ELECTRONIC SUPPLEMENTARY INFORMATION

Colloidally-Synthesized Cobalt Molybdenum Nanoparticles as Active and Stable Electrocatalysts for the Hydrogen Evolution Reaction under Alkaline Conditions

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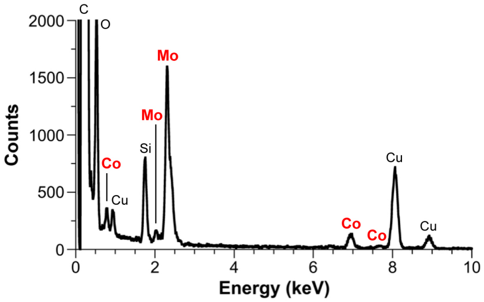

Figure S1. EDS spectrum of Co-Mo nanoparticles. Adventitious C, O, and Si are present, as is the Cu signal from the TEM grid.

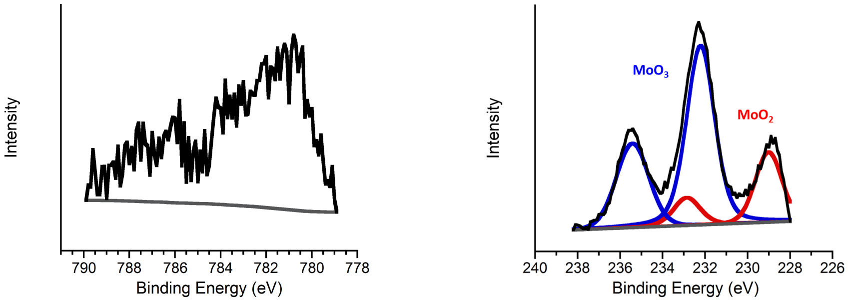

Figure S2. XPS spectra of (left) Co and (right) Mo regions of the Co-Mo nanoparticles after treatment at 300 °C for 2 h under H_2(5%)/Ar(95%). The Co region is consistent with that expected for the $2p_{3/2}$ region of various cobalt oxides.[1-3] although the peaks cannot be reliably deconvoluted due to the low signal, which is a result of the small amount of Co in the Mo-rich nanoparticles. Specifically, CoO and Co_3O_4 would both have an intense peak at ~781 eV, but the presence of a satellite peak between 786 and 790 eV indicates that CoO is likely present.[1] The absence of a peak at 778 eV indicates that Co^0 is not present at the surface.[1] The profile in the Mo region, which is commonly observed in literature for a mixture of MoO_2 (red) and MoO_3 (blue) surface species, originates from overlapping $3d_{5/2}$ and $3d_{3/2}$ peaks.[4,5] The relative atomic Co:Mo ratio is 19:81, which, like the EDS data, is consistent with a Mo-rich composition.

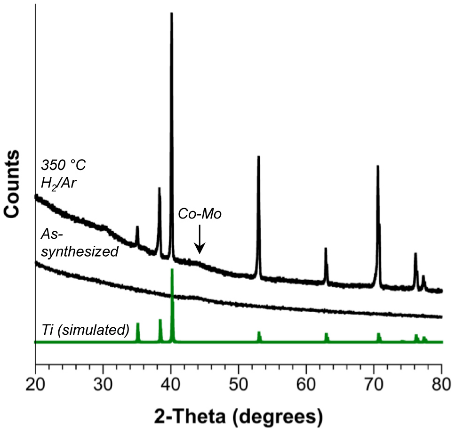

Figure S3. Powder XRD data for the Co-Mo/Ti electrode annealed at 350 °C in H_2(5%)/Ar(95%) prior to electrochemical testing. The XRD pattern for the as-synthesized Co-Mo nanoparticles, as shown in Figure 1c, is shown for comparison, as is the simulated pattern for Ti. The Co-Mo nanoparticles remain unchanged upon annealing.

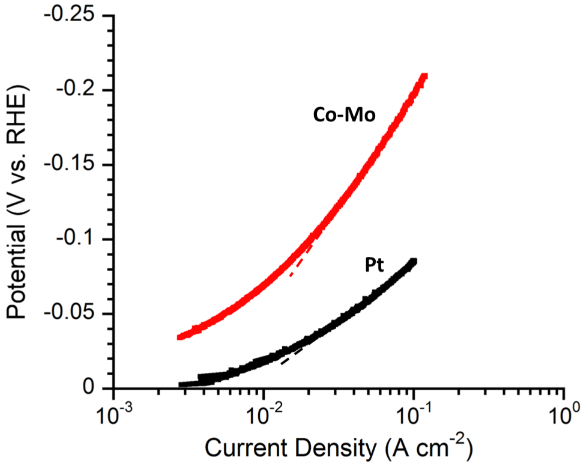

Figure S4. Tafel plot for a Co-Mo/Ti electrode and the Pt mesh control using iR compensated data. The Co-Mo nanoparticle electrode yielded a Tafel slope of 142 mV dec^{-1} (exchange current density of 4.6×10^{-3} A cm^{-2}) in 1 M KOH through the linear region of 100 mV to 200 mV, while the Pt electrode yielded a Tafel slope of 73 mV dec^{-1} (exchange current density of 7.4×10^{-3} A cm^{-2}) through its linear region of 40 mV to 80 mV. Tafel slopes, which correlate to the HER mechanism,[6] can be dependent upon applied potential, pH, and exposed crystal facets. Single crystalline Pt under strongly alkaline conditions can have a Tafel slope of 50-150 mV dec^{-1} depending on the applied potential and exposed facet.[7] The polycrystalline Pt mesh falls within this range and corresponds well with other polycrystalline Pt electrodes reported previously.[7] The Tafel slope of the Co-Mo nanoparticle electrode is comparable to similar materials in the literature under similar conditions (Ni-Co-Mo electrode has a Tafel slope of 125 mV dec^{-1},[8] Co-Mo electrode has a Tafel slope of 116 mV dec^{-1},[9] and Co-Mo electrodes with different Co:Mo ratios have Tafel slopes ranging from 53 – 155 mV dec^{-1}).[10]

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