Operando characterization of atomic-scale structural transformations in cobalt hydroxide catalysts during oxygen evolution reaction

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The oxygen evolution reaction (OER) plays a key role in the electrocatalytic production of clean fuels and valuable chemicals. Nevertheless, the intricate and dynamic changes of the catalysis-related topmost surface structures of the OER catalysts remain unresolved under operando reaction conditions.[1,2] In this study, we present the employment of high-resolution electrochemical atomic force microscopy (EC-AFM), high-energy X-ray diffraction (HE-XRD), and density functional theory (DFT) calculations to reveal the surface-active phases and catalytically active structures under in situ reaction conditions (Figure 1). We provide the first direct atomic-scale surface images that, under applied anodic potentials, cobalt hydroxides ($Co(OH)_2$) heterogeneously reconstructed into coexisting CoOOH and CoO_xH_y structures on the basal plane. The OER-active phases are characterized by about 12% contraction of the lattice spacing and a nonhomogeneous intercalation of ions, specifically at the lateral plane. These surface structural dynamic behaviors are revealed to be different from the bulk structure of $Co(OH)_2$ by operando HE-XRD. Potentiodynamic of $Co(OH)_2$ manifests an oscillation in lattice parameters and irreversible expansion on the basal and lateral planes, respectively. Complementary spectroscopic approaches will be further discussed, and a perspective given on the potential of scanning probe microscopy for nanoscale catalysis and energy conversion materials.

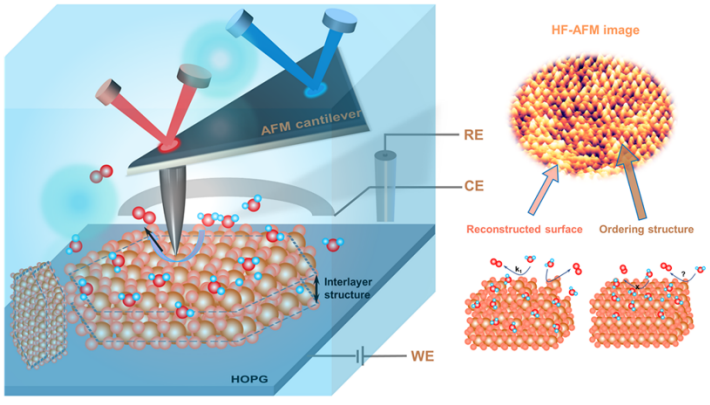

Figure 1 Schematic figure of high-resolution EC-AFM mapping surface structures on $Co(OH)_2$ under OER working conditions.

[1] Fabio D. et al. Nat. Commun., 2020, 11, 2522. [2] Felix, H. et al. Nat. Energy, 2022, 7, 765-773.