



Self-assembly of cobalt-centered metal organic framework and multiwalled carbon nanotubes hybrids as a highly active and corrosion-resistant bifunctional oxygen catalyst



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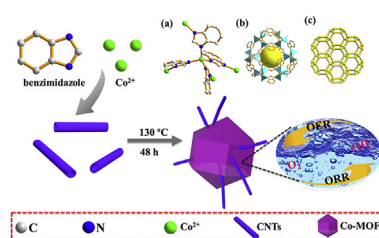
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HIGHLIGHTS

- A self-assembly approach to synthesize Co-MOF@CNTs 3D hybrids.
- CNTs can avoid the carbon corrosion at high positive potentials of OER.
- The structure offers a large surface area and stable anchoring sites.
- A synergistic interaction among Co(II), organic ligands and CNTs.
- The electrocatalyst achieves high performance in OER and ORR.

GRAPHICAL ABSTRACT



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ABSTRACT

Metal organic frameworks (MOF) derived carbonaceous materials have emerged as promising bifunctional oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) catalysts for electrochemical energy conversion and storage. But previous attempts to overcome the poor electrical conductivity of MOFs hybrids involve a harsh high-template pyrolytic process to *in situ* form carbon, which suffer from extremely complex operation and inevitable carbon corrosion at high positive potentials when OER is operated. Herein, a self-assembly approach is presented to synthesize a non-precious metal-based, high active and strong durable Co-MOF@CNTs bifunctional catalyst for OER and ORR. CNTs not only improve the transportation of the electrons but also can sustain the harsh oxidative environment of OER without carbon corrosion. Meanwhile, the unique 3D hierarchical structure offers a large surface area and stable anchoring sites for active centers and CNTs, which enables the superior durability of hybrid. Moreover, a synergistic catalysis of Co(II), organic ligands and CNTs will enhance the bifunctional electrocatalytic performance. Impressively, the hybrid exhibits comparable OER and ORR catalytic activity to RuO₂ and 20 wt% Pt/C catalysts and superior stability. This facile and versatile strategy to fabricating MOF-based hybrids may be extended to other electrode materials for fuel cell and water splitting applications.

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1. Introduction

Oxygen electrocatalysis is central to the development of efficient energy storage and conversion devices such as metal – air batteries

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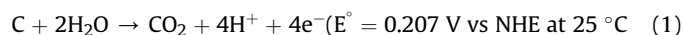
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and regenerative fuel cells to link intermittent renewable energy with energy needs on-demand [1–4]. However, progress is hampered by the sluggish kinetics of oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) [5]. To date, the most active catalysts for both the OER and the ORR are primarily derived from the platinum group metals, such as RuO₂, IrO₂ and Pt [6,7]. Nevertheless, the high cost and scarcity as well as poor stability has restricted their widespread applications. Besides, a major drawback is that good catalysts for OER, such as RuO₂, are often poor for ORR and vice versa, making it very challenging to realize materials that can serve as bifunctional catalysts for both OER and ORR.

With respect to the low cost, earth-abundant transition-metal oxides/hydroxides [8–10], especially Co-based complexes with different structures and dimensions [11–16], are explored as promising alternative catalysts for OER and ORR. However, the strong causticity in alkaline solution and intrinsic low conductivities of many Co-based catalysts hamper their further applications [17]. One recent strategy applied to improve the durability of these composites is to couple them with a conductive support such as graphene [10], carbon nanotubes [18], Ni foam [19]. Studying the general design of the catalysts, it can be seen that most of these conductive support-based composites are fabricated by direct deposition or adsorption of nanocatalysts on the substrates surface [20], yet the biggest problem is that the active centers are directly exposed and they are easily peeled off from the substrates surface during long-term electrochemical reactions, thus resulting in poor stability.

Recently, metal organic frameworks (MOFs), a class of crystal-line inorganic organic hybrid materials, with diverse skeletons and fascinating properties such as well-defined pore structures, high surface areas and large pore volume, are very attractive for applications in catalysis. Moreover, MOFs contain redox-active metals and organic linkers as both redox and proton transfer mediator motifs for catalyzing water oxidation reaction [21]. And a synergistic catalysis of inorganic catalysts and ligands promotes oxygen-evolving systems. Nevertheless, the intrinsic conductivity of most MOFs is less desirable, which excludes them from being used as electrode materials or electrocatalysts. Previous attempts to improve the electrical conductivity of MOFs hybrids involve a harsh high-template pyrolytic process to *in situ* form carbon [22–27], which suffer from extremely complex operation and time-consuming fabrication. What's worse, carbon corrosion is inevitable and disastrous at high positive potentials when OER is operated in the electrolyzer mode as indicated by the following reaction [28,29]:



Oxidation of carbon generally referred to as carbon corrosion, which can accelerate agglomeration or loss of active centers, thus decreasing the activity and lifetime of catalyst. Hence, seeking a direct and mild approach to prepare excellent MOFs-based catalyst for OER and ORR is desired.

Based on the above reasons, we introduce a cobalt-containing zeolitic imidazolate framework (termed Co-MOF) and present a facile self-assembly approach to synthesize a high active and strong durable Co-MOF@CNTs bi-functional catalyst for OER and ORR. Co-MOF, which incorporates the nets of corner-sharing tetrahedral CoN₄, where the bond between the benzimidazolate (phIM) anion and Co(II) is one of the most stable N-donor ligands. Besides, Co-MOF has an open-framework structure adopting sodalite topology with hexagonal symmetry, composed of bridging benzimidazolate anions and cobalt cations with the formula Co(phIm)₂·(DMF)·(H₂O) [30]. In addition, this desirable composite has the following merits. Firstly, the preparation process is facile

and mild. Secondly, CNTs are successfully inserted into the Co-MOF and become an integral component of the Co-MOF framework by acting as struts to link Co-MOF nodes, which not only effectively improve the conductivity but also can sustain the harsh oxidative environment of water oxidation without carbon corrosion. Besides, CNTs are inserted into the Co-MOF and Co(II) is coordinated with nitrogen atoms, which can protect both of them from peeling off and keep robust for maintaining the stable catalytic reactions. Thirdly, a synergistic catalysis of active centers Co(II), organic ligands and CNTs would enhance the bifunctional electrocatalytic performance. Remarkably, the hybrid exhibits comparable OER and ORR catalytic activity to RuO₂-based and Pt-based (20 wt% Pt/C) catalysts and superior stability in comparison to many of the highly active cobalt-based catalysts reported to date.

2. Experimental

2.1. Synthesis of Co-MOF

Co-MOF was prepared as described previously with some modification. 0.84 g of Co(NO₃)₂·6H₂O and 0.68 g of benzimidazole (phIM) were dissolved in 72 mL of N, N-dimethylformamide (DMF) in a 100 mL glass vial and sonicated to ensure homogeneity. The vial was heated at 130 °C in an oven for 36 h followed by slow cooling to room temperature. The purple crystal were collected via filtration and washed with DMF several times and dried under vacuum.

2.2. Synthesis of (CNTs X wt%) Co-MOF

Co(NO₃)₂·6H₂O (0.210 g) and phIM (0.170 g) were dissolved with DMF (72 mL) in a 100 mL glass vial. Different amounts of CNTs (1, 5, 10, 15 and 20 wt% based on the total mass of starting solid materials) were added to the mixtures. After sonication of the solution, the vessel was sealed and heated up to 130 °C in an oven for 48 h followed by slow cooling to room temperature. The purple-grayish crystals were collected filtrated and washed with ample DMF and dried under vacuum.

2.3. Characterizations

A FEI-TECNAI G² transmission electron microscope operating at 200 kV (FEI company) was used to make the transmission electron microscopy (TEM) images, high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM), high resolution TEM images (HRTEM) and element analysis mapping. Elemental composition data was collected by energy dispersive X-ray spectroscopy (EDS) performed using a TECNAI G² microscope. X-ray diffraction (XRD) measurement was performed on a Rigaku D/max-2400 diffractometer, using CuK α radiation as the X-ray source in the 2 θ range of 10°–80°. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI-5702 instrument and the C_{1s} line at 291.4 eV was used as the binding energy reference. Scanning electron microscopy (SEM) samples were prepared by drop-drying the aqueous suspensions onto the copper substrate, and SEM analysis was performed by using a MIRA 3 XMU scanning electron microscope. Fourier transform infrared (FT-IR) spectroscopy of the sample was recorded with BRUKER VERTEX 70 FT-IR spectrometer (America Bruker Corporation) with a KBr plate. Thermogravimetric analysis (TGA) was performed on a PerkinElmer TG Analyzer.

2.4. Electrochemical measurements

All the electrochemical measurements were carried out in an electrochemical cell (V = 15 mL) at room temperature using a three-electrode system with glassy carbon electrode (GCE,

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