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Applied Surface Science

2-Methylimidazole-tuned "4-Self" strategy based on benzimidazole-5-carboxylate for boosting oxygen reduction electrocatalysis

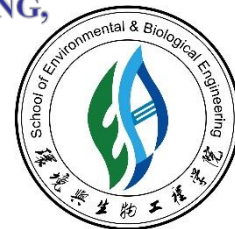
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Abstract:	Rational design highly active transition metal or transition metal oxides/nanocarbon hybrids is one of the feasible way to deliver a cooperative oxygen reduction (ORR) with a synergistic effect of the hybrid interface. Herein, based on benzimidazole-5-carboxylate (BIMC), hierarchical CoO/Co-N-C nanocomposites are fabricated via 2-methylimidazole (MeIM)-tuned "4-Self" strategy, namely, self-templating, self-adapting, self-assembly and self-catalysis. As a base, competitive ligand, N and C sources, MeIM modulates the dispersion of BIMC in methanol to generate colloidal-like BIMC tiny particles, the coordination ability of BIMC to Co(II), the composition and morphology of the self-assembled precursor (Co-BM), and as well as the conductivity of the resultant electrocatalyst. Impressing, carbonization of Co-BM at 800 °C under N ₂ atmosphere endows the pyrolysis product (Co-BM-800) with the well-dispersed Co/CoO riveted on nitrogen-doped carbon, as well as the enhanced ORR performance in terms of positive onset-potential (0.890 V vs. RHE), large diffusion limiting current density (5.21 mA cm ⁻²), and high stability.
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Manuscript title: 2-Methylimidazole-tuned “4-Self” strategy based on benzimidazole-5-carboxylate for boosting oxygen reduction electrocatalysis

By Yu-Xuan Dai, Wen-Li Xin, Lian-Hua Xu, Ji Li, Yi-Xuan Li, Junji Li, Serge Cosnier, Xue-Ji Zhang, Robert S. Marks, and Dan Shan*

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Please find the above manuscript that I would like you consider for publication in **Applied Surface Science**. The manuscript has not been previously published, is not currently submitted for review to any other journal, and will not be submitted elsewhere before a decision is made by this journal.

Total number of words: 5303

Total number of Tables: 0;

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To further enhance the electro-catalytical performance of cobalt-based nanomaterials for the boosted oxygen reduction reaction (ORR), it is still a great challenge to create a cooperative CoOx/Co-N-C structure. In this work, 2-methylimidazole (MeIM) was genetically used as a modulator to tune the self-templating, self-adapting, self-assembly and self-catalysis based on BIMC, during the preparation process of electrocatalyst. This MeIM-tuned “4-Self” strategy was

proposed based on the following reasons: (1) pKa value of BIMC and MeIM is 3.10 and 14.44, respectively. As a base, the deprotonation degree of BIMC can be altered by MeIM and provide more available carboxylate for coordination with Co(II). (2) Due to its intermolecular hydrogen-bonding and π - π interactions, BIMC poorly dissolves in methanol. Base on the acid/base equilibria of BIMC/MeIM, the aggregated size of BIMC is expected to be regulated by MeIM. The solvophobic BIMC aggregates can be used as templates directing the structure of the self-assembly. Moreover, the BIMC aggregates may be inevitable confine the migration and agglomeration of Co, resulting in the highly-dispersed metal active sites. (3) The rest of MeIM may serve as a competitive ligand at Co(II) center. The coordination state of Co(II) may be self-adaptive. (4) The aggregated BIMC particles using as templates, the coordinated BIMC and the coordinated MeIM can be used as N- and C-sources. The carbonization may be self-catalyzed via the chelated Co(II). The chelated Co(II) in precursor may be further reduced to a low-valence states. Thus, according to the proposed MeIM-tuned “4-Self” strategy, the boosted ORR electrocatalysis may be realized. This proposed “4-Self” strategy could open up significant technological opportunities for the preparation of advanced nanomaterials with high-lever complexities, on-demand functionalities and fascinating performance in the near futures.

Based on the above statement, we believe that this generic work conforms the connotation of this academic journal, and has some enlightenment for audience of **Applied Surface Science**.

Thank you very much for your kind assistances.

Sincerely yours,

Prof. Dan Shan

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2-Methylimidazole-tuned “4-Self” strategy based on benzimidazole-5-carboxylate for boosting oxygen reduction electrocatalysis

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ABSTRACT

Rational design highly active transition metal or transition metal oxides/nanocarbon hybrids is one of the feasible way to deliver a cooperative oxygen reduction (ORR) with a synergistic effect of the hybrid interface. Herein, based on benzimidazole-5-carboxylate (BIMC), hierarchical CoO/Co-N-C nanocomposites are fabricated via 2-methylimidazole (MeIM)-tuned “4-Self” strategy, namely, self-templating, self-adapting, self-assembly and self-catalysis. As a base, competitive ligand, N and C sources, MeIM modulates the dispersion of BIMC in methanol to generate colloidal-like BIMC tiny particles, the coordination ability of BIMC to Co(II), the composition and morphology of the self-assembled precursor (Co-BM), and as well as the conductivity of the resultant electrocatalyst. Impressing, carbonization of Co-BM at 800 °C under N₂ atmosphere endows the pyrolysis product (Co-BM-800) with the well-dispersed Co/CoO riveted on nitrogen-doped carbon, as well as the enhanced ORR performance in terms of positive onset-potential (0.890 V vs. RHE), large diffusion limiting current density (5.21 mA cm⁻²), and high stability.

KEYWORDS

Benzimidazole-5-carboxylic acid; 2-Methylimidazole; “4-Self” strategy; Oxygen reduction reaction (ORR)

1. Introduction

At present, the global energy crisis and environmental pollution force people to explore green and sustainable energy. Oxygen reduction reaction (ORR) is a key technology for sustainable energy development.[1-3] Transition metal catalysts with hollow d orbitals and variable valences are considered to be the best substitutes for noble metal. Transition metal oxides have attracted intense attention for their excellent stabilities, catalytic abilities.[4, 5]

Take cobalt oxide (CoO_x) as an example, it is a semiconductor material with a 3d electronic configuration and high surface activation energy. Nevertheless, its poor conductivity and the uncontrollable size hinder the electron transfer and reaction processes.[6, 7] In contrast, Co-N-C has better conductivity, but it is easy to leak and agglomerate during the ORR process, which inducing the poor stability. Generally, to enhance charge transport capacity and increase the exposure of active sites, CoO_x and Co-N-C were introduced to the carbon surface when combined with carbon nanotubes or graphene.[8, 9] However, during the ORR reaction, lack of bridging bonds between CoO_x and Co-N-C, the electron transfers and electrocatalytic tunability at the interface are greatly restricted.[10, 11] Meanwhile, the introduced CoO_x and Co-N-C are easy to secede or agglomerate, resulting in poor stability. To prevent the leakage and agglomeration of Co-N-C and simultaneously to provide efficient electronic conducting routes for CoO_x, it is still a great challenge to create a cooperative CoO_x/Co-N-C structure. Construction the precursor of the electrocatalyst using self-assembly directed by different non-covalent interactions (coordinate bonds, hydrogen bonds, van der Waals force, etc) can provide us a feasibly way. In particular, cobalt ions can be chelated by a suitable O- and N-donor hybrid ligand.[12, 13]

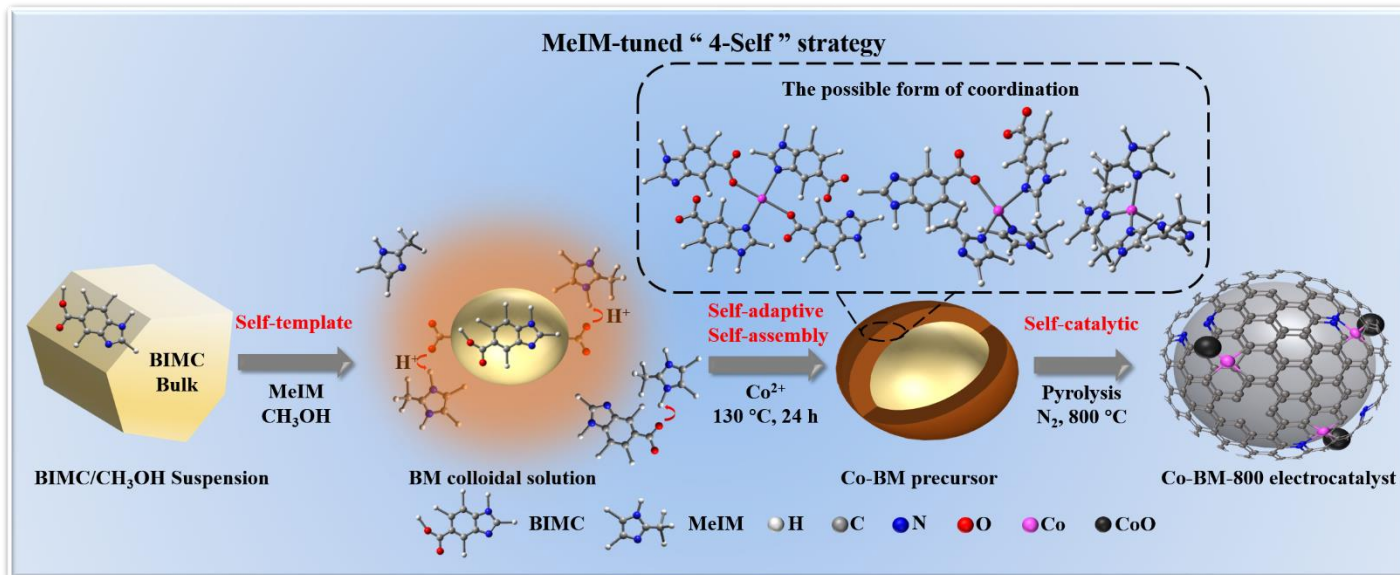
Benzimidazole-5-carboxylic acid (BIMC) has been widely used in the design of therapeutic agents in the last decade, due to its

relevance to DNA, proteins, and other biological system.[14-16] The structure of BIMC possesses a carboxylic acid group and a benzimidazole ring, exhibiting both O- and N-donor functionalities for various coordination modes. Driven by the hydrogen bonds and π - π stacking interactions, benzimidazole groups can aggregate to nanocluster and act as the physical crosslinking network, greatly limiting the movement of the molecules. It is also because of its strong char-formation ability, benzimidazoles are often used as a nitrogen source and carbon source to prepare nitrogen-doped porous materials.[17-19] Besides, the self-assembly of deprotonated BIMC (BIMC⁻¹) with Co(II) by layer-separating diffusion at room temperature gives rise to a 3-D supramolecular architectures consisting of 1-D zigzag chains with two crystallographically independent Co atoms alternately bridged by double BIMC⁻¹ ligands.[20, 21] The shortest intrachain Co...Co separation is 9.205 Å. Based on aforementioned interesting characteristics of BIMC, it implies that BIMC is a promising hybrid ligand to design the precursor for the efficient electrocatalyst. Moreover, the electrocatalytic performance can be further enhanced via tuning the coordination environment of BIMC and Co(II) and controlling the self-assembling process based on BIMC.

In this work, 2-methylimidazole (MeIM) was genetically used as a modulator to tune the self-templating, self-adapting, self-assembly and self-catalysis based on BIMC, during the preparation process of electrocatalyst. This MeIM-tuned “4-Self” strategy was proposed based on the following reasons: (1) pK_a value of BIMC and MeIM is 3.10 and 14.44, respectively. As a base, the deprotonation degree of BIMC can be altered by MeIM and provide more available carboxylate for coordination with Co(II). (2) Due to its intermolecular hydrogen-bonding and π - π interactions, BIMC poorly dissolves in methanol. Base on the acid/base equilibria of BIMC/MeIM, the aggregated size of BIMC is expected to be regulated by MeIM. The solvophobic BIMC aggregates can be used

as templates directing the structure of the self-assembly. Moreover, the BIMC aggregates may be inevitable confine the migration and agglomeration of Co, resulting in the highly-dispersed metal active sites. (3) The rest of MeIM may serve as a competitive ligand at Co(II) center. The coordination state of Co(II) may be self-adaptive.[22, 23] (4) The aggregated BIMC particles using as

templates, the coordinated BIMC and the coordinated MeIM can be used as N- and C-sources. The carbonization may be self-catalyzed via the chelated Co(II). The chelated Co(II) in precursor may be further reduced to a low-valence states. Thus, according to the proposed MeIM-tuned “4-Self” strategy, the boosted ORR electrocatalysis may be realized.



Scheme 1. Schematic illustration of the fabrication process of Co-BM-800.

2. Experimental section

2.1 Chemicals and materials

Cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, AR, 99%), benzimidazole-5-carboxylic acid (BIMC) and methanol (CH₃OH, AR, 99%) were purchased from Aladdin. 2-methylimidazole (MeIM) was bought from Shanghai Meryer Chemical Technology Co. Ltd (China). A commercially available 20 wt% platinum-loaded carbon (Pt/C) loaded on carbon black (Johnson Matthey) was used as received. All other chemicals were of analytical grade and used without further purification. Deionized water (DI) was used throughout the experiment.

2.2 Preparation of electrocatalyst based on BIMC and MeIM as ligands

The protocol of preparation of Co-BM is described as below: Under ultrasonic treatment, 1 mmol BIMC and 6 mmol of MeIM were dissolved in 25 mL of methanol to form the faint yellow transparent solution A (BM). 1.75 mmol Co(NO₃)₂·6H₂O was dissolved in 10 ml methanol under ultrasonic treatment until formed the transparent pink solution B. Solution A was added dropwise into solution B, then the mixed solution was transferred to an autoclave and heated at 130 °C for 24 h. Finally, the obtained precipitate was centrifuged, washed three times with methanol and dried overnight in a vacuum, then Co-BM was obtained. For comparison, the products without MeIM (only adding 7 mmol of BIMC) and without BIMC (only adding 7 mmol of MeIM) were also prepared via the solvothermal reaction under identical conditions, these samples are respectively denoted as Co-BIMC and Co-MeIM.

Under the protection of nitrogen, the obtained precursors were carbonized from room temperature to 800 °C at the heating rate of 5 °C/min for two hours, cooled to room temperature and ground to obtain Co-MeIM-800, Co-HL-800 and Co-BM-800, respectively.

2.3 Electrochemical measurements

All electrochemical studies were performed with a conventional three-electrode cell using a graphite rod as counter electrode, a saturated calomel Hg/Hg₂Cl₂ electrode as reference electrode.

Cyclic voltammetry (CV) and rotating disk electrode (RDE, 0.196 cm², Metrohm) were recorded on CHI660D electrochemical workstation (CH Instrument). Linear sweep voltammetry (LSV) experiments were executed at 10 mV s⁻¹ under rotating speeds varying from 225 to 2500 rpm. During electrochemical measurements a flow of N₂ or O₂ was maintained over the electrolyte (0.1 mol L⁻¹ KOH) for continuous N₂ or O₂ saturation. All catalysts were fabricated follow steps: Firstly, The catalyst ink (5 mg mL⁻¹) of Co-MeIM-800, Co-BIMC-800, Co-BM-800 and 20% Pt/C were prepared by dispersing the catalyst powders in deionized water and ultrasonic dispersion for 5 min. Secondly, spreading 20 μL of the catalyst ink onto pretreated RDE and dried at room temperature. Finally, 5 μL of Nafion/ethanol solution (5 wt%) was dropped on the surface of above-modified electrode and dried in air. Thus, the catalysts modified RDE were fabricated. Herein, all the potentials were converted to a reversible hydrogen electrode (RHE), E (RHE) = E (Hg/Hg₂Cl₂) + 1.008 V.

2.4 Materials characterization

A TENSOR Model 27 FT-IR spectrometer was used for FT-IR spectra test. The X-ray diffraction (XRD) patterns were collected on X-ray diffractometer (Bruker D8) at 40 kV and 40 mA. With 532 nm solid laser as an excitation source, an iHR550 Raman microscope (HORIBA scientific) was used for Raman spectra test. The detailed morphology and size of the catalyst product were analyzed by transmission electron microscope (TEM, FEI Tecnai 20 electron microscope). The element mapping images were carried out on Quanta 250F and FEI. The surface functional properties of our catalysts were investigated by K-Alpha X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI). The particle size of BM was measured by dynamic light scattering (DLS, Malvern ZS90). X-ray absorption fine spectroscopy (XAFS) was performed in transmission mode on the Beamline BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), which used a Si (111) double crystal monochromator for energy selection. Meanwhile, the XAFS of Co foil, CoO, Co₂O₃, and Co₃O₄ were also tested for comparison.

3. Results and discussion

3.1 The interactions between BIMC and MeIM in methanol

The strong intra/inter molecular hydrogen bonds and π - π stacking interactions of the self-aggregated BIMC greatly limit its dissolution in methanol. Generally, the full-dissolved BIMC/methanol can be obtained by the neutralization of BIMC with equal mole of NaOH. Herein, MeIM was used as a Lewis base to promote the deprotonation of BIMC. The interactions between BIMC and MeIM in methanol was initially investigated. 1 mmol BIMC was dispersed in 25 mL methanol by using ultrasonicator. As shown in Figure 1a, the transparency and pH value of the prepared BIMC suspension were greatly influenced by the presence of MeIM. When MeIM amount increased to 6 mmol, the white suspension just transformed into a faint yellow and transparent solution with pH=9. The obtained solution (mole ratio, BIMC:MeIM=1:6) was denoted as BM. Distinguished Tyndall phenomenon could be still observed in BM (Figure 1b). Further increase of MeIM to 10 mmol, the red pillar diminished obviously. It indicated the “solubilization” of MeIM and the existed “colloidal particles” in BM. Thereby, TEM and DLS were performed to study the morphology and distribution state of the particles in BM. Elliptical particles with fade edge were

uniformly distributed, average size of 921.83 nm (diameter) (Figure 1c, Figure S1).[24] Zeta potential test showed the particles charged negatively (Zeta potential = -10.1 mV).

To further reveal the interactions between BIMC and MeIM, FTIR spectroscopy was explored. Figure 1d showed the FTIR spectra of MeIM, BIMC and BM. For the self-aggregated BIMC, the peaks of non-ionized carboxylic group could be observed at 3200 cm^{-1} and 1660 cm^{-1} , assigned to the vibration of O-H and the stretching vibration of -C=O, respectively.[25] Interacted with MeIM, significant change could be found at the spectrum of BM. The broad absorption bands in the range of 3300-2000 cm^{-1} were similar to that of MeIM. The characteristic peaks of non-ionized carboxylic group of BIMC were almost invisible. Meanwhile, the asymmetric and symmetric stretching vibrations of the carboxylate groups at 1628 and 1429 cm^{-1} could be identified.[26] It demonstrated that MeIM could be used to deprotonate the non-ionized carboxylic group of BIMC. Due to acid/base equilibria of BIMC/MeIM, the small BIMC crystals of self-aggregated structure could be well distributed in methanol. Thus, the “colloidal” BM solution contained the ingredients of deprotonated BIMC (BIMC⁻), protonated MeIM, MeIM and the small negatively charged BIMC crystals with the size of 921.83 nm.

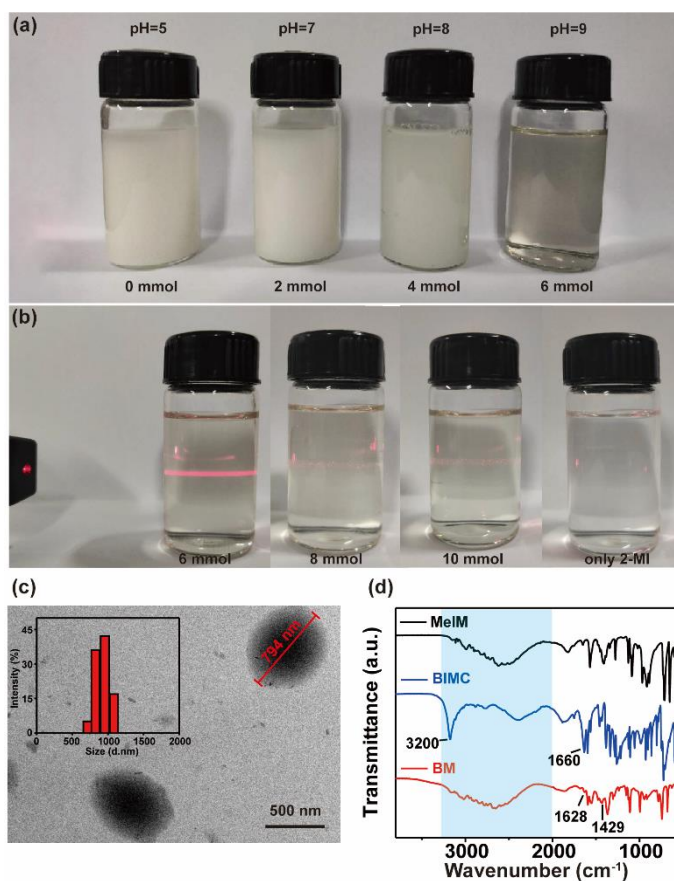


Figure 1. (a) The pH and transparency of 1 mmol BIMC with 0, 2, 4, 6 mmol MeIM in 25 mL methanol solution, respectively. (b) Tyndall phenomenon for 1 mmol BIMC with 6, 8, 10 mmol MeIM in 25 mL methanol, respectively. The last one is 6 mmol MeIM in 25 mL methanol. (c) TEM and Dynamic light scattering (DLS) measures the size of BM (1 mmol BIMC with 6 mmol MeIM in 25 mL methanol). (d) FT-IR spectra of MeIM, BIMC and BM.

3.2 Characterization of precursor

When Co(II) was introduced to BM, the spontaneous self-assembly occurred to form the supramolecular aggregates as the precursor of electrocatalyst. The detail morphologies of the self-assembled precursor (Co-BM) were measured by SEM, Co-MeIM and Co-BIMC as control. As reported in the literature, Co-MeIM was regular rhombic dodecahedrons in shape and about 400 nm in size (Figure 2a).[27] Co-BIMC displays the structure of irregular

blocks (Figure 2b). Strangely, small connected plates (diameter of ~500 nm) could be observed in Figure 2c for the morphology of Co-BM. As the illustrated XRD patterns in Figure 2d, Co-BM was amorphous state, while Co-MeIM and Co-BIMC were crystal states.

The Co(II)-coordination was further confirmed via FTIR (Figure 2e, Figure S2). In the spectrum of Co-BM, the asymmetric and symmetric stretching vibration bands around at 1549, 1435 and 1386 cm^{-1} indicated that the carboxylate groups employ a chelating and

bridging coordinated modes.[25] The $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$ of the free BIMC at 1622 cm^{-1} and 1484 cm^{-1} shift towards lower wave numbers at 1590 cm^{-1} and 1463 cm^{-1} in Co-BM indicating the

coordination of nitrogen atoms of BIMC to Co(II). It should be noted that the $\nu(\text{NH})$ bending vibration for free MeIM at 1153 cm^{-1} in spectrum of BM couldn't be found in spectrum of Co-BM.[28, 29]

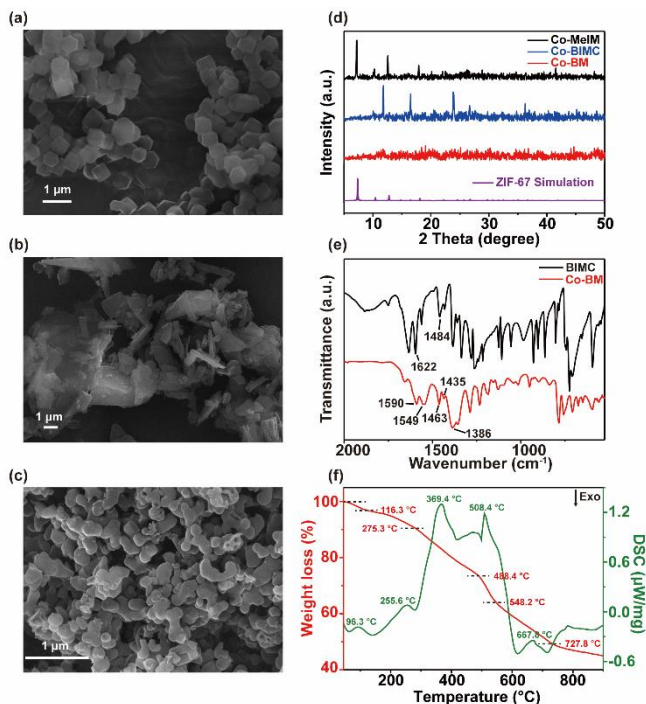


Figure 2. SEM images of (a) Co-MeIM, (b) Co-BIMC and (c) Co-BM. (d) XRD results of Co-MeIM, Co-BIMC and Co-BM. (e) FT-IR spectra of Co-MeIM, Co-BIMC and Co-BM. (f) TG-DSC curves of Co-BM in N_2 atmosphere with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

To further confirm the existence of MeIM in the structure of the self-assembled Co-BM, thermogravimetric/differential scanning calorimetry (TG/DSC) was then performed. The TG plot for Co-BM displayed a loss of mass in six stages (Figure 2f). In the first stage, the mass loss of (2.9%) occurred before $116.3\text{ }^\circ\text{C}$ (DSC endothermic peak at $96.3\text{ }^\circ\text{C}$), which corresponded to the removal of physically adsorbed methanol and water. In the second stage from 116.3 to $275.3\text{ }^\circ\text{C}$, an endothermic peak at $255.6\text{ }^\circ\text{C}$ was in accordance with the boiling point of MeIM (Figure S3). Nevertheless, the melting endothermic peak of MeIM at $149.9\text{ }^\circ\text{C}$ was not observed. It indicated that there existed the coordinated form of MeIM in Co-BM and the weight loss (about 6.3%) of this stage assigned to the decomposition of the coordinated MeIM.[30] The third stage ($275.3\text{--}488.4\text{ }^\circ\text{C}$), with mass loss of 17.2% and an endothermic peak at $369.4\text{ }^\circ\text{C}$, were attributed to the volatilization of BIMC.[31] The mass loss during the fourth stage from $488.4\text{ }^\circ\text{C}$ to $548.2\text{ }^\circ\text{C}$ with an endothermic peak at $508.4\text{ }^\circ\text{C}$ was due to the decomposition of Co-BIMC. The sample was further graphitized and gradually formed Co/CoO during the last two stages.

3.3 Characterization of catalyst

The crystalline nature of the obtained pyrolysis products was identified by XRD analysis. As illustrated in Figure 3a, Co-MeIM-800, Co-BIMC-800 and Co-BM-800 presented the similar

diffraction peak at 44.22° indexes to the (111) plane of metallic Co (PDF#15-0806). The Raman spectrum of the pyrolysis product was measured to figure out the detail structure information of carbon. It was observed that the D and G bands of carbon locate at $\sim 1350\text{ cm}^{-1}$ and $\sim 1580\text{ cm}^{-1}$, respectively (Figure 3b). Co-BM-800 possessed the relatively harmonious I_d/I_g ratio (1.10) compared with those for Co-MeIM-800 ($I_d/I_g=1.35$) and Co-BIMC-800 ($I_d/I_g = 0.93$), as well as the distinguished peak for CoO. The SEM revealed that Co-BM-800 retained the initial morphology of its precursor with reduced size of 300 nm (Figure 3c, Figure S4). TEM image of Co-BM-800 in Figure 3d indicated the well-dispersed nanoparticles with diameter from 200 to 300 nm . Such nanoparticles exhibited obvious lattice fringes with spacing of 0.205 , 0.214 and 0.334 nm for crystal plane of Co(111), CoO(200) and C(002), respectively (Figure 3e).[32, 33] The element distribution of Co-BM-800 was then analyzed by EDS (Figure 3f). The pyrolysis product had a chemical composition of Co, O, C and N. The distribution of Co was highly overlapped with that of O elements. Meanwhile, the similar evenly elemental distribution manner can be observed for N and C. It was evident that Co/CoO was wrapped in few graphitic N-doped carbon layers, which is favorable to the enhanced electrocatalytic performance, such as conductivity, stability.

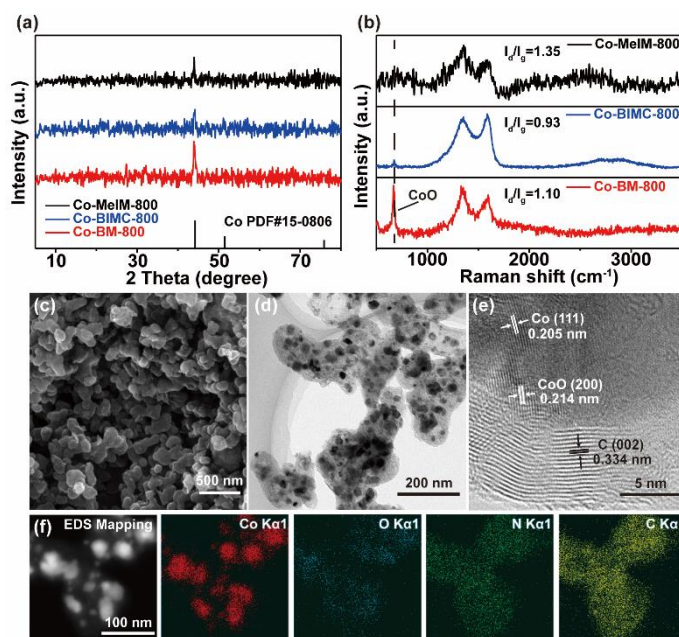


Figure 3. (a) XRD results of Co-MeIM-800, Co-BIMC-800 and Co-BM-800. (b) Raman spectra of Co-MeIM-800, Co-BIMC-800 and Co-BM-800. (c) SEM, (d) HRTEM, (e) lattice image and (f) EDS images of Co-BM-800.

The detailed elemental composition and surface chemical state of Co-BM-800 were further investigated by XPS, Co-MeIM-800 and Co-BIMC-800 as control. The XPS survey spectra reveal the expected photoelectron peaks due to Co, O, N and C elements in all samples (Figure 4a). In Figure 4a, XPS spectra simply proved the existence of Co, N, C and O. Generally, the Co 2p spectrum could be divided into two peaks arising from the orbitals of Co 2p_{3/2} and Co 2p_{1/2}, respectively. The Co 2p_{3/2} spectrum had a further peak separation as demonstrated in Figure 4b, corresponding to three peaks at 781.9, 780.3 and 778.6 eV for Co-N, Co-O and Co⁰, respectively.[34, 35] The CoO content of Co-BM-800, Co-MeIM-800 and Co-BIMC-800 were 52.4%, 42.9% and 4.8%, respectively. Similarly, the metal oxygen content of Co-BM-800 (530.4 eV) (12.5%) in O 1s was almost twice more than that of Co-BIMC-800 (6.1%)(Figure 4c).[36] According to the previous article, CoO was crucial for ORR catalyst.[6] The high-resolution N 1s spectra of all samples indicated the existence of four dominating signals of doping N, including pyridinic-N, pyrrolic-N, graphitic-N, and Co-N (Figure 4d).⁶ The content of the aforementioned N species in Co-BM-800 (22.6% pyridinic N, 20.0% graphitic N and 29.6% Co-N) exceeded that of Co-BIMC-800 (19.2% pyridinic N, 23.0% graphitic N and 21.3% Co-N). In general, pyridinic N, graphitic N and Co-N were believed to be present in the active sites of ORR.

X-ray absorption spectroscopy (XAS) measurements were performed to further analyze the coordination environment of cobalt and the chemical state of metal species at the atomic level (without phase correction Figure 4 e and f, Figure S5, Table S1). The X-ray absorption near-edge structure (XANES) of Co-MeIM-800, Co-BIMC-800, Co-BM-800 and the reference sample at the K edge showed that the absorption edges of Co-MeIM-800, Co-BIMC-800, Co-BM-800 were located between Co foil and CoO (Figure 4e), suggesting that the valence states of Co-MeIM-800, Co-BIMC-800, and Co-BM-800 were located between Co⁰ and Co²⁺. In Co-MeIM-800, Co-BIMC-800 and Co-BM-800, cobalt existed as a mixture of cobalt element and cobalt oxide. Extended X-ray absorption fine structure (EXAFS) spectra of Co-MeIM-800, Co-BIMC-800, and Co-BM-800 showed that the main peaks are located at 2.12 Å, 2.09 Å, and 2.18 Å, respectively (Figure 4f). Considering their bond length was similar to Co foil (2.15Å), it could be speculated that it was a Co-Co coordination structure.[37, 38] In addition, the coordination of cobalt species was inferred by fitting (Table S1). Combined with XPS, we believed that Co-BM-800 contained more Co⁰ and CoO, and CoO is mainly distributed on the surface of the particles, which was conducive to the reaction kinetics of ORR.

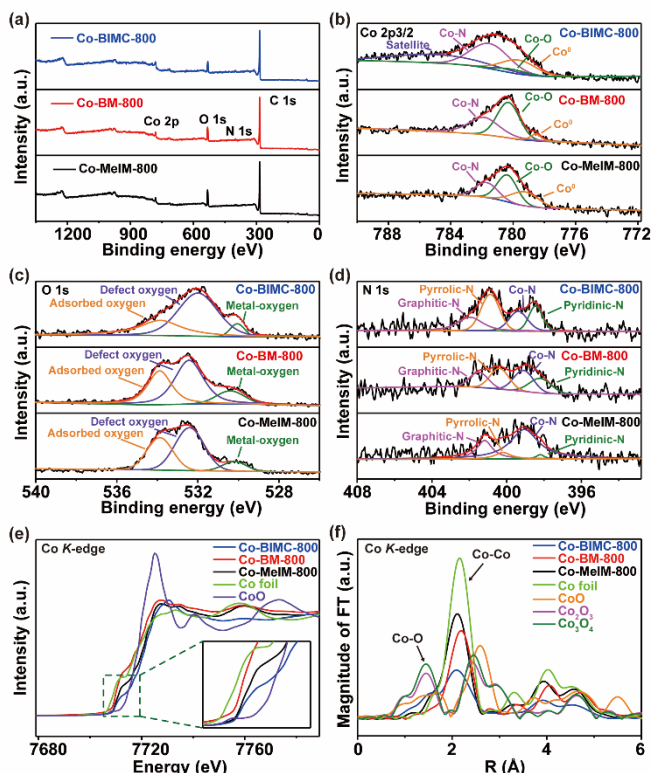


Figure 4. (a) XPS survey spectra for Co-BIMC-800, Co-BM-800 and Co-MeIM-800. XPS spectra of (b) Co 2p_{3/2} (c) O 1s, and (d) N 1s for Co-BIMC-800, Co-BM-800 and Co-MeIM-800, respectively. (e) XANES profiles and (f) FT-EXAFS spectra of Co K-edge of Co-MeIM-800, Co-BIMC-800, Co-BM-800 and the reference materials.

3.4 Electrocatalytic activity in ORR

The ORR activity of Co-BM-800 was assessed with the RDE technique, using Co-BIMC-800, Co-MeIM-800 and commercially available 20 wt.% platinum-loaded carbon (20% Pt/C) as control. Figure 5a presented the CVs of the four samples in N₂ and O₂-saturated 0.1 mol L⁻¹ KOH at a scan rate of 10 mV s⁻¹. The reduction peak was found at 0.80, 0.83, 0.84 and 0.86 V for Co-BIMC-800, Co-MeIM-800, Co-BM-800 and 20% Pt/C, respectively. A distinguishable oxidation peak at around 1.10 V was observed, which might be ascribed to the existence of Co/CoO at the lower valence state. This oxidized state of Co/CoO in turn accelerated ORR. Figure 5b showed the ORR polarization curves of the four

samples in the same conditions at a rotation speed of 1600 rpm. The corresponding electrocatalytic performances such as onset potential, half-wave potential and limiting current density were summarized in Table S2. Obviously, Co-BM-800 possessed a relative high onset potential (0.890 V) comparable to that of 20% Pt/C and the largest limiting current density (5.21 mA cm⁻²). In addition, the stability and durability in relation to use methanol as fuel were evaluated through chronoamperometric measurements at 0.4 V. As shown in Figure 5c, Co-BM-800 retained 98.9% of its initial signal, which higher than that of 20% Pt/C (90.6%), suggesting the good stability for ORR in alkaline electrolyte. The tests of methanol tolerate abilities displayed in Figure 5d indicated a good tolerance of Co-BM-800 to methanol.

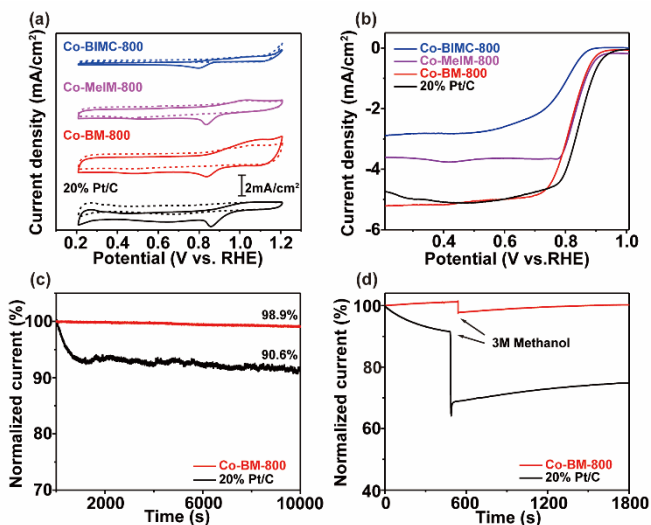


Figure 5. (a) CV curves of Co-MeIM-800, Co-BIMC-800, Co-BM-800 and 20% Pt/C in N₂/O₂-saturated 0.1 mol L⁻¹ KOH solution at a scan rate of 10 mV s⁻¹. (b) LSV curves of Co-MeIM-800, Co-BIMC-800, Co-BM-800 and 20% Pt/C in O₂-saturated 0.1 mol L⁻¹ KOH solution at a scan rate of 10 mV s⁻¹ (rotating speed=1600 rpm). (c) Relative current intensities of Co-BM-800 and 20% Pt/C recorded at 0.6 V versus RHE in O₂-saturated 0.1 mol L⁻¹ KOH solution (rotating speed=1600 rpm). (d) Chronoamperometric responses of Co-BM-800 and 20% Pt/C at 0.4 V in O₂-saturated 0.1 M KOH (rotating speed=1600 rpm) with the addition of 3 M methanol.

The decent ORR performance of Co-BM-800 owed to its special composition and structural characteristics. On one hand, enriched N-doped graphitic carbon simultaneously improved the dispersion of the active component, the electronic conductivity and the electrochemical stability of the electrocatalyst. On the other hand, highly dispersed Co/CoO NPs riveted on nitrogen-doped carbon. The synergistic effect of the active sites (e.g., Co-N, CoO and N-C) greatly increased the electrocatalytic activity.

4. Conclusions

In summary, we have demonstrated a general paradigm for rational design and synthesis of a promising electrocatalyst with cooperative CoO/Co-N-C for ORR via MeIM-tuned “4-Self” strategy (self-templating, self-adapting, self-assembly and self-catalysis). BIMC acts as O- and N-donor hybrid ligand. Due to the equilibria of “acid-base” and coordination, tiny colloidal BIMC particles formed in methanol and served as one of building blocks, the in situ competitive cobalt(II)-coordination subsequently occurred at the interface of the colloidal particles, thereby enabling the creation of supramolecular assembly as the precursor of electrocatalyst. Thus, the resultant Co-BM-800 catalyst possessed the structure of highly dispersed Co/CoO NPs riveted on N-enriched carbon, inducing in good catalytic and conductive properties benefit for the enhanced ORR. We envision this facile and distinctive MeIM-tuned “4-Self” strategy could open up significant technological opportunities for the preparation of advanced nanomaterials with high-lever complexities, on-demand functionalities and fascinating performance in the near futures.

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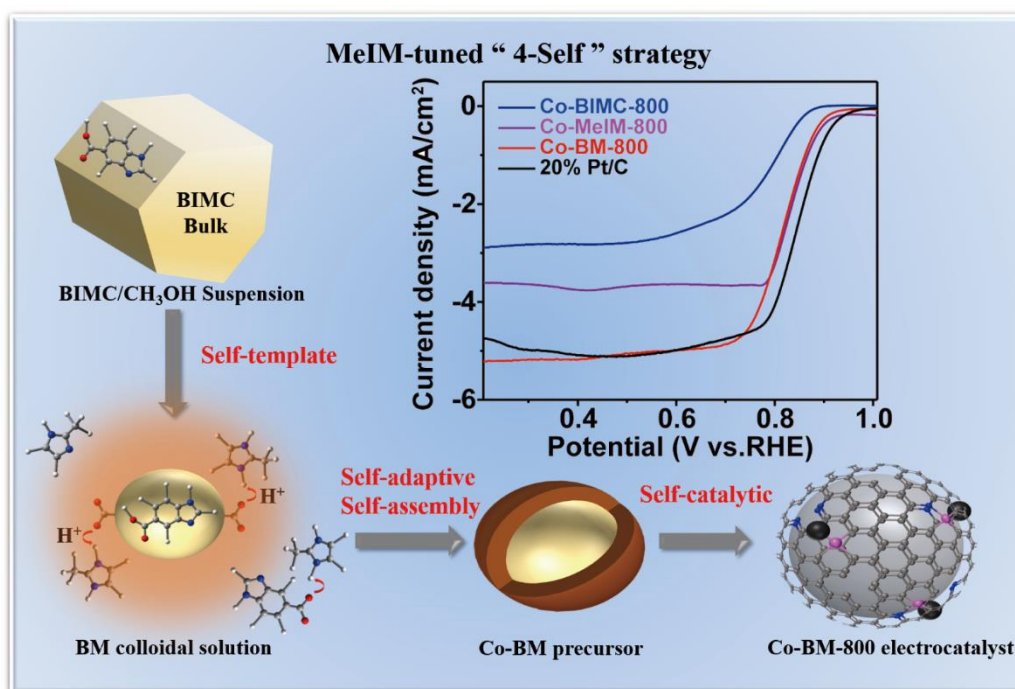
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Highlights

- MeIM-tuned “4-Self” (self-templating, self-adapting, self-assembly and self-catalysis) strategy based on BIMC was used to prepare a highly dispersed and cooperative CoO/Co-N-C for the boosted ORR.
- MeIM modulates the dispersion of BIMC in methanol to generate colloidal-like BIMC tiny particles as self-tempeate for the self-assembled precursor.
- The deprotonated BIMC can be used as hybrid ligand for coordination with Co^{2+} , exhibiting both O- and N-donor functionalities.
- The aggregated colloidal BIMC particles, the coordinated BIMC and the coordinated MeIM can be used as N- and C-sources.

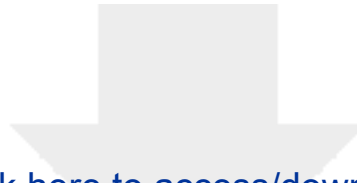


MeIM-tuned “4-Self” strategy based on BIMC for boosting oxygen reduction electrocatalysis

Declaration of interests

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