

## Experimental Procedures

**Synthesis of  $\alpha$ -Co(OH)<sub>2</sub>.**  $\alpha$ -Co(OH)<sub>2</sub> hexagonal particles were synthesized via a modified hydrothermal method<sup>[1]</sup>. Specifically, CoCl<sub>2</sub>·6H<sub>2</sub>O (Adamas-beta), hexamethylenetetraamine (HMT, Sigma-Aldrich), and polyvinylpyridone k30 (PVP, Adamas-beta) were dissolved in 80 mL of ethanol/water solution (with a volume ratio of 1/9) to achieve the final concentrations of 20, 2, and 0.1 mM, respectively. The mixture was stirred for half an hour at room temperature, then heated and refluxed for 2 hours in an oil bath at 95 °C. Stirring was ceased at the end of heating, and the solution was cooled to room temperature. The reaction suspension was separated by centrifugation at 10000 r.p.m. for 10 minutes. After centrifugation, the supernatant was removed, and the precipitate was washed by adding deionized water and ethanol once again. The above centrifugation and cleaning procedures were repeated three times to eliminate any residual PVP on the particle surface, and then dried in an oven at 50 °C overnight.

**Physical characterization.** The bulk phase chemical structure of Co(OH)<sub>2</sub> was characterized by XRD (Bruker, D2 PHASER, Cu K $\alpha$  radiation,  $\lambda=1.5405$  Å). Topographical measurements were performed in air using a Cypher ES scanning probe microscope (Oxford Instruments Asylum Research Inc.) with an Olympus AC240TS probe (tip radius ~7 nm) in tapping mode. XPS (Thermo Kalpha) measurements were carried out using a Al K $\alpha$  source, with energy step size of 0.100 eV.

**Electrochemical test.** Electrochemical tests were conducted in a three-electrode system using an electrochemical workstation (Gammry, Interface 1010) with 1 M KOH as the electrolyte. The reference electrode potentials for all experiments were normalized prior to testing by using a reversible hydrogen electrode (RHE, eDAQ Inc.) in electrolyte. All the working electrode potentials are converted to RHE, and the conversion formula is as follows:

$$E_{(V \text{ vs. RHE})} = E_{(V \text{ vs. RHE})} + E_{(V \text{ Ag/AgCl vs. RHE})}$$

where  $E$  (V Ag/AgCl vs. RHE) represents the potential of the Ag/AgCl electrode relative to the reversible hydrogen electrode after correction with a standard hydrogen electrode in 1 M KOH solution. The potentiostat automatically compensated for 85% of the solution resistance with impedance measurements, while the remaining 15% was manually adjusted for compensation.

### ***In-situ* EC-AFM imaging**

**Electrochemical reaction cell.** As illustrated in Supplementary Figure S1, the cell is suitable for three-electrode electrochemical systems and allows to control the reaction atmosphere. The part of the electrochemical cell in contact with the solution is made of acid-alkali corrosion-resistant PEEK material, capable of holding 200-300  $\mu$ L of electrolyte solution, meeting the requirements of EC-AFM tests in high-concentration electrolyte environments. The 1 cm  $\times$  1 cm working electrode was sealed with a rubber ring, with only the sample part exposed to the electrolyte; the metal wire part was not immersed in the solution to prevent potential contamination. The counter electrode was attached to the PEEK ring, and the reference electrode was inserted into the solution from above.

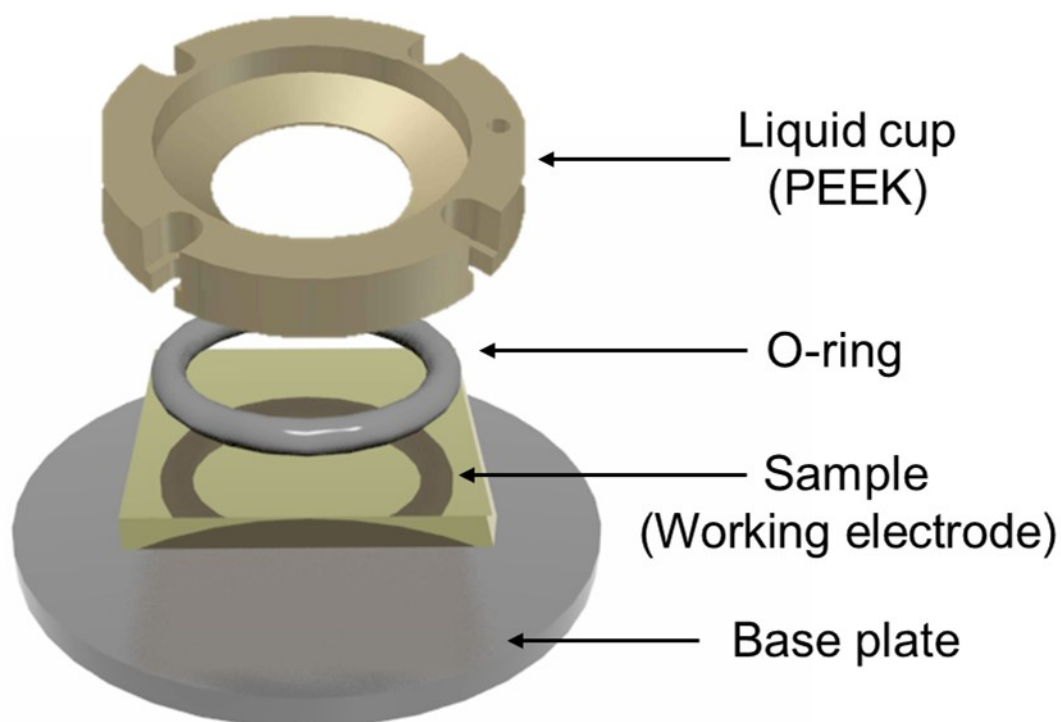


Figure S1 *In-situ* liquid electrochemical reaction cell.

**Three electrode fabrication.** The working electrode was prepared as follows: First, ITO with a size of 1 cm $\times$ 1 cm was selected as the substrate to support the catalyst. Next, the prepared  $\alpha$ -Co(OH) $_2$  was dispersed with ethanol at a concentration of 1 mg mL $^{-1}$ . A 50  $\mu$ L of the dispersion was dropped onto the ITO surface and further dispersed using a homogenizer. The reference electrode preparation involved sanding the surface of a 0.1 cm diameter silver wire with sandpaper to eliminate the oxide film. Subsequently, plating was conducted using a constant current technique in a 1 M KCl solution at a current density of 1 mA cm $^{-2}$  for 5-10 minutes. The counter electrode comprised a platinum wire with a diameter of 1 mm.

**EC-AFM mapping.** *In-situ* topographical measurements of  $\alpha$ -Co(OH) $_2$ -catalyzed water oxidation were performed using EC-AFM in the tapping mode in the liquid phase. The utilized probe was AC-40TS (OLYMPUS) with a tip size of 8 nm and an elastic coefficient of 0.09 N m $^{-1}$ . A 1 M KOH aqueous solution served as the electrolyte. Morphological changes of individual  $\alpha$ -Co(OH) $_2$  platelet under various oxidation potentials were tracked.

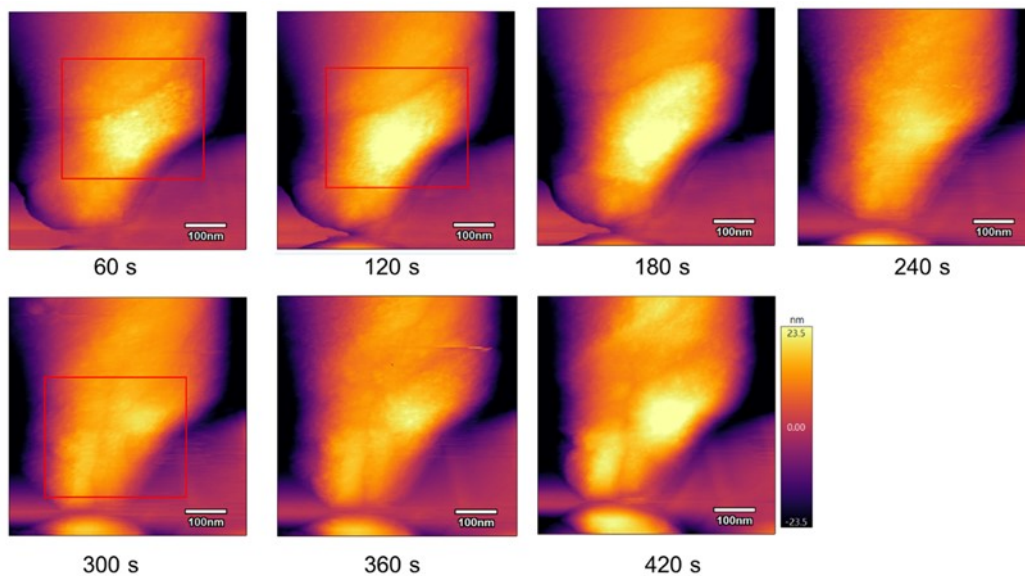


Figure S2 The topological morphology of  $\text{Co(OH)}_2$  particle edge changes with time under 1.5 vs. RHE.

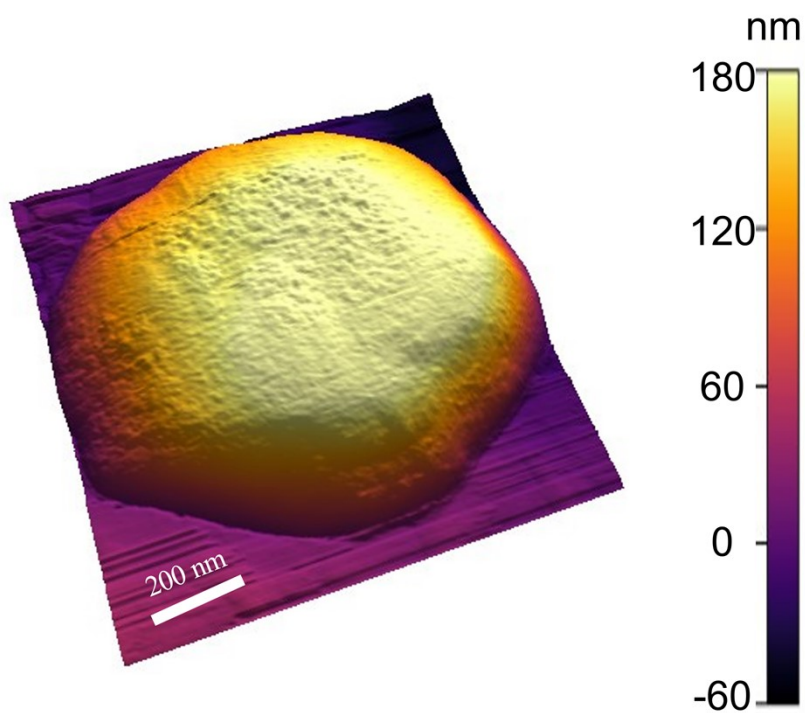


Figure S3 Topography of one  $\text{Co(OH)}_2$  particle after returning from a constant potential to OCP.

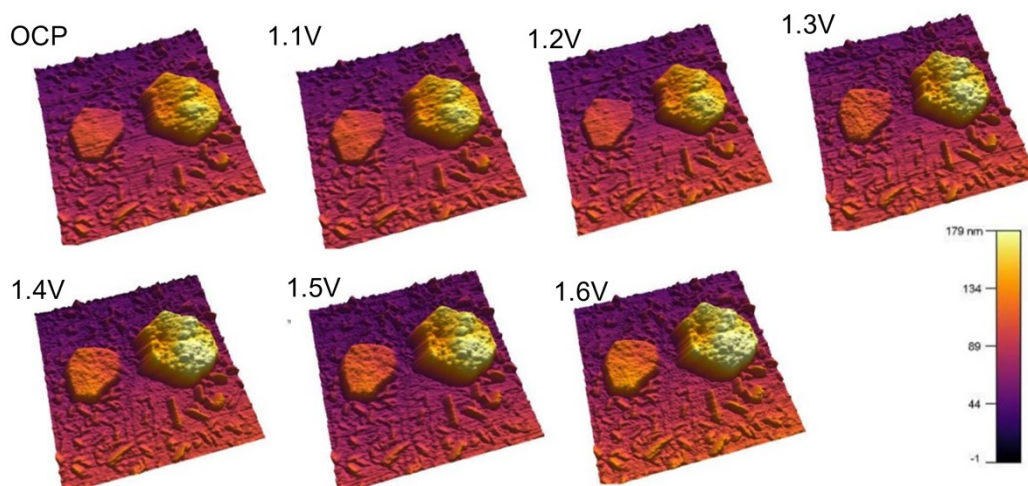


Figure S4 Topological evolution of other two  $\text{Co(OH)}_2$  particles monitored by EC-AFM in 1 M KOH (pH=13.9) electrolyte under different potentials (vs. RHE). At each oxidation potential, the nanosheet morphology images were continuously collected for 600 s.

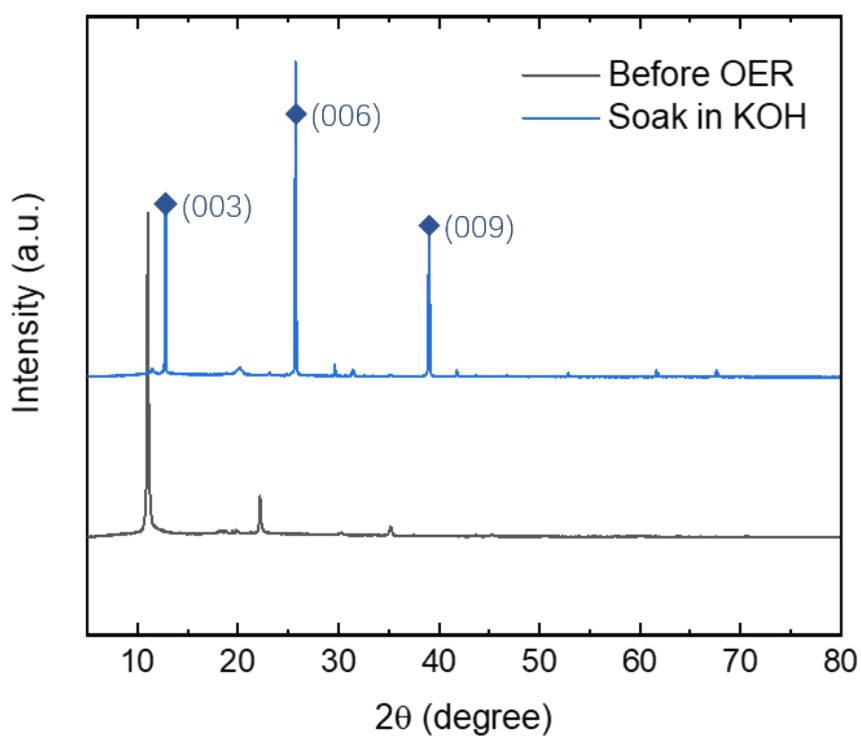


Figure S5 XRD images of  $\text{Co(OH)}_2/\text{ITO}$  samples soaked in 1 M KOH electrolyte for 1 h without applying potential.

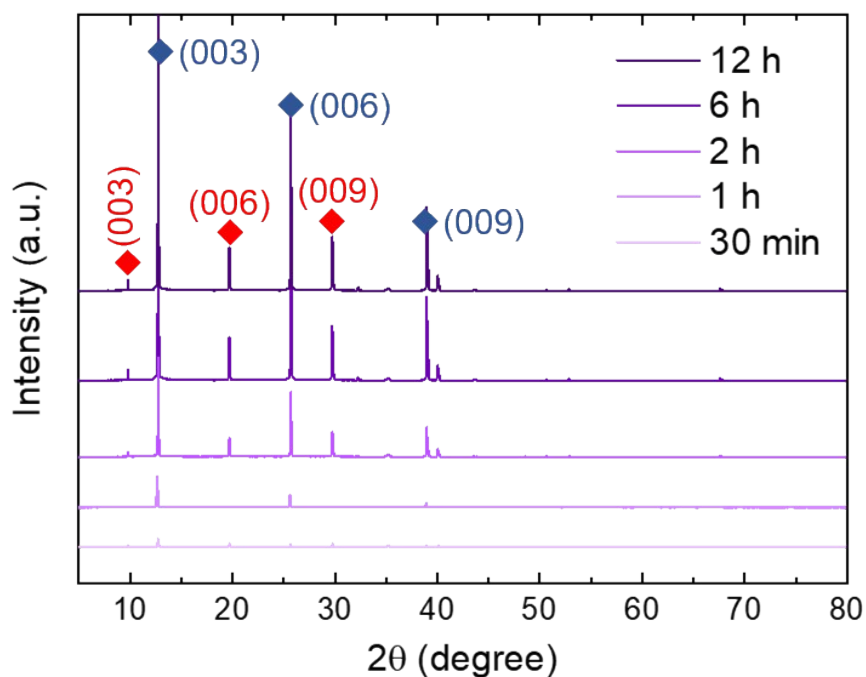


Figure S6 Comparison of XRD patterns of  $\text{Co}(\text{OH})_2$  after different durations (30 min, 1 h, 2 h, 6 h and 12 h) at 1.3 V vs. RHE.

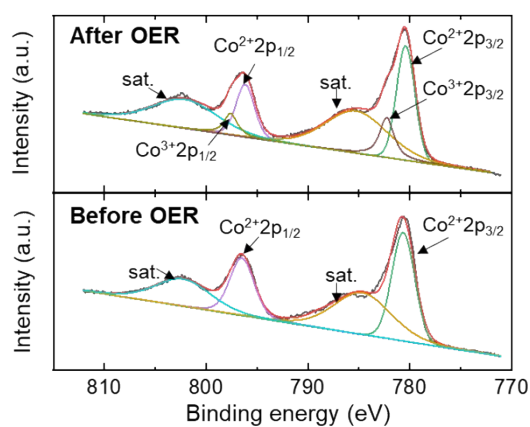


Figure S7 XPS results comparing the oxidation state of Co before and after OER. Before OER: the sample was at OCP; After OER: the sample was electrolyzed for one hour at a potential of 1.6 V vs. RHE in 1 M KOH electrolyte.

## Reference

[1] Xu, W. J.; Lyu, F. L.; Bai, Y. C.; Gao, A. Q.; Feng, J.; Cai, Z. X.; Yin, Y. D. Porous cobalt oxide nanoplates enriched with oxygen vacancies for oxygen evolution reaction. *Nano Energy* **2018**, *43*, 110-116.