptake by NC600 at 273 K. (c) Isothermic heats of adsorption of the NC samples. (d) Selectivities for CO_2 over N_2 and CH_4 for NC700 at 273 K.

porous materials. High microporosities and Q_{st} values would be expected to afford high selectivity for CO_2 over N_2 and CH_4 . At 273 K, the CO_2/N_2 and CO_2/CH_4 selectivities for NC700 are 59:1 and 11:1, respectively (Figure 3d), which is impressive for industrial applications.¹³ The high selectivity can be ascribed to the electron-rich graphite network and the high charge density at the N sites, which might facilitate more favorably the interaction with the polarizable acidic CO_2 molecules through local dipole–quadrupole interactions.

To assess the electrocatalytic properties of these N-decorated carbons, ORR catalytic activities were evaluated using a three-electrode electrochemical station (see the SI). Figure 4a shows

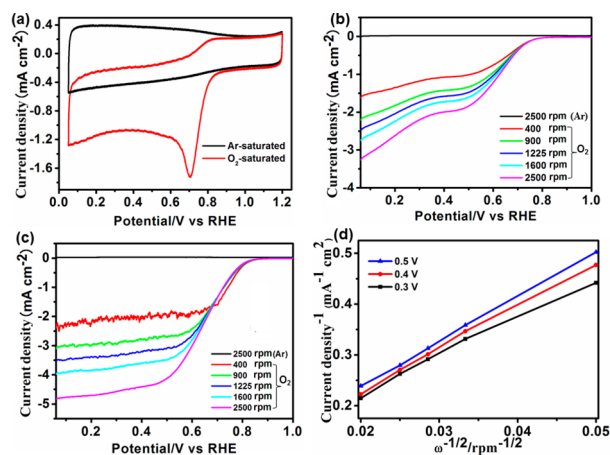


Figure 4. (a) CVs (scan rate = 50 mV s^{-1}) of NC900 on a GC RDE in Ar- and an O_2 -saturated 0.1 M KOH(aq). (b, c) LSVs (10 mV s^{-1}) for (b) NC800 and (c) NC900 on a RDE in O_2 -saturated 0.1 M KOH(aq) at various rotating speeds. (d) Koutecky–Levich plots for NC900 obtained from the LSV curves in (c) at various potentials.

cyclic voltammograms (CVs) of NC900 deposited on a glassy carbon rotating disk electrode (GC RDE) in Ar- and O_2 -saturated 0.1 M KOH(aq). The CVs for NC900 showed nearly rectangular shapes, indicating high conductivity with superior capacitive current. A well-defined reduction peak occurred at $\sim 0.7 \text{ V}$ (vs reversible hydrogen electrode, RHE) in the O_2 -saturated solution, whereas there was no such a peak in the Ar-

saturated one, indicating that O_2 was reduced on the electrode coated with NC900. NC1000 showed a similar sharp reduction peak at 0.7 V (Figure S10). Linear sweep voltammograms (LSVs) showed that these carbons have high electrocatalytic activity for the ORR (Figures 4b,c, S11, and S12). The LSVs for equal masses of NC700, NC800, NC900, NC1000, and commercial 10 wt % Pt/C (HiSPEC 2000, Johnson Matthey) deposited on a GC RDE in O_2 -saturated 0.1 M KOH(aq) were measured at 2500 rpm. The N-decorated NC700, NC800, NC900, and NC1000 showed ORR onset potentials at 0.71, 0.76, 0.83, and 0.82 V, respectively, compared with 0.95 V for the commercial Pt/C catalyst (Figure S13). The ORR current densities for NC900 and NC1000 at 0.7 V (the peak potential) were found to be 1.36 and 1.02 mA cm^{-2} , respectively, which are comparable to those of other N-decorated carbons, including recently reported MOF-derived carbons (Table S2).¹⁰ The high ORR catalytic activity of NC900 is associated with the large number of active basic N sites and the high surface area, which provides proper channels with easy mass diffusion. The appreciable activity of NC1000, which has a N content of only 0.7%, reveals that a small amount of N-decoration in high-surface-area porous carbon could be enough for ORR activity.

To investigate the reaction mechanism, we used Koutecky–Levich plots obtained from the polarization curves (LSVs) at various rotation speeds. The LSVs of NC800 and NC900 measured with an RDE at various rotating speeds (Figure 4b,c) show increasing cathodic current with increasing rotating speed because of the improved mass transport at the electrode surface. From the slopes of the Koutecky–Levich plots in Figure 4d, obtained from the data in Figure 4c, the number of electrons transferred per O_2 molecule in the ORR was calculated to be 3.3 for NC900, suggesting that the four-electron reduction pathway to produce water as the main product is favored, which will benefit the construction of fuel cells with high efficiency. However, the slopes of the Koutecky–Levich plots for NC800 (Figure S14) are much higher than those for NC900, and the electron transfer value calculated from the slopes is 2.1, indicating domination of the two-electron pathway with peroxide as the final product. These observations are consistent with previous studies showing that increased N-decoration may lead to a two-electron process,¹⁴ although NC800 has higher microporous characteristics, a higher Zn content, and a lower degree of graphitization than NC900 or NC1000. These results highlight the effects of carbonization temperature, which can effectively control the degree of graphitization, porosity, and nitrogen content and hence the dominating electrochemical reaction pathway.

In conclusion, we have successfully prepared N-decorated nanoporous carbons with high surface areas and CO_2 uptake capacities and superior selectivities for CO_2 over other gases as well as good electrochemical properties as Pt-free ORR catalysts by employing a robust N-rich MOF as both a precursor and template and FA and NH_4OH as the other precursors via an easily handled method. The high microporosity and N content within porous carbon frameworks could provide selective peroxide formation. This work unambiguously shows the great potential of heteroatom-decorated carbon materials derived from porous MOFs in selective gas separation and energy storage/conversion applications, which opens up an avenue to enrich the functional applications of porous MOFs. With the great number of available MOF structures, nanocasting using MOFs could be highly promising for large-scale synthesis of porous carbon materials as an alternative to nanocasting using silica or other

porous materials because the MOF itself contributes to the formation of high-quality carbon.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and additional data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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