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Two-dimensional metal-organic frameworks for energy-related electrocatalytic applications

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Abstract

In this short perspective we examine recent developments in the design, synthesis and use of metal-organic frameworks (MOFs) for electrocatalytic applications. We discuss the inherent challenges and limitations that continue to plague conventional MOFs and novel strategies for overcoming them. In particular we focus on the growing interest in two-dimensional MOFs as a practical HER/OER/NRR/CO₂RR catalyst. We also consider its exciting value as a tool for probing the underlying reaction mechanism and catalytic function of various metals.

1. Introduction

Nowadays, the rapid and continuous rise of global demand for energy [1], has fostered considerable interest in the development of numerous renewable energy techniques such as water splitting, fuel cells, CO₂ and N₂ electrolysis. During the development of these technologies, nanoporous materials, which can store and transport energy carriers, have come to the forefront as a family of candidate catalysts for such electrochemical energy applications. Factors such as suitable pore-size distribution, rational morphology, and multi-functionality are crucial parameters for achieving favorable reaction kinetics, and thus are directly correlated with the efficiencies of these energy devices. The ordered microporous structure, uniform spatial distribution of components, and tailorable topologies of metal-organic frameworks (MOFs) allows these materials to outperform other traditional inorganic porous counterparts for such energy-related reactions [2].

Conventional bulk MOFs however are generally considered to be poor catalysts for electrochemical reactions due to their very low electrical conductivity ($\sim 10^{-10}$ S m⁻² [3]) which limits the charge transport within electrodes. Further, although MOFs have abundant micropores in their structures, most of the pores are very small (usually within several nanometers), and are deeply embedded inside the architecture, and thus only a relatively low proportion of them can be utilized during electrocatalysis. Strategies reported in the literature have not proven to be effective in solving these issues, for example, calcination at high temperature to improve electrode conductivity sacrifices the MOFs' intrinsic molecular metal active sites [4], whilst hybridization with secondary conductive supports (e.g. graphene [5]), may block the MOFs' intrinsic micropores.

Recently, we and some other groups have proposed a promising strategy of downsizing MOFs into two-dimensional (2D) ultrathin nanosheets [6–9], which has opened up a new direction of using MOFs for various applications. With the witness of fast-growing research in this direction, this perspective will build on relevant works by examining the potential application of such materials, particularly as electrocatalysts. It will first canvass the inherent advantages of 2D nanosheets as electrocatalysts and their current associated challenges, followed by a survey of recent advances and demonstrated application of the nanosheets for water splitting and nitrogen/ carbon dioxide reduction. Finally, this perspective will examine the future prospects of 2D MOF nanosheets as electrocatalysts and suggest some strategies for overcoming their current obstacles in the aforementioned electrochemistry fields.

2. Advantages of 2D metal-organic frameworks

The downsizing of MOFs into 2D nanosheets has attracted increasing attention in research due to its many unique properties originating from its ultrathin thickness [2, 6, 10–13]. 2D MOF-related research is one of the fast-growing directions in the fields of chemistry, materials, and renewable energy. Owing to their ultrathin nanosheet architecture, 2D MOFs can have an extremely large surface area and high surface-to-volume atom ratios at highly exposed molecular metal active sites (see figure 1 below).

Moreover, the electrical conductivity of 2D MOFs is significantly higher than bulk MOFs, due to the dramatically decreased electron transfer distance from the ultrathin nanosheets to the current collector of the electrodes [8]; and thus mitigates the MOFs' inherent challenging poor electrical conductivity. Further, if assembled in a suitable way, MOF nanosheets can form an appropriate structure with a combination of hierarchical pores. The combination of these factors can give rise to highly exposed active sites, and in principle make 2D MOFs a versatile and high performance catalyst.

3. Synthesis of 2D metal-organic frameworks

Over the past few years, significant advances have been made in the fabrication process of 2D MOFs. Two strategies employed for the synthesis of 2D MOF sheets includes the so called 'top-down' and 'bottom-up' approaches. The former usually requires synthesis of bulk MOF followed by destruction of the weak van der Waals bonding between the MOF layers to achieve the nanosheets. This typically involves extra physical and chemical forces to promote exfoliation of the sheets from the bulk MOF. These forces may also result in inefficient exfoliation and aggregation of the nanosheets. By contrast, the bottom-up method which aims for the direct synthesis of the MOF-based nanosheets through controlled growth can avoid these disadvantages. The importance of synthesis parameters and precursors is well reported in the literature [7].

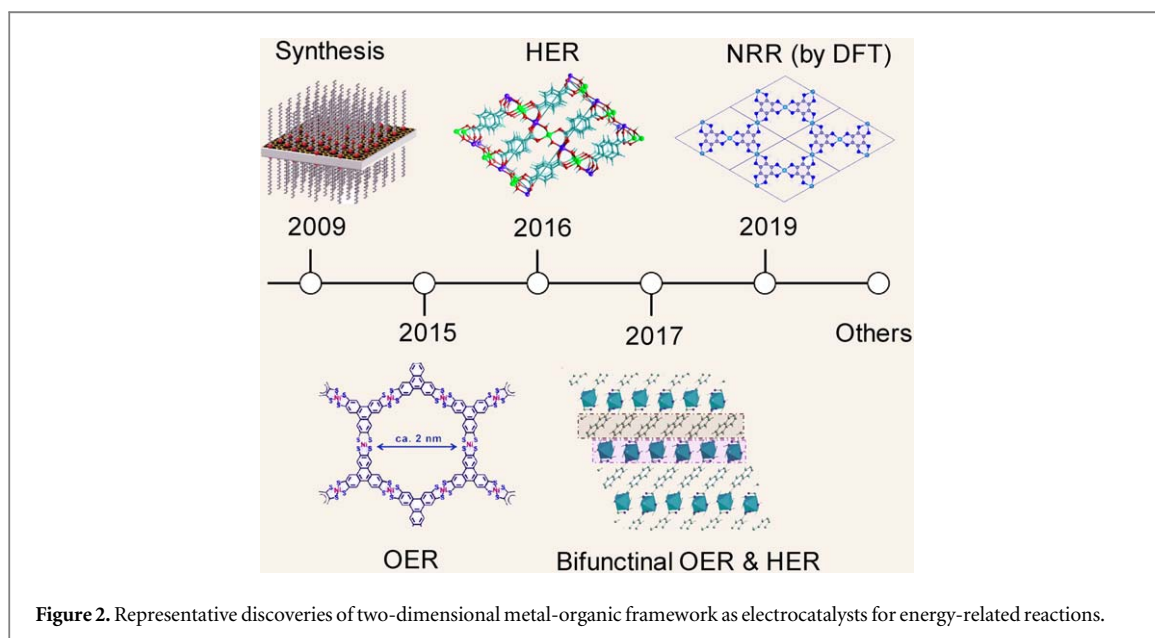
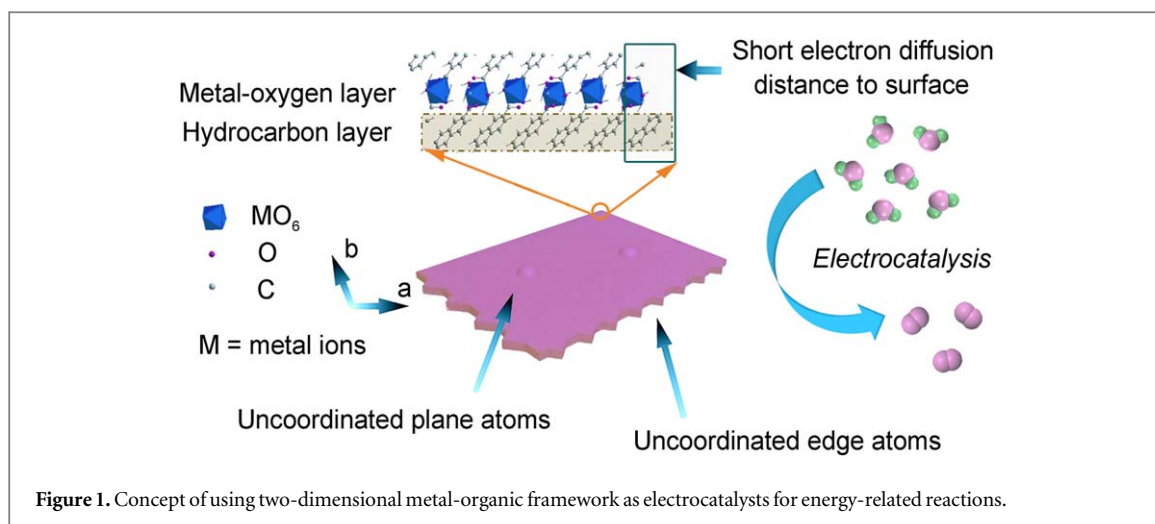
Technically, a number of methods have been developed to synthesize various 2D MOFs [2, 6, 10–13], including top-down processing through sonication exfoliation, Li-intercalation exfoliation, and chemical exfoliation. In addition, the bottom-up approach has been through procedures such as interfacial synthesis, three-layer synthesis, and surfactant-assisted synthesis. These reports have opened up enormous opportunities for the application of versatile 2D MOFs to energy-related applications.

4. Energy-related applications of 2D metal-organic frameworks

So far, several 2D MOFs have been applied as electrocatalysts for cathodic hydrogen evolution reaction (HER) and/or anodic oxygen evolution reaction (OER) in water splitting (figure 2) [14–16]. 2D Ni-THT MOF nanosheet with a thickness of only 0.7–0.9 nm has been prepared by a Langmuir–Blodgett method at the air/water interface, and exhibited excellent activity with a small overpotential of 333 mV at 10 mA cm⁻² for HER [12]. For the OER, ultrathin NiCo-MOF nanosheet has been demonstrated to require an overpotential of 250 mV at 10 mA cm⁻² [13], which is much lower than that of its bulk counterpart (317 mV). These significantly enhanced activities may be attributed to the unsaturated metal atoms and/or the strong coupling effect between different metal sites in 2D MOF nanosheets.

As reported in our previous work [6], we developed a bottom-up method for the assembly of 2D MOFs into nanosheet arrays on a nickel foam substrate, which works as a bifunctional catalyst for both HER and OER. The vertically grown NiFe-MOF nanosheets have a lateral size of several hundred nanometers, with a distance between adjacent MOF nanosheets around tens of nanometers. The nanosheets demonstrated superior catalytic activity with an overpotential of 134 mV for HER and 240 mV for OER at 10 mA cm⁻² in 0.1 M KOH solution. When used as the catalyst for both the anode and cathode in a water splitting setup, the electrochemical cell can deliver a current density of 10 mA cm⁻² at a voltage of only 1.55 V, which is 70 mV smaller than that of the benchmark catalysts composed of Pt/C cathode and IrO₂ anode.

In addition, Chao *et al* [17] recently demonstrated that a thiophene-2,5-dicarboxylate and 4,4'-bipyridine based MOF resulted in an effective 2D bifunctional catalyst for water splitting in alkaline media. The authors attribute the low over potentials and Tafel slopes of 240 and 110 mV at 10 mA cm⁻² and 62 and 94 mV dec⁻¹ for OER and HER respectively to the thinner thickness, more defects and larger specific surface area of electrocatalyst; all characteristics of 2D MOF derived nanosheets. Similarly, Wang *et al* [18] employed a top-down ultrasonication based methodology to obtain cobalt MOF nanosheets which exhibited an overpotential of 309 mV at 10 mA cm⁻² and Tafel slope of 75.71 mV dec⁻¹. Of particular interest is also another work of Zhuang and colleagues [19] who employed a 2D oxide sacrifice approach to synthesize ultrathin MOF nanosheets which bypass traditional bottom-up or top-down strategies.



In other applications, 2D MOFs can also be viable candidates for the nitrogen reduction reaction (NRR) in N_2 electrolysis. Sun *et al* [11] have used density functional theory to propose a 2D MOF-based on molybdenum for NRR. With highly ordered structure and exposed metal active sites, the Mo-based MOF could exhibit an excellent catalytic performance for the conversion of N_2 into NH_3 at room temperature with a very low overpotential of 0.18 V. Further, Wu *et al* [20] have demonstrated copper porphyrin metal-organic framework nanosheets as highly selective and efficient electrocatalysts for the electroreduction of CO_2 to formate and acetate (CO_2RR), with a maximum faradaic efficiency of 61.5% and 12.3% respectively. The authors attribute the efficiency of the electrocatalyst to its flat and high-aspect-ratio which promoted electron transfer and reduced the diffusion kinetic barrier, confirming that MOF downsizing is a feasible method for the further improvement of 2D nanosheet conductivity. Other examinations of 2D MOF nanosheets based materials for CO_2RR was undertaken by Sun *et al* [21–24].

5. Challenges and future directions

In future works, a number of specific challenges need to be addressed for the development of 2D MOFs as practical electrocatalysts. As compared to conventional inorganic catalysts, 2D MOFs still possess far poorer intrinsic electrical conductivity, and have greater difficulty in binding with inorganic electrically conducting substances. Therefore, improving the electrical conductivities both inside the 2D MOF sheets and between the MOFs could be an effective method for enhancing the desired electrocatalytic activities.

One method of achieving this involves ‘doping’ the MOF with conductive cross linked species into the framework as conductive pathways for electron transport. Some potential obstacles includes loss of the MOF structure resulting in decreased porosity and exposure of active sites, and reduced thermal and phase stability of the MOF structure. Further research into the synthesis of MOFs which possess intrinsic high electrical conductivity is therefore highly desirable. Interesting solutions include careful selection of planar, conjugated and redox active organic linkers which promote conduction mechanisms such as hopping, through space or through bond [25]. It is hypothesized that selective pairing of ligands with appropriate metal precursors can result in enhanced p-d orbital overlap and promote charge delocalization and thus the electrical conductivity of the overall structure.

Furthermore, rational optimization of the thickness, lateral size, and arrangement, by *in situ* growth of closely attached 2D MOFs on electrically conductive substances should be particularly helpful for increasing the electrocatalytic performances and mechanical durability of 2D MOF-based electrodes.

For electrocatalysis, the relative chemical instability of 2D MOF sheets may also be a cause for concern, as many electrocatalytic reactions operate in aqueous electrolytes, and frequently in highly acidic/alkaline solutions. This has resulted in comparatively fewer studies of 2D MOFs as electrocatalysts compared to other porous materials like carbon, metal oxides, and their hybrids. It is noted however that a number of bulk MOFs with high chemical stabilities in water and even in highly acidic/alkaline conditions have been reported [3], and thus could be used as precursors in the synthesis of durable 2D MOF electrocatalysts.

Finally, it is also important to utilize the inherent advantages and properties of 2D MOFs for the elucidation of catalytic mechanisms and use the findings in the subsequent design/optimization of the catalysts’ structure. The metal-site isolation of 2D MOFs’ is analogous to well-defined molecular catalysts; and thus, they may be studied with more comprehensive electrochemical characterization methods, typically used for homogeneous catalysts. This may include *in situ* spectroscopy techniques such as x-ray photoelectron spectroscopy, Fourier-transform infrared spectroscopy, Raman and extended x-ray absorption fine structure, and isotope tracing experiments. It is suggested that these fundamental experiments which improve our understanding of the underlying mechanism are crucial for the rational design of electrocatalysts with enhanced efficiencies and tuned selectivity to the desired products.

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