Shrimp-shell Derived Carbon Nanodots as Carbon and Nitrogen Source to Fabricate Three-dimensional N-doped Porous Carbon Electrocatalyst for Oxygen Reduction Reaction

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Rongrong Liu,^{a,b} Haimin Zhang,^{*a} Shengwen Liu,^a Xian Zhang,^{a,b} Tianxing Wu,^a Xiao Ge,^{a,b} Yipeng Zang,^{a,b} Huijun Zhao^{a,c} and Guozhong Wang^{*a}

Development of cheap, abundant and metal-free N-doped carbon materials as high efficiency oxygen reduction electrocatalysts is crucial for their practical applications in future fuel cell devices. Here, three-dimensional (3D) N-doped porous carbon (NPC) materials have been successfully developed by a simple template-assisted (*e.g.*, SiO₂ spheres) high temperature pyrolysis approach using shrimp-shell derived N-doped carbon nanodots (N-CNs) as carbon and nitrogen source obtained through a facile hydrothermal method. The shrimp-shell derived N-CNs with a product yield of ~5% possesses rich surface O- and N-containing functional groups and small nanodot sizes of 1.5–5.0 nm, which is mixed with surface acidification treated SiO₂ spheres with an average diameter of ~200 nm in aqueous solution to form a N-CNs@SiO₂ composite subjected to a thermal evaporation treatment. The resultant N-CNs@SiO₂ composite is further thermally treated in N₂ atmosphere at different pyrolysis temperatures, followed by acid etching, to obtain 3D N-doped porous carbon (NPC) materials. As electrocatalysts for oxygen reduction reaction (ORR) in alkaline media, the experimental results demonstrate that 3D NPC obtained at 800 °C (NPC-800) with a surface area of 360.2 m² g⁻¹ exhibits the best ORR catalytic activity with an onset potential of -0.06 V, a half wave potential of -0.21 V and a large limiting current density of 5.3 mA cm⁻² (at -0.4 V, *vs.* Ag/AgCl) among all NPC materials investigated, comparable to that of commercial Pt/C catalyst with an onset potential of -0.03 V, a half wave potential of -0.17 V and a limiting current density of 5.5 mA cm⁻² at -0.4 V. Such 3D porous carbon ORR electrocatalyst also displays superior durability and high methanol tolerance in alkaline media, apparently better than commercial Pt/C catalyst. The findings of this work would be valuable for development of low-cost and abundant N-doped carbon materials from biomass as high performance metal-free electrocatalysts.

1 Introduction

As a vital cathodic reaction, the catalytic oxygen reduction reaction (ORR) in alkaline media has been widely investigated for applications in numerous promising renewable energy technologies,

such as fuel cells and metal-air batteries.^{1–5} It is well known that the electrocatalyst plays a key role in determining the ORR performance in respect to catalytic activity, operation durability and resistance to small fuel molecules (*e.g.*, methanol).^{1–5} Among varieties of ORR electrocatalysts developed to date, metal-free carbon materials with heteroatom (*e.g.*, N, S, B, P *etc.*) doping/co-doping, such as carbon nanotubes, graphene and metal-organic frameworks derived carbon materials and so on, have demonstrated a huge potential as a kind of promising electrocatalysts to substitute for expensive and scarce Pt-based catalysts.^{4–16} So far, heteroatom doped/co-doped metal-free carbon materials are mainly synthesized by high temperature pyrolysis approach, for example, *in situ* doping in the process of carbon structure formation in the presence of heteroatom-containing sources and post-doping by post treatment of as-prepared carbon materials with heteroatom-containing precursors.^{4–16} No matter what synthetic approach is

^aKey Laboratory of Materials Physics, Centre for Environmental and Energy Nanomaterials, Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China. Email: zhanghm@issp.ac.cn; gzhwang@issp.ac.cn; Tel: +86 551 65591973.

^bUniversity of Science and Technology of China, Hefei 230026, China.

^cCentre for Clean Environment and Energy, Griffith University, Gold Coast Campus, QLD 4222, Australia.

Electronic Supplementary Information (ESI) available: SEM image of SiO₂ spheres, SEM images of NPC-500, NPC-600, NPC-700, NPC-800 and NPC-900, surface survey XPS spectra and high resolution C 1s spectra of NPC-500, NPC-800 and NPC-900, and electrochemical measurements of NPC-500, NPC-600, NPC-700 and NPC-900. See DOI: 10.1039/x0xx00000x

adopted, the heteroatom doped/co-doped metal-free carbon materials reported to date are almost exclusively fabricated by fossil oil derived chemicals as reaction precursors, which undoubtedly enhances the cost of practical applications.⁴⁻¹⁶ Therefore, it is highly desirable for development of cheap and abundant biomass-derived materials as carbon and nitrogen sources to fabricate heteroatom doped/co-doped metal-free carbon materials to meet the application requirements of high catalytic activity, good durability and low cost for ORR.

Recently, N-doped carbon nanodots (N-CNs) derived from biomasses such as soy milk and grass have successfully demonstrated the great potentials as superior ORR electrocatalysts in our and others works.¹⁷⁻¹⁹ However, our studies have indicated that the obtained N-CNs cannot be directly used as electrocatalyst to prepare ORR electrode because the carbon nanodots possess high water adsorption property (especially in alkaline solution) owing to their surface rich O- and N-containing hydrophilic functional groups, leading to poor uniformity and stability of the catalyst film onto glassy carbon electrode.^{18, 19} Similar conclusions are also drawn by Li *et al.* using N-doped graphene quantum dots with oxygen-rich functional groups as ORR electrocatalyst.²⁰ To overcome this, the N-doped carbon nanodots or graphene quantum dots have been successfully immobilized onto conductive carbon or graphene substrates to form carbon-based composites by simple post-treatment approaches, effectively avoiding the catalyst falling off and showing good ORR performance.¹⁸⁻²⁰ The above reported works give us a further inspiration to fully utilize the biomass-derived N-CNs properties, such as small sizes, rich surface O- and N-containing functional groups, and concurrently acting as carbon and nitrogen source, for fabrication of metal-free N-doped carbon materials as high performance ORR electrocatalysts. Although biomass-derived N-doped carbon nanodots have shown great potentials as ORR electrocatalysts, low-temperature hydrothermal converted carbon nanodots (*e.g.*, at 180 °C) generally possess low graphitization degree, possibly unfavorable for high efficient electron transfer in ORR.^{21, 22} This may be well solved by a simple high temperature pyrolysis of the as-synthesized carbon nanodots. Generally, high temperature treatment approach inevitably arouses serious agglomeration of carbon structure to form discrete carbon particles with low surface area and poor electrical conductivity, leading to low ORR performance.^{6, 7, 12, 13, 23, 24} Therefore, it is of great importance for developing a facile approach of using biomass-derived N-doped carbon nanodots as carbon and nitrogen source to fabricate N-doped carbon material with large surface area and superior electron transfer network for high efficiency ORR. Recently, template-assisted approach (*e.g.*, SiO₂ spheres as templates) has been widely applied to fabricate three-dimensional (3D) porous carbon network structures with large surface area, porous structure, high graphitization degree and superior electrical conductivity, as ORR electrocatalysts, exhibiting superior electrocatalytic activity owing to their high active loading, good mass transport properties of ORR-relevant species in alkaline media such as OH⁻, O₂, H₂O and superior electron transfer.^{6, 15, 24-26} This template-assisted method may be an efficient means to fabricate high performance 3D porous carbon ORR electrocatalyst with high surface area and superior mass transport and electron transfer properties using biomass-derived N-doped carbon nanodots as carbon and nitrogen source.

Herein, we report a simple template-assisted high temperature pyrolysis method to fabricate 3D N-doped porous carbon (NPC) materials using shrimp-shell derived N-doped carbon nanodots (N-CNs) as carbon and nitrogen source. Firstly, N-CNs is prepared by hydrothermal treatment of dried shrimp shells at 180 °C for 15 h. Subsequently, surface acidification treated SiO₂ spheres with an average diameter of ~200 nm are added to N-CNs solution under stirring, followed by thermal evaporation treatment at 80 °C for overnight, to form a N-CNs@SiO₂ composite. 3D NPC materials are finally obtained by high temperature pyrolysis of N-CNs@SiO₂ composites in N₂ atmosphere at different temperatures, followed by acid etching. Scheme 1 shows a schematic preparation process of 3D NPC material. As electrocatalysts for ORR, the 3D NPC material obtained at pyrolysis temperature of 800 °C (NPC-800) exhibits superior catalytic activity, good durability and high resistance to methanol crossover effect, comparable to that of commercial Pt/C catalyst. The high ORR performance of NPC-800 can be attributed to the high active loading, good mass transport and superior electron transfer properties, resulting from its high surface area, suitable N doping type, porous structure, high graphitization degree and 3D carbon network structure.

Scheme 1 A schematic illustration of the preparation process of 3D NPC material.

2 Experimental section

Synthesis of N-doped carbon nanodots (N-CNs)

N-doped carbon nanodots (N-CNs) were synthesized by hydrothermal treatment of dried shrimp shells in deionized water without addition of any other chemicals. In a typical synthesis, 3.0 g dried shrimp shells were firstly ground to powder and added to 50 mL of deionized water, and then the mixture was transferred to a 100 mL of Teflon-lined autoclave. The hydrothermal reaction was kept at 180 °C for 15 h. After that, the obtained solution was filtrated by 0.2 µm cellulose membrane and centrifugated at 14,000 rpm to remove large particles, and the rest of supernatant was collected for further use. The product yield of N-CNs is ~5% and the concentration of N-CNs solution is around 3.0 mg mL⁻¹.

Synthesis of three-dimensional (3D) N-doped porous carbon (NPC)

Silica (SiO₂) spheres with an average diameter of ~200 nm were firstly fabricated by a Stöber method.²⁷ In a typical synthesis, 200 mL of absolute ethanol was mixed with 16 mL of deionized water

and 8.0 mL of 25 wt.% ammonia aqueous solution. The mixture was stirred vigorously for 0.5 h and then quickly added 12 mL of tetraethylorthosilicate (TEOS). The above mixture was continuously stirred for another 4 h at room temperature. Finally, SiO₂ spheres were collected by centrifugation at 14,000 rpm for 15 min, followed by 3 times washing with ethanol and 2 times with deionized water and dried at 80 °C in vacuum for 12 h. The obtained white solid was subsequently heated to 550 °C for 4 h in air at a ramp rate of 5 °C min⁻¹. The calcined SiO₂ spheres were then treated by 0.01 M H₂SO₄ at 50 °C for 1 h, followed by adequate washing with deionized water and drying at 80 °C in vacuum for further use.

0.2 g acidification treated SiO₂ spheres were firstly mixed with 40 mL of 3.0 mg mL⁻¹ N-CNs solution derived from shrimp shells under stirring to form a homogeneous solution. Then the mixture was treated by thermal evaporation at 80 °C for 10 h to obtain a N-CNs@SiO₂ composite. The as-prepared N-CNs@SiO₂ composite was subsequently pyrolyzed in N₂ atmosphere as follows: the N-CNs@SiO₂ composite was firstly heated to 400 °C for 30 min at a temperature rising rate of 2 °C min⁻¹, and then the pyrolysis temperature was further increased to a certain temperature (e.g., 500, 600, 700, 800 or 900 °C) at a temperature rising rate of 5 °C min⁻¹ for 2 h in N₂ atmosphere. The pyrolytic products were subsequently immersed in 40 wt.% HF solution for overnight to completely remove SiO₂ templates. The resultant N-doped porous carbon (NPC) materials obtained at different pyrolysis temperatures (denoted as NPC-X, X represents pyrolysis temperature of 500, 600, 700, 800 and 900 °C) were adequately washed with deionized water and dried at 80 °C in vacuum for further characterization and electrochemical measurements.

Characterizations

Powder X-ray diffraction (XRD) patterns of the samples were recorded on a Philips X-Pert Pro X-ray diffractometer with Cu K α radiation ($\lambda_{K\alpha1} = 1.5418$ Å). Field emission scanning electron microscopy (FESEM) images of the samples were taken on a FESEM (Quanta 200FEG) operated at an accelerating voltage of 10.0 kV. Transmission electron microscopy (TEM) images of the samples were obtained by a high resolution TEM (JEOL 2010), operated at an acceleration voltage of 200 kV. FT-IR spectra were performed on a Nexus FT-IR spectrophotometer. Raman spectra of the samples were recorded on a LabRAM HR800 confocal microscope Raman system (Horiba Jobin Yvon) using an Ar ion laser operating at 632 nm. X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, America) equipped with Al K $\alpha_{1,2}$ monochromatized radiation at 1486.6 eV X-ray source. The surface area and porosity of samples were measured by a Surface Area and Porosity Analyzer (Tristar 3020M).

Electrochemical measurements

All the electrochemical measurements were performed on an electrochemical workstation (CHI 760D, CH Instruments, Inc., Shanghai, China) and a PINE rotating disk electrode (RDE) system (Pine Instruments Co. Ltd. USA) in a conventional three-electrode cell. Catalyst coated glassy carbon (GC) electrode with a diameter of 5.0 mm, Ag/AgCl and platinum wire were used as working electrode, reference electrode and counter electrode, respectively. The

electrolyte was 0.1 M KOH solution prepared from deionized water. Prior to measurements, a GC electrode was polished carefully with 5.0, 0.3 and 0.05 μ m alumina slurry, respectively, and then ultrasonically cleaned in water and absolute ethanol to remove residues. The electrocatalyst ink was prepared by ultrasonically dispersing 2.0 mg catalyst into a mixture composed of 10 μ L of 5% Nafion, 190 μ L of absolute ethanol and 800 μ L of deionized water, resulting in a catalyst ink concentration of 2.0 mg mL⁻¹. To prepare catalyst coated GC electrode, 20 μ L of the catalyst ink was firstly cast onto the cleaned GC electrode surface, and then dried at room temperature. After that, another 20 μ L of the catalyst ink was cast again to obtain completely covered GC surface with catalyst, followed by drying at room temperature, to obtain catalyst coated GC electrode (catalyst loading amount of ~ 0.41 mg cm⁻²). **For comparison, a commercial Pt/C coated GC electrode was also prepared as the same procedure as the NPC catalyst mentioned above, and the Pt/C loading amount on GC electrode was ~ 0.41 mg cm⁻².** All electrochemical measurements, including cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry, were carried out in an O₂- or N₂-saturated 0.1 M KOH solution. The electrochemical impedance spectroscopy (EIS) measurements were performed by applying an AC voltage with 10 mV amplitude in a frequency range from 100,000 to 1 Hz and recorded at -0.35 V vs. Ag/AgCl electrode.

The transferred electron numbers *per* oxygen molecule involved in an ORR process were determined using the Koutecky-Levich (K-L) equation:^{1, 20, 28}

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}$$

$$B = 0.2nFC_0(D_0)^{2/3}\nu^{-1/6}$$

$$J_K = nFkC_0$$

where J is the measured current density, J_L and J_K are the diffusion- and kinetic-limiting current densities, ω is the rotation speed, n represents the number of electron transferred *per* oxygen molecule, F is the Faraday constant (96485 C mol⁻¹), C_0 is the O₂ concentration in the electrolyte (1.26 $\times 10^{-6}$ mol cm⁻³), D_0 is the diffusion coefficient of O₂ in the electrolyte (1.9 $\times 10^{-5}$ cm² s⁻¹), and ν is the kinetic viscosity (0.01 cm² s⁻¹).

3 Results and discussion

In this work, shrimp-shell derived N-doped carbon nanodots (N-CNs) were used as cheap and abundant carbon and nitrogen source to prepare three-dimensional (3D) N-doped porous carbon (NPC) materials. After hydrothermal treatment of dried shrimp shells at 180 °C for 15 h, uniformly dispersed carbon nanodots can be clearly observed with nanodot sizes of 1.5–5.0 nm (Fig. 1A and inset). The FT-IR spectrum (Fig. 1B) of shrimp-shell derived carbon nanodots indicates the characteristic absorption bands of O-H, N-H and C-H stretching vibrations at around 3410 cm⁻¹, 3248 cm⁻¹ and 2960 cm⁻¹, respectively.^{18, 29–32} The peaks centred at 1408 cm⁻¹ and 1638 cm⁻¹

are corresponding to the stretching vibrations of C=O/C=N and in-plane bending vibration of O-H, respectively.^{18, 29-32} The absorption band concentrated at 1043 cm^{-1} can be attributed to the vibration of C-O/C-N bonds.^{18, 29-32} The above FT-IR analysis confirms the presence of rich surface O- and N-containing functional groups in shrimp-shell derived carbon nanodots. Our previous work has demonstrated that N doping in carbon nanodots can effectively change the charge distribution of carbon atoms around the doped N atom, resulting in superior electrocatalytic activity of oxygen reduction reaction (ORR).¹⁸ In this work, small sized N-CNs with rich surface O- and N-containing functional groups can be used as cheap and abundant precursor as “building blocks” to first assemble N-CNs@SiO₂ composite with surface acidification treated SiO₂ spheres possessing surface O-containing functional groups. Fig. S1 (ESI[†]) shows the surface SEM image of surface acidification treated SiO₂ spheres, indicating uniformly dispersed sphere-shape structures with an average diameter of $\sim 200\text{ nm}$. After pyrolysis treatment of N-CNs@SiO₂ composite at $800\text{ }^{\circ}\text{C}$, followed by acid etching, 3D porous carbon network structure can be observed with an average pore size of $\sim 200\text{ nm}$ resulting from the removal of SiO₂ spheres (Fig. 1C). Further TEM characterization shown in Fig. 1D indicates that the formed 3D porous carbon network structure possesses an average pore size of $\sim 200\text{ nm}$ and the thickness of the formed carbon wall is $\sim 8\text{ nm}$ (top inset in Fig. 1D). The high resolution TEM (HRTEM) image shows the formed carbon wall with highly distorted graphitic lattice structure (bottom inset in Fig. 1D), which may mean more defects formed in carbon structure, thus providing more catalytic active sites for electrocatalysis applications.³³⁻³⁵

Fig. 1 (A) TEM image of N-CNs and corresponding size distribution (inset). (B) FT-IR spectrum of N-CNs. (C) SEM image of 3D porous carbon network structure obtained at $800\text{ }^{\circ}\text{C}$. (D) TEM image of pyrolytic carbon sample obtained at $800\text{ }^{\circ}\text{C}$ and corresponding high magnification TEM (top inset) and HRTEM (bottom inset) images of an individual carbon wall.

In this work, we also investigate the effect of pyrolysis temperature on the morphology and structure of resulting porous carbon materials, as shown in Fig. S2 (ESI[†]). Apparently, low pyrolysis temperatures of $500\text{ }^{\circ}\text{C}$ and $600\text{ }^{\circ}\text{C}$ (Fig. S2A, B, ESI[†]) result in the obtained carbon materials with incompletely porous structure, possibly owing to low carbonization degree at these

temperatures unfavorable for the formation of 3D porous structure. With increasing pyrolysis temperature to $700\text{ }^{\circ}\text{C}$ (Fig. S2C, ESI[†]), the obtained carbon material with uniform porous structure can be observed, and an intact 3D porous carbon network structure can be obtained at pyrolysis temperature of $800\text{ }^{\circ}\text{C}$ (Fig. 1C, D), while too high pyrolysis temperature (e.g., $900\text{ }^{\circ}\text{C}$) arouses serious structure damage to form discrete large carbon particles (Fig. S2D, ESI[†]). The above results demonstrate that the pyrolysis temperature has important influence on the morphology and structure of pyrolytic carbon products, thus possibly affecting their electrocatalytic performance when used as electrocatalysts.

Fig. 2 (A) XRD patterns of NPC-500, NPC-600, NPC-700, NPC-800 and NPC-900. (B) Raman spectra of NPC-500, NPC-600, NPC-700, NPC-800 and NPC-900. (C) High resolution N 1s XPS spectrum of NPC-800. (D) N₂ adsorption-desorption isotherm of NPC-800 and corresponding pore size distribution.

The N-CNs@SiO₂ composites derived porous carbon materials at different pyrolysis temperatures were further characterized by XRD technique. As shown in Fig. 2A, all carbon materials investigated exhibit strong inter-plane (002) diffraction at around 24.7° and gradually enhanced inner-plane (101) diffraction at around 43.7° with pyrolysis temperature, attributed to graphitic carbon.^{11, 36} The gradually enhanced inner-plane (101) diffraction peak indicates an improvement of graphitization degree of the carbon material with pyrolysis temperature. This can be further confirmed by Raman spectra investigation. Fig. 2B shows the Raman spectra of pyrolytic carbon materials, indicating D and G bands located at around 1353 cm^{-1} and 1588 cm^{-1} , respectively arising from the disordered graphitic carbon structures and the vibration of sp^2 -bonded carbon atoms.³⁷ The relative ratios of the D band to the G band are generally used to evaluate the degree of graphitization of carbon materials. The I_D/I_G values at around 1353 cm^{-1} and 1588 cm^{-1} of pyrolytic carbon products gradually decrease with pyrolysis temperature, indicating an improvement of graphitization degree. The I_D/I_G value of carbon product obtained at $800\text{ }^{\circ}\text{C}$ is about 1.01, suggesting the presence of a great deal of disordered carbon in carbon structure, which is consistent with the HRTEM result (bottom inset in Fig. 1D). The disordered carbon structure contained in pyrolytic carbon material may mean more defects, thus contributing more catalytic active sites for high efficiency

electrocatalysis.³³⁻³⁵ In this work, X-ray photoelectron spectroscopy (XPS) measurements were performed to measure the chemical composition of pyrolytic carbon materials. The surface survey XPS spectra (Fig. S3, ESI[†]) of the carbon materials (take NPC-500, NPC-800 and NPC-900 as examples) show that only C, N and O elements can be observed with N contents of 11.8, 8.1 and 6.8 at.% for NPC-500, NPC-800 and NPC-900, respectively, suggesting a decrease of N doping amount in carbon structure with pyrolysis temperature. The high resolution C 1s XPS spectra (Fig. S4, ESI[†]) of NPC-500, NPC-800 and NPC-900 can be deconvoluted into four different peaks with bonding energies of 284.3, 285.1, 286 and 288.7 eV, corresponding to C-C, C-N, C-O and C=O/C=N, respectively, further confirming the presence of doped N and O-rich functional groups.^{18, 20} Further, the high resolution N 1s XPS spectra (take NPC-800 as an example, Fig. 2C) show three deconvoluted peaks at 398.2, 399.4 and 401.0 eV, which can be ascribed to pyridinic-N (37.9%), pyrrolic-N (25.2%) and graphitic-N (36.9%), respectively.^{18, 20} The above results demonstrate that pyridinic-N and graphitic-N are predominant among all doped N types for NPC-800, which are generally considered as catalytic active sites for ORR.^{5, 13} Fig. 2D shows the N₂ adsorption-desorption isotherm (Barrett-Joyner-Halenda, BJH method) of NPC-800, confirming the Brunauer-Emmett-Teller (BET) surface area of 360.2 m² g⁻¹ and presence of trimodal-pore structures calculated on adsorption branch in N₂ adsorption-desorption isotherm (micropores, mesopores and macropores, inset in Fig. 2D). The microporous structures are resulted from the spherical thin layer graphitic carbon formed on SiO₂ spheres and the mesoporous structures are attributed to the formed cavities of neighborhood SiO₂ spheres, which significantly contribute the large surface area of NPC-800. The macroporous structures are formed by the removal of SiO₂ spheres, combining with mesoporous structures, which are very favorable for mass transport of ORR-related species such as OH⁻, O₂, H₂O during electrocatalysis. This enables full utilization of material pore inner catalytic active sites to improve ORR electrocatalytic performance.^{15, 38} By comparison, lower surface areas of 13.4, 30.2, 70.8 and 88.6 m² g⁻¹ are obtained for NPC-500, NPC-600, NPC-700 and NPC-900, respectively. Low pyrolysis temperatures (e.g., 500 °C, 600 °C and 700 °C) have demonstrated the obtained carbon products with low carbonization degree, resulting in the formation of incomplete porous structures, while high pyrolysis temperature of 900 °C readily causes structural damage to form discrete large carbon particles (Fig. S2, ESI[†]). These collectively contribute lower surface area of the carbon products obtained at these pyrolysis temperatures compared to that of NPC-800. The above results further evidence that a suitable pyrolysis temperature is critically important for the formation of 3D porous carbon network structure with high surface area.

The electrocatalytic activities of NPC samples obtained at different pyrolysis temperatures were evaluated toward ORR using a rotating disk electrode (RDE) system. As shown in Fig. 3A, the cyclic voltammetry (CV) responses of all NPC and commercial Pt/C coated glassy carbon (GC) electrodes exhibit a featureless voltammetric current within the potential range investigated in N₂-saturated 0.1 M KOH solution. By comparison, the CV curves of all NPC and commercial Pt/C coated GC electrodes in O₂-saturated 0.1 M KOH solution show obviously well-defined cathodic current peaks attributed to oxygen reduction reactions at -0.424 V, -0.381 V, -

0.313 V, -0.242 V, -0.308 V and -0.195 V for NPC-500, NPC-600, NPC-700, NPC-800, NPC-900 and Pt/C, respectively. The above results indicate that NPC-800 possesses the lowest overpotential toward oxygen reduction among all NPC catalysts investigated, close to that of commercial Pt/C catalyst. Fig. 3B shows that the linear sweep voltammogram (LSV) curves of all NPC and commercial Pt/C coated GC electrodes in O₂-saturated 0.1 M KOH solution at a scan rate of 10 mV s⁻¹ and a rotation speed of 1600 rpm. The onset potentials of NPC-500, NPC-600, NPC-700, NPC-800, NPC-900 and Pt/C are -0.30 V, -0.23 V, -0.15 V, -0.06 V, -0.17 V and -0.03 V, respectively. Obviously, NPC-800 coated GC electrode exhibits more positive onset potential than that of other NPC catalysts, which is very approximate to that of commercial Pt/C catalyst, suggesting its high catalytic activity. Also, the limiting current (e.g., 5.3 mA cm⁻² at -0.4 V) of NPC-800 coated GC electrode is dramatically higher than that of other NPC catalysts, close to commercial Pt/C catalyst (e.g., 5.5 mA cm⁻² at -0.4 V). The above results further demonstrate NPC-800 possessing high electrocatalytic performance.

Fig. 3 (A) Cyclic voltammetry (CV) curves of all NPC and commercial Pt/C catalysts in N₂- or O₂-saturated 0.1 M KOH solution; the scan rate of 50 mV s⁻¹. (B) Linear sweep voltammogram (LSV) curves of all NPC and commercial Pt/C catalysts in O₂-saturated 0.1 M KOH solution at a scan rate of 10 mV s⁻¹ and a rotation speed of 1600 rpm. (C) Linear sweep voltammogram (LSV) curves of NPC-800 obtained at different rotating speeds in O₂-saturated 0.1 M KOH solution at a scan rate of 10 mV s⁻¹. (D) Koutecky-Levich plots of NPC-800 derived from Fig. 3C at different potentials, the inset of electron transfer number (*n*) of NPC-800.

Fig. 3C shows the linear sweep voltammogram (LSV) curves of NPC-800 coated GC electrode obtained at different rotating speeds in O₂-saturated 0.1 M KOH solution at a scan rate of 10 mV s⁻¹. An increase in the rotation speed results in an increase of the cathodic current, implying a mass transfer controlled process.¹¹ The electron transfer number (*n*) per oxygen molecule for ORR can be calculated from the LSV curves at different rotating speeds using Koutecky-Levich (K-L) equation to further evaluate the ORR catalytic performance of NPC catalysts. The K-L plots (Fig. 3D) of NPC-800 coated GC electrode derived from Fig. 3C exhibit good linear relationships with a close slope for all plots obtained under various rotation speeds for the potential range investigated, suggesting a first-order reaction with respect to the dissolved O₂. The electron

transfer number (n) of NPC-800 calculated from K-L plots is found to be between 3.75 and 3.95 over the potential range of -0.40 V to -0.65 V (inset in Fig. 3D), indicating a four-electron ORR process.^{10, 20} By comparison, the calculated electron transfer numbers over the potential range of -0.40 V to -0.65 V are 1.36~1.62, 1.24~2.14, 2.53~2.95 and 2.12~2.24 for NPC-500, NPC-600, NPC-700 and NPC-900, respectively (Fig. S5, ESI[†]), further confirming the high ORR catalytic performance of NPC-800. For a meaningful comparison, we also evaluated the ORR catalytic activity of N-doped carbon materials obtained by direct pyrolysis of shrimp-shell derived N-doped carbon nanodots without SiO₂ spheres and shrimp-shell powder at 800 °C, respectively (denoted as NC-800 and SSC-800). As shown in Fig. S6 (ESI[†]), the obtained NC-800 shows discrete particle morphology, and as an ORR electrocatalyst, the NC-800 coated GC electrode displays much lower catalytic performance than NPC-800 (Fig. 4A). Interestingly, the shrimp-shell powder derived SSC-800 exhibits better ORR performance than that of NC-800, but still lower than that of NPC-800. It is believed that N doping in SSC-800 derived from shrimp-shell powder containing natural nitrogen element should be mainly responsible for its relatively high ORR catalytic activity, which deserves a further investigation in future work. Compared to NC-800, the high ORR performance of NPC-800 can be due to its 3D porous carbon network structure, contributing high surface area, superior mass transport and electron transfer. This can be further confirmed by electrochemical impedance spectrum (EIS) measurement. Fig. 4B shows the EIS curves of NC-800 and NPC-800 electrodes. As shown, NPC-800 exhibits smaller semicircular diameter in EIS than that of NC-800, due to smaller contact and charge transfer impedance in NPC-800,³⁹ confirming the 3D porous carbon network structure favorable for electron transfer and thus improving ORR performance.

Fig. 4 (A) Linear sweep voltammetry (LSV) curves of NC-800, SSC-800 and NPC-800 at 1600 rpm in O₂-saturated 0.1 M KOH solution with a scan rate of 10 mV s⁻¹. (B) Electrochemical impedance spectrum (EIS) of NC-800 and NPC-800 catalysts recorded at -0.35 V. The inset of corresponding equivalent circuit diagram, consisting of an electrolyte resistance (R_s), a charge-transfer resistance (R_t) and a constant-phase element (CPE). (C) Crossover effect measurements of NPC-800 and commercial Pt/C catalysts. (D) Durability tests of NPC-800 and commercial Pt/C catalysts at an applied potential of -0.35 V and a rotation speed of 1600 rpm.

As we know, heteroatom doped/co-doped carbon materials as ORR electrocatalysts possess high resistance to crossover effect of small fuel molecules (e.g., methanol).^{5, 15, 18} In this work, the stability test of NPC-800 is also performed in the presence of 3.0 M methanol. As shown in Fig. 4C, NPC-800 electrode exhibits high resistance to 3.0 M methanol without noticeable crossover effects, while commercial Pt/C catalyst shows a sharply decreased current after the addition of methanol due to the methanol crossover oxidation reactions happened on Pt/C.^{18, 40} The above results demonstrate that NPC-800 possesses higher ORR selectivity with strong tolerance to methanol crossover effect when compared with the commercial Pt/C. The durability is critically important for evaluating an ORR electrocatalyst for its practical application. Fig. 4D shows the stability test of NPC-800 and commercial Pt/C catalysts. As shown, the NPC-800 exhibits only 12% decrease in current density over 20,000 s of continuous operation at a rotation speed of 1600 rpm, under an applied potential of -0.35 V, while almost 26% decrease in current density is observed from the Pt/C catalyst, indicating a superior operation stability of NPC-800 in alkaline media compared to commercial Pt/C catalyst.

It has been widely accepted that doping N into carbon structures can effectively create electrocatalytic active sites for high performance ORR.^{1, 5} Moreover, our and others studies have demonstrated that pyridinic-N and graphitic-N are effective N doping types for creating electrocatalytic active sites for ORR.^{1, 5, 13, 15, 18} In this work, the superior ORR performance of NPC-800 can be ascribed to the obtained porous carbon with predominant pyridinic-N and graphitic-N doping types creating catalytic active sites for ORR.^{1, 5, 13, 15, 18} Additionally, the high ORR performance of NPC-800 is also due to its high surface area, porous structure and 3D carbon network structure, contributing high active loading, effective mass transport and superior electron transfer.^{13, 15}

4 Conclusions

In summary, 3D N-doped porous carbon materials have been successfully synthesized using shrimp-shell derived N-doped carbon nanodots as carbon and nitrogen source by a facile template-assisted high temperature pyrolysis method. The 3D N-doped porous carbon obtained at 800 °C exhibits a trimodal-pore structure and high surface area, as an ORR electrocatalyst, demonstrates superior electrocatalytic activity with a typical four-electron oxygen reduction process, good stability and high resistance to methanol crossover oxidation reaction. This work demonstrates the feasibility of using biomass as the starting material to fabricate cheap, abundant and high efficiency metal-free electrocatalysts.

Acknowledgements

This work was financially supported by the Natural Science Foundation of China (Grant No. 51372248 and 51432009), the CAS/SAFEA International Partnership Program for Creative Research Teams of Chinese Academy of Sciences, China, and the CAS Pioneer Hundred Talents Program.

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