Cobalt Phosphide Nanoparticles for Hydrogen Evolution Electrocatalysis

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Late transition metal phosphides have been reported to have high activity for catalyzing hydrogen evolution reaction (HER), yet their active site and stability are not well-understood. Here we report systematic activity and stability study of CoP for HER by combining electrochemical measurements for CoP nanoparticles (NPs) with ex situ and in situ synchrotron X-ray absorption (XAS) spectroscopy at phosphorus and cobalt K edges, as well as density functional theory (DFT) calculations. Colloidally synthesized CoP NPs showed high HER activity in both acid and base electrolytes, comparable to previous work, where no significant pH dependence was observed. Transmission electron microscopy-energy dispersive spectroscopy study of CoP NPs before and after exposure to potentials in the range from 0 to 1.4 V vs. the reversible hydrogen electrode (RHE) revealed that the P/Co ratio reduced with increasing potential in the potentiostatic measurements prior to HER measurements. The reduced P/Co ratio was accompanied with the emergence of (oxy)phosphate(s) as revealed by XAS, and reduced specific HER activity, suggesting the important role of P in catalyzing HER.