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# Nitrogen-doped cobalt nanoparticles/nitrogen-doped plate-like ordered mesoporous carbons composites as noble-metal free electrocatalysts for oxygen reduction reaction

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## ABSTRACT

In this work, nitrogen-doped cobalt nanoparticles/nitrogen-doped plate-like ordered mesoporous carbons (N/Co/OMCs) were used as noble-metal free electrocatalysts with high catalytic efficiency. Compared with OMCs with long channel length, due to more entrances for catalytic target accessibility and a short pathway for rapid diffusion, the utilization efficiency of cobalt nanoparticles inside the plate-like OMCs with short pore length is well improved, which can take full advantage of porous structure in electrocatalysis and increase the utilization of catalysts. The active sites in N/Co/OMCs for oxygen reduction reaction (ORR) are highly exposed to oxygen molecule, which results in a high activity for ORR. By combination of the catalytic properties of nitrogen dopant, incorporation of Co nanoparticles, and structural properties of OMCs, the N/Co/plate-like OMCs are highly active noble-metal free catalysts for ORR in alkaline solution.

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## 1. Introduction

Fuel cells (FCs) are believed to be the alternative and environmentally friendly source of energy to replace fossil fuels in the future. FCs are clean and high-efficiency devices that directly convert chemical energy from a fuel into electricity through chemical reaction with oxygen ( $O_2$ ) or another oxidizing agent. Platinum (Pt)-based materials are currently the most effective catalysts for the oxygen reduction reaction (ORR) at the cathode in FCs. However, the high cost of Pt, its limited reserve in nature, poor durability, and sluggish kinetic towards ORR restricts its large-scale commercialization for the FCs technology. Thus, much effort has been put forward to replace the Pt-based materials with low cost electrocatalysts with high electrocatalytic activity, excellent selectivity, and stability. Recent effort has led to exploration of doping of heteroatom (N, B, S, P, F, Se, or halogen) into nanostructured carbon materials as a desirable alternative to replace the high cost Pt-based catalysts in FCs [1–3].

Ordered mesoporous carbons (OMCs) are kinds of nanostructured carbon materials which are regarded as suitable catalyst materials because of well-ordered pore structure, high specific pore volume, high specific surface area, and tunable pore diameter in

the mesopore range and have attracted much attention for their application in electrochemistry [4]. The well-ordered porous structure provides a favorable path for mass transport, while the high surface area and a large number of mesopores of OMCs facilitate the exposure of active sites for catalysis. Noble-metal free ORR catalysts based on OMCs templated from ordered mesoporous silica exhibited high activity towards ORR. Different heteroatom-containing precursors, including melamine-formaldehyde resin [5], ethylenediamine [6], organic dyestuff [7], polyaniline [8], pyrrole [9], and honey [10], have been used for preparation of OMCs-based ORR catalysts, which displayed much high catalytic activity with better long-term durability for ORR. In addition to ordered mesoporous silica, amorphous [11], fumed [12–14], and mono-dispersed silica [15–17] were similarly used as template for preparation of noble-metal free ORR catalysts. For example, a series of noble-metal free ORR catalysts with high porosity derived from pyrolyzed iron-containing compounds and nitrogen-containing polymeric precursors were prepared using amorphous silica as template [11]. These ORR catalysts exhibited high surface area and high performance towards ORR. In other notable studies, ORR catalysts templated from fumed silica similarly showed high activity [12–14]. Recently, mono-dispersed silica was also selected as template for preparation of nitrogen-doped ORR catalysts [15–17], which exhibited high performance for ORR. Noting the low activity of heteroatom-doped carbon materials compared to the noble metals in ORR, some researchers have studied and confirmed the introduction of transition metal into N-doped carbon is a desired way

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to promote the ORR activity efficiently [18–21]. The earlier work of metal/nitrogen/carbon (M/N/C) type electrocatalysts in 1964 identified that  $N_4$ -chelate complex with a cobalt metal center was active for ORR [18]. In the subsequent work, the Co-containing M/N/C catalysts obtained from thermal treatment of nitrogen-rich compounds and transition-metal salts had a competitive ORR performance for practical FCs applications [19–21]. Recently, many novel Co-based M/N/C catalysts, such as cobalt oxides/N-carbon nanomaterials [22–26], cobalt nanoparticles/N-carbon nanomaterials [27–29], and N-carbon shells encapsulated cobalt nanoparticles [30–32], are also interesting noble-metal free electrocatalysts displaying high ORR activities. These novel M/N/C materials have found use as heterogeneous catalysts in ORR with long-term stability and four-electron selectivity towards the ORR [3,33–38]. The synergistic catalytic effects between the N dopants and Co-based materials lead to the superior electrocatalytic performance for ORR, as summarized in recent reviews [1–3,39–41]. Notably, noble-metal free ORR electrocatalysts treated by ammonia gas exhibited interestingly high electrocatalytic activity for the ORR [42–56]. Inspired by capability of M/N/C for efficiently catalyzing ORR, researchers quickly identified that N/M/OMCs composites are good alternative catalysts for ORR in hope of replacing Pt. For example, in 2013, Kong et al. found that N/Fe/OMCs prepared by the pyrolysis of tetrapyrrolyl porphyrin iron inside the pores of SBA-15 are active ORR catalysts under acidic and alkaline solution [57]. Fe/N/OMCs prepared by this simple one-pot method showed high ordered structure and large surface area, which facilitates the exposure of active sites and mass transport. Around the same time, Cheon et al. reported the synthesis of N/FeCo/OMCs and their application in ORR [33]. Recently, a ferrocene-based ionic liquid was used as a metal and N-containing precursor for preparation of N/Fe/OMCs. The catalysts of N/Fe/OMCs exhibited comparable catalytic activity but superior long-term stability to 20 wt% Pt/C for ORR with four-electron transfer pathway under alkaline media [38]. Additionally, some N/M/OMCs materials prepared by the pyrolysis of phenanthroline metal chelates [36], 2,2-bipyridine and Fe chelates [58], vitamin B12 and polyaniline-Fe [15], Fe-phthalocyanine [59,60], and hemin [61] also showed high activity towards ORR. Unlike these one-pot methods, N/M/OMCs obtained by pyrolysis of M source/N-containing organic precursors [62,63] or metal-organic frameworks [64] inside the pores of OMCs were also demonstrated to be active ORR catalysts. Insights from these authors informed that the synergistic effects between the N dopants and  $MN_x$  active sites can be proposed to account for their enhanced catalytic activity towards ORR [58]. Along with introduction of M into N/OMCs, the multi heteroatom-doped OMCs also exhibited high activity for ORR compared with solely doped OMCs [8,65–67].

The development of noble-metal free ORR catalysts by doping OMCs with heteroatoms produces remarkable ORR electrocatalytic activity. However, there are setbacks in the performances of noble-metal free ORR catalysts based on OMCs which are attributed to their morphological structures and inefficient utilization of active sites, as illustrated in Fig. 1. For instance, the widely used OMC in the literatures is CMK-3 (one kind of OMCs templated from SBA-15) with channel length of  $\sim 2$  nm. The channel in the large particle of SBA-15 is U-shaped, whereas the channel in the small particle is straight [68]. So the U-shape of the channel at large length scale was also inherited by CMK-3. Due to the tortuosity, connectivity, pore packing defect, and shape of the pores of CMK-3, the exact transport of catalytic target within porous textures is very complex [68,69]. Therefore, the transportation of molecule and product in the mesopores could be rather inefficient and decreased with the increase of pore length [70–72]. In addition, the utilization of catalysts which are inside the long pore channel of OMCs might not be efficient (Fig. 1a). Furthermore, for the one step method, the active sites (N and  $MN_x$ )

for ORR are always secluded into the wall of OMCs (Fig. 1b). This means that the partially embedded active sites cannot be fully exposed to catalytic target which accordingly limit their ORR activity. For multi-step method, OMCs were used as a support for the growth of M source/N-containing organic precursors and then thermally treated at high temperature. Although most of N-containing organic precursors are decomposed at high temperature, direct pyrolysis of N-containing organic precursors in the absence of OMCs at inert atmosphere can also produce carbon materials. Therefore, carbon residues derived from N-containing organic precursors are more or less remained inside the pores of OMCs during the pyrolysis of M source/N-containing organic precursors/OMCs. The carbon residues inside the pore may cause the channel blockage, which is not favorable for mass transport and exposure of active sites (Fig. 1c). Recently, phosphorus-doped OMCs [72] and Fe/N/OMCs [59,60] with short pore channel showed high activity for ORR due to the fast mass transport in short channel. The use of OMCs with short pore length can effectively improve the activity of OMCs-based catalysts and take full advantage of porous structure in electrocatalysis. Inspired with these work about the advantages of OMCs with short pore channel, in this work, we synthesized the non-precious metal ORR catalysts of N/Co/OMCs using the available OMCs with short channel as support, and  $Co(NO_3)_2$  and  $NH_3$  as the cobalt and N sources. Three OMCs were CMK-3 plate with short and straight channel, CMK-3 with long and curving channel, and CMK-8. The structure and porous properties of CMK-8 are different to CMK-3 and CMK-3 plate. Both CMK-3 and CMK-3 plate exhibit highly ordered 2D hexagonal  $p6mm$  mesostructure. CMK-8 has an ordered pore arrangement with 3D cubic  $la3d$  symmetry. In addition, the pore size and surface area of CMK-8 is different to CMK-3 and CMK-3 plate. The comparison of electrocatalytic activity of electrocatalysts supported on different OMCs provides information about the relationship between structure and activity, thus yielding new insights for further design of high-performance ORR electrocatalysts. The doping of N and deposition of Co nanoparticles into the OMCs framework create a high density of active surface sites in N/Co/OMCs, promoting more exposure for the  $O_2$  molecule in the ORR processes and resulting in higher electrocatalytic activity for ORR with much better long-term durability and methanol tolerance than the commercial Pt/C in alkaline medium. The excellent electrocatalytic performance of N/Co/OMCs in ORR is mainly attributed to synergistic effect arising from combining the catalytic properties of N, the incorporation of Co nanoparticles, and the structural properties of OMCs. Although heteroatom-doped OMCs and N/Fe/OMCs with short pore channel have been used as noble-metal free ORR catalysts [59,60,72], the differences of our methodology are: (1) The utilization efficiency of Co nanoparticles inside the OMCs plate with short pore length is well improved due to the less pore blockage, which can take full advantage of porous structure in electrocatalysis; (2) The active sites in N/Co/OMCs promoted ORR are highly exposed to  $O_2$  molecule, which result in a high activity for ORR.

## 2. Experimental

### 2.1. Synthesis of catalyst

Three forms of OMCs, namely the CMK-3 [73], CMK-8 [74], and CMK-3 plate [34], were prepared according to literatures. The cobalt nitrate ( $Co(NO_3)_2$ ), ethanol and methanol were obtained from Beijing Chemical Reagent, and the 0.1 M potassium hydroxide (KOH) was used as the electrolyte. Nafion was obtained from Sigma-Aldrich. To prepare the N/Co/OMCs catalysts, 30 mg of the as-synthesized OMCs and 29 mg of  $Co(NO_3)_2$  were dissolved in 50 mL of distilled water. The mixtures were then exposed to ultrasonication for about 2 h so that the pores on the OMCs are

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