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Direct Growth of Well-aligned MOF Arrays onto Various Substrates

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The directed conversion of metal-organic framework (MOFs) nanocrystals to well-aligned MOF superstructures is still a significant challenge. In a recent publication in Chem, Jiang and co-workers have developed a versatile strategy to realize controllable grown of three-dimensional MOF hybrid arrays on a variety of substrates.

Metal-organic frameworks (MOFs) are a family of crystalline porous solids with supramolecular structure consisting of metal ions and organic ligands linked together by coordination bonds.¹ With the availability of regular crystalline, tailored and periodic porous texture of MOFs, their derived porous carbon composites (MOFCs), with high porosity and surface area as well as uniform active heteroatom doping, exhibit broad applications in energy conversion and storage fields, especially in electrocatalysis.² However, the MOF particles are prone to aggregate during pyrolysis at high temperature, which makes the resultant MOFC unfavorable for the transfer of electrons/charges and the transport of reactants/products in the electrocatalytic reactions. One of the best solutions is directly converting MOF nanocrystals to well-shaped superstructures like nanowire, nanorod, nanofiber, etc. to maintain the oriented arrangement of MOFCs.³⁻⁷ However, there are still some challenges in the synthetic approach to control the shape and size of the MOF superstructures and MOFCs. In a recent publication in Chem, Jiang and co-workers have rationally developed a versatile strategy to realize controllable grown of three-dimensional MOF hybrid arrays on a variety of substrates. The oriented and close arrangement of MOFCs inherited from MOF arrays showed excellent water

electrolysis processes, which is one of the oldest electrochemical processes but is still used to produce high-purity hydrogen fuel for hydrogen-based fuel cells and other hydrogen-based energy sources.⁸

Taking well-aligned CoO@ZIF-67 hybrid arrays on Ni foam (simply as Ni@CoO@ZIF-67) as a model, The CoO nanowire arrays were vertically grown on Ni foam in a regular hydrothermal way (Figure 1a), which were then chosen as self-sacrificial precursors/templates that provide Co²⁺ ions and skeleton for the growth of ZIF-67, by dissolving themselves with the assistance of solvent and ligand. This process endows hybrid arrays with a uniform rod-like nanostructure (Figure 1b), indicating that the morphology is well preserved with local corrosion of the metal oxide arrays. A close observation by transmission electron microscopy (TEM) images and energy-dispersive X-ray spectroscopy (EDS) analysis indicating that part of CoO nanowire is left in the interior along with outer MOF shell, forming a core-shell heterostructure in a rod-like morphology of Ni@CoO@ZIF-67 hybrid arrays. Then the as-prepared Ni@CoO@ZIF-67 has been facilely converted to CoO@Co/N-doped porous carbon arrays on Ni substrate (denoted as Ni@CoO@CoNC) by pyrolysis in N₂ atmosphere, featuring favorable electrical conductivity and porosity as a free standing electrode directly applicable in electrocatalysis. As a result, the free standing electrocatalyst reaches an overpotential of 190 and 309 mV at a current density of 10mA/cm² for half process of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), respectively.

A time-dependent reactions were further investigated to track the process of conversion and reveal The growth mechanism of well-aligned MOF hybrid arrays. as the reaction proceeds, the ZIF-67 shell become thicker and thicker via the corrosion of the CoO core. This phenomenon reveals that the ligand is able to penetrate into the pores of ZIF-67 and react with

the inner CoO species, accompanying with deprotonation to produce H^+ , which would lead to the dissolution of CoO to Co^{2+} . The Co^{2+} ions diffuse outward to react with the ligand at the outer surface of ZIF-67 layer for continuous growth. ZIF-67 grows much more slowly when the MOF shell becomes thick, possibly due to the diffusion limitation. The thickness of ZIF-67 almost reached a maximum value and stopped the growth after reaction for ~12 hr. The above process strongly suggests a competing mechanism that the dissolution of metal oxide at the solid-liquid interface and the precipitation of ZIF-67 particles by the coordination between metal ions and 2-methylimidazole (2-MeIM) linkers 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 on Ni foam.

The generality and versatility of the template-directed strategy for MOF-based hybrid arrays. Given that various metal oxide and even hydroxide arrays (NiO, ZnO, $ZnCo_2O_4$, $Cu(OH)_2$, etc.) can be easily grown on different substrates (Ti foil, Cu foil, and conductive glass et al),⁴⁸⁻⁵² it is expected that the above self-sacrificing template strategy can be extended to the growth of a variety of MOF arrays on different substrates, which would be highly desired for diverse applications. To demonstrate this, in addition to the above Ni foam, other substrates, such as Cu mesh, Fe mesh and Cu foil, etc., have been employed and ZIF-67 nanorod arrays can be successfully grown on all of them, by following similar synthetic procedures (Figure 3A-C, and Figure S11-S13). Interestingly, the shape of MOF arrays can be readily adjusted by changing the shape of pristine precursor arrays, for examples, CoO@ZIF-67 nanorods from CoO nanowires, CoO@ZIF-67 nanowalls from CoO nanowalls (Figure 3D and Figure S14-S15). Moreover, on the basis of the same metal oxide arrays, different MOF arrays can be fabricated by introducing corresponding organic ligands. Taking CoO nanowire arrays on Ni foam as an example, not only Ni@CoO@ZIF-67 was obtained by using 2-methylimidazole as

indicated above, but Ni@CoO@Co-MOF-74 can also be achieved by introducing the ligand 2,5-dihydroxyterephthalic acid (Figure 3E and Figure S16). More importantly, diverse metal oxide and even hydroxide arrays can be grown onto the substrates, which guarantees the successful growth of a variety of metal oxide@MOF or metal hydroxide@MOF hybrid arrays, for examples, CoO arrays for CoO@ZIF-67 arrays, NiO arrays for NiO@Ni-MOF-74 arrays (Figure 3F and Figure S17-S18) as well as Cu(OH)₂ arrays for Cu(OH)₂@HKUST-1 arrays (Figure 3G and Figure S19-S22). All these results unambiguously demonstrate the generality and versatility of the current synthetic strategy for MOF-based hybrid arrays.

Finally, as the authors concluded, In summary, we have developed a versatile strategy to the synthesis of metal oxide@MOF or metal hydroxide@MOF hybrid arrays on various substrates by using metal oxide/hydroxide nanostructured arrays as self-sacrificing templates, in which all of substrate, metal oxide/hydroxide, MOF and even the shape (nanorod or nanowall) of the array are alterable. Remarkably, by simple pyrolysis, the obtained MOF-based hybrid arrays can be further transformed into metal oxide/MOF-derived porous carbon hybrid arrays with well-aligned hierarchical and self-supporting structure. The latter directly used as an efficient electrode for both HER and OER exhibit much higher activity, more favorable kinetics and better durability than the corresponding counterparts (Ni@metal oxide or MOF-derived nanocomposite without a self-supporting structure). The excellent electrocatalytic performance should be ascribed to the porous nanoarray electrode configuration, in situ carbon incorporation, increased exposure and accessibility of active sites, accelerated release of gas bubbles, robust structure and great mass/charge transport. It is expected that this self-sacrificing template strategy would provide new opportunities for rational assembly of well-aligned 3D MOF nanocrystals on substrates, which would serve as important platforms for device applications, especially in energy storage and conversion.

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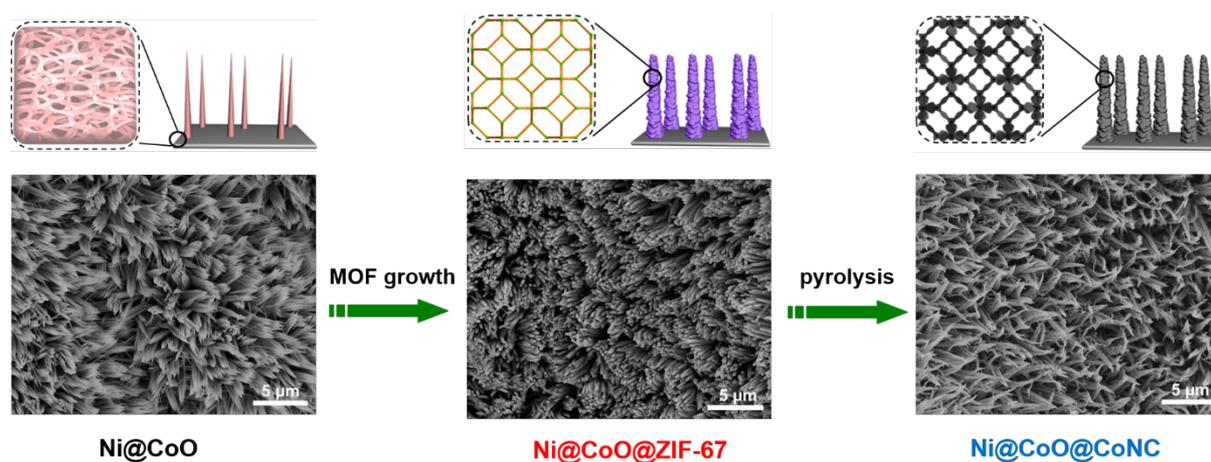


Figure. Schematic illustration of the fabrication of metal oxide@MOF hybrid arrays and their derived metal oxide@MOFC arrays on the 3D conductive matrix substrate (using Ni@CoO@ZIF-67 and Ni@CoO@CoNC as representatives).