

## Previews

## Optimizing MOF electrocatalysis by metal sequence coding

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In this issue of *Chem Catalysis*, Jia et al. realized the precise positioning of diverse metal species into specific sequences within multivariate metal-organic frameworks (MTV-MOFs), and the resultant sequence-coded ZnCo-MOF-699—with sheet-like secondary building units—performed much better for electrocatalytic oxygen evolution than the non-coded counterpart.

Creating heterogeneity in materials by introducing multiple constituents is an emerging way to regulate intrinsic properties and introduce new functions.<sup>1–3</sup> This creates infinite possibilities for the spatial distribution of different constituents, and manipulating their spatial arrangement—such as the sequence of different metal atoms—has become one of research hotspots along this line.<sup>3</sup> Specifically for catalysis, materials with well-controlled atomic arrangements can realize fine regulations on geometric and electronic effects in materials, greatly influencing the microenvironments of active sites and significantly altering the reaction paths.<sup>3,4</sup> In spite of great superiorities, relative works on the control over the sequence of multiple constituents are still in infancy, and efficient construction strategies are highly desired.

Metal-organic frameworks (MOFs), allowing to flexibly design and modulate structures/components with atomic precision, provide great opportunities for the accurate control over alignment of diverse structural motifs in a specific sequence.<sup>5–8</sup> Multivariate MOFs (MTV-MOFs), one representative MOFs that includes multiple metal atoms/organic linkers, can precisely introduce heterogeneity into the same crystal without influencing the original bonding/connectivity of MOFs.<sup>6–9</sup> The unique struc-

tural and component superiorities of MTV-MOF on precision make it promising to code the sequence of multiple metal atoms or organic ligands with MOFs in a well-controlled manner, while relative investigations are still scarcely reported, leaving a big blank ready to be explored.

In this issue of *Chem Catalysis*, Jia et al. have successfully realized precise control over the spatial distribution of diverse metals, even with the same valence and coordination number, within MTV-MOFs. First, two kinds of metals with different preference coordination numbers were prefixed into a heterometallic MOF precursor (named pre-coded MOF) (Figure 1A).<sup>10</sup> Each metal occupied the unique crystallographic position due to their different coordination modes, making them distinguishable within the pre-coded MOF. After a single-crystal-to-single-crystal (SC-to-SC) conversion process, the original sequence of metal atoms could be perfectly inherited into the target MOFs, obtaining sequence-coded MTV-MOFs. The authors demonstrated that such a “coordination number precoding” strategy was applicable for three MTV-MOFs with a 2D sheet-like secondary building units (SBUs), including ZnCo-MOF-699, ZnNi-MOF-699, and ZnCu-MOF-699. When used for electrocatalytic oxygen evolution reaction (OER), the sequence-coded ZnCo-MOF-699 showed much better

activity than the non-coded counterparts, monometallic Zn-MOF-699 and Co-MOF-699, as well as commercial IrO<sub>2</sub>—illustrating the huge potential of metal sequence regulation on catalytic performance optimization.

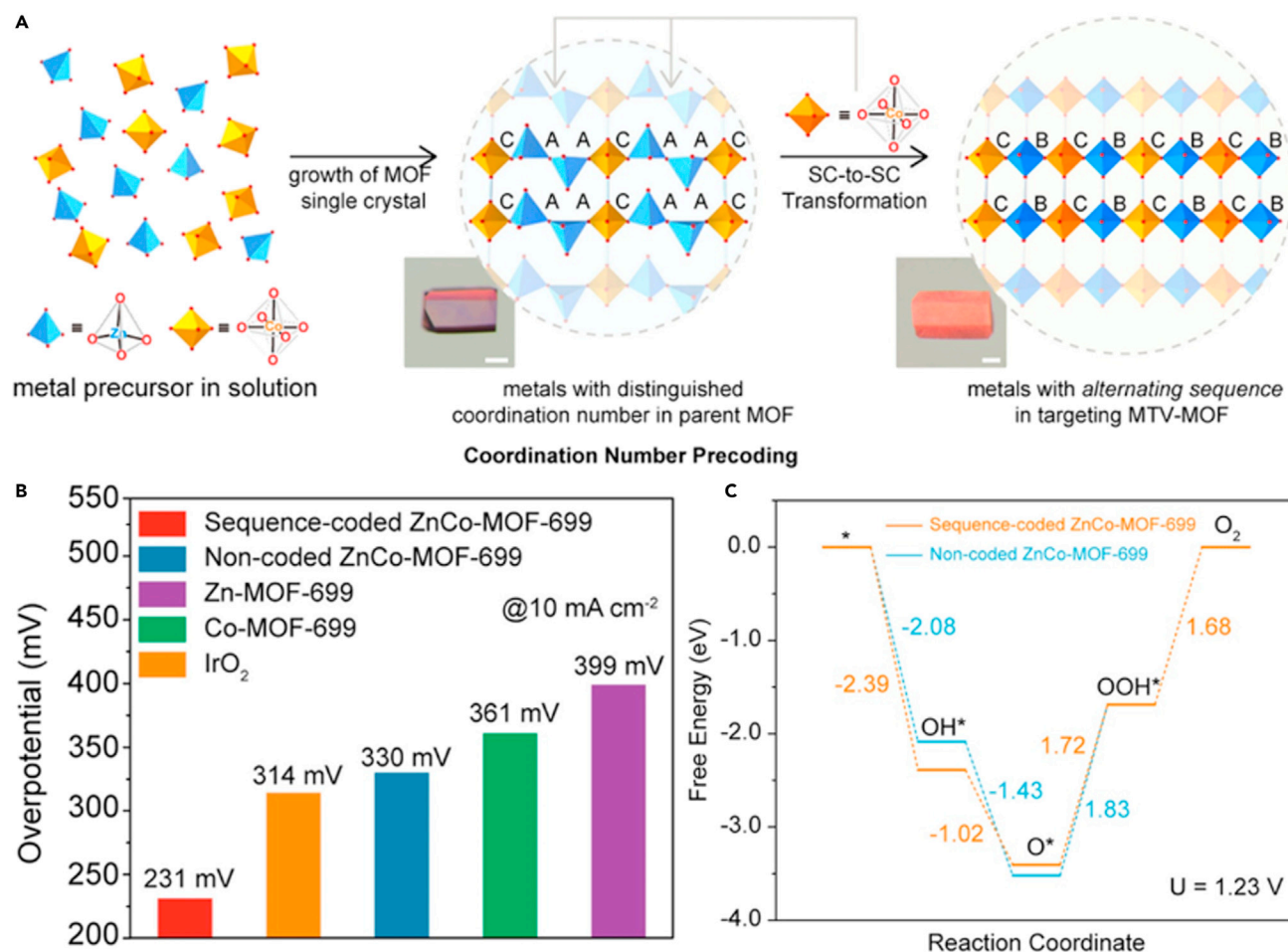
Taking the construction of ZnCo-MTV-MOF-699 as a representative, the authors first obtained single crystals of ZnCo-MOF-69C (the pre-coded MOF) possessing Zn and Co atoms with different coordination environments and crystallographic positions, which can be well identified by single-crystal X-ray diffraction (SCXRD). Crystal structure refinement results showed that Co<sup>2+</sup> of ZnCo-MOF-69C was in octahedral shape sharing vertices with two adjacent four-coordinated Zn<sup>2+</sup> tetrahedral, forming the specific metal sequence of Zn and Co precisely. Via SC-to-SC transformation, the resultant ZnCo-MOF-699 crystal, though with the same coordination number of Co and Zn, perfectly inherited the alternative spatial arrangement of Zn and Co in pre-coded ZnCo-MOF-69C, which was further confirmed by SCXRD. Further, the X-ray photoelectron spectroscopy confirmed the well-retained coordination environment of cobalt and the transformation of Zn coordination environment from tetrahedral to octahedral during SC-to-SC transformation, confirming the results of SCXRD analysis.

To get insights for the SC-to-SC transformation mechanism, the authors carried out the *in situ* time-resolved small-angle X-ray scattering measurements. The peak of (100) in pre-coded ZnCo-MOF-69C was found to be

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**Figure 1. Schematic illustration showing the construction of sequence-coded MTV-MOFs for electrocatalytic oxygen evolution**

(A) Coordination number precoding method to obtain metals with an alternating arrangement in sequence-coded MTV-MOFs. The scale bar represents 200  $\mu\text{m}$ .

(B) Overpotential comparison of the ZnCo-MOF-699 with different heterometallic distribution for OER.

(C) The standard Gibbs free energy diagram of sequence coded and non-coded ZnCo-MOF-699 for OER.<sup>10</sup>

decreased accompanied by increase of (200) peak for the newly formed ZnCo-MOF-699, manifesting the formation of sheet-like SBU. Due to the breathing effect of MOFs, the SBUs located in the opposite position of the pore move to each other. Then, the adjacent rod-like SBUs of ZnCo-MOF-69C integrated with each other, induced by the solvent removal, during which the additional Co ions were inserted, forming alternating sequence of Zn<sup>2+</sup> and Co<sup>2+</sup> in ZnCo-MOF-699. Further, the kinetic studies of conversion mechanism in different solvents showed that oxygen containing solvents (methanol and tetrahydrofuran) decreased the reac-

tion kinetics due to the possible coordination with Co<sup>2+</sup>/Zn<sup>2+</sup>. By replacing these solvents with chloroform or toluene, the reaction kinetics can be enhanced to favor the formation of sheet-like SBUs in ZnCo-MOF-699.

Inspired by the excellent OER performance of layered inorganic materials, ZnCo-MOF-699—with sheet-like SBU similar to the inorganic materials—has been employed as electrocatalyst for OER by the authors. The sequence-coded ZnCo-MOF-699 showed excellent catalytic performance in 1 M KOH with a lower overpotential of 231 mV at the current density of 10 mA/cm<sup>2</sup>,

much superior to its monometallic counterparts containing Zn or Co atoms only as well as the commercial IrO<sub>2</sub> (Figure 1B). More impressively, the non-coded ZnCo-MOF-699 with random metal arrangements, even though they possess crystal structures and compositions identical to sequence-coded ZnCo-MOF-699, presented much inferior activity and kinetic behavior, clearly suggesting the superiority of ordered sequence of metal atoms. Theoretical calculations revealed that the much-enhanced adsorption of OH\* intermediate and the synergy of Co-Co coupling, accompanied by partial electron transfer from Zn to Co, contributed

to the better OER activity of sequence-coded ZnCo-MOF-699 (Figure 1C).

This study provides an elegant example to illustrate the possibility of sequencing the heterometals in MTV-MOFs via SC-to-SC transformation and demonstrates the critical role of metal sequence control in MOFs on regulating the electrocatalytic performance for OER. Inspired by this work, the precise positioning of metals with specific sequence could also be applicable to other MOFs or even other crystalline material. Moreover, other than metal atoms, ordered arrangement of diverse linkers and structural defects are also readily to be investigated for the optimization of material properties, opening up a new avenue to tune the physical or chemical properties of materials at atomic accuracy.

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## An atom economical approach for enantioselective cross dehydrogenative coupling

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**Asymmetric C–H/C–H cross coupling offers an efficient strategy for direct synthesis of enantioriched molecules. In this issue of *Chem Catalysis*, You and coworkers disclosed a Pd catalyzed approach for enantioselective cross coupling between indolizines and dialkylaminomethylferrocenes. Using this protocol, a range of chiral planar ferrocenes have been accessed under mild condition.**

Improving synthetic efficiency of chemical reactions have long been the goal of chemists. Effective synthetic methods are required to be both selective (chemo, regio, diastereo, and

enantioselectivity) and atom economical.<sup>1</sup> Along with these, synthesizing a molecule in lesser number of steps (step economy) also falls under synthetic efficacy. Over the years, transi-

tion metal catalyzed C–H functionalization has come up as one of most efficient strategies that fulfills the conditions of synthetic efficacy.<sup>2</sup> Whether it is aryl, heteroaryl, or aliphatic molecules, this approach has been successful across a myriad of substrates. These strategies enable the transformation of unactivated C–H bonds into C–C and C–heteroatom bonds in a step and atom economical manner starting from readily available starting materials.<sup>3</sup> In this regard, C–H functionalization of indolizines have gained tremendous

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