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Paper-derived cobalt and nitrogen co-doped carbon nanotube@porous carbon as a nonprecious metal electrocatalyst for the oxygen reduction reaction

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ABSTRACT

The oxygen reduction reaction (ORR) is a vitally important process in fuel cells. The development of high-performance and low-cost ORR electrocatalysts with outstanding stability is essential for the commercialization of the electrochemical energy technology. Herein, we report a facile synthesis of cobalt (Co) and nitrogen (N) co-doped carbon nanotube@porous carbon (Co/N/CNT@PC-800) electrocatalyst through a one-step pyrolysis of waste paper, dicyandiamide, and cobalt(II) acetylacetonate. The surface of the hierarchical porous carbon supported a large number of carbon nanotubes (CNTs), which were derived from dicyandiamide through the catalysis of Co. The addition of Co resulted in the formation of a hierarchical micro/mesoporous structure, which was beneficial for the exposure of active sites and rapid transportation of ORR-relevant species (O_2 , H^+ , OH^- , and H_2O). The doped N and Co formed more active sites to enhance the ORR activity of the electrocatalyst. The Co/N/CNT@PC-800 material exhibited optimal ORR performance with an onset potential of 0.005 V vs. Ag/AgCl and a half-wave potential of -0.173 V vs. Ag/AgCl. Meanwhile, the electrocatalyst showed an excellent methanol tolerance and a long-term operational durability than that of Pt/C, as well as a quasi-four-electron reaction pathway. The low-cost and simple synthesis approach makes the Co/N/CNT@PC-800 a prospective electrocatalyst for the ORR. Furthermore, this work provides an alternative approach for exploring the use of biomass-derived electrocatalysts for renewable energy applications.

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1. Introduction

Fuel cells are one of the most promising energy conversion devices for providing sustainable and clean energy [1,2]. The

oxygen reduction reaction (ORR) is the cathode reaction in fuel cells and is usually catalyzed by precious metals, especially by state-of-the-art platinum (Pt)-based catalysts, because of their excellent catalytic performance [3]. However, the Pt materials

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are expensive and suffer from limited natural reserves, sluggish kinetics, poor durability, the crossover effect, and low tolerance to methanol, which pose a key obstacle to its development and commercialization [4–7]. Therefore, the development of low-cost, high-performance non-Pt catalysts to replace Pt-based catalysts is considered as one of the best ways to achieve large-scale commercialization of fuel cells.

To endow non-Pt catalysts with superior ORR performance, various carbon-based materials are a great choice. Carbon-based materials have some unmatched versatility for electrocatalysis including good electrical conductivity, chemical inertness, versatile morphology, and large surface area. Various carbon-based materials have been extensively applied for the ORR such as graphene [8], carbon nanotubes (CNTs) [9], and carbon microspheres [10]. However, pure carbon materials have few active sites and display poor ORR activity. Numerous studies have demonstrated that the doping of heteroatoms (B [11,12], N [13,14], P [15,16], S [17,18]) within the skeleton of carbon materials can change their electron donor properties and form active sites to boost the ORR [19,20]. Specifically, N-doped carbon materials with unique structures, favorable flexibility, and excellent mechanical and electrochemical properties have been widely used as effective electrocatalysts for the ORR [21]. In N-modified carbon materials, the nitrogen atoms have a higher electronegativity than that of the carbon atoms. The electron density of the carbon atoms adjacent to the nitrogen atom is lowered, which favors the dissociative chemisorption of oxygen [22]. Furthermore, the earth-abundant transition metals (Fe [23], Co [24], Ni [25], Cu [26]) have also been introduced to enhance ORR activity, which could immobilize the dissociative oxygen species and promote electrical conductivity [23,27]. In particular, transition metals (such as Co) in N-doped carbon can effectively improve the ORR properties by constructing Co–N_x active sites [28]. Cao *et al.* [29] synthesized Co and N co-doped bamboo-like CNTs (NBCNT), which showed an enhanced ORR performance compared with individual Co- or N-doped materials. The synergistic effect of the co-doped Co and N promoted the ORR process.

Recently, carbon-based materials derived from carbon-enriched biomass (seaweed [30], fermented rice [31], typha orientalis [32]) have also been widely exploited for the ORR. Biomass is sustainable, renewable, ecofriendly, cheap, and ubiquitous in nature. All these merits imply that biomass is a potential candidate for the ORR for large-scale applications. Paper is one of the most common biomass-derived materials used in daily human life, but its recycling rate is still very low. Wei *et al.* [33] have prepared Fe-based N-doped carbon materials as ORR catalysts using tissue and filter paper. Carbon materials prepared from waste paper have a large specific surface area. The large specific surface area is favorable for the transmission of ORR-related species (O₂, H⁺, OH[−], and H₂O) and accelerates the reaction rate. Furthermore, it is an environmentally friendly process, which would not only reduce the cost but would also be conducive to large-scale preparation.

Herein, we designed a readily scalable approach for the fabrication of Co and N co-doped porous carbon (Co/N/CNT@PC-800) electrocatalysts, which were prepared

through a simple annealing of a mixture of waste paper, dicyandiamide, and cobalt(II) acetylacetonate at 800 °C. Because of the catalytic effect of cobalt, the Co/N/CNT@PC-800 catalyst with a porous structure had many nanotubes on its surface. The numerous micropores and mesopores are beneficial for exposure of the active sites and the transportation of ORR-relevant species. The Co and N co-doped carbon materials can generate more active sites to enhance the ORR activity. For these reasons, the low-cost catalyst exhibited good ORR performance with a quasi-four-electron reaction pathway, good stability, and methanol tolerance in an alkaline medium. This work will open up a new way to utilize biomass waste to obtain value-added materials through an economic and environmentally friendly method.

2. Experimental

2.1. Chemicals

Cobalt(II) acetylacetonate (99%), dicyandiamide, and methanol were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Nafion (10% wt%) was obtained from Sigma-Aldrich (Missouri, USA). Commercial 20 wt% Pt/C was obtained from Alfa Aesar (China) Chemicals Co., Ltd. (Shanghai, China). The waste paper obtained from our laboratory. (Zhenjiang, China). All these chemicals were used as delivered without further treatment.

2.2. Material synthesis

The shredded paper was washed with an appropriate amount of distilled water to remove the impurities. Then, the paper pulp was filtered by suction and vacuum dried at 60 °C before further use.

The synthesis of Co/N/CNT@PC-800 is shown in Scheme 1. In a typical synthesis, 2.0 g dicyandiamide and 0.5 g of cobalt(II) acetylacetonate were dissolved in 50 mL methanol and defined as solution A. Then, 1.0 g pretreated paper was distributed in 50 mL of distilled water to obtain mixture B. Solution A was added into mixture B and then stirred for 12 h. The intermediate product was dried in an oven. Afterwards, the obtained dark-green material was ground and placed into a ceramic boat. The material was heated to 500 °C for 2 h with a ramp rate of 5 °C min^{−1} under an argon atmosphere in a tubular furnace. Then, the temperature was raised to 800 °C and main-

Scheme 1. Schematic of the synthesis process for the Co/N/CNT@PC-800.

tained for 2 h. Finally, the carbon composite was immersed in 6 mol L⁻¹ HCl for 12 h to remove any unstable and inactive species.

C-800 was fabricated by using the same procedure as that for Co/N/CNT@PC-800 without adding cobalt(II) acetate and dicyandiamide.

N/C-800 was fabricated by using the same procedure as that for Co/N/CNT@PC-800 without adding cobalt(II) acetate.

Co/PC-800 was fabricated by using the same procedure for Co/N/CNT@PC-800 without adding dicyandiamide.

2.4. Material characterization

The morphology and microstructure of the materials were verified by scanning electron microscopy (SEM; JEOLJSM-7001F) and transmission electron microscopy (TEM; JEOLJEM-2010). The elemental composition of the electrocatalysts was determined by element mapping (JSM-6010PLUS/LA). The crystalline structures of the products were recorded with a Shimadzu XRD-6000 X-ray diffractometer in the 2θ range of 10°–80° with Cu Kα radiation at room temperature (λ = 0.15418 nm). The surface states of the samples were analyzed by X-ray photoelectron spectroscopy (XPS) with a monochromatic Mg Kα source operated at 20 kV. The specific surface area and pore size distribution of the products were measured by adsorption–desorption isotherms of N₂ on a TriStar II 3020 surface area and porosity analyzer (Micromeritics Instrument Corporation, USA). The Raman spectra were obtained with a micro Raman spectrometer (Renishaw Invia) in a backscattering geometry with a 532 nm laser as the excitation source.

2.5. Electrochemical measurements

The ORR experiments were performed in a three-electrode cell connected to an electrochemical analyzer (CHI 760E) at room temperature. A rotating disk electrode (RDE, 3 mm diameter), Pt wire, and Ag/AgCl electrodes were used as working electrode, counter electrode, and reference electrode, respectively. 4 mg of prepared catalyst was distributed in 1 mL mixed solvent (2-propanol/water = 1:3 (v/v)) with 15 μL of 10% Nafion. 20 μL of the catalyst ink was loaded on the surface of the RDE and dried at room temperature. Cyclic voltammetry (CV) measurements were recorded at 50 mV s⁻¹ from 0.2 to -0.8 V vs. Ag/AgCl. Linear sweep voltammetry (LSV) measurements were performed at a rotating speed from 400 to 2500 r min⁻¹ at 5 mV s⁻¹ in 0.1 mol L⁻¹ KOH solution. O₂ or N₂ were introduced into the electrolyte 30 min before the test.

Koutecky-Levich (K-L) plots were analyzed at different rotation speeds of the ORR polarization curves. The electron transfer number (*n*) was calculated by using the K-L equation [34]:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_L} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}} \quad (1)$$

$$B = 0.62nFC_{O_2}D_{O_2}^{2/3}\nu^{-1/6}, J_K = nFkC_{O_2} \quad (2)$$

$$J_K = nFkC_{O_2} \quad (3)$$

in which *J* is the measured current density, *J_k* and *J_L* are the kinetic- and diffusion-limiting current densities, respectively. *B* is the Levich slope, ω is the angular velocity, *F* is the Faraday constant (*F* = 96485 C mol⁻¹), *C_{O₂}* is the concentration of dissolved O₂ (*C_{O₂}* = 1.2 × 10⁻⁶ mol cm⁻³), *D_{O₂}* is the diffusion coefficient of O₂ in 0.1 mol L⁻¹ KOH (*D_{O₂}* = 1.9 × 10⁻⁵ cm² s⁻¹), ν is the kinetic viscosity of the electrolyte (ν = 0.01 cm² s⁻¹), and *k* is the electron transfer rate constant.

Rotating ring-disk electrode (RRDE) measurements: In the RRDE system, the rotating speed of the working electrode was fixed at 1600 r min⁻¹ with a scan rate of 5 mV s⁻¹. The potential of the ring electrode was set to 0.5 V vs. Ag/AgCl. The electron transfer number and hydrogen peroxide yields were calculated by the following equations [35]:

$$n = \frac{4I_D}{I_D + I_R / N} \quad (4)$$

$$\%(\text{H}_2\text{O}_2) = 200 \times \frac{I_R / N}{I_D + I_R / N} \quad (5)$$

in which *I_D* and *I_R* are the disk and ring currents and *N* is the collection efficiency, which was reported to be 42.4% by the manufacturer.

3. Results and discussion

The SEM and TEM images were used to elucidate the morphology and microstructure of the prepared samples. As shown in Fig. S1(a) and (b), C-800 and N/C-800 exhibited a similar microstructure with a wrinkled surface. This indicated that the introduction of dicyandiamide did not change the original microstructure of the waste paper. After the addition of Co, many pore structures appeared on the surface of the Co/PC-800 catalyst (Fig. S1(c) and (d)). Therefore, the doped Co played a critical role in the formation of the porous structures. As shown in Fig. 1(a) and (b), the surface of the Co/N/CNT@PC-800 catalyst had a porous structure and many carbon nanotubes with diameters of approximately 20 nm. The synergetic coupling of doped Co and N was essential for the formation of carbon nanotubes [29]. As shown in Fig. 1(c) and (d),

Fig. 1. SEM (a, b) and TEM (c, d) images of the Co/N/CNT@PC-800 catalyst.

Co/N/CNT@PC-800 had an obvious hollow tube structure and some residual Co nanoparticles were wrapped in the carbon layer and CNTs. Moreover, the element mapping ascertained that both Co and N were uniformly distributed in the Co/N/CNT@PC-800 catalyst (Fig. S2).

The crystal structure of the C-800, N/C-800, Co/PC-800 and Co/N/CNT@PC-800 catalysts was further characterized by powder X-ray diffraction (XRD) patterns (Fig. 2(a)). The well-defined diffraction peaks of the XRD patterns of the Co/N/CNT@PC-800 and Co/PC-800 catalysts at approximately $2\theta = 44.2^\circ, 51.5^\circ, 75.9^\circ$ were assigned to the (111), (200), (200) plane of Co [28]. All the carbon materials showed a sharp peak corresponding to the (002) plane of the graphite structure. In stark contrast, the C-800 catalyst displayed a broad peak at approximately 23.7° , which signified a low graphitization degree in this sample [36]. Raman spectra were obtained to further analyze the graphitization degree and defects of these

catalysts (Fig. 2(b)). The peaks at approximately 1350 cm^{-1} (D-band), 1580 cm^{-1} (G-band), and 2680 cm^{-1} (2D-band) in the Raman spectra indicated a typical characteristic signature of crystalline graphite [37,38]. The G-band indicated the presence of sp^2 -hybridized carbon atoms. The presence of defects in the doped carbon materials was indicated by the D-band [39]. The relative intensities of the G-band (I_G) and D-band (I_D) were used to study the characteristics of the carbon materials. A lower I_D/I_G ratio indicates a higher degree of graphitization of carbon materials [40]. As displayed in Fig. 2(b), the I_D/I_G values of the C-800, N/C-800, Co/PC-800, and Co/N/CNT@PC-800 catalysts were 0.98, 1.02, 1.10, and 1.04, respectively. The increase in defects and disorder for N/C-800, Co/PC-800, and Co/N/CNT@PC-800 after Co or N doping was clearly observed. The I_D/I_G ratio of the Co/N/CNT@PC-800 catalyst was lower than that of Co/PC-800. This may be owing to the formation of a large number of carbon nanotubes, which further improved

Fig. 2. XRD patterns (a) and Raman spectra (b) of C-800, N/C-800, Co/PC-800 and Co/N/CNT@PC-800 catalysts.

Fig. 3. (a) Wide XPS survey of Co/N/CNT@PC-800. (b) Element contents for C, N, O, Co from XPS data. High-resolution spectra of N 1s (c), C 1s (e), Co 2p (f). The proportion of N with different chemical states (d).

the graphitization degree.

XPS measurements were performed to further elaborate the doped element and bonding states. The survey XPS spectrum of the Co/N/CNT@PC-800 catalyst demonstrated the presence of C (89.75 at%), N (4.43 at%), O (5.6 at%), Co (0.22 at%) (Fig. 3(a) and (b)). The high-resolution N 1s spectrum showed four peaks at 398.45 ± 0.3 , 399.53 ± 0.3 , 400.73 ± 0.3 , and 402.50 ± 0.3 eV, which were pyridinic-N (42.15%), pyrrolic-N (12.79%), graphitic-N (32.70%), and oxidized-N (12.36%), respectively (Fig. 3(c), 3(d) and S3). This suggested that pyridinic-N and graphitic-N were the dominant species, which has been demonstrated to boost O₂ reduction [41]. As shown in Fig. 3(e), there were four types of bonding states in the C 1s spectrum: C=C, C=N&C=O, C=O&C=N, and O=C=O, which indicated the existence of N and O heteroatoms in the hybrids. The high-resolution spectrum of Co 2p_{3/2} and Co 2p_{1/2} can be fitted with three components in accordance with Co⁽⁰⁾, Co-N_x and the shake-up peaks (Fig. 3(f)). The peaks at 780.8 and 796.7 eV were assigned to the zerovalent state cobalt, which was consistent with the results of the XRD. The peak at 779.5 eV was the Co-N_x peak, which demonstrated the existence of a coordination bond between Co and N atoms [28].

The specific surface area and pore size of the hybrids were determined by the nitrogen adsorption isotherms. The surface area of the Co/N/CNT@PC-800, Co/PC-800, N/C-800, and C-800 catalysts was 421.146, 304.801, 358.220 and 476.675 m² g⁻¹ respectively (Fig. 4 and Table S1). The type IV isotherm with

a distinct hysteresis loop in the medium- and high-pressure regions ($P/P_0 = 0.4\text{--}1.0$) implied the presence of multiple micropores and mesopores in the structure of the prepared catalysts. The pore size distributions diagrams (inset) indicated that the size of the micro/mesopores was between 1 and 10 nm. The number of mesopores increased after doping of Co. The results also confirmed the appearance of the porous structure in the SEM patterns after the doping of Co, which indicated that the Co was beneficial for the formation of a porous structure. It has been reported that a hierarchical porosity is favorable for mass transfer of ORR-related species and the formation of abundant active sites for ORR [42].

The ORR activities of the Co/N/CNT@PC-800, Co/PC-800, N/C-800 and C-800 catalysts were investigated by rotating disk electrode measurements. Fig. S4(a) and (b) showed the cyclic voltammogram tests of the Co/N/CNT@PC-800 and Pt/C catalysts in a O₂-saturated and N₂-saturated solution. No cathodic peaks could be observed in the N₂-saturated solution for the two samples. In contrast, when the electrolyte solution was saturated with O₂, cathodic peaks appeared for those catalysts in the CV potential range, demonstrating the ORR activity of the catalysts, which was attributed to the reduction of O₂. As presented in Fig. 5(a), Co/N/CNT@PC-800 showed a better oxygen reduction performance with a more positive onset potential, half-wave potential ($E_{1/2}$), and higher limited current density than the other three prepared materials (Table S2). Compared with the C-800 curve, the N/C-800 showed a more positive

Fig. 4. N₂ adsorption-desorption isotherms (the inset: the corresponding pore size distribution) of Co/N/CNT@PC-800 (a), Co/PC-800 (b), N/C-800 (c) and C-800 (d) catalysts.

Fig. 5. (a) Linear scan voltammograms of C-800, N/C-800, Co/PC-800, Co/N/CNT@PC-800 and Pt/C catalysts in O_2 -saturated 0.1 mol L^{-1} KOH at a rotation rate of 1600 r min^{-1} with a scan rate of 5 mV s^{-1} . (b) Electron transfer number of Co/N/CNT@PC-800 and Pt/C catalysts.

initial potential and the Co/PC-800 displayed a more positive initial potential and higher limited current density. This indicated that the N- or Co-doped carbon materials can boost the ORR properties, but the activity promotion was limited. The Co/N/CNT@PC-800 possessed optimized ORR activity than that of Co or N single-doped materials, which was owing to the synergistic interaction between both N and Co co-doped in the carbon materials. The Co/N/CNT@PC-800 catalyst showed a superior ORR performance than most catalysts derived from biomass under similar conditions (Table S2). The (K-L) plots of

the Co/N/CNT@PC-800 and Pt/C catalysts were obtained from the LSV curves at different rotation speeds; both showed a good linearity (Fig. S5(c) and (d)). The electron transfer number of the Co/N/CNT@PC-800 catalyst was calculated to be approximately 3.4–3.5 at potentials ranging from -0.4 to -0.8 V (Fig. 5(b)). The result suggested that the Co/N/CNT@PC-800 exhibited a quasi-four-electron pathway in the ORR process. All the results indicated that both the Co- and the N-functionalized carbon species were essential for the active site in M-N_x/C type catalysts [43].

Fig. 6. (a, b) Cyclic voltammograms of Co/N/CNT@PC-800 and Pt/C catalysts in O_2 -saturated 0.1 mol L^{-1} KOH without any methanol and with methanol at a scan rate of 50 mV s^{-1} . (c, d) Linear scan voltammograms (the inset: cyclic voltammograms) of Co/N/CNT@PC-800 and Pt/C catalysts for ORR in O_2 -saturated 0.1 mol L^{-1} KOH before and after 3000 cycles.

The tolerance to methanol and stability are significant criteria to evaluate the performance of an ORR catalyst. As shown in Fig. 6(a) and (b), after the addition of methanol (1 mol L⁻¹), the CV curve of the Pt/C catalyst clearly changed and displayed a typical inverse methanol oxidation peak. However, there was only a slight effect on the CV curve of the Co/N/CNT@PC-800 catalyst. The results showed that the Co/N/CNT@PC-800 catalyst had a tolerance to methanol. Finally, the durability tests of the Co/N/CNT@PC-800 and Pt/C catalysts were recorded by performing 3000 cycles of cyclic voltammogram measurements in O₂-saturated 0.1 mol L⁻¹ KOH with a scan rate of 50 mV s⁻¹. The Co/N/CNT@PC-800 catalyst could maintain high activity with a limited current density loss of 0.27 mA cm⁻² and there was no significant change in the initial potential (Fig. 6(c)). Nevertheless, the limited current density of the Pt/C catalyst showed a decrease of approximately 0.80 mA cm⁻² at -0.8 V, and the initial potential became more negative (Fig. 6(d)). In addition, the $E_{1/2}$ of the Co/N/CNT@PC-800 catalyst showed a negative shift of 15 mV, which was much smaller than that of commercial Pt/C ($\Delta E_{1/2} = 37$ mV). As shown in the inset of Fig. 6(c), a well-defined reduction peak in the CV curves of Co/N/CNT@PC-800 was still evident after 3000 cycles. However, the peak potential of Pt/C shifted negatively from -0.138 to -0.168 V, almost 30 mV (inset of Fig. 6(d)). These results indicated that the Co/N/CNT@PC-800 demonstrated a more remarkable methanol crossover effect and long-term stability for the ORR.

To further study the ORR performance of Co/N/CNT@PC-800 in an alkaline environment, rotating ring-disk electrode (RRDE) measurements were performed to investigate the electron transfer number and H₂O₂ yield. Fig. 7 recorded the ring (Fig. 7(a)) and disk (Fig. 7(b)) currents of the Co/N/CNT@PC-800 and Pt/C catalysts. The limiting current of Co/N/CNT@PC-800 was -553 μ A at -0.8 V, which was slightly different from that of Pt/C (-625 μ A). The electron transfer number and the H₂O₂ yield was directly calculated from the disk currents and the ring currents by Eqs. (4) and (5), respectively. As shown in Fig. 7, the electron transfer number of the Co/N/CNT@PC-800 and Pt/C catalysts was approximately 3.5–3.7 and 3.8–3.9 (Fig. 7(c)), respectively. The H₂O₂ yields of the Co/N/CNT@PC-800 and Pt/C catalysts were 26.6% and 8.9%, respectively, at -0.8 V in 0.1 mol L⁻¹ KOH solution (Fig. 7(d)). All the electrochemical experiments suggested that the oxygens were directly reduced to hydroxyls through a quasi-four-electron reaction in the ORR process and the Co/N/CNT@PC-800 is a good choice as a cathode catalyst.

Based on above results, the Co/N/CNT@PC-800 catalyst showed an optimized ORR performance, which illustrated the mechanism controlling the ORR active sites in the electrocatalyst. First, doped N could improve the electron donor-acceptor properties, enhance the adsorption of dissociative oxygen, and weaken the O–O bonding [44–46]. Second, doped metal atoms can form active sites and intimate bonds (M–N_x) more efficiently and boost the ORR activity of the material [23]. Third,

Fig. 7. Ring currents (a) and disk currents (b). Electron transfer number (c) and hydrogen peroxide yield (d) during ORR process of Co/N/CNT@PC-800 and Pt/C catalysts in O₂-saturated 0.1 mol L⁻¹ KOH at a rotation rate of 1600 r min⁻¹ with a scan rate of 5 mV s⁻¹.

the Co nanoparticles also activated the protective carbon layers, which allowed the carbon layer of the outer surface to participate in the ORR process [28]. Finally, the Co nanoparticles catalyzed the dicyandiamide into CNTs on the surface of the porous carbon, affording more exposed active sites and facilitating the transportation of ORR-relevant species.

4. Conclusions

We successfully employed an uncomplicated process that effectively combines the advantages of porous carbon and biomass to obtain catalysts for the ORR. Cheap waste paper was used as carbon source, which was doped with Co and N to prepare a Co/N/CNT@PC-800 electrocatalyst. The Co and N co-doped carbon material greatly improved the ORR performance. The Co catalyzed the *in situ* formation of carbon nanotubes, which promoted the exposure of active sites. The porous carbon substrate was favorable for mass transfer. The Co/N/CNT@PC-800 catalyst exhibited excellent ORR activity, a positive half-wave potential, and a quasi-four-electron reaction pathway. The tolerance of methanol and stability of Co/N/CNT@PC-800 was also better than that of commercial Pt/C. This work will provide a new idea for the use of biomass for the synthesis of low-cost electrocatalysts with effective performance for metal-air batteries and fuel cells.

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Graphical Abstract

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Paper-derived cobalt and nitrogen co-doped carbon nanotube@porous carbon as a nonprecious metal electrocatalyst for the oxygen reduction reaction

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Paper-derived cobalt and nitrogen co-doped carbon nanotube@porous carbon was fabricated as a nonprecious metal electrocatalyst and showed excellent catalytic performance for the oxygen reduction reaction.

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非贵金属钴、氮共掺杂碳纳米管负载纸衍生多孔碳电催化剂的制备及其氧还原性能研究

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摘要: 燃料电池可以直接将化学能转化为电能, 是一种极具前景的能量转换设备。目前, 铂碳是燃料电池阴极氧还原反应(ORR)常用催化剂, 但是铂储量低、价格昂贵、稳定性差且容易受CO毒化, 极大地限制了其在燃料电池商业化中的应用。因此, 探索价格低廉、性能优越的非贵金属氧还原催化剂显得尤为重要。

大量研究发现, 碳基材料具有优越的氧还原性能和良好的电化学稳定性。同时, 自然界的生物质种类丰富, 是很好的碳基材料来源。本文选取日常生活中最常见的富碳生物质废纸作为碳源, 二氰二胺和乙酰丙酮钴分别作为氮源和钴源, 经过特定气氛下的梯度升温制得非贵金属钴、氮共掺杂碳纳米管负载多孔碳氧还原催化剂(Co/N/CNT@PC-800)。考察了杂原子N掺杂、过渡金属Co掺杂对材料形貌和性能的影响, 采用扫描电子显微镜(SEM)、透射电子显微镜(TEM)、X射线衍射(XRD)、拉曼(Raman)光谱、氮气吸附-脱附和X射线光电子能谱(XPS)等表征方法探究了Co/N/CNT@PC-800材料的组成与结构, 通过循环伏安法(CV)以及线性扫描伏安法(LSV)等电化学测试探究了其氧还原反应性能。

SEM和TEM结果表明, Co/N/CNT@PC-800材料为表面生长着大量碳纳米管的多孔碳结构。这是因为二氰二胺和钴引入后, 钴催化二氰二胺转化成碳纳米管。金属纳米粒子被封装在碳层之间和碳纳米管中而得到有效的保护, 使之不易被酸腐蚀。同时, Co和N元素可以形成更多的活性位点(Co-N_x), 增强材料ORR活性。SEM和氮气吸附-脱附结果显示, 掺杂Co后, 材料的介孔结构会进一步增加, 形成微孔/介孔结构。多孔结构可以增强ORR相关物质(O₂, H⁺, OH⁻, H₂O)的传质速率, 提升反应速率, 达到增强ORR活性的效果。除此之外, 多孔的结构也可以促进活性位点的暴露, 进而提升材料的ORR性能。XPS结果显示, Co/N/CNT@PC-800材料中N主要以吡啶氮和石墨氮两种形式存在, 而这两种类型的氮有利于促进ORR的进行。Raman光谱结果显示, 在引入N和Co元素后, 材料的缺陷结构有所增加, 因而有利于电催化氧还原反应性能的提升。

另外, LSV测试结果表明, 在引入Co或者N后, 材料催化ORR的起始电位、半波电位、极限电流密度均有小幅改善; 同

时引入Co和N后, Co/N/CNT@PC-800材料催化ORR的起始电位(0.005 V vs. Ag/AgCl)、半波电位(−0.173 V vs. Ag/AgCl)、极限电流密度(−4.117 mA cm^{−2})均有较大幅度的改善. 通过Koutecky-Levich (K-L)方程计算以及旋转环盘电极测得的氧还原极化曲线结果均表明, Co/N/CNT@PC-800材料的氧还原反应是通过准四电子反应转移路径进行. 此外, 循环(3000圈CV)稳定性测试结果证明, Co/N/CNT@PC-800材料比商业化的Pt/C具有更好的稳定性.

总之, 本文采用简单的梯度升温法制备出非贵金属钴、氮共掺杂的碳基氧还原催化剂(Co/N/CNT@PC-800), 为探索利用生物质制备电催化剂用于燃料电池提供了一种可供选择的途径.

关键词: 氧还原反应; 废纸; 生物质; 多孔碳; 钴

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