

1 **Facile synthesis of Co-N₄-doped mesoporous carbon for oxygen reduction reaction**

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16

17 **Abstract**

18 The oxygen reduction reaction (ORR) is a critical factor in fuel cells that has attracted
19 significant research attention. Non-precious metal catalysts have improved the ORR
20 activity considerably, but they still exhibit poorer ORR performance than commercial
21 Pt-based catalysts. In this study, Co-N₄-doped mesoporous carbon (Co-N₄-MC) was
22 prepared for the ORR using cobalt-azides as the Co-N₄-containing precursor, and
23 ordered mesoporous silica SBA-15 as a template for achieving mesoporous structures.
24 The Co-N₄-MC electrode exhibited remarkable ORR activity in an alkaline medium (a
25 half-wave potential of -0.15V vs. MMO, only ~ 19 mV deviation from the commercial
26 Pt/C catalyst), high selectivity (electron-transfer number ~ 4) and excellent
27 electrochemical stability (~ 8 mV negative shift of the half-wave potential after 1000
28 cycles). The good performance of the Co-N₄-MC electrode was attributed to the
29 synergetic effects of N₄, C and Co. In particular, the existence of graphitic pores in the
30 Co-N₄-MC catalyst facilitated the diffusion of O₂ to the catalytic active sites, which
31 benefited the progression of the ORR on the Co-N₄-MC catalyst.

32

33 Keywords: Co-N₄-doped mesoporous carbon; Oxygen reduction reaction; Graphitic
34 pores

35

36 **1. Introduction**

37 The activity of the oxygen reduction reaction (ORR) is a critical factor in fuel cells
38 and other electrochemical technologies (1). The low reaction rate of the ORR can be
39 overcome using expensive nano-sized Pt catalysts in fuel cells (2, 3). In addition to the
40 scarcity and high-cost, the long-term operation of fuel cells may lead to dissolution and
41 agglomeration of the noble metal particles, which will degraded the performance of the
42 electrocatalysts (4-6). The search for efficient, durable and inexpensive non-precious
43 metal catalysts has become one of the most active and competitive endeavors in the
44 study of energy conversion (7-12). Recently, these non-precious metal and nitrogen
45 doped carbon catalysts prepared from transition metal macrocyclic compounds, such as
46 Co-N₄-C and Fe-N₄-C, are considered the best alternative ORR electrocatalysts (13-16).
47 On the other hand, the unavoidable agglomeration of carbon materials hinders the
48 diffusion of electrolyte ions to the catalytic active sites, thereby reducing the catalytic
49 performance. Mesoporous carbon (MC)-based catalysts can effectively allow the
50 reactants to access the catalytic active sites efficiently, leading to improved mass
51 transport in electrochemical reactions. (17-19). Therefore, Co-N₄-MC could be a good
52 candidate for the ORR, combining the good catalytic activity of the Co-N₄-C catalyst
53 with the excellent mass-transfer performance of MC (20, 21). Despite this, there are few
54 reports on the activity of the ORR over Co-N₄-MC (22, 23), which may be due to the
55 expensive Co sources, such as Vitamin B12 (24, 25) and cobalt
56 tetramethylphenylporphyrin (CoTMPP) (9, 26, 27). Large amounts of CoTMPP are
57 required to produce Co-N₄-C catalysts, making it an expensive preparation process.

58 Although some simple inorganic salt containing Co are used as the Co source (28),
59 however, Co nanoparticles formed in the catalyst composite instead of Co-N₄ clusters
60 (29). According to density functional theory analysis (30), only Co-N₄ clusters near the
61 graphite material can promote the four-electron pathway of the ORR. Therefore, it is
62 still a challenge to develop a low-cost and effective Co source to produce stable Co-N₄
63 doped carbon materials as the ORR catalysts.

64 This paper reports a novel, effective and low-cost method to produce Co-N₄-MC via a
65 high temperature graphitizing process. The novelties in this work, compared to the
66 earlier works (31), are (i) the synthesis of organo-cobalt compounds as the
67 Co-N₄-containing precursor in a low-cost manner, and (ii) use of commercial SBA-15
68 (pore size of 20 nm) as the template to produce Co-N₄-MC with a mesoporous structure
69 (pore size of 4.2 nm) to enhance the accessibility of O₂ and the electrolyte to the
70 catalytic activity sites. SBA-15 has been successfully large-scale produced in industries,
71 which would benefit to the industrial production of Co-N₄-MC catalyst which achieved
72 a stable and high performance comparable to the commercial Pt/C catalyst in ORR, as
73 supported by the current study.

74

75 **2. Experimental Section**

76 *2.1. Preparation of the Co-N₄ complex*

77 The Co-N₄ complex was synthesized via four reactions, as shown in step 1 of Figure
78 1. The first three reactions were based on a previous study (32), which is a typical
79 method to synthesize the N₄ complex. To the best of the authors' knowledge, this is the

80 first report of the preparation of a Co-N₄ complex using the proposed method.
81 Compound a (20g) was heated with K₂CO₃ (10% wt.) and 1-iodopropane (7% wt.) in
82 anhydrous CH₃CN under reflux in a N₂ atmosphere. Compound b was obtained from
83 the reaction mixture by extraction with CH₂Cl₂, and subsequent precipitation with
84 methanol. Compound d was obtained by the purification of compound c (20g) with
85 N-bromosuccinimide and azobis in CCl₄. Subsequently, compounds b and d were heated
86 under reflux in anhydrous CH₃CN (200ml) in the presence of Cs₂CO₃ (5% wt.) under
87 nitrogen to synthesize compound e. Finally, the Co-N₄ complex was prepared by mixing
88 Co²⁺ ions and compound e at a molar ratio of 1:1.

89 2.2. Preparation of Co-N₄-MC

90 Ordered mesoporous silica, SBA-15 (Sigma-Aldrich), was used as a template to
91 produce the mesoporous carbon structures [19]. The SBA-15 template (1 g) was
92 impregnated with a solution of 50 mg of anhydrous oxalic acid in 200 mL ethanol (pure
93 grade) for 20 min (33). In step 2, the oxalic acid-treated SBA-15 was then impregnated
94 with 2 g of the Co-N₄ complex for 45 min at room temperature. In step 3, the resulting
95 composite was then subjected to a series of thermal treatments including 60 °C for 30
96 min, 100 °C for 5 h and 200 °C for 5 h. Stepwise heating was used to evaporate and
97 decompose the organic solvent. At the final thermal treatment, the resulting sample was
98 transferred to a tube furnace for carbonization at 900 °C for 3 h under a N₂ atmosphere
99 at a heating rate of 10 °C/min. In step 4, the SBA-15 template was removed using 15%
100 hydrofluoric acid (200 mL). Co-N₄-MC was obtained after rinsing the sample three
101 times with 50 mL butanol (pure grade). For comparison, the graphitic N₄-C and the

102 template-free Co-N₄-C were also prepared by heating the compound e and the target
103 compound, respectively, at the same heating conditions. The commercial
104 carbon-supported Pt catalyst from Sigma-Aldrich (labeled as Pt/C, with 10 wt.% of Pt
105 metal loading) was used for comparison (34).

106 *2.3. Sample characterizations*

107 The morphology of the samples was analyzed by scanning electron microscopy /
108 energy dispersive X-ray spectroscopy (SEM/EDX, JEOL JMS820). Transmission
109 electron microscopy (TEM, JEOL Model JEM-2000F) images were obtained using a
110 high-resolution system with a LaB₆ filament at 200 kV. The sample powder was
111 dispersed in ethanol by sonication for 3 h, and drops of the suspension were deposited
112 on a copper grid with a holey carbon film. The sample was air-dried and kept in a
113 microscope vacuum for 15 min before the tests. X-ray diffraction (XRD, Philips, model
114 PW 1830) of the prepared samples were obtained using Cu-K α radiation ($\lambda = 0.1542$ nm)
115 at 40 kV and 30 mA. The scanning speed was $0.25^\circ \text{ min}^{-1}$ with a 0.02° step. The BET
116 (Brunauer, Emmett and Teller) surface areas of the samples were investigated using a N₂
117 adsorption–desorption apparatus (Micromeritics ASAP 2020M) at liquid nitrogen
118 temperature (-196°C). The surface elemental composition of the samples was
119 determined by X-ray photoelectron spectroscopy (XPS, VG Scientifics ESCALAB250).
120 Raman spectroscopy was performed using a micro-Raman spectrometer (Renishaw,
121 InVia). A glassy carbon electrode (GCE) with an area of 0.125 cm^2 was used as the
122 working electrode. Pt foil was employed as the counter electrode, and Hg/HgO/KOH
123 (1.0 M) (MMO, 0.098 V versus SHE) was used as the reference electrode. The working

124 electrode was modified with the catalyst layer by placing the catalysts on the GCE. The
125 catalyst ink was prepared by dispersing 10 mg of the each sample ultrasonically in 1.9
126 mL of ethanol, to which 0.1 mL of a 5 wt.% Nafion solution was added. The dispersion
127 was ultrasonicated for 30 min to obtain a homogeneous solution. Approximately 10 μ L
128 of the dispersion was pipetted out on the top of the GCE and dried in air.

129

130 **3. Results and Discussion**

131 *3.1. Characterizations of Co-N₄-MC*

132 Formation of the Co-N₄ complex was first confirmed by UV-vis spectra, which shows
133 the UV-vis spectra of the N₄ complex before and after complexing with Co²⁺ ions. The
134 N₄ compound had an absorption band at 286 nm, which was assigned to the absorption
135 of the phenyl and 2,2-dipyridyl moieties. The addition of Co²⁺ ions to the N₄ compound
136 caused a shift of the ligand absorption band from 286 nm to 308 nm. These results
137 indicated the formation of the Co-N₄ complex. Interestingly, the formation process of
138 Co-N₄-MC can be traced by TEM. As shown in Figure S2a, the skeletons and the pore
139 channels of SBA-15 were observed, whereas only the skeletons of SBA-15 were
140 observed after the pore channels of SBA-15 had been filled with the Co-N₄ complex
141 (Figure S2b). After removing the SBA-15 template with hydrofluoric acid, the skeletons
142 and pore channels of SBA-15 became invisible (Figure S2c). Figure 2a-c shows TEM
143 images of the Co-N₄-MC sample at different magnifications. EDX confirmed the
144 presence of C, N and Co in the Co-N₄-MC sample (Figure 2b). Figure 2c showed that
145 the Co and N doped pyrolytic carbon consisted of graphene-like sheets. On the other

146 hand, no Co NPs were observed, even at high magnification. This is because when
147 Co-macrocyclic compounds were used as the Co source, Co-N₄ nanoclusters were
148 generally formed [21] instead of Co NPs [23]. Figure 2d-f show SEM images with
149 mapping, clearly indicating the density of CK α 1, NK α 1 and CoK α 1. As shown in
150 Figure 3a, the Co-N₄-MC sample exhibited the typical shape for a mesoporous material
151 (20, 35). The mesopore radius distribution was centered at approximately 4.2 nm
152 (Figure 3b). In Figure 3c, the Raman spectra revealed the characteristic peaks of
153 graphitic carbon at 1350 cm⁻¹ (D-band), 1580 cm⁻¹ (G-band) and 2750 cm⁻¹ (2D-band).
154 The narrow D- and G-bands as well as an intense 2D-band indicated that the Co-N₄-MC
155 sample had high crystallinity.

156 As shown in Figure 4a, the atomic percentage of N, C and Co in the Co-N₄-MC
157 sample were 4.36 %, 94.67 % and 0.97 %, respectively (impurities, such as trace
158 amounts of O, Si and F were not detected). Figure 4b-d show the high-resolution N1s,
159 C1s and Co2p spectra. The C1s peak (Figure 4b) was shifted to a higher binding energy
160 (284.9 eV), which was attributed to the incorporation of nitrogen (36, 37). In Figure 4c,
161 the N1s peak was fitted to peaks of pyridinic-N (398.2 eV), pyrrolic-N (4001 eV), and
162 graphitic-N (400.7 eV). Among them, pyridinic-N (up to 42 at.% of the total
163 amount of N atoms) was found to critically affect the ORR performance (38-40). In
164 addition, the peaks for Co2p_{3/2} and Co2p_{1/2} (Figure 4d) were observed in the Co-N₄-MC
165 sample, confirming the existence of Co (0) atoms.

166 3.2. Electrochemical activity of Co-N₄-MC electrode for ORR

167 To evaluate the ORR performance of the Co-N₄-MC electrode and other electrodes,

168 the polarization curves for the ORR of the electrodes were recorded in a 0.1 M KOH
169 solution saturated with pure oxygen. Figure 5a shows the linear sweep voltammetry
170 curves of the electrodes. Typically, the positive onset potential and half-wave potential,
171 and high current density are good metrics for a good ORR catalyst. These results
172 indicated that the onset potential (-0.02 V vs. MMO) and half-wave potential (-0.15 vs.
173 MMO) of the Co-N₄-MC electrode are similar to those of the Pt/C electrode. The onset
174 potential of the Co-N₄-MC electrode is much higher than those of the N₄-C electrode
175 (-0.15 V vs. MMO) and the Co-N₄-C electrode (-0.017 V vs. MMO) and the half-wave
176 potential is higher than those of the N₄-C electrode (-0.25 V vs. MMO) and the Co-N₄-C
177 electrode (-0.20 V vs. MMO) as well. The limited current (5.4 mA cm⁻²) of the
178 Co-N₄-MC electrode approached that of the Pt/C electrode (5.5 mA cm⁻²), and was
179 higher than those of the N₄-C electrode (3.8 mA cm⁻²) and the Co-N₄-C (4.5 mA cm⁻²)
180 electrode (15). For the Co-N₄-MC electrode, the Co atoms could facilitate the
181 incorporation of active N species into the carbon matrix with strong Lewis basicity,
182 which enhances the electron-donor properties of the N-doped carbon and weakens the
183 O-O bond via bonding with the oxygen and nitrogen and/or the adjacent carbon atom
184 (36). The N atoms, particularly pyridinic-N, make an important contribution to the ORR
185 performance (38-40). In addition, the existence of the graphitic pores in the Co-N₄-MC
186 electrode sample could facilitate the diffusion of O₂ to the Co-N₄ active sites, and
187 benefit the progression of the ORR on the Co-N₄-MC electrode (41, 42). However, the
188 N₄-C electrode, without the Co catalysts, showed a different ORR mechanism from the
189 Co-N₄-MC electrode (43). For the Co-N₄-C electrode, without the mesoporous carbon

190 structure, although it has similar onset potential, the limit current is much lower than
 191 that of the Co-N₄-MC electrode, which could be due to the poor mass transfer
 192 performance (44). The results suggest that the high performance of the Co-N₄-MC
 193 electrode is due to the synergetic effects of N, Co and MC structure in the Co-N₄-MC
 194 sample.

195 To confirm the 4e-ORR reaction path, a series of rotating disk voltammograms of
 196 the ORR by the Co-N₄-MC electrode at different rotation rates in a 0.1 M KOH
 197 saturated with oxygen were tested (Figure 5b). The RDE data was analyzed using the
 198 Kouteckye–Levich equation (45):

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

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

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

199 where J is the measured current density, J_K and J_L are the kinetic and diffusion limiting
 200 current densities, respectively, ω is the electrode rotation rate, n is the overall number of
 201 electron transfer, F is the Faraday constant (96,485 C mol⁻¹), C_o is the bulk
 202 concentration of O₂ dissolved in the electrolyte (1.2×10^{-6} mol cm⁻³), D_o is the O₂
 203 diffusion coefficient (1.9×10^{-5} cm² s⁻¹), and ν is the kinematic viscosity of the
 204 electrolyte ($\nu = 0.01$ cm² s⁻¹) (46). Based on the ring and disk currents, the calculated
 205 number (n) of electrons transfer is approximately 3.85 for the Co-N₄-MC electrode
 206 (Figure 5c), which was confirmed by the measured n value (Figure 5d) using
 207 the rotating ring-disk electrode (RRDE). These results indicate that the ORR occurred

208 mainly via a four-electron mechanism.

209 Figure 6a shows the Tafel plots for the ORR on the Co-N₄-MC and Pt/C electrodes.
210 The Co-N₄-MC electrode has a similar Tafel plot to the Pt/C electrode, indicating that
211 the Co-N₄-MC sample has comparable kinetic performance to the Pt/C catalyst.
212 Durability is a major issue in fuel-cell technology. Therefore, the stability of the
213 Co-N₄-MC electrode was evaluated further. As shown in Figure 6b, no obvious change
214 in the performance of the Co-N₄-MC electrode was observed before and after 1000
215 cycles. The good stability of the Co-N₄-MC electrode was attributed to the mesoporous
216 carbon structure, which enhanced their interfacial contact and facilitated the transport of
217 electrolyte ions (47). The unique features of the Co-N₄-MC sample, such as the
218 graphitic mesopore framework with moderate nitrogen content, resulted in high
219 electrocatalytic activity and excellent long-term stability.

220

221 **4. Conclusion**

222 In summary, a high-performance Co-N₄-MC electrocatalyst was prepared for the
223 ORR. A cobalt-azide compound was used as the Co-N₄-containing precursor. An
224 ordered mesoporous silica SBA-15 was used as a template to achieve the mesoporous
225 structure of the Co-N₄-MC sample. The Co-N₄-MC electrode exhibited good ORR
226 performance (similar to that of the Pt/C electrode) with good stability, which was
227 attributed to the synergetic effects of N₄, Co and MC. Moreover, the ORR by the
228 Co-N₄-MC sample occurred through the preferred four-electron reaction pathway. This
229 study suggests that the Co-N₄-MC sample can be used as a non-precious electrocatalyst

230 for the ORR in alkaline fuel cells.

231

232 **Acknowledgements**

233 This work was supported by the Science and Technology Development Fund from
234 Macau SAR (FDCT-098/2015/A3), the Start-up Research Grant (SRG2015-00057-FST)
235 from Research & Development Office at University of Macau, and the UEA funding.

236 **Appendix A. Supplementary data**

237 Supplementary data associated with this article can be found in the online version.

238

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308

309 **Figure Captions**

310 **Fig. 1.** Schematic diagram of the synthesis of Co-N₄-MC.

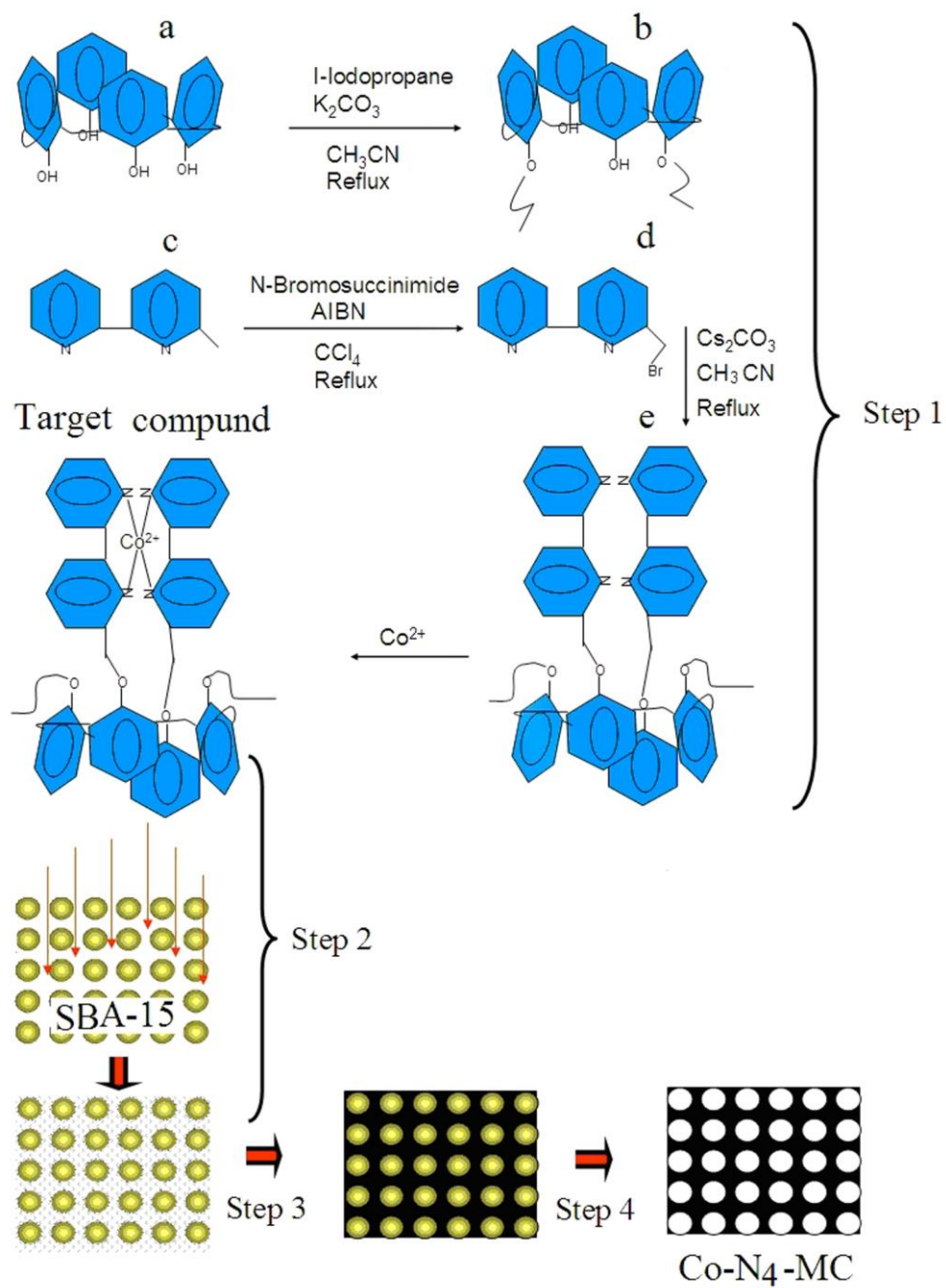
311 **Fig. 2.** TEM images (a, b, and c) and EDS (inset of c), SEM image (d) and mapping (e,
312 f and g) of the obtained Co-N₄-MC.

313 **Fig. 3.** Adsorption/desorption curve (a), pores diameter (b) and Raman spectrum of
314 Co-N₄-MC (c).

315 **Fig. 4.** Wide-scan X-ray photoelectron spectra (XPS) of various Co-N₄-MC (a). The
316 XPS spectra of C1s (b), N1s (c) and Co2p (d) of Co-N₄-MC.

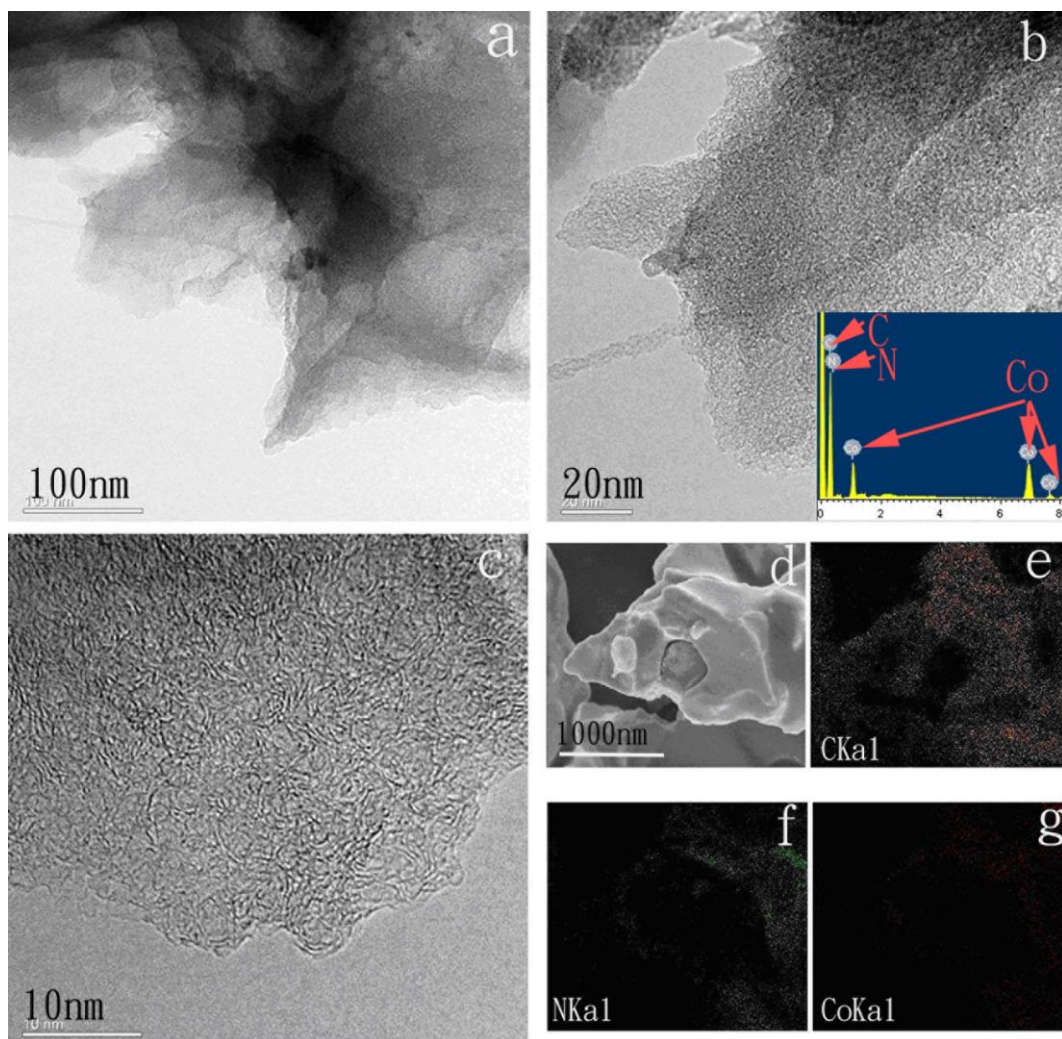
317 **Fig. 5.** Linear sweep (5 mV s⁻¹) of N₄-C, Co-N₄-C, Co-N₄-MC, and Pt/C in 1.0 M KOH
318 solution saturated with oxygen (a). Linear sweeps (5 mV s⁻¹) at different rotating speeds
319 (b). *n* value over the entire range of potentials studied (c). *n* value was measured by
320 RRDE (d).

321 **Fig. 6.** Tafel slopes of Co-N₄-MC and Pt/C electrodes (a). Linear sweep (5 mV s⁻¹) of the
322 Co-N₄-MC electrode before (black line) and after (red line) 1000 cycles (b).



323

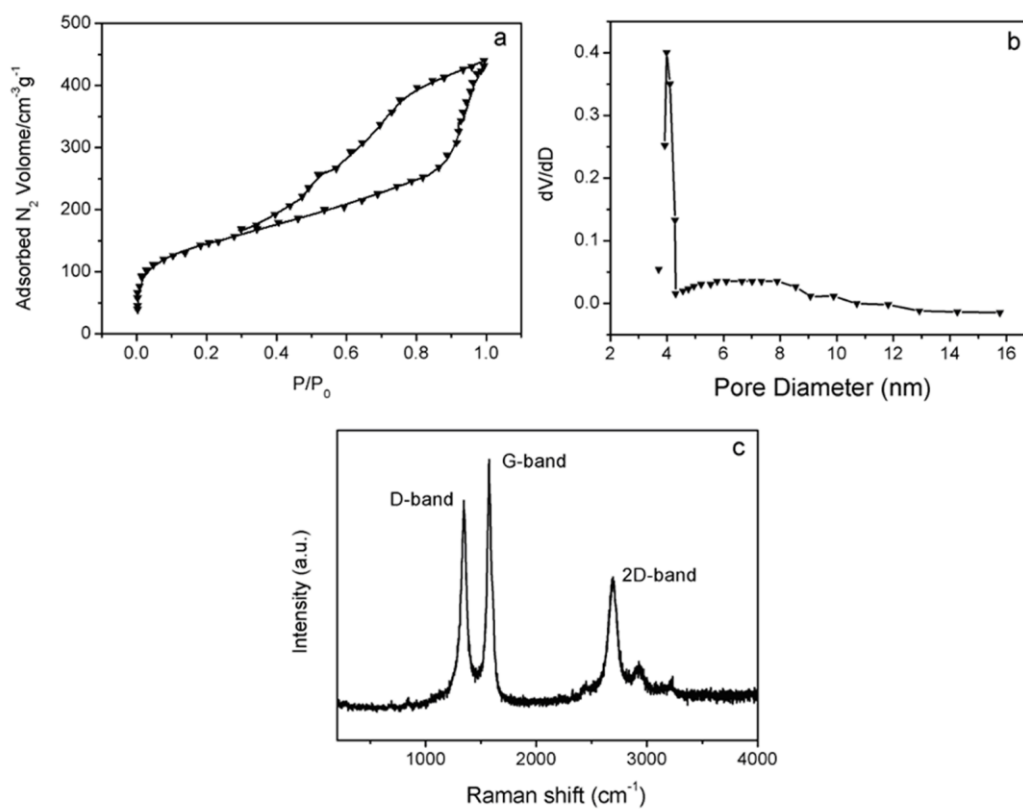
324 **Fig. 1.** Schematic diagram of the synthesis of Co-N₄-MC.



325

326 **Fig. 2.** TEM images (a, b, and c) and EDS (inset of c), SEM image (d) and mapping (e,

327 f and g) of the obtained Co-N₄-MC.

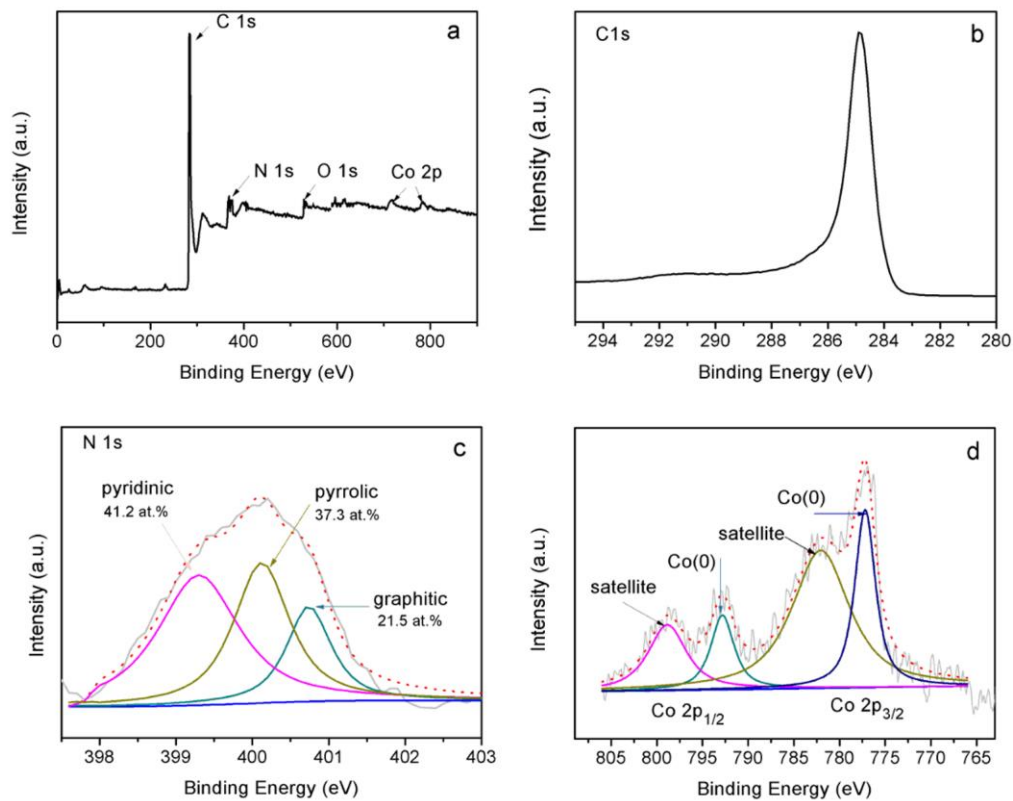


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329 **Fig. 3.** Adsorption/desorption curve (a), pores diameter (b) and Raman spectrum of

330 Co-N₄-MC (c).

331

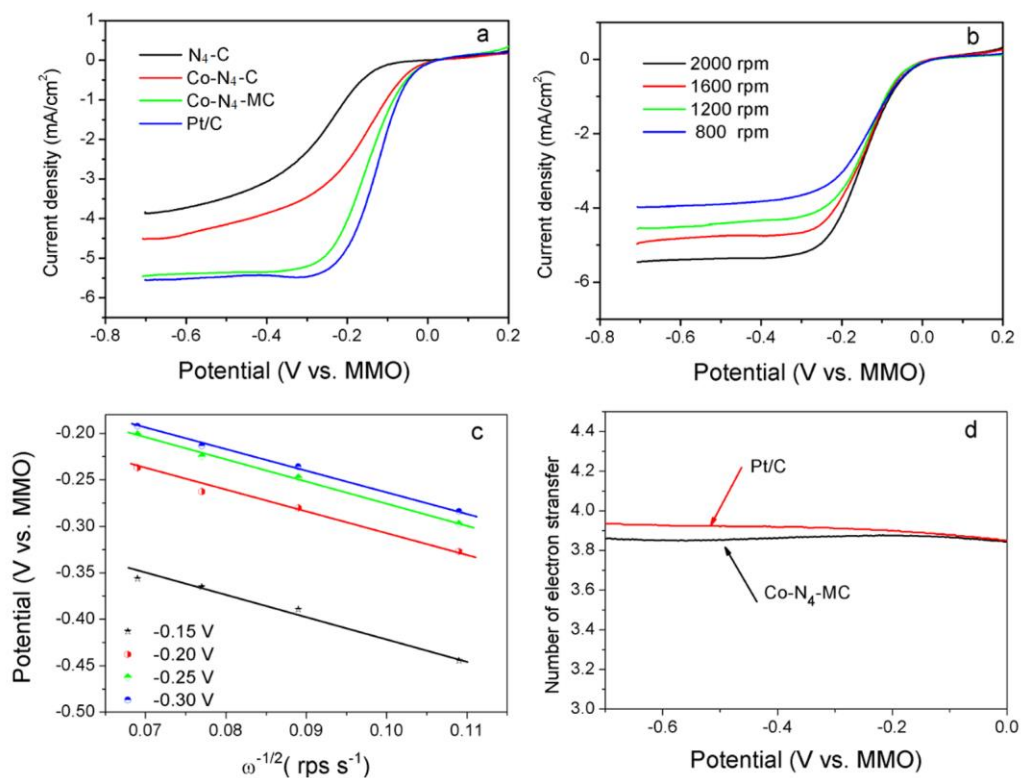


332

333 **Fig. 4.** Wide-scan X-ray photoelectron spectra (XPS) of various Co-N₄-MC (a). The

334 XPS spectra of C1s (b), N1s (c) and Co2p (d) of Co-N₄-MC.

335



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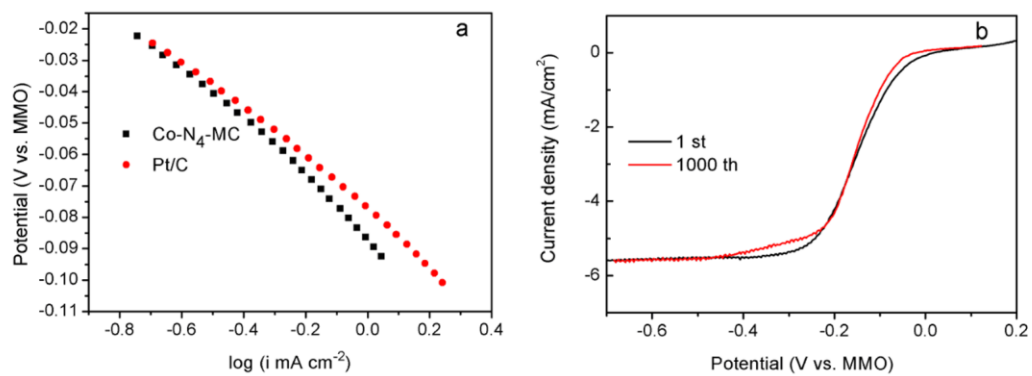
337 **Fig. 5.** Linear sweep (5 mV s⁻¹) of N₄-C, Co-N₄-C, Co-N₄-MC, and Pt/C in 1.0 M KOH

338 solution saturated with oxygen (a). Linear sweeps (5 mV s⁻¹) at different rotating speeds

339 (b). *n* value over the entire range of potentials studied (c). *n* value was measured by

340 RRDE (d).

341



342

343 **Fig. 6.** Tafel slopes of Co-N₄-MC and Pt/C electrodes (a). Linear sweep (5 mV s⁻¹) of the
 344 Co-N₄-MC electrode before (black line) and after (red line) 1000 cycles (b).