Metal-organic-framework-derived formation of Co–N-doped carbon materials for efficient oxygen reduction reaction

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ABSTRACT

Non-precious metal nitrogen-doped carbonaceous materials have attracted tremendous attention in the field of electrochemical energy storage and conversion. Herein, we report the designed synthesis of a novel series of Co-N-C nanocomposites and their evaluation of electrochemical properties. Novel yolk-shell structured Co nanoparticles/polymer materials are fabricated from the facile coating polymer strategy on the surface of ZIF-67. After calcination in nitrogen atmosphere, the Co-N-C nanocomposites in which cobalt metal nanoparticles are embedded in the highly porous and graphitic carbon matrix are successfully achieved. The cobalt nanoparticles containing cobalt metal crystallites with an oxidized shell and/or smaller (or amorphous) cobalt-oxide deposits appear on the surface of graphitic carbons. The prepared Co–N–C nanoparticles showed favorable electrocatalytic activity for oxygen reduction reactions, which is attributed to its high graphitic degree, large surface area and the large amount existence of Co–N active sites.

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1. Introduction

Electrocatalysis of the oxygen reduction reaction (ORR) have drawn enormous interest in electrochemical energy storage and conversion fields such as fuel cells and metal-air batteries [1–12]. Pt-based catalysts are well-known to be the most active catalysts for ORR [13,14], but high costs and low abundance of Pt still restrict their widespread application. In addition, they still suffer from intermediate poisoning, fuel crossover and poor stability in the electrochemical system. To overcome these problems, recent intensive research has focused toward to fabricate alternative nonprecious electrocatalysts with high activity, long-term stability, and better tolerance to poisons [15,16]. Among them, cobalt and nitrogen co-doped carbon (Co–N–C) electrocatalysts prepared from the pyrolysis of nitrogen and cobalt containing precursors such as aniline [17], melamine [18], pyrrole [19], and metal-organic frameworks [20–23] are very promising candidates. Therefore, it is important to develop a facile approach to prepare Co–N–C nanoparticles with low cost, relatively good electrical conductivity and high specific surface area in a simple and effective way to synergistically enhance the ORR catalytic activity.

Zeolite imidazolate frameworks (ZIFs), one kind of typical metal-organic frameworks (MOFs), have been widely used for heterogeneous catalysts due to uniform pore size, well-defined morphology and excellent chemical stability [24–27]. ZIF-derived carbon materials such as Co–N–C materials have been demonstrated as excellent electrocatalysts with relative low-cost, high activity and stability [28–32]. These catalysts usually possess high crystallinity and electrical conductivity of carbon matrix with the assistance from catalytic graphitization of transitional metals.
[33]. Additionally, the synergistic effects among metal species, the doped N species, and carbon lattice provide enough reactive sites and local work function for O2 adsorption through the modification of the charge distribution on carbon surface, promoting electron transfer and facilitating the ORR process [34–36].

With the advancement of the extended Stöber method for preparation of carbon spheres [37,38], this strategy has been successfully developed for the synthesis of core@polymer and core@carbon structures. For example, this versatile coating technique can be used for fabrication of various particles with complicated structures and compositions such as polymer@polymer [39], Ag@polymer [40], α-Fe2O3 nanoparticles@polymer [41], Fe3O4 box@polymer [42] and ZnO@carbon [43]. Therefore, it is really desired to develop a facile approach to synthesize Co–N–C particles as low-cost and efficient ORR catalysts starting from the Stöber method by using ZIF particles as the precursors.

Herein, we present a spontaneous phase transformation of ZIF-67@polymer core-shell structure to Co nanoparticles@polymer yolk-shell structure under mild solvent hydrothermal conditions. Coating resin polymer on the surface of ZIF-67 creates a “nanoreactor” to complete the phase transformation. After pyrolysis in nitrogen atmosphere, Co–N–doped carbon materials are achieved. This unique synthetic strategy empowered the rational design of Co–N–doped carbon materials with large surface area, high graphitization as well as N dopants are all beneficial to the superb ORR activity.

2. Experimental

2.1. Materials

The following provides information on chemicals used in this work: formaldehyde (37% solution), aqueous ammonia (25% solution), ethanol (95%–100%), 3-aminophenol (99%), methanol (99%), cobalt nitrate hexahydrate (Co(NO3)2·6H2O) and 2-methylimidazole were purchased from Sigma-Aldrich and used as received without any further purification. Washing was achieved with ultrapure water and reagent grade ethanol where required. Ultrapure water was used for solution preparations.

2.2. Synthesis of ZIF-67

Typically, Co(NO3)2·6H2O (0.87 g) was dissolved in 30 mL of methanol to form a solution. 20 mL of methanol containing 2-methylimidazole (1.97 g) was poured into Co(NO3)2 solution. The mixture was kept stirring at room temperature for 24 h. The resulting white precipitates were collected by centrifuging, washed with methanol three times, and finally dried at 100 °C overnight.

2.3. Synthesis of Co nanoparticles@polymer (CP)

In a typical synthesis, CTAB (0.1 g) was dissolved in a mixture of water (20 mL) and ethanol (8 mL). Then, an aqueous solution of ammonia (NH4OH, 0.2 mL, 25 wt%) was added and stirred at room temperature for 0.5 h, followed by addition of 0.1 g ZIF-8. After stirring for 0.5 h, 3-aminophenol (0.08 g) was added into that suspension. After stirring for an additional 30 min, a solution of formaldehyde (0.112 mL) was added. The mixture was stirred for 24 h at room temperature and subsequently heated for 24 h at 100 °C under static conditions in a Teflon-lined autoclave. The solid products were recovered by centrifugation and dried at 100 °C for 24 h.

2.4. Synthesis of Co–N–C samples

The ZIF-67@polymers were carbonized in flowing N2 in a tube furnace using a heating rate of 1 °C min−1 up to 350 °C, dwell for 2 h, and resuming heating rate at 1 °C min−1 up to different temperatures (700, 800, and 900 °C) and dwell for 4 h. The final products were denoted as Co–N–C–X (X represents pyrolysis temperature of 700, 800, and 900 °C, respectively).

2.5. Oxygen reduction reaction (ORR) performance test

Catalyst inks were prepared by ultrasonically dispersing catalyst (4.0 mg) in a solution containing 0.5 mL of ethanol isopropanol (1:1 vol) and 16 μL of 5 wt% Nafion solution (Alfa Aesar). The dispersion was sonicated for 1 h. Then, 5 μL of the ink was dropped onto a rotating disk electrode (RDE, 5 mm diameter, 0.196 cm2 geometric surface areas). Cyclic voltammetry (CV) data were recorded on an electrochemical workstation (Electrochemical Workstation ZENNIUM, USA) equipped with a three-electrode cell system. An Ag/AgCl electrode (saturated KCl solution, 3.5 mol/L) and a Pt wire were used as the reference electrode and the counter electrode, respectively. The electrolyte was 0.1 M KOH aqueous solution. CV curves were collected at a scan rate of 50 mV s−1 at room temperature. RDE measurements were conducted at a scan rate of 10 mV s−1 and rotating rates under different disk rotation rates of 400, 625, 900, 1225, 1600 and 2025 rpm at room temperature. All the potentials in this work were recorded with respect to the Ag/AgCl reference electrode. The electrode transfer number (n) per oxygen molecule was calculated by the Roughtey-Levich (K–L) equation:

\[
J = J_k^{-1} + \frac{(Bo^{1/2})^{-1}}{B} = \frac{nFkC_0}{v}
\]

where J is the measured current density during ORR, Jk is the kinetic current density, ω is the electrode rotating angular velocity (rpm), B is the slope of K–L plots, n represents the electron transfer number per oxygen molecule, F is the Faraday constant (96,485 C mol−1), Do is the diffusion coefficient of O2 in 0.1 M KOH (1.9 × 10−5 cm2 s−1), v is the kinetic viscosity (0.01 cm2 s−1), C0 is the bulk concentration of O2 (1.2 × 10−3 mol L−1).

2.6. Materials characterization

The sample morphology was characterized by using a transmission electron microscope (TEM, JEOL EM-2100), High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) imaging and element mapping were carried out using a FEI Titan G2 80-200 TEM/STEM with ChemiSTEM Technology operating at 200 kV. The elemental maps were obtained by energy dispersive X-ray spectroscopy using the Super-X detector on the Titan with a probe size ~1 nm and a probe current of ~0.4 nA. Powder X-ray powder diffraction (XRD) analysis was performed on an X-ray diffractometer (Bruker D8 Advance) using Cu Kα radiation at 40 kV and 30 mA. The BET specific surface area and single-point pore volume were obtained from nitrogen adsorption isotherms measured at k −196°C using a nitrogen sorption instrument (Micromeritics TriStar II Surface Area and Porosity Analyzer). Prior to nitrogen adsorption measurements, the samples were degassed at 250°C overnight. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD spectrometer.

3. Results and discussion

The synthesis strategy of yolk-shell structured Co nanoparticles@polymer (CP) is schematically depicted in Scheme 1. Two methanol solution of zinc nitrate hexahydrate (Co(NO3)2·6H2O) and 2-methylimidazole (HMI) are mixed and stirred for 24 h at room temperature to generate uniform ZIF-8 particles as templates.
In the first step, the extended Stober coating method is used to deposit polymer layer on the surface of ZIF-67. After generating ZIF-67@polymer core-shell structures, hydrothermal treatment is used to prepare yolk-shell structured Co nanoparticles@polymer. Carbonization of these yolk-shell structured CP in nitrogen atmosphere can generate Co-N-C samples.

The structures formed at different procedures are characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM) and Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) imaging and element mapping. The XRD pattern of ZIF-67 crystals (Fig. S1) agrees well with previous reports [444] and the TEM image of ZIF-67 particles (Fig. 1(a)) shows a polyhedral structure with a smooth surface. Fig. S2 reveals that polymer layer has been successfully coated on the surface of ZIF-67 nanoparticles. After hydrothermal treatment for 24 h, yolk-shell structured materials with shell thickness about 81 nm are achieved. Noticeably, it is also very interesting to find that needle-like Co nanoparticles are generated in the inside of hollow polymer shell. The scanning transmission electron microscopy (STEM) and the corresponding energy dispersive X-ray spectroscopy (EDS) elemental mapping (Fig. 1(d)) are obtained to identify the distribution of nitrogen, carbon, cobalt and oxygen in this hollow structure. Elemental carbon and nitrogen are homogenously distributed in the carbon shell, but cobalt and most oxygen atoms are only present in the core materials, confirming that elemental cobalt were confined in the hollow carbon shell.

After calcination of CP in the flowing nitrogen at 700°C, a stacked carbon structure with the deposition of cobalt-related nanoparticles can be observed (as shown in Fig. 2(a)). As shown in HRTEM image in Fig. 2(b), tiny Co nanoparticles were wrapped in the graphitic carbon layers rather than exposed on the outer surface. The interlayer distance of 0.34 nm is determined, corresponding to the (002) plane of graphitic carbon [45]. Fig. 2(b) also displays clear lattice fringes with d-spacing of about 0.20 nm, which is attributed to the (111) crystal plane of cubic Co metal, indicating a high degree of crystallinity. The scanning transmission electron microscopy (STEM) and the corresponding energy dispersive X-ray spectroscopy (EDS) elemental mapping (Fig. 2(c)) are obtained to identify the distribution of nitrogen, carbon, oxygen and cobalt. As shown in Fig. 2(c), nitrogen and oxygen atoms are homogeneously distributed in the graphitic carbon structure and cobalt nanoparticles are wrapped with elemental oxygen.

The compositions of Co–N–C samples are shown in the X-ray diffraction (XRD) patterns in Fig. 3(a). The diffraction peaks at 44.3°, 51.6° and 76.1° can be ascribed to cubic cobalt metal (ICPDS No.15-0806). By using the Scherrer equation for the cobalt (111) peak in the XRD patterns, approximate cobalt particle size was calculated to be 42, 48 and 68 nm for Co–N–C-700, Co–N–C-800 and Co–N–C-900. This indicates that higher temperatures resulted in severe Co aggregation. The surface areas of these as-prepared nanoparticles were determined by nitrogen adsorption measurements, and the results are shown in Fig. 3(b) and Table S1. As shown in Fig. 3(b), the nitrogen adsorption isotherms of the three samples were type IV with a distinct H3 hysteresis loop. As presented in Table S1, the Brunauer–Emmett–Teller (BET) surface area and the pore volume obtained on the basis of the adsorption isotherm for Co–N–C-700 were 514 m² g⁻¹ and 0.57 cm³ g⁻¹. After elevating the calcination temperatures, the BET surface area decreased with the growth of pore volume, 498 m² g⁻¹ and 0.90 cm³ g⁻¹ for Co–N–C-800, 472 m² g⁻¹ and 0.83 cm³ g⁻¹ for Co–N–C-900, respectively. This tendency demonstrated that the specific surface areas are associated with the increase of calcination temperatures that could not only control the cobalt nanoparticle size but also regulate the specific surface area of the final products. It also indicates that the as-prepared Co–N–C samples possess abundant porous channels ensuring high permeation and mass transfer rates for species involved in a catalytic reaction. In addition, analysis of N2 adsorption-desorption isotherm (Fig. 3(b)) measured for the Co–N–C composites indicates the presence of mesopores, which is confirmed by Barrett–Joyner–Halenda (BJH) calculation of the pore size distribution with peak centered at 3.9 nm (Fig. S3).

X-ray photoelectron spectroscopy (XPS) measurement is performed to investigate the chemical composition and the content of nitrogen in the Co–N–C samples. The XPS patterns of Co–N–C-700, Co–N–C-800 and Co–N–C-900 exhibit four typical peaks for C 1s, N 1s, O 1s and Co 2p on the survey spectrum (Figs. S4a-S6a) and their corresponding contents of each element have been
shown in Table S2. It is found that with the increasing calcination temperature the nitrogen content in Co-N-C samples was reduced, which was attributed to the loss of unstable nitrogen. The symmetric C1s peaks for the Co–N–C samples (Figs. S4b–S6b) were centered at approximately 284.5 eV, which can be attributed to sp$^2$ graphitic carbon. After deconvolution, six peaks at 779.4, 779.9, 788.2, 786.1, 794.5, 795.0 and 803.7 eV are displayed in the high-resolution Co 2p spectrum of Co–N–C-700, Co–N–C-800 and Co–N–C-900 (Fig. 3(c)). Among them, the peaks at 779.4 and 779.9 eV are corresponded to the binding energies of the 2p$_{3/2}$ orbitals of Co$^{2+}$ species and the peak at 794.5 and 795.0 eV can be ascribed to the 2p$_{1/2}$ orbitals of Co$^{3+}$ species [46]. The intense peaks at 788.2 and 803.7 eV are satellite peaks that can be ascribed to the shakeup excitation of the high-spin Co$^{2+}$ ions [47]. The presence
of Co\(^{2+}\) and Co\(^{3+}\) may derive from the surface oxidation of the Co metal deposits exposing to air. Furthermore, Co\(_2\)O\(_3\) and CoO are not observed in the XRD pattern of Co-N-C-700 as shown earlier in Fig. 3(a). The inability of XRD to detect Co\(_2\)O\(_3\) and CoO is likely to be resulted from the resolution of the technique providing information mainly on the bulk particle and not the surface [48]. The XPS high resolution N 1s scan (Fig. 3(d)) displays four overlapping N 1s peaks corresponding to pyridinic nitrogen (398.2 eV), pyrrolic nitrogen (400.0 eV), quaternary nitrogen (400.9 eV) and N-oxide (403.4 eV) [49] and their corresponding relative concentrations for Co-N-C-700, Co-N-C-800 and Co-N-C-900 are shown in Table S3. Generally, pyridinic-N and pyrrolic-N can be considered as metal-coordination sites due to their lone-pair electrons, whereas pyridinic-N and quaternary-N are responsible for ORR [50,51]. Considering the XRD, TEM and XPS results together, it appears the cobalt nanoparticles containing cobalt metal crystallites with an oxidized shell and/or smaller (or amorphous) cobalt-oxide deposits appear on the surface of graphitic carbons. The high surface area and pore structure of Co–N–C nanoparticles is expected to be beneficial for fast mass transfer processes and facile access to active sites. To confirm this, the electrocatalytic activity of Co–N–C-700 was first studied by cyclic voltammetry (CV) in both N\(_2\) and O\(_2\) saturated 0.1 M KOH electrolyte at a scan rate of 50 mV s\(^{-1}\). As presented in Fig. 4(a), no redox peaks can be observed for Co–N–C-700 in the range −1.0–0.2 V in the N\(_2\)-saturated condition. However, when it is tested in O\(_2\)-saturated electrolyte, a well-defined oxygen reduction peak at −0.19 V was shown, indicating a good ORR electrocatalytic activity. To further investigate the reaction kinetics, rotating disk electrode (RDE) measurements with rotating speeds ranging from 400 to 2025 rpm were conducted (Fig. 4(b)). As revealed from their corresponding Koutecky-Levich plots in Fig. 4(c), the calculated electron-transfer number (n) on per O\(_2\) molecule is 3.7, presenting an effective 4-electron transfer pathway. It is also worth-mentioning that RDE measurements of Co–N–C-800 and Co–N–C-900 in Figs. S7 and S8 also reveal a 4-electron transfer process. The calcination temperature is one of the most significant synthetic parameters for Co–N–C electrocatalysts. The electrocatalytic behavior of Co–N–C samples prepared at different calcination temperatures was compared with RDE experiments shown in Fig. 4(d). The Co–N–C-900 presented the best ORR catalytic activity among the samples prepared. The half-wave potential (E\(_{1/2}\)) and the diffusion-limited current density (−0.17 V and 5.2 mA cm\(^{-2}\)) of Co–N–C-800 were superior to Co–N–C-800 (−0.19 V and 3.6 mA cm\(^{-2}\)) and Co–N–C-700 (−0.17 V and

![Fig. 4. Electrochemical characterizations of Co–N–C nanoparticle as an electrocatalyst for ORR. (a) CV curves of Co–N–C-700 in N\(_2\)-saturated and O\(_2\)-saturated 0.1 M KOH solution with a sweep rate of 50 mV s\(^{-1}\). (b) RDE polarization curves of Co–N–C-700 in O\(_2\)-saturated 0.1 M KOH solution with a sweep rate of 10 mV s\(^{-1}\) at different rotating speeds ranging from 400 to 2025 rpm. (c) The corresponding Koutecky-Levich plots (J\(^{-1}\) vs. \(ω^{-1/2}\)) of Co–N–C-700 at different potentials from −0.2 to −0.6 V from the polarization curves. (d) LSV curves for Co–N–C-700, Co–N–C-800 and Co–N–C-900 at an RDE rotation rate of 1600 rpm with a scan rate of 10 mV s\(^{-1}\).]
3.7 mA cm⁻²). The Tafel slope of Co-N-C-900 (71 mV decade⁻¹) at low over potential was apparently smaller than that of Co–N–C-800 (79 mV decade⁻¹) and Co–N–C-700 (76 mV decade⁻¹) (Fig. S9). The relatively lower tafel slope value of Co–N–C-900 reveals more favorable kinetics and also indicates the good chemical and electronic coupling among Co–N–C nanoparticles.

It is worth-mentioning that the content of nitrogen in carbon materials especially the portion of pyridinic and quaternary N plays an important role in promoting the electrocatalytic reaction in ORR [52,53]. XPS results (Fig. S10a and Table S2) illustrate a decrease of nitrogen and cobalt content in Co–N–C samples with increasing calcination temperature. Fig. S10(b) shows the content difference of pyridinic N, pyrrolic N, quaternary N atoms, and N-oxide obtained from the deconvolution of the high resolution of N 1s spectra and atomic percentage from the full survey. It is found that the highest amount of pyridinic N was observed within Co–N–C-700 sample and quaternary N was observed on Co–N–C-900 sample catalyst, which is responsible for ORR activity [54,55]. This agrees well with that Co–N–C-700 and Co–N–C-900 had superior electrochemical activity than Co–N–C-800. Higher percentages of quaternary N and N-oxide were detected using relatively high temperatures, indicating that more pyridinic and pyrrolic N are transformed into quaternary N as the temperature increases. In addition to the nitrogen contents in the Co–N–C nanoparticles, large BET surface area, high porosity and graphitization degree can contribute to the enhanced excellent ORR activity. More active sites can be exposed through tuning the porosity for carbon spheres, which benefits for the reactants transfer to active sites and further for the improvement of the ORR activity [36]. As shown in Fig. 3(b) and Table S1, the pore volume of Co–N–C-900 is significantly higher than that of Co–N–C-700 with comparable surface area, revealing an increased ORR activity. This also agrees well with the highest degree of graphitization among the three samples, which is proved from the XRD patterns (Fig. 3(a)) that Co–N–C-900 presents the highest intensity of broad peak at 26° indexed to the (002) plane of the graphitic carbon. Therefore, the best cat-

4. Conclusions

In summary, we have developed a facile method to prepare a new family of Co–N–C porous nanocomposite by pyrolysis of yolk-shell structured Co nanoparticles@polymer. Novel yolk-shell structured Co nanoparticles@polymer was prepared through coating polymer on the surface of ZIF-67 and the following hydrother-

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Supplementary materials

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