

Nitrogen-Doped Hierarchical Porous Carbons Derived from Sodium Alginate as Efficient Oxygen Reduction Reaction Electrocatalysts

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Abstract: Exploring earth-abundant and low-cost eco-friendly materials with superior electrocatalytic performance is crucial for sustainable energy development. In this work, three-dimensional nitrogen-doped hierarchical porous carbon (NC) materials with interconnected mesoporous/macroporous structure have been successfully synthesized via a simple single-step pyrolysis of naturally available sodium alginate in the presence of urea. The systematical investigation of pyrolysis temperature on the oxygen reduction reaction (ORR) performance in 0.1 M KOH solution indicates that the catalyst obtained at 900 °C (NC-900) exhibits the most predominant catalytic performance due to high graphitization degree and unique hierarchical porous structure. Furthermore, NC-900 exhibits excellent durability and remarkable resistance to methanol poisoning relative to Pt/C in alkaline solution. This work highlights the significance and great potential of biomass-derived hierarchical porous carbon materials for applications in energy conversion devices.

Introduction

The Developing highly efficient, cost-effective catalysts for the oxygen reduction reaction (ORR) has been a pivotal issue in the commercialization of fuel cells and metal-air batteries.^[1] Currently, Pt-based compounds are reported to possess the highest activity toward the ORR.^[2] However, it is not practical and economical to apply Pt-based catalysts in the large scale due to their high cost, scarcity, poor durability and fuel crossover deactivation.^[3] Numerous efforts have been devoted to exploring high-efficient and stable catalysts such as transition metal based catalysts^[4] and carbon materials^[5,6] with low-cost and earthabundant resources.^[7] Among those catalysts, porous carbon materials doped with heteroatom have been regarded as the far more promising alternatives toward the ORR.[3,8-11] Nitrogendoped porous carbon materials have been attracted considerable concerns since the incorporation of nitrogen atoms can improve the surface polarity, electric conductivity, as well as

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electron-donor propensity of carbon significantly, which can improve the ORR performance efficiently.^[12,13]

Recently, biomass as one of attractive starting materials has been attracted much attention in virtue of its low-expense, ready availability and environmentally friendly properties. Extensive efforts have been made towards the synthesis of heteroatomdoped carbon by using biomass (e.g. crab shells,^[14] eggshell membranes,^[15] and fermented rice^[16]) as the precursor. Therefore, it is immensely preferable but still an enormous challenge to prepare heteroatom-doped carbon materials via an efficient approach from natural resources^[17]. Herein, we proposed a cost-effective, facile and readily route for the scalable synthesis of three-dimensional (3D) nitrogen-doped hierarchical porous carbon material via a one-pot pyrolysis strategy with eco-friendly sodium alginate and urea as the carbon and nitrogen source, respectively. The as-prepared Ndoped carbon annealed at 900 °C showed excellent catalytic activity in alkaline solution towards ORR, comparable to Pt/C. Besides, this material exhibited outstanding methanol tolerance and long-term cycle life toward the ORR.

Results and Discussion

Fabrication of nitrogen doped porous carbon materials was accomplished via one-step calcination of well-mixed alginate and urea at 900 °C under inert atmosphere (Figure 1).

The morphology of the resulting NC-0.5-900 was first examined by transmission electron microscopy (TEM). It is interesting to note that the as-synthesized NC-0.5-900 is composed of interconnected 3D porous structures with entangled and crumpled morphology (Figure 2a and 2b). The STEM image displayed in Figure 2c reveals that the nanosheets were interleaved with each other to form foam-like porous carbon materials. The formation of such unique porous morphology is probably due to the release of a large amount of NH₃ from the decomposition of urea in the process of thermal treatment.^[18-20] Nitrogen adsorption-desorption measurements were conducted to further evaluate the porous structure as well as the specific surface area of NC-0.5-900. Figure 2d clearly shows that the N₂ adsorption-desorption isotherm displays a striking feature of type IV profile with an H2 hysteresis loop, revealing that NC-0.5-900 exhibits mesoporous feature. The nitrogen volumes absorbed increasing steeply at high relative pressure indicate the presence of macroporous structure.^[21] Brunauer-Emmett-Teller (BET) surface area of NC-0.5-900 is detected to be 470.9 m² g⁻¹. Based on the Barrett-Joyner-Halenda (BJH) method, the pore size distribution curve can be obtained from the desorption branch. In addition, the insert of Figure 2d also clearly demonstrates that NC-0.5-900 exhibits the feature of mesoporous/macroporous, coinciding with the TEM

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characterization. The 3D porous architecture and the high surface area could be conducive to the fast absorption and diffusion of ions from the electrolyte and provide abundant active sites, which would enhance the electrochemical performance of NC-0.5-900 when it is used as oxygen reduction electrocatalysts.



Figure 1. Schematic illustration of synthesis process for N-doped hierarchical porous carbon materials.



Figure 2. (a) and (b) TEM images of NC-0.5-900 at different magnification. (c) STEM image of NC-0.5-900. (d) Nitrogen adsorption/desorption isotherms of NC-0.5-900, and the corresponding pore size distribution (inset).

Raman spectroscopy is the most powerful means to directly detect the doping effect of carbon materials.^[22] As shown in Figure 3a, all the Raman spectra of electrocatalysts annealed at different temperature exhibit three peaks at around 1350 cm⁻¹, 1585 cm⁻¹, and 2750 cm⁻¹, corresponding to the D band, G band, and 2D band, respectively. Among them, the D band, arising from the structural imperfection as the A_{1g} mode, is the common feature of amorphous carbon. The G band, corresponding to the first-order scattering of the E_{2g} mode, has close relevance to a graphitic carbon phase with a sp2 electronic configuration.^[23-26] The 2D band originating from a two-phonon double resonance process, is associated with the disorder-induced feature of carbon materials.^[23-26] Compared with C-900, the peak position

of G band for NC-0.5-900 slightly shifted toward the lower frequency, which could be attributed to nitrogen doping.^[27] Generally, the intensity ratio of D-band to G-band (I_D/I_G) is utilized to evaluate the disorder degree of carbon materials. It turned out that the intensity ratios of I_D/I_G are 1.01 and 0.99 for C-900 and NC-0.5-900, respectively, indicating that the nitrogen doping generates defects in the carbon structure, thereby increasing active sites as well as enhancing the electrochemical performance.^[22] Moreover, the I_D/I_G of NC-0.5-700, NC-0.5-800 and NC-0.5-1000 are calculated to be 1.12, 1.05 and 0.99, respectively, suggesting an enhancement of sp2-carbon degree and electron conductivity of as-prepared materials with increasing pyrolysis temperature. ^[28,29]

The chemical structure of NC-0.5-900 was assessed using FT-IR spectroscopy (see Figure 3b). In the spectrum of sodium alginate (SA), the peaks at ~3440 cm⁻¹ (broad) and ~1030 cm⁻¹ could be attributed to hydroxyls and C-O structure, respectively; the bands at ~1625 and ~1420 cm⁻¹ correspond to asymmetric and symmetric stretching peaks of carboxylate salt groups.[30] In the spectrum of urea, peaks at 3445, 3347, 1683, 1627, 1465 and 1153 cm⁻¹ are assigned to N-H stretching vibration, C=O stretching vibration, N-H bendina vibration. C-N stretching vibration, N-H rocking vibration, respectively.^[31,32] After pyrolysis at 900 °C, the characteristic peaks relating to amino groups as well as carbonyls could not be detected in the spectrum of NC-0.5-900, suggesting that the decomposition of these groups occurred during calcination process. Furthermore, a wide peak at ~1160 cm⁻¹ observed may be owing to the generation of C-N bonds and the remaining C-O groups in NC-0.5-900.[27] XPS was further measured to assess the chemical compositions and the element bonding configurations of NC because the ORR catalytic property of NC mainly hinges on the content and type of the doped nitrogen.[33] Figure 3c displays that the XPS survey spectra clearly indicate the existence of C, O, and N, confirming that nitrogen was successfully introduced into the carbon materials. The N content decreases as the temperature rises from 700 °C to 1000 °C (Figure 3d).

The C1s spectrum of NC-0.5-900 was deconvoluted into four peaks, seen in Figure S1. And the peaks located at 284.5, 285.3 286.3 and 289 eV can correspond to C=C, C-N, C-O, as well as O-C=O, respectively,[18,34] indicating nitrogen has been effectively incorporated into the carbon. The deconvoluted highresolution N1s spectra of NC-0.5-700, NC-0.5-800, NC-0.5-900 as well as NC-0.5-1000 are displayed in Figure 4a-d. Peaks located at ~398.3, ~400.0, ~401.0 eV correspond to pyridinic N, pyrrolic N, and graphitic N groups, [35-37] respectively. Remarkably the pyridinic N is predominant at low temperature and its content decreases along with the annealing temperature increasing from 700 to 1000 °C. While graphitic N is the main existing type of nitrogen at high temperature, suggesting that graphitic N has a much better stability compared to pyridinic N when the temperature was high. Moreover, the pyrrolic N and/or pyridinic may be converted into graphitic N at higher annealing temperature.^[38] The results demonstrate that the content along with the chemical state of nitrogen doped into carbon materials could be easily adjusted by changing the calcination temperature. Moreover, pyridinic as well as graphitic nitrogens

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are perceived to serve a crucial part in enhancing the ORR catalytic properties of carbon materials.^[15,39] Thus, the relative content of pyridinic and graphitic nitrogens was calculated. As depicted in Figure S2, NC-0.5-900 possesses a relatively high percentage of pyridine nitrogen and graphitic nitrogen. All the above results imply that NC-0.5-900 would harvest superior performance toward ORR benefiting from the porous structure, high surface area, optimal nitrogen content and chemical composition.



Figure 3. (a) Raman spectra of NCs obtained at different annealing temperature. (b) FTIR spectra of sodium alginate, urea, and NC-0.5-900. (c) XPS survey spectra of NCs obtained by annealing the precursors at the different temperature. (d) Total content of carbon, oxygen, and nitrogen of NC-0.5-700, NC-0.5-800, NC-0.5-900 and NC-0.5-1000 from XPS measurement.

The ORR electrocatalytic performances of the resulting materials were studied via cyclic voltammetry (CV) detection in N₂-saturated and O₂-saturated 0.1 M KOH aqueous solution at a scan rate of 50 mV s⁻¹, illustrated in Figure 5a. In comparison with C-900, NC-0.5-900 exhibits a pronounced oxygen reduction peak centered at around 0.8 V in the O₂-saturated aqueous solution with the comparison of no cathodic reduction peak observed in the N₂-saturated 0.1 M KOH media, suggesting the excellent ORR catalytic activity of the NC-0.5-900 due to nitrogen atoms incorporated into the carbon architecture promote the ORR. Then, in order to examine the influences of annealing temperature on ORR activity, CV measurements of the as-prepared materials at different annealing temperature were performed in N₂- and O₂-saturated 0.1 M KOH electrolyte. Figure 5b clearly shows that NC-0.5-900 exhibits a distinct oxygen reduction peak (~0.80 V) in O2-saturated 0.1 M KOH aqueous solution, much more positive than those samples calcined at other temperatures demonstrating that the ORR activity of NC-0.5-900 was improved to the maximum extent.



Figure 4. High-resolution N1s XPS spectra of (a) NC-0.5-700, (b) NC-0.5-800, (c) NC-0.5-900 and (d) NC-0.5-1000.

To obtain the further perception of the significance of nitrogen incorporation and annealing temperature for ORR, linear sweep voltammetry (LSV) curves were measured on a rotating disk electrode (RDE) in an O2-saturated 0.1 M KOH media at a scanning rate of 5 mV s⁻¹. As shown in Figure 5c, NC-0.5-900 presented a remarkably enhanced oxygen reduction onset potential (E_0) along with half-wave potential ($E_{1/2}$) (0.94 V and 0.83 V), much more positive than that of C-900 (0.80 V and 0.66 V) and other reported non-Pt catalysts^[40-42] and even comparable to Pt/C (0.95 V and 0.83 V). The more positive E_{c} and E1/2 of NC-0.5-900 demonstrate that nitrogen atoms doped into the carbon material are conducive to the ORR. Figure 5c also shows that NC-0.5-900 possesses a pronounced electrocatalytic activity toward the ORR than NC-0.5-700, NC-0.5-800, and NC-0.5-1000 in the aspects of onset potential and half-wave potential. Combined the experiment data with the XPS analysis, it can come to the conclusion that annealing at different temperature could produce different catalytic sites which affect the ORR activity^[43] and the high nitrogen content may do not facilitate the ORR performance.[18,29] Furthermore, the high percentage content of pyridinic N as well as graphitic N is favorable for enhancing the ORR activity.[44-46] To further appraise the kinetic characteristic of ORR, the Tafel slopes of different samples were obtained from the LSVs (Figure 5c) at 1600 rpm. [44,47] As illustrated in Figure 5d, NC-0.5-900 presents a Tafel slope of ~68 mV decade⁻¹, approximating the ~70 mV decade⁻¹ of Pt/C, suggesting that NC-0.5-900 follows a similar ORR mechanism to Pt/C that the first electron transfer might be the primary rate-determining step.^[48] The effects of the mass of urea added on the ORR catalytic activity were also evaluated by the CV and LSV curves. Figure S3a, b and Figure S4 show that the NC-0.5-900 with best ORR catalytic performance was obtained when annealing the mixture of 0.5 g urea and 0.5 g alginic acid sodium salt.

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Figure 5. (a) CV curves of NC-0.5-900 and C-900 in N₂- (dash line) and O₂- (solid line) saturated 0.1 M KOH solution at a scan rate of 50 mV s⁻¹. (b) CV curves of NCs obtained at different annealing temperature in N₂-(dash line) and O₂- (solid line) saturated 0.1 M KOH solution at a scan rate of 50 mV s⁻¹. (c) ORR polarization curves of C-900, NC-0.5-700, NC-0.5-900, NC-0.5-1000 and Pt/C at a rotating speed of 1600 rpm in O₂-saturated 0.1 M KOH solution at a scan rate of 5 mV s⁻¹. (d) Tafel plots of C-900, NC-0.5-700, NC-0.5-800, NC-0.5-900, NC-0.5-1000 and Pt/C in O₂-saturated 0.1 M KOH electrolyte. (e) ORR polarization curves of NC-0.5-900 in O₂-saturated 0.1 M KOH solution at various rotating speeds with a scan rate of 5 mV s⁻¹, and the Koutecky–Levich plots of NC-0.5-900 under potentials of 0.6 V, 0.65 V, 0.7 V and 0.75 V (inset). (f)The electron-transfer number n and H₂O₂ yield for NC-0.5-900.

The kinetics of the ORR for the as-prepared catalysts at different annealing temperature were investigated by RDE voltammetry measurements with various rotation speeds. The increase of the limiting current density was presented in Figure 5e and Figure S5 when increasing the rotation speed on NC-0.5-700, NC-0.5-800, NC-0.5-900, and NC-0.5-1000 electrodes, respectively. In

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addition, Figure 5e clearly displays that good linearity is obtained from the Koutecky-Levich (K-L) plots at different electrode potentials on NC-0.5-900 electrodes revealing first-order reaction kinetics which is related to the oxygen concentration.[49] Besides, the electron transfer number (n) of NC-0.5-900 was calculated to be 4 according to the K-L equation, illustrating a 4electron pathway toward ORR. In order to further illustrate the predominated procedure of oxygen reduction, rotating ring-disk electrode (RRDE) measurements were implemented on NC-0.5-900 catalyst. The n value and HO2⁻ yield can be calculated from RRDE voltammogram on the basis of Eqn. (3) and (4). As shown in Figure 5f and Figure S6, the HO₂ yield during the ORR process is less than 5 % below 0.9 V and the electron transfer number at potential from 0.2 to 0.9 V is nearly 4, approaching commercial Pt/C, suggesting a dominant 4-electron pathway. The RRDE experimental results performed on NC-0.5-900 were coincide with the results from the RDE investigation. The superior ORR catalytic properties of NC-0.5-900 catalyst could be ascribed to the following elements: the large surface area of NC-0.5-900 is favorable for the mass transport during ORR process; besides, the nitrogen doping could introduce defects in the carbon material, causing changes in the charge density distribution of adjacent carbon atoms in virtue of the difference of atomic radius between nitrogen and carbon, thereby offering many active sites for the adsorption of oxygen molecule and promote the ORR process. $\ensuremath{^{[18,21]}}$

For actual applications in direct methanol fuel cells, the methanol tolerance effects of the catalysts on ORR are indispensable for methanol molecules are susceptible to cross over the membrane, causing serious activity degradation of the catalyst.^[50] Thus, the methanol tolerance of NC-0.5-900 and commercial Pt/C were both assessed by chronoamperometric measurements at the specific potential of 0.7 V in O₂-saturated 0.1 M KOH aqueous media. Figure 6a evidently presents that the relative current of the Pt/C decreased dramatically after adding 1 M methanol. However, the NC-0.5-900 retained a virtually invariant current response after the addition of methanol In consistent with CV curves in Figure 6b, NC-0.5-900 exhibited almost unchanged CV curve while Pt/C displayed an obvious methanol oxidation peak after adding 1 M methanol into 0.1 M KOH aqueous media,^[51,52] indicating NC-0.5-900 possessed much better catalytic selectivity toward ORR against methanol oxidation than Pt/C. Alternatively, the durability of NC-0.5-900 and Pt/C was also assessed by chronoamperometry in an O2saturated 0.1 M KOH at 0.7 V. As shown in Figure 6c, after 20000 s of the i-t test, the NC-0.5-900 displayed a better longterm stability with almost 81% relative current retention than Pt/C with only 62 % retention.



Figure 6. (a) The chronoamperometric response of NC-0.5-900 and commercial Pt/C in O₂-saturated 0.1 M KOH media in the presence of 1 M methanol at a rotating speed of 1600 rpm. (b) CV curves of Pt/C and NC-0.5-900 in O₂-saturated 0.1 M KOH electrolyte with or without 1 M methanol at a scan rate of 50 mVs⁻¹. (c) The chronoamperometric responses of NC-0.5-900 and Pt/C at 0.7 V in O₂-saturated 0.1 M KOH media at a rotating speed of 1600 rpm. (d) CV curves of NC-0.5-900 between 0.05 and 1.0 V in O₂-purged 0.1M KOH media before and after 10000 potential cycles.

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laser excitation. X-ray photoelectron spectroscopy (XPS) were detected using an AXIS-ULTRA DLD-600W Instrument.

Electrochemical measurement

Electrochemical determination was implemented in 0.1 M KOH aqueous media at room temperature (298K) on electrochemical workstation CHI 760e with high-speed rotators from Pine Instrument. The three-electrode system utilized in the electrochemical tests includes a GCE or modified GCE, a reverse hydrogen electrode, and a Pt wire, which were served as working electrode, the reference electrode, as well as the counter electrode, respectively. 5 mg of samples was added into Nafion/isopropyl alcohol mixed solution (1 mL) followed by sonicating to form a homogeneous ink dispersion. Catalyst ink (16.5 µL) was dropped onto a GCE before dried in the air naturally. The loading amount of the catalysts and commercial Pt/C is about 0.42 and 0.08 mg cm⁻², respectively. Cyclic voltammogram (CV) was performed in N2 or O2-saturated 0.1 M KOH aqueous media. The rotating disk electrode (RDE) and the rotating ring-disk electrodes (RRDE) measurements were both implemented in O₂-saturated 0.1 M KOH electrolyte at a scan rate of 5 mV s⁻¹, and RDE was conducted at various rotation speeds (400, 600, 900, 1200, 1600 and 2000 rpm) while RRDE at 1600 rpm. The resistance to methanol poisoning investigation was realized at the rotating speed of 1600 rpm via the addition of 1 M methanol into O₂-saturated KOH aqueous media. The stability detection was performed at a specific potential of 0.7 V for 20000 seconds with a rotating speed of 1600 rpm.

For the RDE detection, the electron transfer numbers and the kinetic current density can be obtained on the basis of the Koutecky-Levich (K-L) equations:

$$\frac{1}{j} = \frac{1}{j_K} + \frac{1}{j_D}$$
(1)

$$j_D = 0.062 n FAD^{2/3} v^{-1/6} \omega^{1/2} C_{O_2}$$
 (2)

Where *j*, *j*_K, and *j*_D are the measured current density, kinetic current density as well as diffusion-limiting current density, respectively, n is the overall number of electrons transferred in oxygen reduction, F is the Faraday constant (F = 96485 C mol⁻¹), A is the electrode area (A = 0.196 cm²), D is the O₂ diffusion coefficient (D = 1.9×10^{-5} cm² s⁻¹), v is the kinematic viscosity of the electrolyte (v = 1.13×10^{-2} cm² s⁻¹), ω is the rotating speed of RDE, and C_{O2} is the concentration of O₂ (C_{O2}= 1.2×10^{-3} mol L⁻¹).

For the RRDE measurements, the HO_2^- % as well as the electron transfer numbers (n) could be detected by utilizing the following equations:

$$n = \frac{4 J_D}{j_D + \frac{j_R}{N}}$$
(3)
$$H_2 O_2 \% = \frac{\frac{2 j_R}{N}}{j_D + \frac{j_R}{N}} \times 100\%$$
(4)

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The ORR durability of NC-0.5-900 was also investigated via potential cycling ranging from 0.05 to 1.0 V in O_2 -saturated 0.1 M KOH aqueous solution at a scan rate of 200 mV s⁻¹. Figure 6d shows that NC-0.5-900 exhibited negligible oxygen reduction peak potential shift after 10,000 potential cycles, revealing excellent ORR electrocatalytic stability. The results demonstrated that NC-0.5-900 possessed an outstanding methanol tolerance and long-term cycle life, much better than the Pt/C, revealing the prospective use such as in fuel cells and metal-air batteries.

Conclusions

In summary, 3D nitrogen-doped hierarchical porous carbon has been effectively synthesized by a facile single-step approach. In this procedure, alginate, as the renewable natural resources, was used as the carbon source, and urea as the nitrogen source for the preparation of functional carbon materials. The nitrogen content doped into carbon structure could be adjusted easily by changing the annealing temperature. The as-prepared carbon material at the high pyrolysis temperature of 900 °C, exhibiting an interconnected 3D porous structure with mesoporous/macroporous feature, shows excellent catalytic activity for ORR. Benefiting from the costless and readily available materials, simple synthetic method, controllable nitrogen doping level, and favorable interconnected 3D porous structure, the proposed method may provide a facile and green route to prepare other functional porous metal-free carbon materials on a large scale for high-performance renewable energy conversion devices.

Experimental Section

Synthesis of N-doped porous carbon materials

Sodium alginate (0.5 g) was dissolved into 50 mL of urea aqueous solution (with 0.1, 0.5, 1.0, 1.5 g urea was denoted as NC-0.1, NC-0.5, NC-1.0 and NC-1.5, respectively). The solution was then concentrated by heating at 100 °C in an oven overnight. After that, the obtained material was placed in the tube furnace and then heated under flowing N₂ at 200 °C for 2 h following annealed at different temperature (700, 800, 900, 1000 °C) for 6 h. The resulting black products were washed several times with water and ethanol before dried at 60 °C overnight. The as-prepared material was denoted as NC-x-T, where x and T represent the mass of urea added and the annealing temperature, respectively.

Material characterization

Scanning transmission electron microscopy (S-TEM) and Transmission electron microscopy (TEM) images were obtained on Tecnai G2 F30. Fourier transform infrared spectroscopy (FTIR) characterization was conducted at ambient temperature with an FTIR spectrometer (VERTEX 70). Raman spectra were collected via a LabRam HR800 spectrometer with a 532 nm

Where j_D and j_R represent the faradic disk current density as well as the faradic ring current density, respectively, and N = 0.37 refers to as the current collection efficiency.

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Keywords: N-doping • hierarchical porous carbon • biomass • metal-free catalysts • oxygen reduction reaction

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3D N-doped hierarchical porous carbon derived from sodium alginate provides high surface area with unique interconnected structure and exhibits efficient ORR activity as well as excellent durability and methanol tolerance.



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Nitrogen-Doped Hierarchical Porous Carbons Derived from Sodium Alginate as Efficient Oxygen Reduction Reaction Electrocatalysts