

## Preview

# Direct Growth of Well-Aligned MOF Arrays onto Various Substrates

Yao Zheng<sup>1</sup> and Shi-Zhang Qiao<sup>1,\*</sup>

The controlled conversion of metal-organic framework (MOF) nanocrystals into well-aligned MOF superstructures is still a major challenge. In this issue of *Chem*, Jiang and co-workers have developed a versatile strategy for realizing controllable growth of MOF hybrid arrays on a variety of substrates.

Metal-organic frameworks (MOFs) are a class of porous crystalline solids with a supramolecular structure linked by metal ions and organic ligands.<sup>1</sup> MOF-derived porous carbon composites (MOFCs), which have high surface area and uniform active heteroatom doping, exhibit broad applications in energy conversion and storage fields, especially in electrocatalysis.<sup>2</sup> However, MOF particles are prone to aggregation during pyrolysis at high temperatures, making the resultant MOFC unfavorable for the transfer of electrons and the transport of reactants and products in electrocatalytic reactions. One of the best solutions to this problem is the direct conversion of MOF nanocrystals into well-shaped superstructures, such as nanowires, nanorods, and nanofibers, to maintain the oriented arrangement of the MOFCs.<sup>3–6</sup> However, there are still some challenges in the synthetic approach to controlling the shape and size of the MOF superstructures and MOFCs. In this issue of *Chem*, Jiang and co-workers have systematically developed a versatile strategy for realizing the controllable growth of well-aligned MOF hybrid arrays on a variety of substrates. The resultant MOFCs, which inherited their orientation and close arrangement from the MOF arrays, showed excellent activity toward water splitting, which is one

of the oldest electrochemical processes but is still used to produce high-purity hydrogen fuel for fuel cells and other hydrogen-based energy sources.<sup>7</sup>

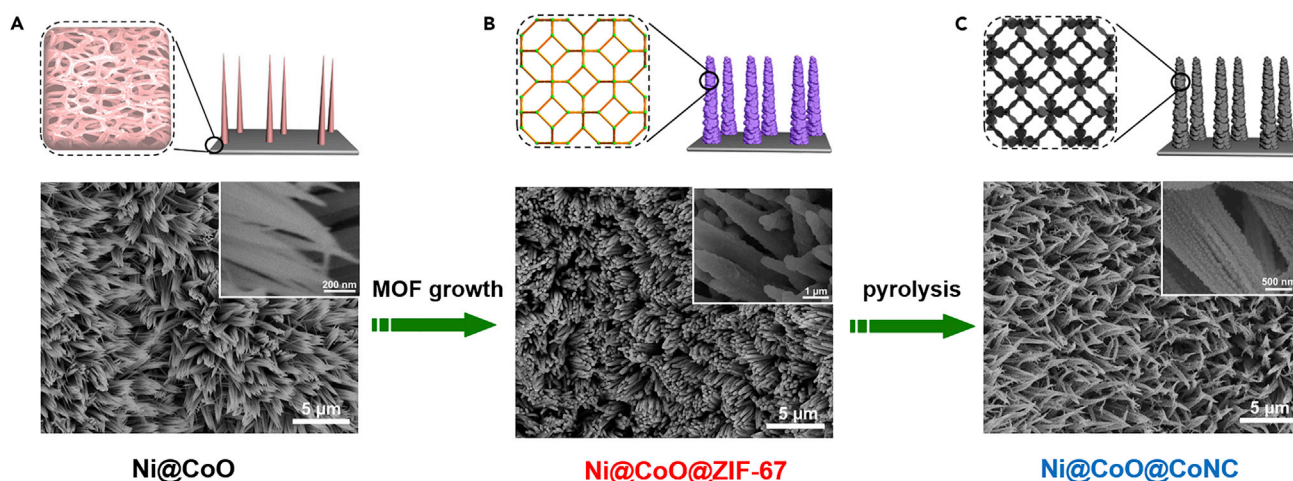
Using CoO@ZIF-67 hybrid arrays on Ni foam (Ni@CoO@ZIF-67) as a model, the authors grew the CoO nanowire arrays vertically on Ni foam via a common hydrothermal process (Figure 1A). Here, the nanowire arrays acted as self-sacrificial precursors and templates, providing Co<sup>2+</sup> ions and skeletons for the growth of ZIF-67 with the assistance of solvents and ligands. Close observation through imaging and spectral analysis indicated that part of the CoO nanowire was located in the interior along with the outer MOF shell, and together they formed a core-shell heterostructure on the CoO@ZIF-67 hybrid. The as-prepared array was then converted into Ni@CoO@CoNC by a facile pyrolysis technique in a N<sub>2</sub> atmosphere, which featured favorable electrical conductivity and porosity as a free-standing electrode. When applied as a hydrolysis electrocatalyst, it achieved an overpotential of 190 and 309 mV to reach a current density of 10 mA/cm<sup>2</sup> for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), respectively, which are the half-reactions of water splitting.

The authors then conducted a series of time-dependent reactions to track the process of conversion and reveal the growth mechanism of these well-aligned MOF hybrid arrays. They found that as the reaction proceeded, the ZIF-67 shell became thicker via the corrosion of the CoO core. This indicates that the ligand was able to penetrate the pores of ZIF-67 and react with the inner CoO species while deprotonation produced H<sup>+</sup>. Then, Co<sup>2+</sup> ions dissolved from CoO diffused outward to react with the ligand at the surface of the ZIF-67 layer for continuous growth. The authors also propose a competing mechanism whereby the dissolution of CoO at the solid-liquid interface and the precipitation of ZIF-67 particles occur at the same time. Therefore, the balance between the dissolution and coordination rate is crucial for the formation of well-defined CoO@ZIF-67 nanorod arrays.

The self-sacrificing template strategy can be extended to the growth of a variety of MOF arrays on different substrates, demonstrating its generality and versatility. Besides Ni foam, the authors also employed Cu mesh, Fe mesh, and Cu foil as the substrate to grow ZIF-67 nanorod arrays. They could readily adjust the shape of the MOF arrays by changing the shape of the pristine precursor arrays, such as nanowires or nanowalls. In addition, they could fabricate different MOF arrays by introducing the corresponding organic ligands. For example, 2-methylimidazole could be used for growing Ni@CoO@ZIF-67, and 2,5-dihydroxyterephthalic acid could be used for growing Ni@CoO@Co-MOF-74. The authors were also able to

<sup>1</sup>University of Adelaide, Adelaide, SA 5005, Australia

\*Correspondence: [s.qiao@adelaide.edu.au](mailto:s.qiao@adelaide.edu.au)  
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**Figure 1. Synthetic Approach of Different MOF-Based Structures**

Top: schematic illustration of the fabrication of metal oxide@MOF hybrid arrays (B) and their derived metal oxide@MOFC arrays (C) on the 3D conductive matrix substrate (A) (Ni@CoO@ZIF-67 and Ni@CoO@CoNC are shown as representatives).

Bottom: scanning electron microscopy and transmission electron microscopy (insets) images of different stage products.

grow a range of metal oxide and hydroxide arrays on the substrates to create a variety of hybrids, such as CoO@ZIF-67, NiO@Ni-MOF-74, and Cu(OH)<sub>2</sub>@HKUST-1.

In conclusion, the authors developed a versatile strategy for the synthesis of metal oxide@MOF or metal hydroxide@MOF hybrid arrays on various substrates. The type of substrate, use of metal oxide or hydroxide, type of MOF, and shape of the array are tunable by the application of various reaction conditions. By simple pyrolysis, the obtained MOF-based hybrid

arrays can be further transformed into porous carbon hybrid arrays with a well-aligned hierarchical and self-supporting structure. The latter can be directly used as an efficient electrode for both HERs and OERs with enhanced activity, kinetics, and durability in alkaline solutions. It is expected that the self-sacrificing template strategy will provide new opportunities for the rational assembly of well-aligned 3D MOF nanocrystals on substrates, which could serve as important platforms for device applications, especially in energy storage and conversion.

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