ZIF-67-aerogel-derived N-doped carbon nanotubes encapsulated with Co nanoparticles as efficient electrocatalysts

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Abstract. Electrocatalyst for oxygen reduction reaction (ORR) are essential for metal-air batteries. Herein, we design a self-catalyzed growth strategy for in-situ encapsulation of Co nanoparticles with N-doped carbon nanotubes (NCNT) on carbon aerogel (CA) (Co/NCNT/CA-1000). Using the zeolite imidazole framework (ZIF-67) as the cobalt source can catalyze the graphitization of melamine and facilitate the growth of NCNTs on the CA. Thanks to its unique structure, the Co/NCNT/CA-1000 exhibits favourable ORR properties (E_{1/2} = 0.80 V). This work offers an effective method for preparing high-active Co-based electrocatalysts and provides a foundation for the future development of electrochemical energy applications.

1 Introduction
Regenerative metal-air batteries have spurred many research in the past decades due to the high energy-conversion efficiency and environmental benignity [1]. In particular, the oxygen reduction reaction (ORR) plays the significant roles in these devices [2]. Yet the ORR with multiple electron transfer process is always inherently inevitably slow in kinetics, which demands suitable electrocatalyst to accelerate its reaction efficiency. It has been known to date that Pt/C is the most efficient electrocatalyst with excellent activity [3]. Nevertheless, the poor durability, high cost and scarcity of Pt/C remain as the primary barriers for their widespread utilization. Accordingly, the major and expected goal of researchers is to explore the low-cost, naturally abundant and high-efficiency materials.

At present, tremendous efforts have been made to seek the alternatives for Pt/C [4-5]. In this regard, Co-based catalysts have been frequently studied towards ORR because of their cost competitiveness and high catalytic properties. Unfortunately, they are not satisfactory ORR catalysts due to the fact that the easy aggregation of the Co nanoparticles and poor corrosion resistance [6]. To tackle the problems, an efficient solution is to encapsulate Co nanoparticles into nitrogen-doped carbon nanotubes (NCNTs) by introducing melamine containing carbon and nitrogen sources [7]. However, such simple encapsulated structures cannot avoid aggregation, which is not conducive to the long-term stability. Recently, carbon aerogel (CA) with the large specific surface area and high porosity appears to be an ideal substrate [8]. Using CA as a support can ensure a good dispersion of active materials and expose more accessible active sites.

In this report, we have successfully fabricated NCNT-encapsulated Co nanoparticles supported on CA (Co/NCNT/CA-1000) through high-temperature pyrolysis. During the process, melamine is used as the carbon and nitrogen source, while zeolite imidazole framework (ZIF-67) can be used as the cobalt source and catalyze the graphitization of melamine, thereby enabling the growth of Co nanoparticles-
encapsulated NCNTs. Co-encapsulated NCNTs can be well dispersed in CA, which can naturally enhance the conductivity. As expected, the obtained Co/NCNT/CA-1000 displays good electrocatalytic activity for ORR.

2 Experimental Section

2.1 Materials
Agarose (AG), melamine (C₃H₆N₆, 99%), 2-methylimidazole (2-MeIM, 98%) and cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 99%) were purchased from Aladdin Reagent. Pt/C (20 wt% platinum in carbon) was purchased from Shanghai Hesen Electric Co., Ltd.

2.2 Materials Characterizations
The crystal structure of Co/NCNT/CA-1000 was measured by X-ray powder diffractometer (XRD) patterns recorded on a Rigaku-Dmax2500 diffractometer. The morphology of Co/NCNT/CA-1000 was displayed by field emission scanning electron microscopy (SEM Hitachi S-4800).

2.3 Electro催化剂 Synthesis

2.3.1 Synthesis of ZIF-67
First, Co(NO₃)₂·6H₂O (0.6 g) was dispersed (40 mL methanol), while 2-MeIM was dispersed in 10 mL methanol. After ultrasonic dispersion (15 min), two types of solution were quickly mixed for 18 h. The resulting purple precipitate (ZIF-67) was washed for many times, and then dried under vacuum (60 °C).

2.3.2 Synthesis of ZIF-67/AG-A
Typically, 0.1 g ZIF-67 was added into 10 mL water with sonication until it was well dispersed. After that, 0.1 g AG was added with stirring at 65 ℃ for 4 h. After cooling down the room temperature, ZIF-67/AG hydrogel (ZIF-67/AG-L) was obtained. Then, it was freeze-dried to form ZIF-67/AG aerogel (ZIF-67/AG-A).

2.3.3 Synthesis of Co/NCNT/CA-1000
Briefly, 0.1 g melamine and 0.1 g ZIF-67/AG-A were added to an agate mortar and ground for 1 h. Then, the above mixture was carbonized at 1000 ℃ under N₂ (5 °C/min). Finally, the obtained product was named as Co/NCNT/CA-1000.

2.4 Electrochemical characterizations
The ORR catalytic activities of Co/NCNT-1000 were evaluated with a three-electrode system containing a rotating disk electrode (RDE) as working electrode, saturated calomel electrode as reference electrode, and graphene rod as counter electrode. 50 μL Nafion solution, 1 mL ethanol and 5 mg catalyst were used to prepare the working electrode (electrocatalyst ink). After that, the ultrasonically dispersed electrocatalyst ink (10 μL) was deposited on the RDE and naturally dried.

ORR measurements were performed in a O₂/N₂-saturated 0.1 M KOH solution. The scan rate are 50 mV s⁻¹ (CV) and 10 mV s⁻¹ (LSV), respectively. Moreover, the electron transfer number (n) could be calculated according to the Koutecky-Levich (K-L) equations:

\[ \frac{1}{J} = \frac{1}{J_D} + \frac{1}{J_K} = \frac{1}{(Bω)^{1/2}} + \frac{1}{(nFC_mC_{O_2})} \]  
\[ B = 0.62nFC_m(D_{O_2})^{1/2}V^{1/6} \]

The recorded potential values versus SCE were converted to a RHE scale according to the Nernst equation:

\[ E_{RHE} = E_{SCE} + 0.241 + 0.0592pH \]
Furthermore, HER tests were performed in a N2-saturated 1 M KOH solution, with a scan rate of 5 mV s\(^{-1}\) for LSV.

3 Results and discussions

The phase compositions for Co/NCNT/CA-1000 is firstly investigated by the XRD pattern. Fig. 1 shows that the peak at around 26.4° is assigned to (002) planes of graphitic carbon. Furthermore, the specific diffraction peaks are located at 44.2°, 51.5°, and 75.8°, respectively, corresponding to (111), (200), and (220) planes of Co (JCPDS card No.15-0806). Obviously, the above confirm the successful synthesis of metallic Co.

![Fig. 1. XRD pattern of Co/NCNT/CA-1000.](image)

The morphology of Co/NCNT/CA-1000 is further investigated using SEM. As shown, the obtained Co/NCNT/CA-1000 shows a large amount of interlaced NCNTs on the CA, which embedded Co nanoparticles on the top of the NCNTs (Fig. 2). Such unusual structure can well inhibit the aggregation of Co nanoparticles and the interlaced NCNTs can significantly increase the conductivity of Co/NCNT/CA-1000.

![Fig. 2. SEM image of Co/NCNT/CA-1000.](image)

Inspired by the above unusual structure, the ORR electrochemical behaviors of Co/NCNT/CA-1000 are assessed in 0.1 M KOH medium. As shown, the cyclic voltammetry (CV) measurements in O\(_2\)- and N\(_2\)- saturated electrolyte are firstly investigated in Fig. 3. The Co/NCNT/CA-1000 exhibits the intensive responses (0.79 V) during cathode scan in O\(_2\)-saturated electrolyte, revealing its inherent ORR activity. At the same time, there is no obvious reduction peak under N\(_2\) condition.
Further, the polarization curves (LSV) shows that the limited current density ($J_L$) is 4.95 mA cm$^{-2}$, and the half-wave potential ($E_{1/2}$) of Pt/C is 0.86 V. As for Co/NCNT/CA-1000, the LSV curve exhibits a $J_L$ of 4.72 mA cm$^{-2}$ and a $E_{1/2}$ of 0.80 V. It can be found that the Co/NCNT/CA-1000 exhibits ORR performance comparable to Pt/C. Such high ORR electrocatalytic activity of Co/NCNT/CA-1000 is mainly derived from the Co active material encapsulated in NCNTs and CA. Moreover, the Tafel slopes are used to evaluate the catalytic kinetics of Pt/C and Co/NCNT/CA-1000 (Fig. 5). Compared with Pt/C (64.5 mV dec$^{-1}$), the Co/NCNT/CA-1000 exhibits smaller Tafel slope of 57.4 mV dec$^{-1}$, which demonstrate its faster kinetic process.
Fig. 5. Tafel plots of Pt/C and Co/NCNT/CA-1000 for ORR.

Furthermore, the RDE tests of Co/NCNT/CA-1000 are conducted under different rotating speeds from 400 to 1600 rpm (Fig. 6a). The higher rotation speed results in the higher current density, which is due to the shorter diffusion distance of the O$_2$-saturated solution. Moreover, the K-L plots of Co/NCNT/CA-1000 are calculated using the LSV curves at different voltages (0.1-0.6 V), showing good parallelism and linearity. The result reveals the first-order reaction kinetics (Fig. 6b).

Fig. 6. (a) LSV curves of Co/NCNT/CA-1000 at different rotation rates. (b) K–L plots of Co/NCNT/CA-1000.
In addition, the calculated electron transfer number (n) is approximately 4, as shown in Fig. 7, which proves that the Co/NCNT/CA-1000 has undergone an ORR four-electron reaction.

Fig. 7. The n value of Co/NCNT/CA-1000.

Fig. 8. LSV curves of Pt/C and Co/NCNT/CA-1000 for HER.

Fig. 9. Tafel plots of Pt/C and Co/NCNT/CA-1000 for HER.
Particularly, the electrochemical behaviors of Co/NCNT/CA-1000 and Pt/C as catalysts for HER are also investigated in Fig. 8. The Co/NCNT/CA-1000 presents a small potential of 316 mV at 10 mA cm$^{-2}$, while the potentials of Pt/C (18.3 mV) are also provided for the purpose of comparison. Further, the catalytic kinetics of Co/NCNT/CA-1000 and Pt/C are evaluated using the Tafel slopes (Fig. 9). The Co/NCNT/CA-1000 (81.7 mV dec$^{-1}$) shows a Tafel slope closer to that of Pt/C (33.9 mV dec$^{-1}$), indicating that it has a good kinetic process for HER.

4 Conclusion
In summary, we develop a simple method to form Co nanoparticles encapsulated in NCNTs and CA through high-temperature calcination. The unusual encapsulation structure endows such Co-based catalyst with fast diffusion kinetics and highly electrons transport. As a result, the Co/NCNT/CA-1000 exhibits favourable catalytic activity for ORR. We believe that such eco-friendly and convenient synthetic strategy can be universally used to synthesize other Co-based electrocatalysts for wider practical applications.

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