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Silica-assisted fabrication of N-doped porous carbon for efficient electrocatalytic nitrogen fixation

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Abstract: Here we demonstrate a silica-assisted strategy for the synthesis of N-doped porous carbon nanoparticles from zeolitic imidazolate framework precursors. As a metal-free electrocatalyst for N₂ reduction to NH₃ at ambient conditions, such porous carbon shows an improved catalytic performance compared with the counterpart without the assistance of silica, delivering a higher NH₃ formation rate of 7.22 µg h⁻¹ mg_{cat}⁻¹ and a Faradic efficiency of 7.42% in 0.1 M HCl solution. The mesopores involved in the carbon catalyst are supposed to be responsible for the efficient electroreduction of N₂.

The Haber–Bosch process for the formation of NH₃ from N₂ and H₂ has been considered a revolutionary technology, because it enabled an exponential explosion of population through the 20th century by affording NH₃-based fertilization.^[1] However, this process is not particularly efficient, accounting for 1-3% of the world's energy consumption and releasing large amounts of CO2 annually. Electrocatalytic N2 reduction reaction (NRR) driven by renewable electricity has been proposed as a promising alternative for NH₃ synthesis since it can be energy-efficiently operated under ambient conditions.^[2] The challenge for the electrocatalytic NRR is the slow kinetics of N2 adsorption and the subsequent N \equiv N triple bond cleavage. Besides, the side reaction, i.e. the hydrogen evolution reaction (HER), should be suppressed because of its comparable standard reduction potential (0 V vs. standard hydrogen electrode, SHE) with that of NRR (0.057 V vs. SHE). To solve these issues, effective NRR catalysts with high catalytic activity and selectivity are urgently required. Noble metal materials have been proven to be active toward electrocatalytic NRR; however, their commercial use is largely hindered by high price and low abundance.^[3] Carbon materials, especially doped with heteroatoms (such as N, B, S and P), normally exhibit highperformance catalytic activity toward various electrochemical reactions.^[4] Recently, reported studies have also demonstrated that metal-free N-doped zeolite-imidazolate-framework (ZIF) derived carbon materials have electrocatalytic activity toward NRR.^[5] Theoretical calculations have also revealed that pyridinic defects involved within the carbon matrix may be responsible for the NRR activity.^[5b, 6] However, the ZIF precursor tends to fuse and aggregate together at high carbonization temperature, resulting in larger particles with a declined specific surface area and decreased active sites accessible to reactants.

In this research, we synthesize a N-doped porous carbon electrocatalyst by coating a silica layer on the surface of ZIFs, followed by carbonization and etching to remove the silica. With this silica-assisted synthetic strategy, the resultant ZIF-derived Ndoped porous carbon exhibited a higher specific surface area and more exposed active sites compared with the contrast sample without silica coating, and showed an improved performance for electrocatalytic NRR.

For a typical procedure, ZIFs were first synthesized using the reported method.^[5b] A silica shell was then coated onto the surface of ZIFs through the alkaline catalyzed hydrolysis of tetraethyl orthosilicate. After carbonization at 1100 °C in Ar atmosphere and HF etching to remove the silica layer, the resultant N-doped carbon nanoparticles (NCNPs) were finally obtained. For comparison, N-doped carbon nanoparticles without silica coating (NCNPs-w/o) were also fabricated under the identical conditions. Scanning electron microscopy (SEM) image in Figure 1a shows a cross-linked aggregated morphology for NCNPs-w/o, while NCNPs have a better monodispersed particle shape with an average diameter of ca. 200 nm (Figure 1d). Transmission electron microscopy (TEM) images further reveal that NCNPs have a morphology which is different from that of NCNPs-w/o (Figure 1b, 1c, 1e and 1f). From the high-resolution TEM image of NCNPs shown in Figure 1g, a lattice spacing of 0.37 nm could be evidently confirmed, which is indexed to the (002) crystal face of graphitic domains involved within an amorphous carbon matrix. High-angle annular dark field scanning TEM and the corresponding energy dispersive X-ray spectroscopy images show that C and N atoms are

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Figure 1. (a-c) SEM and TEM images of NCNPs-w/o. (d-f) SEM and TEM images of NCNPs. (g) High-resolution TEM image of NCNPs. (h, i) HAADF-STEM images of NCNPs (h) and NCNPs-w/o (i), and the corresponding EDS mappings for C and N elements.

homogeneously dispersed on the surface of NCNPs and NCNPsw/o (Figure 1h and 1i).

The characteristic structures of NCNPs and NCNPs-w/o were also confirmed by X-Ray diffraction (XRD) patterns and Raman spectroscopy. In the XRD patterns shown in Figure 2a, broad peaks at 23° and 40° attributable to the (002) and (100) planes of graphitic carbons, respectively, could be readily observed in both NCNPs-w/o and NCNPs. The Raman spectra given in Figure 2b show two peaks located at 1350 and 1580 cm⁻¹, indicating the existence of disordered sp³ carbon (D-band) and graphitic sp² carbon (G-band), respectively.^[7] The ratio of the D and G band intensities (I_D/I_G) of NCNPs was calculated to be 1.03, which is similar to that of NCNPs-w/o (1.02). X-ray photoelectron spectroscopy (XPS) was employed to probe the composition and chemical states of the component elements on the surface of samples. The nitrogen content of NCNPs was determined to be 5.5 at%, which is comparable to that of NCNPs-w/o (5.4 at%) based on the XPS analysis. High-resolution XPS N 1s spectra of NCNPs further reveal the presence of pyridinic, pyrrolic, and graphitic nitrogen atoms for both NCNPs and NCNPs-w/o, with

the pyridinic nitrogen being the highest in content. Based on the above structure and composition analysis, we could deduce that NCNPs and NCNPs-w/o have similar crystalline structures and surface heteroatom-doped states.

To figure out the protective effect of the silica layer for NCNPs, the surface area and pore structure of NCNPs and NCNPs-w/o were further analyzed by N_2 adsorption/desorption measurements at 77 K. As shown in Figure 2e, NCNPs displays the type IV isotherm, indicating that micropores and mesopores are both involved in the sample. In contrast, NCNPs-w/o shows the type I isotherm, which is mainly governed by adsorption in micropores at low relative pressures. As shown in Table 1, the specific surface area and total pore volume of NCNPs are 1122.3 m² g⁻¹ and 0.456 m³ g⁻¹, respectively, much higher than the corresponding values for NCNPs-w/o (800.5 m² g⁻¹ and 0.316 m³ g⁻¹). The pore size distribution (Figure 2f) calculated for NCNPs has a distinct micropore with the diameter of 1.2 nm, and a broader mesopore with the average diameter of ca. 11.3 nm. For NCNPs-w/o, only a micropore with the diameter of 1.2 nm is present, indicating the material possesses far less mesoporosity

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Figure 2. (a) Raman spectra, (b) XRD patterns, (c) XPS spectra, (d) High-resolution XPS N1s spectra, (e) N₂ adsorption/desorption isotherms, and (f) pore size distribution curves of NCNPs and NCNPs-w/o.

than NCNPs. These results reveal the pivotal role of the silica layer, which prevents the aggregation and fusion of ZIF nanoparticles during the high-temperature pyrolysis and carbonization process.

All the electrocatalytic NRR experiments were carried out in a two-compartment cell (H-cell) separated by a Nafion membrane at the ambient temperature and atmospheric pressure. Ag/AgCl electrode (filled with saturated KCl electrolyte) and Pt plate $(1 \times 1 \text{ cm}^2)$ were used as the reference and the counter electrodes, respectively. The working electrode was prepared by dispersing catalyst inks onto a carbon cloth. N₂ was continuously fed into the cathodic electrolyte (0.1 M HCl solution) with a flow rate of 20 mL min⁻¹. After reacting for one hour, the electrolyte from the cathodic

compartment was collected and the as-obtained products, i.e. NH_3 and N_2H_4 , were determined by the indophenol blue method and the Watt and Chrisp method, respectively.^[3b, 8] The initial analysis showed that only NH_3 could be detected. Isotope labeling experiments were performed to verify the nitrogen source of the produced NH_3 . As shown in Figure 3a, $^{15}NH_4^+$ and $^{14}NH_4^+$ could be detected when NRR occurred in $^{15}N_2^-$ and $^{14}N_2^-$ saturated electrolytes, respectively. We also performed a series of control experiments using NCNPs in alternating N_2^- and Ar-saturated electrolytes. Compared with electrolysis in Ar-saturated electrolyte, NCNPs showed much higher NH_3 formation rates and Faradaic efficiencies (FEs) in N_2 -saturated electrolyte. The NCNP sample in N_2 -saturated electrolyte without applied potentials was

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Figure 3. (a) ¹H NMR spectra of the cathodic electrolytes after 6 h of electrochemical NRR at -0.1 V (vs. RHE) using ¹⁵N₂ and ¹⁴N₂ as the feeding gas. (b) NH₃ formation rates and FEs of NCNPs at different potentials in N₂-saturated 0.1 M HCl solution. (c) Recycling test of NCNPs at -0.1 V (vs. RHE). (d) NH₃ formation rates and FEs of NCNPs-w/o at different potentials in N₂-saturated 0.1 M HCl solution.

Table 1. Surface areas and pore volumes of NCNPs and NCNPs-w/o.

Sample	BET surface area (m²/g)	External surface area (m²/g)	Micropore area (m²/g)	Total pore volume (m ³ /g) ^[a]	Micropore volume (m ³ /g) ^[b]
NCNPs-w/o	800.5	143.6	656.9	0.316	0.255
NCNPs	1122.4	673.7	448.7	0.456	0.185

[a] Total pore volume was calculated at P/P₀=0.142; [b] Micropore volume was calculated using the t-plot method.

also tested, just showing the same amount of NH₃ tested in Arsaturated electrolyte. These results suggest that most of the produced NH₃ is derived from electrocatalytic NRR. The trace of NH₃ detected in Ar-saturated electrolyte under tested potentials or N₂-saturated electrolyte at an open circuit voltage may originate from the NH₃ species wafting through the air, and the doped nitrogen involved in catalysts may also contribute the NH₃ formation.^[6] Therefore, the accurate NH₃ formation rate and FE should be determined by subtracting the calculated values in Arsaturated electrolyte from the ones in N2-saturated electrolyte. The NH₃ formation rates and FE values for NCNPs at different applied potentials were then measured and shown in Figure 3b, in which the highest FE of 7.42% could be obtained at -0.1 V (vs. reversible hydrogen electrode, RHE). The highest NH₃ formation rate was achieved at -0.3 V (vs. RHE), with the value reaching as high as 7.22 $\mu g \ h^{-1} \ m g_{cat}^{-1}.$ As the potential negatively shifted, the formation rate and FE significantly decreased because of the competitive HER. The NCNP sample showed a negligible decline in formation rate and FE after five cycles (Figure 3c), indicating good stability toward electrocatalytic NRR. The catalytic performance of NCNPs-w/o under the identical test conditions was also investigated for comparison. As depicted in Figure 3d, the highest NH₃ formation rate of 6.06 μ g h⁻¹ mg_{cat}⁻¹ and highest FE of 2.56% were obtained at -0.3 and -0.1 V (*vs.* RHE), respectively. Nevertheless, the performance of NCNPs-w/o was inferior to that of NCNPs under the tested potentials.

Clearly, the silica coating plays a critical role for NCNPs in improving the electrocatalytic performance toward NRR, because of its function of preventing the catalyst from fusion and aggregation and creating more mesopores for N₂ to reach active sites. The electrocatalytic activity toward NRR is supposed to be associated with the pyridinic N atoms involved in NCNPs and NCNPs-w/o,[5b, 6] while the differences in activity and selectivity may be attributed to morphological factors and especially the pore structure of the two carbon catalysts.^[9] The N₂ molecule can be adsorbed and activated on the active site consisting of three pyridinic N atoms and one adjacent carbon vacancy.^[5b] The hydrogenation process for ammonia synthesis on NCNPs is as follows: *N–N \rightarrow *N–NH \rightarrow *N–NH₂ \rightarrow *N+NH₃ \rightarrow *NH+NH₃ \rightarrow *NH₂+NH₃ \rightarrow 2NH₃. As shown in Figure 2e and Table 1, NCNPs are rich in mesopores and the external surface area is as high as 673.66 m² g⁻¹, which is much larger than that of NCNPs-w/o (143.64 m² g⁻¹). The presence of mesopores maybe beneficial for NCNPs in achieving high NH₃ selectivity and formation rate, just

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Figure 4. Tafel plots for NCNPs and NCNPs-w/o.

as the mesopore-rich carbon-based catalysts have performed in electrocatalytic reactions.^[10] The mass transport other requirements for HER and NRR are different, while the competitive HER reaction could be severely restrained within a mesoporous catalyst.^[11] Furthermore, the wetting properties of porous carbon materials are largely dependent on their morphology and pore structure, and the pore-rich carbon shows a relatively more hydrophobic surface with a lower surface energy.^[10a] We infer that the change in surface energy of NCNPs with the hierarchical porous structure may be beneficial for affording a solid-liquid-gas three-phase reaction interface that facilitates the NRR.^[12] In addition, the Tafel plots derived from the partial current density of N₂ reduction versus cathode potential show that the NCNPs electrode has a smaller Tafel slope than the NCNPs-w/o electrode (100.9 mV dec⁻¹ for NCNPs versus 132.1 mV dec⁻¹ for NCNPs-w/o), suggesting that the NCNPs electrode exhibits faster kinetics than the NCNPs-w/o electrode (Figure 4).

In summary, we have developed a silica-assisted strategy for the fabrication of N-doped porous carbon electrocatalyst for NRR. Owing to its mesopore-rich structure with an enlarged specific surface area and increased number of active sites, the obtained catalyst shows an improved electrocatalytic performance compared with the micropore-rich counterpart. More importantly, these results highlight the observed selectivity for NRR cannot be exclusively related to intrinsic active sites on the surface of catalysts, but also the morphological factors should be taken into consideration when defining the experimental selectivity. This research would shed new light to boost the NRR performance by only morphological design of NRR electrocatalysts.

Experimental Section

Catalyst preparation: $Zn(NO_3)_2 \cdot 6H_2O$ (5.9498 g) and 2methylimidazole (6.5680 g) were dissolved separately in 200 mL of methanol. The solution of 2-methylimidazole was gradually added to the metal salt solution and stirred for 1 h, then aged at ambient temperature for 24 h. The solid product (ZIFs) was collected by centrifugation and washed with methanol, and dried at 60 °C for 6 h. ZIFs (600 mg) were dispersed in 240 mL of H₂O, and then 6 mL of an aqueous cetyltrimethylammonium bromide solution (25 mg mL⁻¹) and 9.6 mL of an aqueous NaOH solution (6 mg mL⁻¹) were added. Tetraethyl orthosilicate (1.2 mL in 6 mL of methanol) was injected into the above solution, and the resulting dispersion was stirred for 0.5 h. The resulting ZIF@SiO₂ nanoparticles were collected by centrifugation and washed with ethanol. The obtained ZIF@SiO₂ was pyrolyzed at 1100 °C for 1 h under N₂, followed by cooling to room temperature. To remove the SiO₂ shell, the pyrolyzed sample was immersed in aqueous HF (10 wt.%), followed by centrifugation and washing with deionized water and ethanol. For comparison, N-doped carbon nanoparticles without SiO₂ protection (NCNPs-w/o) were prepared by directly pyrolyzing the ZIF precursors at 1100 °C for 1 h under N₂.

Characterization: The X-ray diffraction (XRD) patterns of the samples were recorded on a Shimadzu XRD-6100 diffractometer with Cu Ka X-rays operating at 30 mA and 40 kV, using Cu Ka as the radiation source (λ =0.15418 nm). The scanning electron microscopy (SEM) images of the samples were taken on a TESCAN MAIA3 at a working voltage of 5 kV. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100Plus transmission electron microscope. The FT-IR spectra were recorded within the 6000-400 cm⁻¹ region on a Nicolet iS50 spectrometer using KBr pellets. Raman spectroscopy was performed using HORIBA Laser Raman Spectrometer at 532 nm excitation. X-ray photoelectron spectroscopy (XPS) was conducted using a Thermo Fisher ESCALAB 250Xi+ spectrometer with monochromatized AI Ka radiation operating at a power of 300 W. The specific surface area measurements were carried out using (SRET) N₂ adsorption/desorption at 77 K on a Micromeritics ASAP 2460 apparatus. Samples were degassed at 200 °C for 5 h under vacuum prior to nitrogen physisorption measurements. The absorbance data of spectrophotometer were measured on SHIMADZU UV-2600 ultraviolet-visible (UV-Vis) spectrophotometer.

Electrochemical NRR measurements: All electrochemical measurements were performed on a CHI 660E electrochemical workstation (CH Instrumental Corporation, Shanghai, China) using a two-compartment cell, which was separated by Nafion 211 membrane. Different catalyst inks were deposited on a carbon cloth used as the working electrode. The Ag/AgCl electrode (saturated with KCl electrolyte) was used as the reference electrode and a Pt plate was used as the counter electrode. The polarization curves were measured with a scan rate of 5.0 mV s⁻¹ at room temperature. For N₂ reduction reaction (NRR) experiments, the potentiostatic test was conducted for 1 h in N₂-saturated 0.1 M HCl solution (30 mL) by continuously supplying N₂ into the electrolyte was bubbled with N₂ for 30 min before the measurement.

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Conflict of interest

The authors declare no conflict of interest.

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This paper revealed that the morphological and pore structural changes in the N-doped ZIF-derived carbon catalyst have a particularly significant impact on its performance toward electrochemical N_2 reduction to NH_3 .