

Supporting Information

**On the reconstruction of NiMo electrocatalysts by *operando*  
spectroscopy**

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## Experimental

### General method for preparation of films.

For NiMo, an aqueous solution with 0.25 M NiSO<sub>4</sub>·6H<sub>2</sub>O, 0.25 M Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, and 0.3 M sodium citrate tribasic was used for deposition. Electrodeposition was carried out at a current density of  $-10 \text{ mA cm}^{-2}$  for 1 h, although different deposition times and current densities (as low as  $-2 \text{ mA cm}^{-2}$ ) could also be used. The film was washed with de-ionized water (18 M $\Omega$  cm) then dried. The deposition solution was stirred at 800 rpm for slower but more conformal deposition, as was the case for Raman samples. Au substrates were used. Ni films were deposited at  $-10 \text{ mA cm}^{-2}$  for 40 s from a pH 3.5 solution of 1 M NiSO<sub>4</sub>·6H<sub>2</sub>O, 37 mM NiCl<sub>2</sub>·6H<sub>2</sub>O, and 45 mM H<sub>3</sub>BO<sub>3</sub> without agitation.<sup>1</sup> For MoO<sub>x</sub> films, a H<sub>2</sub>-saturated pH 2.8 solution of 0.1 M KClO<sub>4</sub> and 10 mM H<sub>2</sub>MoO<sub>4</sub> with an applied current density of  $-282 \text{ }\mu\text{A cm}^{-2}$  for 10 min.<sup>2</sup> MoS<sub>x</sub> was prepared by cathodic deposition as previously reported.<sup>3</sup> All electrochemical experiments were carried out using a SP-150 potentiostat (Bio-Logic).

### Operando synchrotron XAS experiments.

XAS spectra at the Mo-edge were obtained at the European Synchrotron Radiation Facility (Grenoble, France) on the CRG-FAME-UHD beamline (BM16).<sup>4</sup> The sample cell used was the same as previously described,<sup>2</sup> and the scheme is described in Fig. S1a. A hole is bored into the side of a plastic cell and a 0.1 mm-thick glassy carbon (GC) electrode is epoxied to cover the hole. A wire can then be soldered onto a side of the GC electrode (not covering the opposite side of the hole). The ring was operated at 6 GeV with a nominal current of 200 mA in uniform mode. The beamline was equipped with a liquid-nitrogen-cooled double-crystal Si(220) monochromator surrounded by two Rh-coated mirrors for harmonic rejection. The beam size on the sample was 220 × 100  $\mu\text{m}$  (H × V, FWHM). The monochromator was energy-calibrated by measuring the molybdenum K absorption edge using a metallic molybdenum foil (20000 eV). Spectra were recorded in fluorescence using a Silicon Drift Detector (Vortex-60EX) with a 50 mm<sup>2</sup> active area.

### **Operando Raman spectroscopy experiments.**

Raman spectroscopy was performed using a LabRAM Aramis microscope (HORIBA) with an Olympus 60× water immersion lens. A PTFE film (American Durafilm) was used to protect the lens, which was separated from the film by a drop of deionized water.<sup>5</sup> Three lasers (473 nm (Cobolt), 633 nm (Melles-Griot), and 785 nm (Sacher Lasertechnik)) at an incident power of 2 mW (as measured by a Coherent Lasercheck power meter) were used. The spot size of the system was 1  $\mu\text{m}^2$ . The substrates were NiMo or Ni films, and the solutions used were a combination of 0.1 M KOH, 0.1 M KOH/1 mM  $\text{Na}_2\text{MoO}_4$ , or 0.5 M NaCl/1 mM  $\text{Na}_2\text{MoO}_4$  (pH measured as 7 as prepared). The Raman cell was a custom PTFE operando cell with a face-up electrode and side ports for reference (Hg/HgO, 1 M NaOH) and counter (Ni foam epoxied into PTFE port) electrodes as well as Ar purge line. The scheme of the cell is demonstrated in Fig. S1b. The Raman cell was machined from PTFE with screw joints that could be used to place lines and electrodes in gas- and liquid-tight seals into the cell. Any conductive substrate can be mounted onto a hollow glass tube that fits into the bottom of the cell and serves as the working electrode.

### **Photoelectrochemical deposition of $\text{MoO}_x$ .**

Generally, a solution of 0.1 M  $\text{Na}_2\text{MoO}_4$ /0.1 M KOH was purged with Ar in a photoelectrochemical cell. A 300 W Xe lamp with cold mirror (allows irradiation only < 450 nm) was used to irradiate a FTO working electrode, with a carbon cloth counter electrode and an Hg/HgO 1 M NaOH reference electrode. The applied potential for photoelectrochemical deposition was  $-0.4$  V vs. RHE. For patterning, sticker paper was cut using a  $\text{CO}_2$  laser and applied to the surface of FTO.

### **Small volume reactions for ICP-MS.**

Five mL of 0.1 M KOH was placed into a 10 mL beaker and mounted so that a rotating disc electrode could be held into the electrolyte. A Hg/HgO reference electrode, Ni foam counter electrode, and Ar gas line (with low flow) were also placed in the electrolyte. For HER, a  $-2$   $\text{mA cm}^{-2}$  current density was applied to the electrode and 1 mL aliquots were taken every hour. For OCV, the same was done except no current was applied. The 1

mL aliquots were subsequently individually digested with 6 mL 70% HNO<sub>3</sub> and 1 mL 50% HF using a microwave digester. The samples were diluted with water and analyzed with a Perkin-Elmer ELAN DRC-II ICP-MS.

### Other characterization.

Atomic force microscopy was carried out using a Dimension Icon AFM (Veeco) in tapping mode at a scan rate of 1 Hz and Bruker FESP AFM Probes. UV-visible spectroscopy was carried on a V-670 spectrophotometer (JASCO).

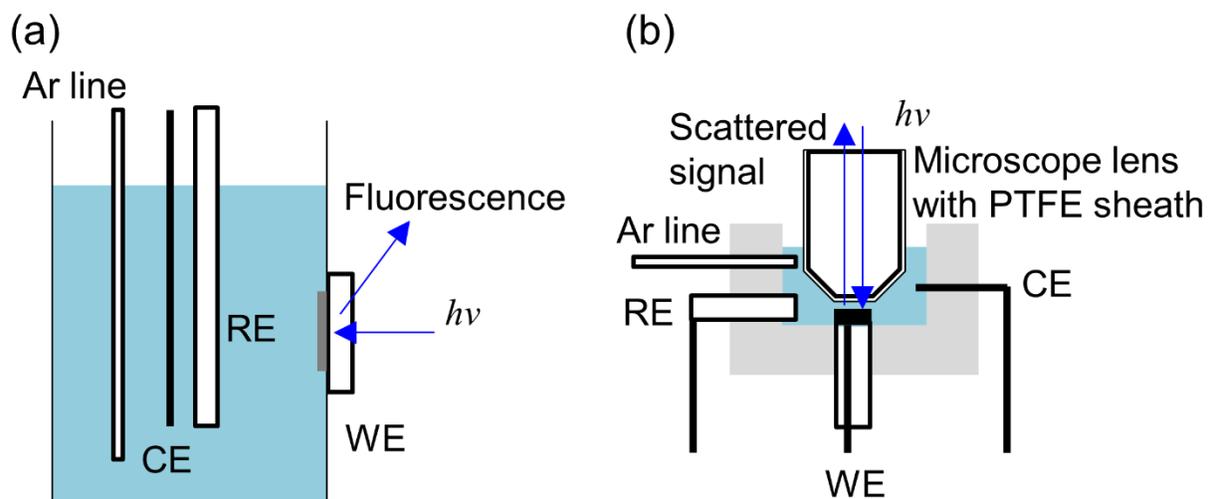


Fig. S1. Experimental setups for (a) XAS and (b) Raman cells. WE, working electrode; CE, counter electrode; RE, reference electrode. See experimental details for experimental descriptions.

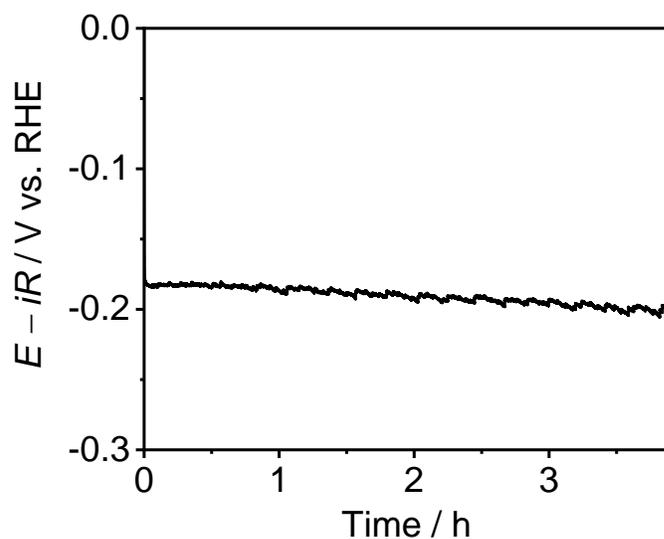


Fig. S2. Chronopotentiometric measurement of NiMo electrode at a current density of  $-2 \text{ mA cm}^{-2}$  in 0.1 M KOH under XAS irradiation.

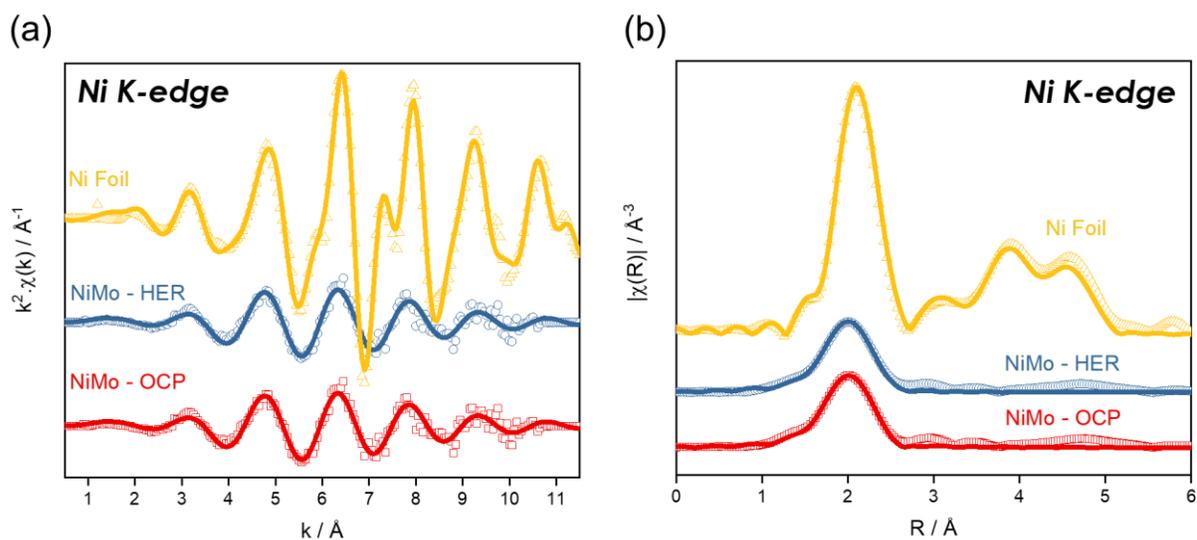


Fig. S3. (a) Ni EXAFS spectra and (b) FT-EXAFS spectra (no phase correction) of NiMo film at before HER (open circuit potential (OCP)), NiMo film during HER at a time course of 7 h, and Ni foil (reference). HER conditions:  $-2 \text{ mA cm}^{-2}$  in 0.1 M KOH measuring  $\sim 200 \text{ mV}$  overpotential.

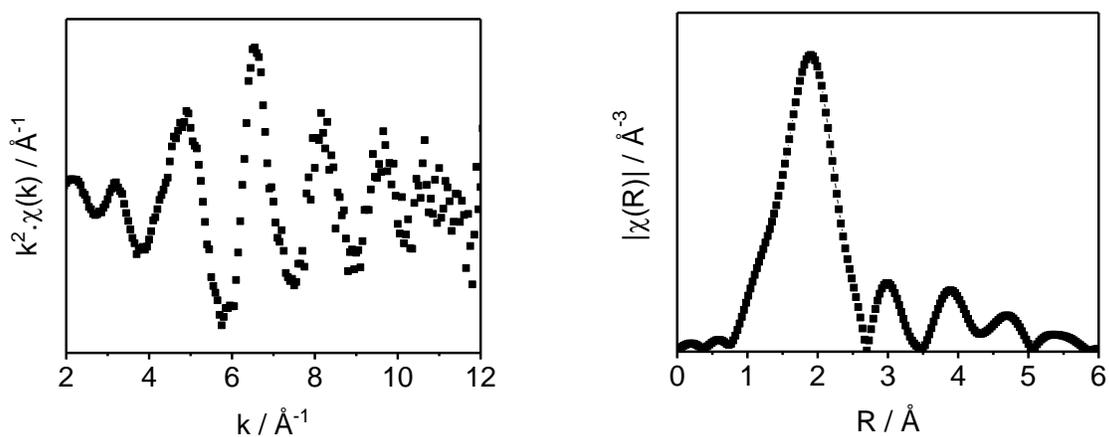


Fig. S4. Mo EXAFS (left) and FT-EXAFS (right) spectra (no phase correction) of NiMo film at the end of oxidative treatment at 0.3 V vs. RHE in 0.1 M KOH.

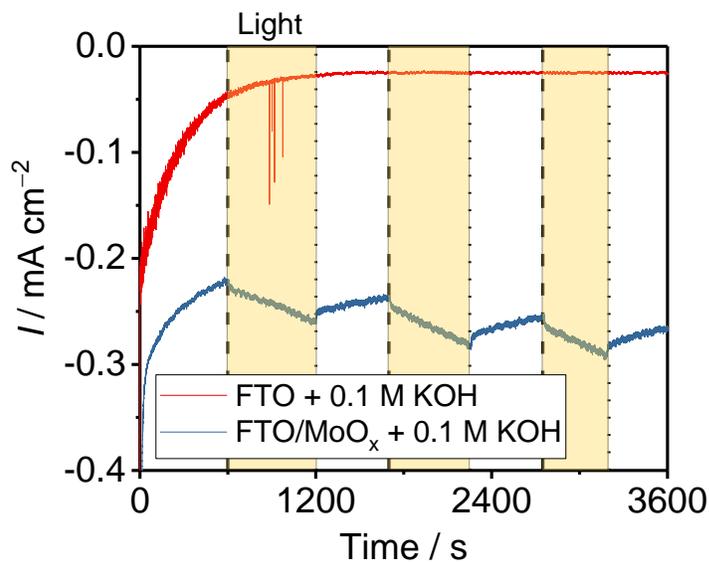


Fig. S5. Chronoamperometry of FTO slides held at  $-0.4 \text{ V}$  vs. RHE in the absence and presence of  $0.1 \text{ M MoO}_4^{2-}$ . Illumination was performed using a 300 W Xe lamp.

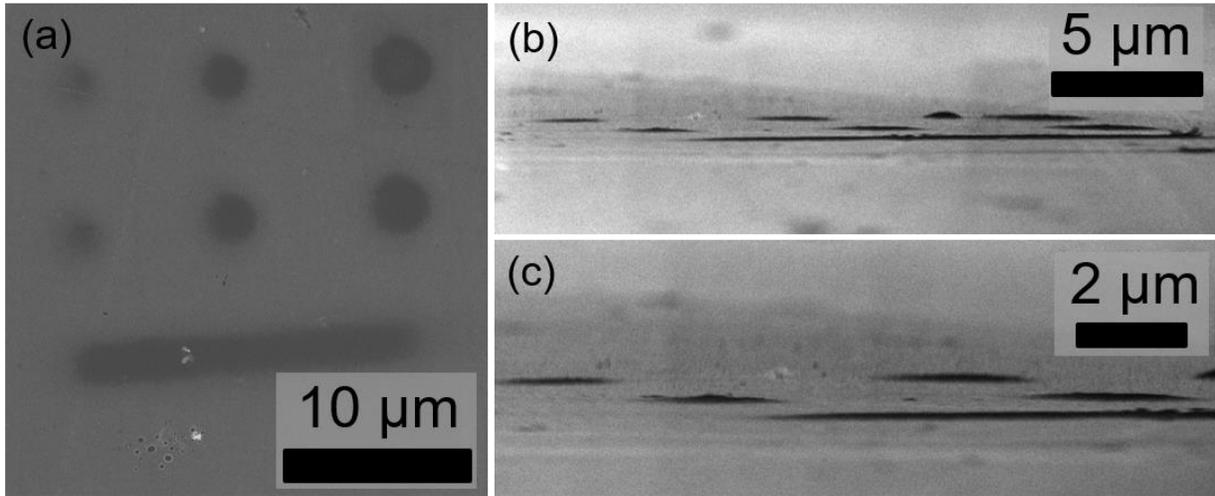


Fig. S6. Scanning electron microscopic (SEM) images of  $\text{MoO}_x$  pattern in Fig. 3c of the main manuscript. (a) Top-down image, (b) side view of entire pattern, and (c) close-up side view of left side of pattern.

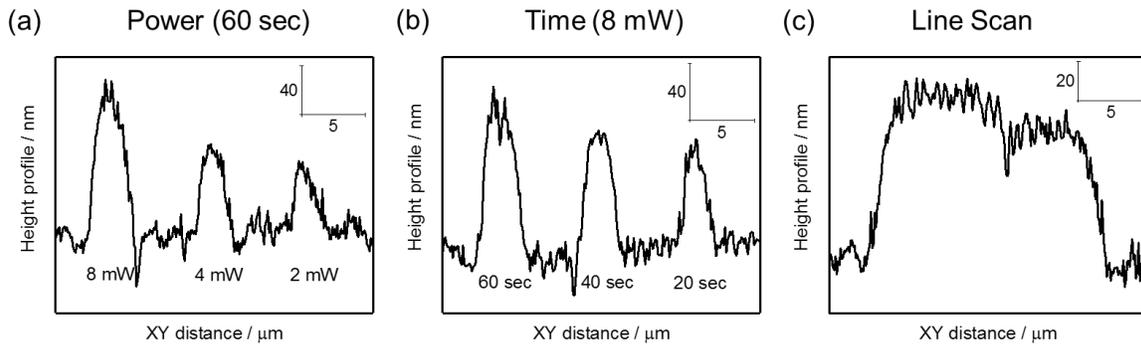


Fig. S7. Atomic force microscopic (AFM) profiles of the patterns in Fig. 3c of the main manuscript. (a) Effect of power for 60 s exposure time, (b) effect of time for 8 mW laser power, and (c) profile of line feature.

## References (Electronic Supplementary Information)

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