A “MOFs plus ZIFs” Strategy toward Ultrafine Co Nanodots Confined into Superficial N-Doped Carbon Nanowires for Efficient Oxygen Reduction

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ABSTRACT: N-doped carbon-confined transition metal nanocatalysts display efficient oxygen reduction reaction (ORR) performance comparable to commercial Pt/C electrocatalysts because of their efficient charge transfer from metal atoms to active N sites. However, the sheathed active sites inside the electrocatalysts and relatively large-size confined metal particles greatly restrict their activity improvement. Here, we develop a facile and efficient “MOFs plus ZIFs” synthesis strategy to successfully construct ultrafine sub-5 nm Co nanodots confined into superficial N-doped carbon nanowires (Co@C@NC) via a well-designed synthesis process. The unique synthesis mechanism is based on low-pressure vapor superassembly of thin zeolitic imidazolate framework (ZIF) coatings on metal−organic framework substrates. During the successive pyrolysis, the preferential formation of the robust N-doped carbon shell from the ZIF-67 shell keeps the core morphology without shrinkage and limits the growth of Co nanodots. Beneiting from this architecture with accessible and rich active N sites on the surface, stable carbon confined architecture, and large surface area, the Co@C@NC exhibits excellent ORR performance, catching up to commercial Pt/C. Density functional theory demonstrates that the confined Co nanodots efficiently enhance the charge density of superficial active N sites by interfacial charge transfer, thus accelerating the ORR process.

KEYWORDS: low-pressure vapor superassembly, MOF composite design, superficial N-doped carbon, nanowires, oxygen reduction

1. INTRODUCTION

The oxygen reduction reaction (ORR) is of crucial importance in sustainable energy storage and conversion devices, including fuel cells and metal-air batteries.1−3 The materials based on Pt are the benchmark ORR catalysts, but their practical applications are constrained by the scarcity, high cost, and poor stability.4−6 Developing efficient nonprecious metal-based catalysts is desirable to replace the catalysts based on Pt.7−9 However, the performance of these catalysts is mainly limited by their intrinsic activity and accessible number of active sites.10 To obtain catalysts with high intrinsic active sites, a variety of nonprecious metal-based materials have been explored. Among them, the catalysts based on transition metal/metal carbide/metal oxide nanoparticles encapsulated in nanostructured N-doped carbon (M@NC, M = Fe, Co, Cu, etc.) have been widely studied in which the accessible surface N boosted by transition metal is considered as the active site.11 Wang et al. reported Fe/Fe3C nanoparticles encapsulated in N-doped graphene and carbon nanotubes with N active sites boosted by Fe.12 To further enhance ORR performance, increasing accessible active sites of M@NC is believed to be a key factor. Generally, the architecture of these catalysts is always determined by the morphology and structure of
precursors. Therefore, it is essential to design suitable precursors to synthesize M@NC catalysts with a high surface area and rich accessible active sites.\textsuperscript{13,14}

Metal−organic frameworks (MOFs) are porous crystal compounds assembled from metal ions/clusters coordinated with organic ligands.\textsuperscript{15−18} Benefiting from the fantastic properties of controllable architecture and high surface area, MOFs have been considered to be promising precursors for fabricating M@NC catalysts with high surface area and tunable surface properties.\textsuperscript{19−22} Lai et al. reported controllable Cu@NC nanocatalysts by annealing adjustable Cu–zeolitic imidazolate framework (ZIF)-8 nanoparticles.\textsuperscript{23} Zhang et al. designed CoFe@NC hollow spheres by pyrolyzing MIL-101/ZIF-67 composites.\textsuperscript{24} As expected, these M@NC catalysts achieved a high specific surface area. However, because of homogeneous N doping in MOF precursors during the synthesis process, the M@NC catalysts derived from these MOFs have doped N sites through the whole carbon materials.\textsuperscript{25,26} Despite some accessible N sites activated on the surface, most N sites are deeply sheathed without accessibility because the ORR is performed on the surface.\textsuperscript{27} In addition, most these catalysts have relatively large metal particles (>10 nm), further reducing the accessible active sites on the surface.\textsuperscript{28} So far, it is still necessary to develop a suitable strategy to design M@NC catalysts with ultrafine metal

Figure 1. Schematic illustration of the synthesis process and structure of Co@C@NC.

Figure 2. (a) XRD patterns of MOF-74, ZIF-67, and MOF-74@ZIF-67 nanowires. (b) FTIR spectra of MOF-74, ZIF-67, and MOF-74@ZIF-67 nanowires. (c) SEM image, (d) TEM image, and (e) HAADF-STEM image with the corresponding EDS element mapping of the MOF-74@ZIF-67 nanowire.
nanodots confined and most accessible active N sites focusing on the surface.

Herein, a facile “MOFs plus ZIFs” strategy following controlled pyrolysis has been developed to design a new type of ultrafine sub-5 nm Co nanodots confined into superflcal N-doped carbon nanowires (Co@C@NC). This “MOFs plus ZIFs” strategy achieves the uniform growth of thin ZIF-67 coating on MOF-74. The preferential pyrolysis of ZIF-67 can generate stable N-doped carbon shells and hinder the growth of Co nanodots. Benefiting from the well-designed process, the resultant Co@C@NC can simultaneously achieve a high surface area and rich accessible active sites doping on the surface. The as-prepared catalyst exhibits high catalytic activity in alkaline electrolyte with a half-wave potential of 0.83 V, catching up to the commercial Pt/C catalyst. The enhanced charge transfer between Co nanodots and N-doped carbon shells is also proved by density functional theory (DFT) calculations.

2. RESULTS AND DISCUSSION

The overall fabrication process of Co@C@NC is shown in Figure 1. MOF-74 nanowires (~70 nm in diameter and ~20 μm in length) (Figure S1) were prepared by the reported hydrothermal method.29 Then, these nanowires were activated to remove water molecules from the channels and avoid water participating in the subsequent reaction. The activated MOF-74 nanowires and 2-methylimidazole (2-MIM) powders were both placed in a common system and treated at 120 °C for 24 h. Then, the gaseous 2-MIM was converted from solid to gas and filled the entire reaction system. The gaseous 2-MIM ligands reacted with MOF-74 on the surface, forming in situ ZIF-67 shells. During this process, 2-MIM released protons and coordinated with Mo2+ to form ZIF-67, while the ligands of MOF-74 accepted protons and released 2, 5-dihydroxyparaxic acid (DHTA).30,31 The reaction equation could be described as follows:

\[
2 \text{MIM (g)} + \text{MOF} \rightarrow \text{MOF-74@ZIF-67(s) + DHTA(g)} \quad (1)
\]

The formation of uniform ZIF-67 shells on MOF-74 nanowires was proved. The X-ray diffraction (XRD) pattern of MOF-74@ZIF-67 revealed typical diffraction peaks corresponding to MOF-74 and ZIF-67 (Figure 2a). Fourier transform infrared spectroscopy (FTIR) of MOF-74@ZIF-67 also revealed the feature vibrations of MOF-74 and ZIF-67 (Figure 2b). The adsorption band at 421 cm−1 represented the C=N vibration, indicating that Co2+ ions were successfully coordinated with deprotonated 2-MIM.32,33 The scanning electron microscopy (SEM) image showed most MOF-74@ZIF-67 maintained the nanowire morphology (Figure 2c). The transmission electron microscopy (TEM) image clearly indicated the core-shell feature of the MOF-74@ZIF-67 nanowire (Figure 2d). The thickness of the uniform ZIF-67 shell is ~20 nm and the diameter of the MOF-74 core remained at ~60 nm. Comparing the diameter of MOF-74 before reaction (~70 nm), it can be estimated that the transformation content of the MOF-74 core in the ZIF-67 shell is ~27%. High-angle annular dark-field scanning TEM (HAADF-STEM) and the corresponding energy-dispersive X-ray spectroscopy (EDS) mapping images of MOF-74@ZIF-67 showed the homogeneous distribution of C, O, N, and Co elements in the overall MOF-74@ZIF-67 (Figure 2e).

Therefore, all the above results indicated uniform ZIF-67 shells were formed on the surface of MOF-74.

Co@C@NC was prepared by the controlled pyrolysis of the MOF-74@ZIF-67 precursor in an Ar/H2 atmosphere. For insight into the morphology evolution after pyrolysis, MOF-74 was directly sintered into Co@C nanowires under the same condition for comparison. The Co@C@NC sample retained the morphology of nanowires in the SEM image (Figure 3a).

The TEM image revealed the Co@C@NC had a smooth surface with ultrafine Co nanodots uniformly confined (Figure 3b). There was no obvious shrinkage in the Co@C@NC (~100 nm in diameter) compared to the MOF-74@ZIF-67 precursor. However, the surface of Co@C was rough with many protrusions and most large Co particles (>10 nm) were exposed (Figure S2). The diameter of Co@C (~40 nm) had a significant shrinkage compared to that of the MOF-74 precursor (~70 nm). It could be inferred that MOF-74 nanowires suffered from severe collapse during the pyrolysis process, but ZIF-67 had less collapse and provided a relatively stable carbon skeleton to inhibit the growth of Co particles under the same condition. The red dotted circles reflected that the size of most Co nanodots is below 5 nm. These small Co nanodots were expected to boost more accessible N active sites.34 The diffraction ring in the corresponding selected area electron diffraction (SAED) pattern (inset in Figure 3b) and a lattice fringe space of 0.224 nm in the high-resolution TEM (HRTEM) image (Figure 3c) was attributed to the (111) crystal plane of Co.35 The EDS element mapping shown in Figure 3d revealed that C and N elements distributed wider than Co, which was more obvious in high magnification (Figure S3), indicating almost all the Co nanodots were coated by superficial N doped C shells. As shown in Figure S4, N elements are mainly distributed at the edges, indicating superficial N doping along the radial direction of Co@C@NC.

To explore the formation mechanism of core-shell Co@C@NC, thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses were performed for MOF-74, MOF-74@ZIF-67, and ZIF-67 (Figure S5). The TG curve of MOF-74@ZIF-67 demonstrated that its mass loss centered on two distinct temperature ranges, including 16% mass loss in 280-400 °C and 17% mass loss in 440-530 °C.36,37 These two mass losses are the pyrolysis of ZIF-67 and MOF-74, respectively. The DSC curve of MOF-74@ZIF-67 indicated that the exothermic peak position was 460 °C, lower than that of MOF-74 (530 °C), further proving the preferential pyrolysis
of the ZIF-67 shell. Combined with different morphologies of Co@C@NC and Co@C, the preferential pyrolysis of the ZIF-67 shell could form a stable and denser N-doped carbon shell on the surface, which inhibited the collapse of the carbon skeleton and limited the growth of Co nanodots.

XRD patterns of both Co@C@NC and Co@C showed sharp peaks at 75.8°, 51.5°, and 44.2° corresponding to (220), (111), and (200) crystal planes, respectively. The peaks are consistent with the hexagonal phase of graphite (JCPDS card 75-1770).

Raman spectroscopy revealed the presence of D (disordered carbon) and G (graphitic carbon) bands. The intensity ratio I_d/I_g was used to evaluate the graphitic nature of the carbon shell. The value of I_d/I_g for Co@C@NC was lower than that for Co@C, indicating a higher degree of graphitization for the former.

N2 adsorption-desorption isotherms showed type IV behavior with a hysteresis loop, indicating the presence of mesopores. The BET surface area of Co@C@NC was higher than that of Co@C, reflecting the improved porosity in the former.

X-ray photoelectron spectroscopy (XPS) confirmed the presence of Co and C, with a peak at 779.8 eV corresponding to Co 2p3/2 and one at 284.6 eV corresponding to C 1s. The high-resolution N 1s XPS spectrum showed a peak at 399.3 eV characteristic of pyridinic N, indicating the presence of heteroatoms in the carbon matrix.

Electrochemical measurements revealed the ORR activity of the catalysts. The rotating disk electrode (RDE) polarization curves showed a lower onset potential and a higher current density for Co@C@NC compared to Co@C and Pt/C-20%. The K-L plots indicated a lower electron transfer number (n_e) for Co@C@NC, suggesting better ORR kinetics.

Chloroauric acid (HAuCl₄) was added to the reaction system to form Au nanoparticles on the surface of the catalysts. The presence of Au NPs was confirmed by UV-Vis spectroscopy, showing a surface plasmon resonance (SPR) band at 520 nm.

The electrochemical stability of the catalysts was evaluated using chronochronoamperometry (CVA), and the results showed that Co@C@NC exhibited higher stability and durability compared to Co@C and Pt/C-20%.

Overall, the combination of ZIF-67 and Co@C@NC resulted in a promising catalyst for ORR, with enhanced activity, stability, and durability compared to Pt/C-20% and Co@C.
energy in Co@C@NC demonstrated that Co nanodots were multivalent Co bond (Figure S6). The metal Co stronger considered to promote the adsorption of oxygen and the 4e contents of graphite-N and pyridine-N in Co@C@NC were higher than those of Co@C and C@NC, indicating that the active site is at the N atom boosted by Co nanodots. The electrochemically active surface area of the Co@C@NC catalyst is calculated to be as high as 62.8 m² g⁻¹, indicating its excellent methanol tolerance (Figure 5f). However, the current density of the Pt/C catalyst was reduced obviously, which was attributed to the catalytic oxidation of methanol. This synthesized Co@C@NC catalyst showed excellent ORR activity compared to similar electrocatalysts reported recently, further illustrating the superiority of the designed structure (Table S1).

To reveal the effect of Co nanodots on N-doped C shells, DFT simulations were used to calculate the charge density redistributions of four systems: Co nanodots encapsulated in N-free, pyrrole-N, pyridine-N, and graphite-N-doped carbon shells (denoted as Co@C, Co@pyrr-NC, Co@pyri-NC, and Co@grap-NC). The introduction of pyrrole-N, pyridine-N, and graphite-N changed the charge density of the Co@C system and accumulated charge at the N sites (Figure S8). Moreover, the catalytic current increased with speed typically in the LSV curves of Co@C@NC (Figure 5b). The corresponding Koutecky–Levich plots indicated that the average electron transfer number (n) was ~3.9 in the voltage range from 0.3 to 0.7 V (Figure 5c). The ring-shaped RDE examination revealed that the electron transfer number was maintained at 3.99–4.00 in the potential range of 0.2–0.8 V (Figure 5d), consistent with the RDE results. The yield of H₂O₂ did not exceed 4% in the same potential range. The results above suggested that the Co@C@NC catalyst experienced a near 4e⁻ ORR process. The durability and methanol tolerance of Co@C@NC and Pt/C were compared. The stable current at 10 s was recorded as 100% activity in these examinations. The activity retention rate of Co@C@NC was as high as 95% after 20,000 s, significantly higher than that of Pt/C (88%) (Figure 5e).

Figure 6. Differential charge density redistributions of (a) Co@C, (b) Co@pyrr-NC, (c) Co@grap-NC, and (d) Co@pyri-NC systems. Atoms with blue, brown, and white represent Co, C, and N atoms. Blue and yellow contours represent charge loss and charge accumulation.
parameter to analyze the catalytic activity for carbon-based catalysts. 48 In the DOS of spin down, the states near the Fermi level of these four systems were almost consistent (Figure S11a). However, the DOS of spin up showed the systems containing N had more states than Co@C near the Fermi level (Co@pyrr-NC > Co@grap-NC > Co@pyri-NC > Co@C) (Figure S11b). The extra DOS near the Fermi level was expected to enhance the electrochemical activity. 49 The charge density redistribution and the DOS indicated that the local dipoles formed between Co nanodots and external N-doped C shells, which promoted the electron transfer in the ORR process. 50

3. CONCLUSIONS
In summary, a facile “MOFs plus ZIFs” synthesis strategy was developed to successfully construct a new type of ultrafine sub-5 nm Co@C@NC. The “MOFs plus ZIFs” synthesis mechanism is the in situ growth of a thin ZIF-67 shell on MOF-74 substrates by low-pressure vapor superassembly. Under controlled pyrolysis, the preferential pyrolyzed ZIF-67 can form stable superficial N-doped carbon shells, which inhibit the structural collapse and growth of Co nanodots. Benefiting from the well-designed process, this Co@C@NC catalyst achieves rich and accessible active sites focusing on the surface and high specific surface area, thus exhibiting excellent ORR performance. The experimental and DFT analyses indicate the effects of Co nanodots on N-doped carbon shells. These effects change charge density redistributions and increase the DOS near the Fermi level, enhancing the electron transfer in the ORR process. Considering the diversity of substrates and MOFs, this strategy provides a new direction for the rational design of high-performance catalysts.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c14112.

Synthesis and characterization of materials; SEM and TEM images of MOF-74 nanowires and Co@C; HAADF-STEM and EDS element mapping of a Co@C@NC nanowire; HAADF-STEM image and N distribution of Co@C@NC; TG-DSC curves; high-resolution XPS spectra; XRD patterns; TEM images; CV curves; spin polarized DOS of all systems; and summary of various similar electrocatalysts reported recently for the ORR (PDF).

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Notes
The authors declare no competing financial interest.

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