



# Dual-metal zeolitic imidazolate frameworks and their derived nanoporous carbons for multiple environmental and electrochemical applications

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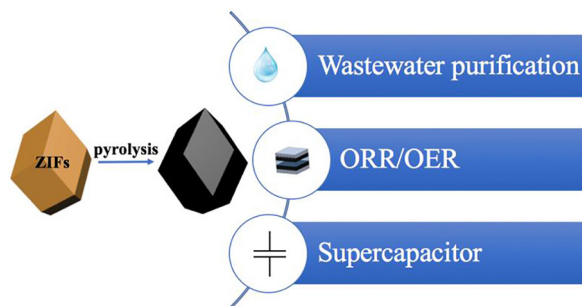
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## HIGHLIGHTS

- Dual Zn-ZIF-8/Co-ZIF-67 and their derived nanoporous carbons (NPCs) were prepared.
- Pristine ZIFs exhibited excellent adsorption of organic pollutants in wastewater.
- High graphitic NPCs presented better organic degradation with peroxymonosulfate.
- NPCs from Co-ZIF-67 also showed the best catalytic activity in ORR and OER.
- NPC from Zn-ZIF-8 performed as the best supercapacitor electrode.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Nanoporous carbons were prepared by thermal conversion of zinc/cobalt-based zeolitic imidazolate frameworks (ZIF-8/ZIF-67) and their bimetallic ZIFs, and used for environmental remediation, energy storage and conversion. For wastewater treatment by adsorption, pristine ZIFs presented high adsorption capacities of phenol while the carbon derivatives showed a negligible capacity, due to the collapse of frameworks during the pyrolysis, resulting in a sharp decrease in specific surface area and micropore fraction. However, the as-derived carbons exhibited excellent catalytic performances in degradation of phenol and *p*-hydroxybenzoic acid by advanced oxidation using peroxymonosulfate. Moreover, ZIF-67 derived carbons also produced the best performances in electrochemical oxygen reduction and evolution reactions due to a high graphitic degree, while ZIF-8 derived carbons showed the highest specific supercapacitance, attributing to the large mesopore volume and specific surface area. This study illustrated that the structures of ZIFs-derived carbon materials are determined by the metal species and constituents of the parental ZIFs as well as the pyrolysis conditions, making the carbons varying performances in environmental and electrochemical applications.

## 1. Introduction

Nanoporous carbons (NPCs), as environmental-friendly and

nontoxic functional materials, hold a great promise to relieve the burden of environmental crisis and energy shortage [1–3]. Their applications in supercapacitors, fuel cells, and pollutant removal were

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widely explored [4–8]. Metal-organic frameworks (MOFs), consisting of organic linkers and metal centers, are extremely advantageous as sacrificial precursors to yield various NPCs via facile carbonization [9–11]. Zeolitic imidazolate frameworks (ZIFs) are the sub-family of MOFs, which could generate NPCs and metal-NPC composites by rational choices of metal centers [12–14]. The volatile zinc and stable cobalt have been frequently used as the metal centers of ZIF-8 and ZIF-67, respectively.

ZIF-8 is an ideal precursor for high-surface-area amorphous carbon due to the volatility of zinc during carbonization and easy removal by acid digestion. Xu's group successfully synthesized nitrogen-doped NPC with high surface area and hierarchical pores from ZIF-8, showing excellent CO<sub>2</sub> adsorption, good performances in oxygen reduction reaction (ORR) and energy storage [15,16]. ZIF-67 was employed as a template for graphitic carbon with high crystallinity and conductivity, attributing to the catalytic graphitization of amorphous carbon by cobalt in the pristine ZIF-67 [17]. As previously reported, highly graphitic carbons, carbon nanotubes, and carbon networks were obtained from ZIF-67, exhibiting outstanding electrochemical performances in energy storage and conversion [18–20]. In order to combine the merits of both amorphous and graphitic carbons, bimetallic Zn-Co-ZIFs have been designed as the precursors. Cobalt-nitrogen-carbon hybrids and porous carbons were synthesized, and their performances in ORR and oxygen evolution reaction (OER) could be tuned by the carbonization conditions and molar ratios of zinc and cobalt in the parental ZIFs [21,22]. Yamauchi's group designed core-shell structured ZIF-8@ZIF-67 to make hybrid carbon materials consisting of nitrogen-doped carbon core and graphitic carbon shell, showing as an excellent supercapacitor [23].

Apart from the electrochemical applications, limited study on ZIFs-derived materials for wastewater purification has been conducted. Torad et al. synthesized Co/NPC from ZIF-67, showing excellent adsorption of dyes [24]. Carbons and carbon-ZnO hybrids from ZIF-8 were also investigated for pollutant removal via adsorption or photocatalysis [25–28]. Advanced oxidation processes (AOPs) are promising in wastewater remediation due to the complete degradation of organic pollutants [29–31]. ZIF-67, as well as the carbons derived from ZIF-67 and ZIF-8, was used to activate peroxymonosulfate for degradation of organic pollutants through radical and nonradical pathways [32–35].

Although a variety of MOF-derived carbons have been synthesized and demonstrated good performance in a specific application, few investigations have been focused on the effects of metal centers of MOFs on carbon structure and different applications. In this work, we synthesized NPCs and metal-NPC hybrids derived from ZIF-8, ZIF-67 and Zn-Co-ZIFs with varied molar ratios of zinc and cobalt at mild carbonization conditions, and studied their performances systematically in wastewater treatment (via adsorption and AOPs) and electrochemical applications including ORR, OER and supercapacitors. Phenol and *p*-hydroxybenzoic acid were chosen as the target organic pollutants here, as they are toxic to aquatic fishes, agro-industrial and pharmaceutical plants, and the removal of them has been a great concern of human beings [36,37]. We found that the NPCs have varying performances in those applications depending on ZIF precursors. The molar ratios of zinc and cobalt in the pristine ZIFs, together with the pyrolysis conditions, induced the selective performances of the corresponding carbon derivatives in the above reactions. This study provides new insight in relationship among metal, carbon structure and performance of MOF-based materials for tailored applications.

## 2. Material and methods

### 2.1. Materials and chemicals

Zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 98%), cobalt nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 98%), 2-methylimidazole (Hmim, 99%), methanol (99.8%), potassium peroxymonosulfate (PMS), phenol (99%), *p*-hydroxybenzoic acid (PHBA, 99%) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98%)

were purchased from Sigma-Aldrich. All the chemicals were used without further purification.

### 2.2. Synthesis of ZIFs and their derived materials

In a typical synthesis process of ZIF-8 (or ZIF-67), 6 mmol of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (or Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) was dissolved into 60 mL of methanol to form a clear solution, which was subsequently poured into 20 mL of methanol containing 24 mmol of 2-methylimidazole. The milky solution was incubated at room temperature for overnight and the precipitate was collected by centrifugation with further methanol washing and drying in an oven. The bimetallic ZIFs (named as ZIFs-x) were prepared following the same procedures by controlling the molar ratio (x) of Co<sup>2+</sup> to Zn<sup>2+</sup>. For example, the amounts of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O for synthesis of ZIFs-2.0 were 4 mmol and 2 mmol, respectively.

The above prepared ZIFs were then pyrolyzed in a tube furnace at 700 °C for 3 h under N<sub>2</sub> atmosphere with a heating rate of 2 °C/min. After acid washing with 0.5 M H<sub>2</sub>SO<sub>4</sub> at 80 °C for 24 h, the as-collected materials were named as ZIF-8-C, ZIF-67-C and Cx, using ZIF-8, ZIF-67 and ZIFs-x as the precursors, respectively. Co-C and Co<sub>3</sub>Zn-C derived from ZIF-67 and ZIFs-0.3, respectively, were prepared without acid washing. ZIF-67-C1000 and C0.5–1000 were synthesized by pyrolysis of ZIF-67 and ZIFs-0.5 at 1000 °C, respectively, followed by acid washing. The synthesis strategies of samples were summarized in Table 1. In this study, the pyrolysis temperatures were set as 700 and 1000 °C. As previously reported [38], cobalt species started to catalyze the conversion of the amorphous carbon into graphitic carbon from 700 °C, so that we could obtain ZIFs-derived carbons with various graphitic degrees due to the different contents of cobalt. With the rise of pyrolysis temperature, graphitic degree of the derived carbons would increase correspondingly, so we chose another higher temperature 1000 °C to enhance the catalytic effect of cobalt. In addition, the zinc (vapor point of zinc ≈ 906 °C) in the pristine ZIFs would evaporate at 1000 °C and leave pores in the carbons, tending to enhance the catalytic effect of carbons [22].

### 2.3. Characterizations of samples

Powder X-ray diffraction (XRD) patterns were measured by a Bruker D8-Advance X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). The morphology and elemental composition of the samples were investigated using a transmission electron microscopy (TEM, JEOL 2100) and field emission scanning electron microscopy (FE-SEM, Zeiss Neon 40 EsB) with energy dispersive X-ray spectroscopy (EDS). The chemical states were studied on X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250XI) using monochromatic Al Kα radiation. Raman spectra were obtained on a Micro Raman Spectroscopy system (Horiba, LabRAM HR UV-NIR). Thermogravimetric-differential thermal analysis (TG-DTA) was carried on a TGA/DSC-1 thermogravimetric analyzer from Mettler-Toledo Instrument to detect mass loss of the samples. The surface areas of the ZIFs were measured at –196 °C on a Quantachrome instrument/Autosorb-1. N<sub>2</sub> adsorption/desorption isotherms of the as-derived materials were obtained at –196 °C on a

**Table 1**  
The synthesis conditions of different carbon samples.

Sample name	Precursors	Carbonization condition	Acid washing
ZIF-8-C	ZIF-8	700 °C for 3 h	YES
ZIF-67-C	ZIF-67	700 °C for 3 h	YES
Cx	ZIFs-x	700 °C for 3 h	YES
ZIF-67-C1000	ZIF-67	1000 °C for 3 h	YES
C0.5-1000	ZIFs-0.5	1000 °C for 3 h	YES
Co-C	ZIF-67	700 °C for 3 h	NO
Co <sub>3</sub> Zn-C	ZIFs-0.3	700 °C for 3 h	NO

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