

Ligand Engineering Enhances (Photo)Electrocatalytic Activity and Stability of Zeolitic Imidazolate Frameworks via In-situ Surface Reconstruction

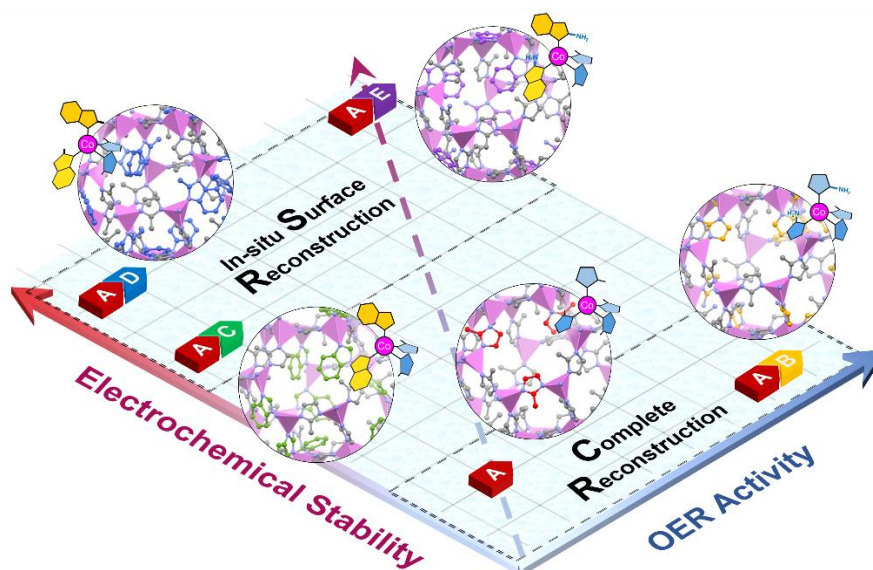
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The current limitations in utilizing metal-organic frameworks (MOFs) for (photo)electrochemical applications stem from their diminished electrochemical stability. In our study, we illustrate a method to bolster the activity and stability of (photo)electrocatalytically active MOFs through ligand engineering. We synthesized four distinct mixed-ligand versions of zeolitic imidazolate framework-67 (ZIF-67), and conducted a comprehensive investigation into the structural evolution and self-reconstruction during electrocatalytic oxygen evolution reactions (OER). In contrast to the conventional single-ligand ZIF, where the framework undergoes a complete transformation into CoOOH via a stepwise oxidation, the ligand-engineered ZIFs (LE-ZIFs) manage to preserve the fundamental framework structure by in-situ forming a protective cobalt (oxy)hydroxide layer on the surface. This surface reconstruction facilitates both conductivity and OER activity by one order of magnitude and considerably enhances the (photo)electrochemical stability. This work highlights the vital role of ligand engineering for designing advanced and stable MOFs for photo- and electrocatalysis.



Schematic diagram of the complete reconstruction mechanism and surface reconstruction mechanism in (photo)electrocatalytic reaction