

# Supporting Information

# An Oxygen-Insensitive Hydrogen Evolution Catalyst Coated by a Molybdenum-Based Layer for Overall Water Splitting

Angel T. Garcia-Esparza<sup>+</sup>, Tatsuya Shinagawa<sup>+</sup>, Samy Ould-Chikh, Muhammad Qureshi, Xuyuan Peng, Nini Wei, Dalaver H. Anjum, Alain Clo, Tsu-Chien Weng, Dennis Nordlund, Dimosthenis Sokaras, Jun Kubota, Kazunari Domen, and Kazuhiro Takanabe<sup>\*</sup>

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# Supporting Information

#### **Author contributions**

A.T.G-E. and T.S. contributed equally. A.T.G-E., T.S., J.K., K.D. and K.T. conceived and designed the experiments. A.T.G-E., T.S. and X.P. performed the material syntheses and conducted the electrochemical measurements. A.T.G-E. and T.S. analyzed the electrocatalytic data. M.Q. conducted the photocatalytic measurements. A.T.G-E., T-C.W., D.N. and D.S. designed and executed the *in operando* spectroscopic characterization. A.T.G-E., S.O-C., N.W. and D.H.A. performed the chemical and physical characterizations. A.T.G-E., S.O-C., T-C.W. and D.S. analyzed the spectroscopic data. A.T.G-E. and S.O-C. defined the theoretical calculations of the absorption spectra. A.C. optimized the theoretical calculations. A.T.G-E., T.S., S.O-C., and K.T. co-wrote the article. All authors read, discussed and approved the final manuscript.

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## **1. Experimental Procedures**

**Materials.** All reagents were provided by commercial suppliers and used without further modification: Na<sub>2</sub>MoO<sub>4</sub>· 2H<sub>2</sub>O (99.99%: Sigma-Aldrich), H<sub>2</sub>MoO<sub>4</sub> ( $\geq$ 85%, MoO<sub>3</sub> basis: Sigma-Aldrich), H<sub>2</sub>SO<sub>4</sub> (99.999%: Aldrich), HClO<sub>4</sub> (99.999%: Aldrich), KOH (99.99%: Aldrich), Na<sub>2</sub>SO<sub>4</sub> ( $\geq$ 99.99%: Aldrich), K<sub>2</sub>SO<sub>4</sub> (99.99%: Aldrich), CsClO<sub>4</sub> (99%: Aldrich), NaClO<sub>4</sub> (99%: Aldrich), LiClO<sub>4</sub> (99.99%: Aldrich), KClO<sub>4</sub> (99%: Aldrich), SrTiO<sub>3</sub> (99.9%: Wako), SrCl<sub>2</sub>· 6H<sub>2</sub>O (99%: Sigma-Aldrich), H<sub>2</sub>PtCl<sub>6</sub>· 6H<sub>2</sub>O (98%: Aldrich), and HCl (trace-metal grade: Fisher Chemical). All gases were provided by AHG Industrial Gases: H<sub>2</sub> (99.9999%), O<sub>2</sub> (99.9995%), and Ar (99.999%). The water used in all experiments was obtained from a Milli-Q Academic system from Millipore (18.2 MΩ cm). The pH was carefully determined using a pH electrode from Fisher Scientific.

**Electrochemistry.** A research-grade BioLogic VMP3 potentiostat was used for all electrochemical measurements. A conventional single-compartment three-electrode system was used for the electrochemical protocols. An airtight, three-electrode cell was used for monitoring gases during the constant potential electrolysis tests. O<sub>2</sub> was used to saturate the electrolyte and as the carrier gas for the analysis of produced H<sub>2</sub>. Gas chromatography ( $\mu$ GC, T-3000) from SRA-Instruments was used with a MolSieve 5A column and a thermal conductivity detector (TCD) for the on-line characterization of gaseous compounds. A Pt wire was used as the counter electrode. Ag/AgCl (saturated KCl) was used as the reference electrode. Before and during the measurements, Ar, H<sub>2</sub>, or O<sub>2</sub> was continuously supplied through the electrolyte. Cyclic and linear sweep voltammograms were recorded at a scan rate of 50 mV s<sup>-1</sup>, unless otherwise noted, at room temperature. All potentials reported were *iR* corrected (i.e., ohmic drop) and presented in reference to the reversible hydrogen electrode (RHE).

**Pt catalysts.** Electrocatalytic experiments were performed using polycrystalline Pt rotating disk electrodes (3.0 mm diameter, 0.071 cm<sup>2</sup> geometric surface area), Pt nanoparticles electrodeposited on glassy carbon disks (GC, 10 mm diameter, 100-200 μm thickness), and sputtered Pt thin-film electrodes on glass or Si wafers.

Custom-made Pt thin-film electrodes were grown using direct current (DC) magnetron reactive sputtering with pure Ti and Pt targets. Deposition of the thin metal layers was performed on glass (18×24 mm, 120 µm thickness from MATSUNAMI) and Si {100} single-crystal wafers. We calculated the sputtered deposition of 5 nm Ti (contact layer) followed by 10 nm Pt (active layer), creating homogeneous films on the substrates. A Cu wire was soldered using In to create resistance-free ohmic contacts. The thin-film electrodes were later isolated with epoxy to cover all the electrical connections while exposing well-defined active areas. The thin-film electrodes were used for constant-potential electrolysis experiments to determine the Faradaic efficiency of the samples and for the *in operando* Mo K-edge XAS, XPS, and transmission electron microscopy characterizations.

The electrochemical deposition of Pt nanoparticles was performed following previously reported methods in the literature from a plating bath composed of sodium hexachloroplatinate (1 mM Na<sub>2</sub>PtCl<sub>6</sub>· 6H<sub>2</sub>O, pH 4.4) by applying a constant potential of -0.1 V vs. Ag/AgCl (2 M NaCl) for 3 s under atmospheric conditions.<sup>[S1]</sup> Glassy carbon disks (100-200 µm thick GC wafers) were used as substrates for the electrodeposition of Pt nanoparticles. To measure the hydrogen desorption region (QH) of the Pt NP surfaces, the pristine materials were tested in perchloric acid (1 M), and the electrochemically active surface area (ECSA) was quantified. Cyclic voltammetry was performed using Pt NPs supported on GC at 300 mV s<sup>-1</sup> between 0.045 V and 1.3 V vs. RHE, and the hydrogen desorption region was integrated under steady-state

conditions, resulting in average values of  $0.13 \pm 0.03$  cm<sup>-2</sup> for electrochemically active Pt. The Pt nanoparticles supported on X-ray transparent GC were used to probe the Pt L3-edge via in operando XAS characterizations of the Pt NPs surface modified with Mo species under working electrocatalytic conditions.

**Mo electrodeposition.** The optimized Mo coating was synthesized via cathodic electrochemical deposition using  $-282 \ \mu A \ cm_{Pt}^{-2}$  constant current density and controlling the amount of charge passed to Pt (169 C cm<sup>-2</sup>). The electrolyte was made by dissolving H<sub>2</sub>MoO<sub>4</sub> (0.01 M) and KClO<sub>4</sub> (0.06-0.12 M). The pH was adjusted to 2.8 using HClO<sub>4</sub> (1 M). H<sub>2</sub> gas was saturated in the electrolyte for at least 20 minutes before and during the electrodeposition step without convection in a standard three-electrode electrochemical cell (see optimization discussion in Figures S1 and S2).

*In operando* characterization of materials. All *in-operando* XAS measurements were performed at the Stanford Synchrotron Radiation Lightsource (SSRL). The Mo K-edge EXAFS and XANES studies were performed at beamline 4-1 using a Si(220) monochromator that delivered a 1mm(v) x 3mm(h) x-ray beam at the sample position; XAS was performed in fluorescence mode using a 30-element Ge detector. The incident photon energy was calibrated using the transmission-mode XAS spectrum of a Mo foil. The high-resolution XAS of Pt L<sub>3</sub>-edge was performed at beamline 6-2 using a Si(111) monochromator in combination with a Rowland circle spectrometer consisting of five spherically bent Ge perfect crystals (R = 1 m).<sup>[S2]</sup> The crystals were aligned in a backscattering geometry, using the (660) Bragg reflection at 80.0°, to select the Pt La1 fluorescence line (9442 eV). The incident photon energy was calibrated using the transmission-mode XAS spectrum of a Pt foil. The incident x-ray beam was focused with a parabolic mirror to a spot size of 200 µm fwhm (V) by 400 µm fwhm (H) at the sample position.

In operando XAS was performed with a custom-made electrochemical cell (described in detail in Figure S8). Briefly, a conventional 3 mL cuvette was modified at the local workshop at SSRL-SLAC to fit the custom-made thin-film electrodes and the Pt NPs supported on GC disk electrodes. A Cu wire and In were used to make ohmic contact with the working electrode before fixing it with epoxy to the cuvette. The epoxy was used to seal, isolate and expose a defined active geometric area that was measured with digital photography and analyzed with the ImageJ image processing and analysis software. Mo was freshly electrodeposited on Pt in the XAS cells before each in operando XAS run. The XAS spectra were analyzed using the HORAE package, a graphical interface to the AUTOBK and IFEFFIT code.<sup>[S3]</sup> The XANES and EXAFS spectra were obtained after performing standard procedures for pre-edge subtraction, normalization, polynomial removal and wave vector conversion. The extracted EXAFS signal was fitted in Rspace using a Kaiser-Bessel window (dk = 1) with a k-range of about [4.6; 12]  $Å^{-1}$  for all materials. For each atomic shell, the following structural parameters were adjusted: coordination number (N), bond length distance (R), and the so-called Debye–Waller factor via the meansquare relative displacement ( $\sigma^2$ ) of the considered bond length. The amplitude factor (S<sub>0</sub><sup>2</sup>) was fitted to the EXAFS spectrum obtained for a Na<sub>2</sub>MoO<sub>4</sub> compound whose crystal structure is known.<sup>[S4]</sup> S<sub>0</sub><sup>2</sup> was then fixed to 0.9 (see Figure S11). The atomic coordinates of the MoO<sub>2</sub> monoclinic form were used as an input to calculate the theoretical phases, amplitudes and electron free mean path with the FEFF6 code implemented in the IFEFFIT programs suite.<sup>[S5]</sup>

**First principles calculations.** Ab initio simulations of the XANES spectra were performed using the FDMNES package. The FDMNES code features mono-electronic calculations, which are carried out in real space using clusters built around each non-equivalent absorbing atom. The finite-difference method (FDM) implemented in the FDMNES code was

used since the latter is a full potential method that introduces no approximation on the shape of the potential, which is particularly important when dealing with highly distorted structures, as in molybdenum oxides.<sup>[S6]</sup> The current implementation at KAUST of the recent FDMNES version with the MUMPS solver allows FDM calculations with a 7 Å cluster radius, which were not possible when using the built-in solver because of the required memory footprint and the CPU runtime.<sup>[S7]</sup> To take into account the core-hole lifetime and other multielectronic phenomena occurring in the absorption process, a convolution procedure was applied to all calculated spectra presented in this work. At the Fermi level, the Lorentzian (FWHM) width is due to the interaction with the core hole and is equal to 4.52 eV at the Mo K-edge.<sup>[S6]</sup> At higher photoelectron energies, the plasmon collective interactions increase the Lorentzian width up to 10 eV.

**Photocatalysis.** As-purchased SrTiO<sub>3</sub> and SrCl<sub>2</sub> (mole ratio of 1:5) were mixed with a mortar and pestle and then underwent flux treatment at 1273 K for 10 h to make highly crystalline SrTiO<sub>3</sub>. Once the powder cooled to room temperature, it was washed with Milli-Q water (18.2 MΩ cm) and then dried at 383 K for 5 h. Pt was deposited on the surface of SrTiO<sub>3</sub> via wet impregnation for a calculated 0.5 wt.% loading using 25 µL H<sub>2</sub>PtCl<sub>6</sub> (0.1 M solution), 5 mL Milli-Q water, and 100 mg (0.54 mmol) SrTiO<sub>3</sub> mixed over a water-bath until all the water evaporated. The Pt/SrTiO<sub>3</sub> was collected and used for the photocatalytic reaction. ICP analysis of the sample indicated a final 0.3 wt.% Pt loading on the SrTiO<sub>3</sub> photocatalyst. Mo was deposited on Pt/SrTiO<sub>3</sub> by mixing 90 mL of Milli-Q water, 10 mL HCl, 100 mg (0.54 mmol) Pt/SrTiO<sub>3</sub>, and 363 mg (1.5 mM to make a 15 mM solution) Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O for 24 h. The powder was collected and used for the photocatalyst powder was placed in a photoreactor with 100 mL Milli-Q water and dispersed by sonication for 5 min. The

photocatalytic reactions were conducted at 100 Torr Ar gas in a circulating batch reactor equipped with an on-line gas chromatograph (GC: Bruker 450 GC, TCD, Ar gas, molecular sieve 13X) connected to a vacuum line.<sup>[S8]</sup> A Xe lamp (CERMAX PE300-BF, 300 W) was used as the light source, and the irradiation wavelength was controlled with the combination of a cold mirror and a water filter ( $300 < \lambda < 800$  nm). The photocatalytic reactor was illuminated for 24 h, then turned off for 6 h to measure the dark reaction. The spectral area of the photocatalytic reactor was 38.5 cm<sup>2</sup>, and the photon flux was measured using the AvaSpec-3648 spectrometer, AvaLight DHS calibration light source, and FC-UV200-2 fiber-optic cable. The apparent quantum efficiency measurements were calculated with a 350 nm band-pass filter at different time points in the experiment (see the photon flux distribution in Figure S16). The photocatalytic reaction measurement was performed three times in this study, and the reported activity was the average of those measurements.

**Characterization.** XPS and AES were performed on a 3400 Amicus/ESCA from Kratos Analytical with an unmonochromatized Al-anode K $\alpha$  X-ray source (1486.6 eV) operated at 15 mA and 10 kV (~1 × 10<sup>-7</sup> Pa). The binding energies were calibrated using adventitious C 1s spectra with a reported binding energy of 284.8 eV, and the associated error was estimated to be  $\pm 0.2$  eV.

Inductively coupled plasma (ICP) measurements were taken using a Varian 720-ES equipped with a charge-coupled device (CCD) detector. All samples were microwave digested in concentrated HNO<sub>3</sub>. The samples were further diluted with 1% HNO<sub>3</sub> prior to all measurements. A standard error of  $\pm$  2 ppm was calculated based on the average of the experimental standard deviations for each set of measurements.

Transmission electron microscopy analysis was performed by employing a probecorrected microscope of model Titan 80-300 ST from FEI Company (Hillsboro, OR), which was equipped with a Gatan Image Filter of model GIF-Quantum 966 from Gatan, Inc. The TEM sample was prepared using an FEI Helios NanoLab 400S FIB/SEM dual-beam system equipped with a  $Ga^+$  ion source. C and Pt layers were deposited on the surface region of interest by electron and ion beam for sample protection. The sample was thinned down to a relative thickness of 80 nm using progressively decreasing ion beam energies in the FIB down to 5 keV. The microscope was operated at an accelerating voltage of 300 kV during the analysis. The microscope was set to image, electron diffraction, and scanning TEM (STEM) modes to acquire bright-field TEM (BF-TEM), selected area electron diffraction (SAED), and high-angle annular dark-field (HAADF) STEM datasets. In addition, electron energy loss spectroscopy (EELS) was used to generate the STEM-EELS spectrum image datasets by setting the GIF-Quantum energy filter in EELS mode. Note that Si K-, Ti L-, O K-, Pt M-, and Mo M-edge absorptions were recorded by EELS to generate the corresponding Si, Ti, O, Pt, and Mo elemental maps. X-ray energy dispersive spectroscopy (EDS) was also used to generate STEM-EDS line profiles to confirm the presence of elements in the elemental maps produced by the STEM-EELS spectrum imaging technique.

## 2. Electrochemical deposition of Mo



Figure S1. Investigation of the Mo electrodeposition conditions.

(a) Chronopotentiometry (CP) over a Pt rotating disk electrode (RDE) electrode in various molybdates containing electrolytes at various pH levels with bubbling Ar ( $-282 \ \mu A \ cm^{-2}$  for 10 min, 298 K). (b) Compilation of steady-state potentials after 10 min of Mo deposition from the electrodeposition step in (a). The square orange symbols followed a 59.1 mV pH<sup>-1</sup> trend as represented by a solid line. (c) Measured open circuit potential (OCV) of a Pt RDE in a molybdate electrolyte under H<sub>2</sub> bubbling and saturation. The inset shows the CP in the subsequent electrodeposition step ( $-282 \ \mu A \ cm^{-2}$  for 10 min, in 0.12 M NaClO<sub>4</sub>, 0.01 M

H<sub>2</sub>MoO<sub>4</sub>, pH 2.8). (d) Koutecky-Levich relation at 400 mV vs. RHE obtained from the CV of the MoO<sub>x</sub>/Pt samples made with changing deposition times under O<sub>2</sub> saturation conditions in Nabased electrolytes (electrodeposition:  $-282 \,\mu\text{A cm}^{-2}$  for 0~10 min, 0.1 M NaClO<sub>4</sub>, 0.01 M Na<sub>2</sub>MoO<sub>4</sub>, pH 2.8; reaction: 50 mV s<sup>-1</sup>, 0.1 M NaClO<sub>4</sub>, pH 1.8, 298 K). The zero-time point refers to the electroless deposition of Mo formed only by supplying H<sub>2</sub> to the molybdate-containing electrolyte.

The CP in various electrolytes was utilized to provide a constant flow of electrons to the Pt electrode in (a). A constant current of  $-20 \,\mu\text{A}$  was applied to the Pt disk (0.071 cm<sup>-2</sup>, 298 K). The pH of the electrolyte was varied along with the concentration and identity of the ions. The investigated pH range was varied from 1 to 5, and the effects of Na, K, Cs, Li, SO4, and ClO4 were explored. All the produced samples were tested for their activity towards the oxygen reduction reaction (ORR), the hydrogen oxidation reaction (HOR) and the hydrogen evolution reaction (HER), and compared to the performance of the pristine Pt RDE (900-3600 rpm). We considered a sample successful if the ORR was inhibited significantly.

Observed potentials for the successful cases (square orange symbols in Figure S1b) during electrodeposition in various electrolyte solutions exhibited a 59.1 mV pH<sup>-1</sup> trend with a *y*-intercept of approximately 0 V vs. the standard hydrogen electrode (SHE), which corresponds to the equilibrium potential of the HER/HOR (i.e., 0 V vs. reversible hydrogen electron -RHE). The observation indicates an involvement of the HER/HOR and may suggest the reduction of Mo species with the evolved H<sub>2</sub> during the deposition. Based on these rationales, we introduced H<sub>2</sub> to the molybdate-based electrolyte and observed that the open circuit potential dropped near 0 V vs. RHE on the Pt RDE without applying potential or current. Moreover, we observed that the Pt

surface changed its color to red/yellow with the presence of H<sub>2</sub> in the molybdate-based solution (a similar optical observation was made when applying constant current to make the Mo coating on Pt). Clearly, it was possible to deposit Mo on Pt by saturation of the molybdate electrolyte with H<sub>2</sub> (Figure S1d). The electroless deposition of Mo may be catalyzed by H<sub>2</sub> dissociation on Pt and the generation of Pt–H, possibly forming a Mo layer on the Pt sites. However, such Mo layer was not stable under potential cycling. Both H<sub>2</sub> saturation and the application of constant current were required to make a chemically and mechanically robust sample. When H<sub>2</sub> was not present during the electrodeposition of Mo, the inhibition effect shown in Figure 1 of the main manuscript was not stable and could be lost after a few electrochemical cycles.

Another noteworthy observation was that there was a range of suitable pH during deposition for the ORR suppression. In electrodeposition baths of  $0.01 \text{ M Na}_2\text{MoO}_4 + 0.05 \text{ M Na}_2\text{SO}_4$ , at pH 2.8 and 3.6, the ORR was successfully suppressed. However, when the pH was higher, e.g., pH 4.9, the suppression was not observed.

A significant influence of the presence/absence of the cations on the ORR suppression was observed. When a bath containing 0.01 M Na<sub>2</sub>MoO<sub>4</sub> + 0.1 M NaClO<sub>4</sub> was used at pH 2.9, the suppression observed in a SO<sub>4</sub><sup>2–</sup>-containing solution was well-reproduced, suggesting a negligible influence of the anion. Interestingly, the ORR was suppressed when the electrodeposition was conducted in 0.01 M Na<sub>2</sub>MoO<sub>4</sub> + 0.05 M Na<sub>2</sub>SO<sub>4</sub>, whereas 0.01 M H<sub>2</sub>MoO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> did not lead to ORR inhibition, although both solutions had the same pH of 3.6. This observation implied that the presence of the alkali metal cation was essential in suppressing the ORR electrochemically (*vide infra*).

Based on the electrochemical results, it is possible to summarize the required conditions for the Mo electrodeposition to result in the inhibition of ORR as follows:

- 1. pH range = 1.1 < pH < 4.9
- 2. Alkaline metal ions are required (see Figure S2 below for more details).
- 3. Any anion can be used (i.e., no difference between  $SO_4^{2-}$  and  $CIO_4^{-}$ ).
- 4. H<sub>2</sub> saturation in the molybdate-based electrolyte is essential.

When the deposition time for Mo was changed while applying the same current density, the amount of deposited Mo could be altered. However, the suppression of the ORR was not significantly affected by the deposition time on Na-containing electrolytes, as shown in Figure S1d. The data points at 0 min in this figure indicate a Mo layer formed only by the saturation of H<sub>2</sub> in the electrolyte, most likely an electroless deposition where Mo replaces Pt-H on the surface of the electrode. Mo on Pt only changed the Koutecky-Levich (KL) slope when the inverse of the current was plotted as a function of the inverse square root of the rotation rate in the case of Na-and Li-based electrolytes. On the other hand, Cs- and K-based electrolytes resulted in a current density which was mostly independent of the rotation rate; hence, the KL analysis was not applied for such cases.

Ultimately, the optimized deposition conditions for our study were as follows: 10 min deposition with a constant current density of  $-282 \,\mu\text{A cm}^{-2}$  in 0.1 M KClO<sub>4</sub>, 0.01 M H<sub>2</sub>MoO<sub>4</sub>, and pH 2.8 with H<sub>2</sub> constantly purged through the electrochemical cell 20 min before, and during the electrodeposition step. The ORR and HER were tested in 0.1 M KClO<sub>4</sub> at pH 1.8 under their respective gas saturation conditions. All the data presented in the main manuscript was obtained from Mo materials made from K-containing electrolytes under H<sub>2</sub> saturation. The influence of the cations is detailed below in Figure S2.



Figure S2. Effects of the alkali metal ions on the ORR with Pt and MoO<sub>x</sub>/Pt.

(a) Linear sweep voltammetry (LSV) recorded under O<sub>2</sub> saturation with MoO<sub>4</sub>/Pt RDE samples measured using different cation-based electrolytes. The MoO<sub>4</sub>/Pt samples were synthesized by changing the alkali metal cation in the electroplating solution during the deposition step and tested in different O<sub>2</sub>-saturated electrolytes (electrodeposition:  $-282 \ \mu A \ cm^{-2}$  for 10 min, 0.12 M *A*ClO<sub>4</sub>, 0.01 M H<sub>2</sub>MoO<sub>4</sub>, pH 2.8; reaction: 50 mV s<sup>-1</sup>, 0.06 M *A*ClO<sub>4</sub>, pH 1.8, 298 K, *A* = Cs, K, Na, Li). All the LSVs in (a) were recorded at a rotation speed of 3600 rpm with O<sub>2</sub> bubbling. (b) LSVs of the pristine Pt RDE under O<sub>2</sub> saturation condition with different alkali metal cations in the electrolyte. The inset shows the details of LSV above 0.4 V vs. RHE (50 mV s<sup>-1</sup>, 0.06 M *A*ClO<sub>4</sub>, pH 1.8, 298 K, *A* = Cs, K, Na, Li). (c) CVs of pristine Pt RDE under Ar saturation,

varying the electrolyte and the alkali metal cation in the solution (50 mV s<sup>-1</sup>, 0.06 M AClO<sub>4</sub>, pH 1.8, 298 K, A = Cs, K, Na, Li).

We observed that the extent of the ORR suppression when using MoO<sub>x</sub>/Pt RDE was dependent on the cations, following the order of Li < Na < K  $\approx$  Cs. Notably, in the Cs-containing electrolyte, precipitates were formed that could alter the concentration of molybdates in the solution. Accordingly, although the ORR was suppressed the most with Cs, K-based electrolytes were chosen in the electrochemical study for consistency. Notwithstanding that there was a clear difference between the ORR LSV over the pristine Pt surface in the presence of different alkali metal cations, we confirmed that the cation itself did not suppress the ORR activity of Pt as in the MoO<sub>x</sub>/Pt case (Figure S2b). Furthermore, the alkali metal cation in the solution did not change the characteristic CV profile of the Pt RDE under Ar saturation at pH 1.8. Moreover, the reducibility of the Pt surface was not drastically changed by the alkali metals, as there were no apparent potential shifts in the redox peaks of PtO<sub>x</sub> (Figure S2c).

## 3. Electrochemical data



Figure S3. HER activity of Mo supported on Au and GC.

CVs of Mo electrochemically deposited on (a) Au and (b) glassy C rotating disk electrodes at 3600 rpm under O<sub>2</sub> gas saturation in the electrolyte (50 mV s<sup>-1</sup>, 0.1 M KClO<sub>4</sub>, pH 1.8, 298 K).



Figure S4. HER Tafel plot of Pt and  $MoO_x/Pt$  (50 mV s<sup>-1</sup>, 0.1 M KClO<sub>4</sub>, pH 1.8, 298 K).

Catalytic cathodic currents ascribed to H<sub>2</sub> formation were clearly observed for both samples (Figures 1b and 1c of the main manuscript). The Tafel relation,  $\eta = a + b \log(i)$ , was used to analyzed the HER kinetics, and the results indicate that Pt exhibited a Tafel slope b = 30~ 40 mV dec<sup>-1</sup> in acidic media (Figure S4). In this case, the rate determining step is ascribable to either the Tafel recombination elementary step or the Heyrovsky step:

)

(Tafel) 
$$2M-H \rightarrow H_2 + 2M$$
 (1)  
(Heyrovsky)  $M-H + H_3O^+ + e^- \rightarrow H_2 + H_2O + M$  (2)

where M denotes an empty site in the Pt surface.

When Mo was present, a potential-dependent Tafel slope was observed with increasing values of 40 to 120 mV dec<sup>-1</sup>. One explanation is a change in the reaction mechanism along with the changing surface coverage: the Heyrovsky step followed by the Volmer step with increasing overpotential. The other possibility is a coverage-induced change in the Tafel slope with the Heyrovsky step being the rate determining step.

(Volmer) 
$$H_3O^+ + e^- + M \rightarrow M - H + H_2O$$
 (3)



Figure S5. Faradaic efficiency and stability measurements.

Chronoamperometry (CA) at 0, -0.09, and -0.18 V vs. RHE of (a) Pt with O<sub>2</sub> bubbling, (b) MoO<sub>x</sub>/Pt with O<sub>2</sub> bubbling, (c) Pt with Ar bubbling, and (d) MoO<sub>x</sub>/Pt with Ar bubbling; recorded in 0.1 M KClO<sub>4</sub> (pH 1.8) at 298 K; and (e) CVs before and after long-term water splitting

stability experiments. Long-term water splitting experiments were performed as presented in the Figures S5a to S5d. The CA experiments were performed sequentially at 0, -0.09 and -0.18 V vs. RHE for 5 h under each applied potential using the thin-film MoO<sub>x</sub>/Pt electrodes described in Figure 2 of the main manuscript (see BF-TEM, HAADF-STEM, and SEM-FIB cross-section in Figures S6 and S7). The solid lines in Figures S5a to S5d represent the measured current density at each applied potential. Filled symbols represent the measured H<sub>2</sub> Faradaic efficiency (FE) at 0 V vs. RHE; open symbols represent the H<sub>2</sub> FE recorded at -0.09 V vs. RHE; and the crossed symbols indicated the H<sub>2</sub> FE at -0.18 V vs. RHE. Figure S5e shows CVs recorded before and after the 15 h of the water splitting experiment to address the stability of the electrocatalyst. The ORR activity of the pristine Pt thin-film electrode is shown in the Figure S5e as a reference. No significant changes were observed in the MoO<sub>x</sub>/Pt CV profile.

## 4. Characterization of electrode

The MoO<sub>x</sub>/Pt thin-film sample was fabricated to pursue the *in operando* X-ray absorption spectroscopy (XAS) characterization to rigorously reveal the identity of the species under the working HER conditions. Custom-made electrodes were fabricated by sequential high-vacuum sputtering of Ti and Pt on either Si  $\{100\}$  wafers or glass slides (120 µm). Then, the Mo electrodeposition was performed (details in Sections 1 and 2 of the Supporting Information). Figures S6 and S7 show the Cs-corrected bright/dark-field imaging coupled with the electron energy loss spectroscopy (EELS) mapping of the cross-sectional nanostructure of the MoO<sub>x</sub>/Pt thin-film electrode after electrocatalytic tests (see also Figure S7 for the focused ion-beam scanning electron microscopy image). A  $160 \pm 15$  nm MoO<sub>x</sub> layer was observed homogenously built on the substrate; consistent with the quantity measured by elemental analysis (ICP), giving a Mo/Pt molar ratio of 232. From bottom to top, the chemical contrast in the bright- and darkfield micrographs identified  $\sim 1 \text{ nm SiO}_2$  layer on the surface of Si {100}, 4 nm amorphous Ti, and 8 nm polycrystalline Pt under the MoO<sub>x</sub> coating (Figures S6a-S6c and EELS mapping in Figure S7). The O K-edge elemental mapping suggested the presence of O species on the top ~5-6 nm region of Pt (Figure S7). The diffusion of Ti atoms into Pt was detected at the substrate side of the catalytic layer (~2-3 nm); however, Mo atoms did not diffuse into Pt within our detection limits, which was consistent with energy-dispersive X-ray spectroscopy (EDX) line profiles across the junction (Figure S7 and S8a). Bright-field high-resolution transmission electron microscopy (BF-HRTEM, Figure S6d) and selected area electron diffraction (SAED, Figure S6e) of the Mo-layer demonstrated the presence of crystallites with a coherent domain size of ~2-4 nm mixed within an amorphous phase. Semi-quantitative elemental analysis by EDX provided an O/Mo atomic ratio of  $3.2 \pm 0.2$ , suggesting the absence of metallic Mo (Figure S8b and O K-

edge for Mo in Figure S7). The limited amount of K in the Mo layer excluded the formation of any K-based crystalline phase (K/Mo =  $0.04 \pm 0.01$ ).



**Figure S6**. (a) TEM cross-section of the MoO<sub>x</sub>/Pt thin-film electrode (from bottom to top: Si/Ti/Pt/Mo). (b) BF-TEM focusing at the Ti/Pt/Mo layers and (c) its HAADF-STEM counterpart. (d) BF-HRTEM of the Mo layer and (e) SAED of the area.



# Figure S7. Electron energy loss spectroscopy (EELS) mapping and Focused ion beam scanning electron microscopy (FIB-SEM) of the cross section.

Upper image indicates chemical composition along the Si/Ti/Pt/Mo electrode cross-section. HAADF-STEM photograph with elemental mappings built with absorption edge extracted from EELS: Si K-edge, Ti L-edge, Pt M-edge, O K-edge, and Mo M-edge. The bottom FIB-SEM image shows the MoO<sub>x</sub>/Pt thin-film electrodes made by sequential high-vacuum direct-current metal sputtering of Ti and Pt on Si {100} single crystal wafers. Next, Mo was electrodeposited following the optimized protocol. The electrodes were then fractured with a diamond knife and processed via FIB-SEM to produce high-quality thin cross-section samples for high-resolution transmission electron microscopy characterization.



Figure S8. Elemental composition of the MoO<sub>x</sub>/Pt electrode evaluated by energy-dispersive X-ray spectroscopy (EDX).

(a) Scanning transmission electron microscopy (STEM) along EDX across the Mo-Pt-Ti layers (inset) and the compositional profile calculated by integrating the peaks related to Mo K $\alpha$ , Pt L $\alpha$ , and Ti K $\alpha$  fluorescence lines. Open symbols are the raw data and the full lines are the outputs resulting from Savitzky-Golay smoothing.<sup>[S9]</sup> (b) EDX spectrum acquired in TEM mode using a 20 nm diameter spot focused in the Mo layer.



Figure S9: In-operando X-ray absorption spectroscopy (XAS).

A conventional 3 ml cuvette was modified at the local workshop at SSRL-SLAC to fit the custom-made Pt electrodes. A Cu wire and In were used to make an ohmic resistance-free electrical connection with the electrode before fixing it with epoxy to the cuvette. The epoxy was used to isolate the electrical connections, expose a defined electrochemically active geometric area, and seal the cuvette to avoid leaking of the electrolyte solution. Several XAS cells were created for our custom-made glass- and glassy carbon (GC)-supported Pt electrodes. Mo was freshly electrodeposited on Pt inside the XAS cells before each operando XAS run. The protocol to obtain XAS spectra under electrocatalytic operation was as follows:

1. The XAS cells were fabricated in advance, and the defined exposed areas were measured with computer-based image analysis software using conventional digital photography.

- 1.1. In the particular case of the experiments related to Pt nanoparticles (NP); the Pt NPs were electrochemically synthesized on the GC before each set of experiments (-0.1 V vs. Ag/AgCl for 3 s, 2 M NaCl, 1 mM Na<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, pH 4.4).
- 1.2. After the electrodeposition of Pt NP, the electrochemically active surface area was measured by the integration of the region assigned to the desorption of adsorbed hydrogen in 1 M HClO<sub>4</sub> at 300 mV s<sup>-1</sup> (see Methods section in the main text for details).
- Before recording the XAS spectra, Mo electrodeposition was performed on fresh electrodes for each experiment, using the optimized electroplating solution under H<sub>2</sub>-saturated conditions (-282 μA cm<sup>-2</sup> for 10 min, 0.1 M KClO<sub>4</sub>, 0.01 M H<sub>2</sub>MoO<sub>4</sub>, pH 2.8).
- 3. Fresh MoO<sub>x</sub>/Pt samples were synthesized for each experiment.
- 4. After the electrodeposition step, the XAS cell was rinsed four times with 0.1 M KClO<sub>4</sub> to remove all molybdates before introducing a fresh reaction solution (0.1 M KClO<sub>4</sub>, pH 1.8).
- 5. The freshly made MoO<sub>x</sub>/Pt electrocatalyst was electrochemically tested for the ORR, HOR, and HER (under O<sub>2</sub> and H<sub>2</sub> atmospheres). The MoO<sub>x</sub>/Pt electrodes were analyzed to determine their ability to suppress the ORR while preserving the HER, as discussed in the main manuscript and Figures S1 and S2.
- 6. The bare Pt and the MoO<sub>x</sub>/Pt samples were subjected to chronoamperometric experiments (CA). After steady-state conditions were achieved, multiple XAS scans were collected at different sample positions at the potentials of interest.
- 7. The electrocatalytic phenomena of the MoO<sub>x</sub>/Pt samples were re-checked after collecting the XAS data to ensure the stability and integrity of the electrocatalysts and the reproducibility of the experiments before and after collecting the XANES/EXAFS spectra.

An important observation when measuring the Mo K-edge XANES was related to the edge step variation between successive spectrum acquisitions for each applied potential. At potentials more positive than 0.2 V vs. RHE, the edge step decreased with time; indicating the plausible dissolution of the Mo film. On the contrary, when applying -0.15 V vs. RHE, a re-deposition of the molybdenum species from the electrolyte solution was evident since the edge step increased with time. Because of the latter dynamic behavior, only the first two spectrums were averaged for each applied potential as a tradeoff between statistics and a meaningful structural analysis. A qualitative assessment of the recorded XANES spectra was performed based on the two main spectral features; which were modified depending of the polarization applied to the thin-film MoO<sub>x</sub>/Pt electrode: i) the position of absorption edge (defined by the maximum of the first derivative) and ii) the intensity of the pre-edge peak located at 20006 eV.



Figure S10. CVs and chronoamperometry (CA) of Pt and MoO<sub>x</sub>/Pt thin film electrodes. CV of the custom-made thin-film Pt electrode under O<sub>2</sub> saturation conditions with and without Mo (50 mV s<sup>-1</sup>, 0.1 M KClO<sub>4</sub>, pH 1.8, 298 K). The data points represented by the crossed circle symbols show the measured average steady-state current density after 30 min of constantpotential electrolysis of water under O<sub>2</sub> saturation conditions in a three-electrode singlecompartment electrochemical cell (0.1 M KClO<sub>4</sub>, pH 1.8, 298 K).



Figure S11. Ex situ core-level X-ray spectroscopy.

(a) Mo 3d and (b) O 1s XPS spectra acquired from the used MoO<sub>x</sub>/Pt electrode after 15 h of cathodic electrocatalytic tests in O<sub>2</sub>-saturated electrolyte (0.1 M KClO<sub>4</sub>, pH 1.8, 298 K).

The surface state of the MoO<sub>x</sub>/Pt electrocatalyst was further studied via ex situ X-ray photoelectron spectroscopy (XPS) after applying consecutive electrode potential steps of 0 V, -0.09 V and -0.18 V vs. RHE for 5 h each under O<sub>2</sub> bubbling, as shown in Figure S5 (pH 1.8, 0.1 M KClO<sub>4</sub>; note that the electrode was exposed to air before XPS analysis). Figure S11 shows the XPS spectra of the Mo 3d and O 1s regions. The survey spectra, the Pt 4f region of the MoO<sub>x</sub>/Pt thin-film electrode, and corresponding control experiments are shown in Figure S12. The Mo 3d spectra exhibited a high energy doublet at 233.2 eV (3d<sub>5/2</sub>) and 236.2 eV (3d<sub>3/2</sub>), attributed to the hexavalent state;<sup>[S10]</sup> and the low energy doublet at 231.6 eV (3d<sub>5/2</sub>) and 234.8 eV (3d<sub>3/2</sub>) was ascribed to the tetravalent state of Mo, consistent with the literature.<sup>[S11]</sup>

Concerning the assignment of the low energy doublet observed on the Mo 3d XPS spectra in Figure S11 at 231.6 eV (3d<sub>5/2</sub>) and 234.8 eV (3d<sub>3/2</sub>); the formation of MoO<sub>2</sub> was readily excluded since the latter phase have been repeatedly reported to produce a prominent doublet at the much lower binding energy of ~ 229 eV (3d<sub>5/2</sub>) and ~ 232 eV (3d<sub>3/2</sub>).<sup>[S12-S16]</sup> Since MoO<sub>2</sub> is

known to be partially oxidized in air, the occurrence of the pentavalent state of Mo seems plausible as a first interpretation and it is consistent with XPS spectra measured on a Mo<sub>4</sub>O<sub>11</sub> phase or on different molybdenum bronzes (H<sub>x</sub>MoO<sub>3</sub>, 0.3 < x < 2.0).<sup>[S17-S20]</sup> Nevertheless, Brox and Olefjord proposed the occurrence of Mo in tetravalent state within a hydrated molybdenum oxyhydroxide phase.<sup>[S12]</sup> Their conclusion was supported by the analysis of the O 1s showing significant contributions from hydroxyl groups and adsorbed water molecules, and our results are in agreement with their study.<sup>[S12]</sup>

The O 1s spectra were deconvoluted into three peaks centered at 531.2, 532.3 and 533.6 eV, attributed to O<sup>2–</sup> anions in a hydrated Mo oxyhydroxide phase, hydroxyl groups, and adsorbed water, respectively.<sup>[S11]</sup> The area of the peaks for the hydroxyl groups and adsorbed water together contribute approximately 46% of the total signal, indicative of the high hydroxylated state of the Mo layer. The ascribed Mo(IV) state is in direct agreement with the in operando Mo K-edge XANES investigation, which highlighted the presence of the tetravalent state as the major component at all the applied potentials.



Figure S12. Ex situ X-ray photoelectron spectroscopy (XPS).

(a) Pt 4f spectra acquired from the used MoO<sub>x</sub>/Pt/Ti thin-film electrode after the electrocatalytic test compared against the pristine Pt/Ti thin-film electrode and a Pt reference. (b) XPS survey spectra of the MoO<sub>x</sub>/Pt/Ti thin-film electrode after the electrocatalysis tests. The inset in (b) shows the Pt 4f and Ti 2p regions taken from the wide scan XPS survey. No signals ascribed to Ti were detected in the MoO<sub>x</sub>/Pt/Ti samples indicating that the Ti layer was not accessible by XPS characterizations. (c) Ti 2p and (d) Mo 3d XPS spectra obtained from the control pristine Pt/Ti thin-film sample shown as the middle signal in (a), which was subjected to similar

treatments and electrocatalytic tests to the studied Mo-modified samples. No signals ascribed to Ti nor Mo were detected in the unmodified Pt-based electrodes.

The escape depth of a Pt 4f photoelectron travelling through an MoO<sub>2</sub> crystal and produced by an aluminum source was estimated as  $\approx 9 \text{ nm.}^{[S21]}$  Since the Mo layer thickness was superior to 100 nm (Figures S6 and S7), it is considered that the observation of the intense Pt signals (Figure S12) was possible due to cracks in the Mo layer created during the XPS sample preparation or due to the dehydration of the hydrated oxyhydroxide Mo coating. The Pt 4f spectra in Figure S12a was decomposed with four single peaks corresponding to two doublets (Pt  $4f_{5/2}$  and  $4d_{7/2}$ ) and attributed to the metallic and oxidized state of Pt. The peak due to the ascribed metallic state at 71.6 eV (Pt 4f<sub>5/2</sub>) was found shifted by  $0.5 \pm 0.2$  eV compared to the Pt reference (Pt  $4f_{5/2} = 71.1 \text{ eV}$ ). The half electron volt shift to higher binding energies from the zero-valent Pt state has been attributed in the literature to the formation of Pt-Mo or Pt-Ti alloys.<sup>[S22-S24]</sup> More importantly, a control experiment ran on an electrode prepared without Mo displayed a similar 0.5 eV energy shift of the metallic state (Figure S12a, middle signal represented as Pt/Ti). Hence, the formation of a Pt-Ti alloy seems feasible at the interface based on the observed energy shift, and the mixing of Ti and Pt atoms observed via transmission electron microscopy (Figures S6 and S7).



Figure S13. Theoretical calculations of MoO<sub>2</sub> and MoO<sub>3</sub> XANES spectra.

Comparison of experimental and theoretical spectra calculated with the FDMNES code for (a) MoO<sub>2</sub> and (b) MoO<sub>3</sub> oxide phases. Overlap of the calculated (c) MoO<sub>2</sub> and (d) MoO<sub>3</sub> spectra with the corresponding projected density of states on the Mo atom.

Concerning the nature of the pre-edge peak at 20006 eV (Figure 2a of the main manuscript), *ab initio* calculations of the MoO<sub>2</sub> and MoO<sub>3</sub> spectra were performed with the FDMNES code to identify its origin. Agreement between the calculated and experimental spectra was excellent for both molybdenum oxides (Figure S13). The spectrum of MoO<sub>3</sub> reference

exhibited a strong pre-edge peak at 20006 eV, whereas only a much weaker structure for the MoO<sub>2</sub> reference was seen at the same photon energy. This difference was explained by the analysis of the calculated local density of states projected on the Mo atoms. In the pre-edge energy region, the Mo 5p orbitals had a much larger contribution in MoO<sub>3</sub> phase compared to the MoO<sub>2</sub> phase (Figures S13c and d). Hence, the pre-edge peak was attributed to the Mo 1s  $\rightarrow$  4d-5p transition and is essentially dipolar (allowed by Laporte selection rule). The intensity of the transition is set by the mixing of molybdenum 5p and 4d orbitals with the oxygen 2p orbitals, whose extent depends on the relative distortion degree of the MoO<sub>6</sub> octahedra in MoO<sub>3</sub> (largest) and MoO<sub>2</sub> (smallest).<sup>[S25,S26]</sup>

The k<sup>2</sup>-weighted EXAFS at Mo K-edge and the corresponding Fourier transforms of the MoO<sub>x</sub>/Pt were compared under different potentials against the experimental monoclinic MoO<sub>2</sub> reference in Figure 2b of the main manuscript. The parameters extracted from the fits of all EXAFS data were summarized in the Table S1 below and the determination of the amplitude reduction factor (So<sup>2</sup>) is presented in Figure S14. The first peak at 1.5 Å (without phase correction) was first fitted using one unique Mo-O scattering path. The coordination number of the corresponding Mo-O bond was found to be in 2-3 range for the highest oxidative potentials, which was unrealistically too low. Instead, two Mo-O scattering paths were used to fit the first shell and the summation of their degeneration was constrained at 6. The latter model assumed an octahedral coordination in accordance with the XANES spectra. In this case, a better agreement with experimental data was obtained and the short and long Mo-O bond distances were respectively calculated being at ~1.7 Å and ~2.0 Å for all applied potentials. Note that the previous interpretation of pre-edge intensity variation was further substantiated by the quantitative analysis of the first shell EXAFS signal: the symmetrization of the MoO<sub>6</sub> octahedral

was enhanced at -0.15 V vs. RHE (Table S1, N(Mo-O<sub>1</sub>) =  $0.5 \pm 0.2$ ) which also corresponded to the weakest pre-edge intensity among the XANES spectra. To discuss the assignment of the second shell (peak at 2.2 Å, without phase correction), it is relevant to introduce beforehand the fitting of MoO<sub>2</sub> EXAFS data. The MoO<sub>2</sub> phase has two allotropes phases crystallizing either with a tetragonal (rutile structure) or a monoclinic crystal system. The rutile structure can be thought of as infinite columns of edge sharing MoO<sub>6</sub> octahedra. In addition, each edge-shared oxygen atoms are corner-shared with an adjacent infinite chain. The monoclinic form is known to result from a distortion of the rutile structure.<sup>[S26]</sup> Indeed, molybdenum cations in MoO<sub>2</sub> have an electronic configuration of  $[Kr]4d^25s^0$  which enables metal-metal bonding between adjacent Mo(IV) cations via electron pairing. The latter introduces a moderate distortion of the edge sharing MoO<sub>6</sub> octahedra which are holding off-centered Mo(IV) cations. This also induces alternating short and long Mo–Mo distances in the infinite chain of edge sharing MoO<sub>6</sub> octahedra.<sup>[S27]</sup> The fitting of experimental  $\chi(k)$  of MoO<sub>2</sub> was thus attempted with theoretical EXAFS functions calculated from the two different crystallographic models: i) the tetragonal MoO<sub>2</sub> structure (22) (*P42/mnm*, a = 4.86 Å, c = 2.79 Å) and ii) the monoclinic MoO<sub>2</sub> structure  $(P21/c, a = 5.610 \text{ Å}, b = 4.857 \text{ Å}, c = 5.626 \text{ Å}, \beta = 120.9^{\circ})$ .<sup>[S28]</sup> The tetragonal model led to a poor agreement with experimental EXAFS function of MoO<sub>2</sub> (R-factor: 9%;  $\chi_v^2 = 5956$ ). On the other hand, the calculated EXAFS function of the monoclinic model resulted in a much better agreement both in k-space and R-space (R-factor: 1%;  $\chi_v^2 = 362$ ). The quantitative EXAFS analysis of the MoO<sub>x</sub>/Pt sample provided a range of degeneration for the Mo-Mo scattering path between 1.3 (1.2 V vs. RHE) and 2.8 (-0.15 V vs. RHE) with rather large uncertainties (±0.6-0.8). While a Mo-Mo coordination number of 1 is indicative of a dimeric structural motif, coordination numbers of 2 and 3 would point respectively towards a trimeric and tetrameric

structural motif. A tetrahedral arrangement of edge sharing MoO<sub>6</sub> octahedra with tetravalent Mo cations would possibly allow a Mo-Mo distance of 2.5 Å. However, to the best of our knowledge there are no isopolymolybdates or crystalline molybdenum oxides displaying such arrangement, so that the tetrameric case was not considered in our studies.

The distinction between the dimeric and trimeric motif was refined by the *ab initio* simulations of XANES spectra corresponding to the two structures presented in Figure 2b of the main manuscript. The dimeric motif was modelled by a  $[Mo_2O_{10}]^{12^-}$  polyanion and its atomic coordinates were simply retrieved from the monoclinic MoO<sub>2</sub> crystal structure. The trimeric motif was modelled by a  $[Mo_3O_{13}]^{14^-}$  polyanion and its atomic coordinates were extracted from the crystal structure of Zn<sub>2</sub>Mo<sub>3</sub>O<sub>8</sub> ternary oxide.<sup>[S29,S30]</sup> For both dimeric and trimeric structural motifs, the unit cell parameters of the parent oxides were slightly tuned (< 1%) by a spherical expansion coefficient to match the Mo-Mo half path length of 2.55 Å as determined by EXAFS spectroscopy. Since XAS provides only an average environment around the Mo metal center, it was not possible to conclusively determine if those structures were included as isolated polymolybdates within a crystalline phase or within the amorphous component of the Mo layer.

**Table S1.** Parameters extracted from the fits of EXAFS data for a reference monoclinic MoO<sub>2</sub> and for the MoO<sub>x</sub>/Pt sample at different applied potentials on the RHE scale. (0.1 M KClO<sub>4</sub>, pH 1.8, 298 K). Fitting range;  $k^2$ :  $\Delta k = 4.6-12$  Å<sup>-1</sup>; N = coordination number; R = bond distance;  $\Delta \sigma^2$  = mean-square disorder in the distribution of interatomic distances;  $\Delta E$  = inner shell potential correction; underlined characters denote fixed parameters, § and  $\infty$  denote pair of constrained parameters.

	Scattering paths	Ν	R [Å]	$\sigma^{2}[\text{\AA}^{2}]$	$\Delta E [eV]$	R-factor
	Mo-O	<u>6</u>	$2.004\pm0.009$	$0.0039 \pm 0.0008$	-2 ± 2	$1.1 \times 10^{-2}$
MoO <sub>2</sub>	Mo-Mo	<u>1</u>	$2.528 \pm 0.008$	$0.0014 \pm 0.0006^{\$}$		
monoclinic model	Mo-Mo	<u>1</u>	$3.124\pm0.009$	$0.0014 \pm 0.0006^{\$}$		
	Mo-Mo	<u>8</u>	$3.714 \pm 0.009$	$0.0045 \pm 0.0005$		
$E = -0.15 \text{ W}_{M}$ DUE	Mo-O <sub>1</sub>	$0.5\pm0.2^\infty$	$1.66\pm0.03$	$0.0054 \pm 0.0007^{\$}$		
E = -0.13  V VS. KILE	Mo-O <sub>2</sub>	$5.5\pm0.2^\infty$	$2.04\pm0.01$	$0.0054 \pm 0.0007^{\$}$	$-4 \pm 2$	$0.1 \times 10^{-2}$
(IILK)	Mo-Mo	$2.8\pm0.8$	$2.562\pm0.009$	$0.006\pm0.002$		
	Mo-O <sub>1</sub>	$1.5\pm0.1^\infty$	$1.70\pm0.01$	$0.0057 \pm 0.0008^{\$}$		
E = 0.2 V vs. RHE	Mo-O <sub>2</sub>	$4.5\pm0.1^\infty$	$2.00\pm0.01$	$0.0057 \pm 0.0008^{\$}$	$-9 \pm 3$	0.8x10 <sup>-2</sup>
	Mo-Mo	$1.7\pm0.6$	$2.55\pm0.01$	$0.005\pm0.002$		
	Mo-O <sub>1</sub>	$1.3\pm0.2^\infty$	$1.70\pm0.02$	$0.010 \pm 0.001^{\$}$		
E = 0.9 V VS. KHE	Mo-O <sub>2</sub>	$4.7\pm0.2^\infty$	$2.00\pm0.02$	$0.010 \pm 0.001^{\$}$	$-8 \pm 3$	1.0x10 <sup>-2</sup>
(001)	Mo-Mo	$1.8\pm0.7$	$2.54\pm0.01$	$0.007\pm0.003$		
	Mo-O <sub>1</sub>	$1.1\pm0.2^\infty$	$1.71\pm0.03$	$0.008 \pm 0.001^{\$}$		
E = 1.2 V vs. RHE	Mo-O <sub>2</sub>	$4.9\pm0.2^\infty$	$2.00\pm0.01$	$0.008 \pm 0.001^{\$}$	$-5 \pm 3$	0.3x10 <sup>-2</sup>
	Mo-Mo	$1.3\pm0.6$	$2.56\pm0.01$	$0.004\pm0.002$		



Figure S14. Determination of the amplitude reduction factor (So<sup>2</sup>) at Mo K-edge with a Na<sub>2</sub>MoO<sub>4</sub> reference.

(a) EXAFS k<sup>2</sup>. $\chi$ (k) functions at Mo K-edge and (b) corresponding Fourier transforms for a Na<sub>2</sub>MoO<sub>4</sub> reference. The fit (full line) of the experimental (open symbols) EXAFS function was performed in R-space within a k-range of [4.3; 12.5] Å using a single Mo-O scattering path with a degeneration fixed at 4. Half path length, mean square displacement parameter, inner shell potential correction and amplitude reduction factor were determined respectively to be R = 1.78  $\pm 0.01$  Å,  $\sigma^2 = 0.0013 \pm 0.0009$  Å<sup>2</sup>,  $\Delta E = 6 \pm 2$  eV, So<sup>2</sup> = 0.90  $\pm 0.1$ .



Figure S15. In operando Mo K-edge EXAFS measurements.

EXAFS  $k^2 \cdot \chi(k)$  functions at the Mo K-edge for the MoO<sub>x</sub>/P electrode taken at various potentials (0.1 M KClO<sub>4</sub>, pH 1.8, 298 K) along with the MoO<sub>2</sub> reference. The open symbols represent experimental data, and the full lines indicate spherical wave theory. Corresponding Fourier transforms (without phase correction) are presented in Figure 2b of the main manuscript.



Figure S16. Electrochemical CV characterization of Pt NPs supported on GC.

CV of Pt NPs electrodeposited on GC electrode under O<sub>2</sub>-saturated conditions with and without Mo (50 mV s<sup>-1</sup>, 0.1 M KClO<sub>4</sub>, pH 1.8, 298 K). The data points represented with the crossed circle symbols show the measured average steady-state current density for the MoO<sub>x</sub>/Pt electrode after 30 min of constant potential electrolysis of water under O<sub>2</sub> saturation conditions in a three-electrode single-compartment electrochemical cell (0.1 M KClO<sub>4</sub>, pH 1.8, 298 K).



Figure S17. *In-operando* Pt *L*<sub>3</sub>-edge of pristine Pt nanoparticles supported on glassy carbon.

The Pt L<sub>3</sub> XAS spectra were obtained after the establishment of a steady state as the potential was increased in steps from -0.1 to 1.5 V on the RHE scale (0.1 M KClO<sub>4</sub>, pH 1.8, 298 K).

The *in operando* high energy resolution fluorescence detection XAS (HERFD-XAS) characterization at the Pt L<sub>3</sub>-edge was assessed to identify the working state of Pt during the HER. Since this is a bulk sensitive technique, to increase the Pt surface contribution, it was necessary to develop electrodes containing Pt NPs supported on glassy carbon disks (GC) by electrodeposition  $(0.13 \pm 0.03 \text{ cm}^{-2} \text{ of electrochemically active Pt supported on 100-200 } \mu\text{m GC}$  wafers, see Methods section).<sup>[S1,S31]</sup> After Mo deposition on the Pt NPs supported on GC, the successful inhibition of the ORR while preserving the HER activity was confirmed, which is in agreement with the previous MoO<sub>x</sub>/Pt thin-film electrodes and RDEs (pH 1.8, 0.1 M KClO4; compare Figure 1b with Figure S16). For the bare Pt NPs (Figure S17), when changing the

applied potential from -0.1 to 1.5 V vs. RHE (pH 1.8, 0.1 M KClO<sub>4</sub>), three regions were identified in the Pt L<sub>3</sub>-edge XANES spectra of the bare nanoparticles: (i) at -0.1 V vs. RHE, the signal was comparable to the spectra of metallic Pt with chemisorbed -H on its surface;<sup>[S32,S33]</sup> (ii) from 0.1 to 0.9 V vs. RHE, the white line increased, ascribed to the increased coverage of chemisorbed oxygen species, such as -O or -OH;<sup>[S33]</sup> and (iii) at over 1.0 V vs. RHE, a new feature appeared in the spectra ascribable to the formation of PtO<sub>x</sub>.<sup>[S33,S34]</sup> The results obtained with bare Pt NPs (pH 1.8, 0.1 M KClO<sub>4</sub>) were in reasonable agreement with results in the literature under similar conditions (Figure S17).<sup>[S32–S34]</sup> Figure 2d in the main manuscript shows the Pt L<sub>3</sub>-edge XANES spectra of the Mo-modified Pt NPs investigated under different applied potentials. The Pt L<sub>3</sub>-edge of MoO<sub>x</sub>/Pt during the HER shows that the Pt state can be ascribed to the metallic form; however, a minor increase in the white line intensity suggested the slight oxidation of the top-most surface of Pt (Figure 2d in the main manuscript).<sup>[S32–S34]</sup> The Pt surface state may be explained by the presence of the MoO<sub>x</sub> layer at the interface with the Pt atoms from the NP surface.

## 5. Photocatalytic overall water splitting



Figure S18. Diffuse reflectance spectra of SrTiO<sub>3</sub>, Pt/SrTiO<sub>3</sub>, and MoO<sub>x</sub>/Pt/SrTiO<sub>3</sub>, together with photon flux spectra using a Xe lamp (CERMAX PE300-BF, 300 W) as the light source.

The irradiation wavelength was controlled with a combination of a cold mirror and a water filter. (a) The photon flux using a 350-band-pass filter, and (b) the photon flux of the full spectra of the Xe lamp under the studied experimental conditions. The inset values are the number of photons integrated over the area of the reactor (38.5 cm<sup>2</sup>). The photon flux was measured using an AvaSpec-3648 spectrometer, AvaLight DHS calibration light source, and FC-UV200-2 fiber-optic cable.



Figure S19. Transmission electron microscopy characterization of the MoO<sub>x</sub>/Pt/SrTiO<sub>3</sub> photocatalyst after the photocatalytic water splitting experiment.

(a-d) TEM micrograph showing Mo particles on the surface of SrTiO<sub>3</sub>. (b) Crystalline Mo domains were observed embedded in amorphous Mo phases supported on the semiconductor; in concurrence with our thin-film electrode characterizations. Randomly distributed amorphous Mo covering the surface of SrTiO<sub>3</sub> can be observed without the presence of Pt particles. (d) HAADF-STEM of Mo layers and the SrTiO<sub>3</sub> semiconductor photocatalyst.

## 6. Membrane-covered rotating disk electrode theory



**Figure S20. Simulations of the diffusion current density for a membrane-covered rotating disk electrode.** Solid lines represent the theoretical diffusion current density for (a) HOR and (b) ORR for an ideal rotating disk covered with homogeneous membranes of different permeabilities for H<sub>2</sub> and O<sub>2</sub> gases. Squared and diamond symbols represent the experimental measurements for HOR and ORR at different rotation rates, respectively; as obtained from Figure 1 of the main manuscript. The broken lines indicate ideal Levich behavior.

The simulations presented in Figure S20 were based on the work of Gough and Leypoldt.<sup>[S35]</sup> They reported a theoretical framework based on the work of Levich.<sup>[S36]</sup> A standard rotated disk electrode of radius *R* under rotation  $\omega$  was assumed to evaluate the mass transport of a solute in a membrane of thickness  $\delta_m$  homogeneously covering a reactive electrode that may undergo a simple electrochemical reaction at the surface. A one-dimensional model perpendicular to the flat electrode surface assumes that changes in concentration only occur across this dimension *Z*. The solution filled confined space at the interface of the electrode and the membrane was assumed negligible. The origin of the dimension *Z* = 0 was modeled as the

membrane-solution boundary and Z is positive in direction to the bulk of the electrolyte. Departing from the general diffusion equation without convection within the membrane, we describe the solute concentration  $C_m$  in the membrane as

$$\frac{d^2 C_m}{dZ^2} = 0 \qquad \qquad -\delta_m \le Z \le 0$$

Then, the convective diffusion equation describes the solute concentration C

$$v_z \frac{dC}{dz} = D \frac{d^2 C}{dZ^2} \qquad -\delta_m \le Z \le 0$$

where *D* is the diffusion coefficient of the solute in the solution and  $v_z$  is the fluid velocity. Employing the conservation of mass at Z = 0 we may obtain the following expression while defining a partition coefficient  $\alpha$  as the equilibrium ratio of solute concentration in the membrane over the concentration in the solution.

- $D_m \frac{dC_m}{dZ} = D \frac{dC}{dZ} \qquad \qquad Z = 0$
- $\frac{c_m}{c} = \alpha \qquad \qquad Z = 0$
- $C = C_B$   $Z \to \infty$
- C = 0  $Z = -\delta_m$

By using the specified boundary conditions, we may evaluate the integration of the diffusion equations following the method of Levich. Finally, after derivations from the obtained concentration profiles along Z,<sup>[S35]</sup> Gough and Leypoldt proposed the following expression to describe the resulting diffusion current as:

$$j_d = nFD_m \left[\frac{\partial C}{\partial Z}\right]_{Z=-\delta_m} = j_L \left(\frac{1}{1+\frac{P_S}{P_m}}\right) = 0.62nFC_B D^{2/3} \nu^{-1/6} \omega^{1/2} \left(\frac{1}{1+\frac{P_S}{P_m}}\right)$$

$$P_{s} = \frac{D}{\delta_{d}}$$

$$P_{m} = \frac{\alpha D_{m}}{\delta_{m}}$$

$$\delta_{d} = 1.6 D^{1/3} v^{1/6} \omega^{-1/2}$$

where *n* is the number of electrons transferred in the reaction, *F* is the Faraday constant,  $\omega$  is the rotation rate of the electrode,  $\delta_d$  is the thickness of the diffusion boundary layer, *v* is the kinematic viscosity, *C*<sub>B</sub> is the concentration of the solute in the bulk of the solution, *D*<sub>m</sub> is the molecular diffusion constant in the membrane, *P*<sub>m</sub> is the permeability of the membrane, *P*<sub>s</sub> is the permeability of the solution as described below, and *j*<sub>L</sub> is the ideal Levich current density.<sup>[S36]</sup>

At sufficiently low rotation rates when  $P_s/P_m \ll 1$  the diffusion current can be described with ideal Levich behavior and in this limit the system is in solution mass transport control.<sup>[S35]</sup>

$$\lim_{\omega^{1/2} \to 0} j_d = j_l$$

whereas at sufficiently high rotation rates when  $P_s/P_m >> 1$  the diffusion current density is limited by mass transport in the membrane as a function of its permeability as observed in our simulations for HOR and ORR for the MoO<sub>x</sub> membrane protecting the Pt rotating disk electrode in Figure S20, and in our experimental rotation independent ORR and HOR current density observed in Figure 1 of the main manuscript.

$$\lim_{\omega^{1/2} \to \infty} j_d = nFC_B P_m$$

From our experimental data in Figure 1 of the main manuscript we estimated a permeability of  $9 \times 10^{-7}$  m s<sup>-1</sup> and  $2 \times 10^{-5}$  m s<sup>-1</sup> for O<sub>2</sub> and H<sub>2</sub> respectively. From those values,

we can expect diffusion coefficients in the membrane in the order of  $10^{-13}$  and  $10^{-12}$  m<sup>2</sup> s<sup>-1</sup> for O<sub>2</sub> and H<sub>2</sub> respectively.

Compare diffusion  $D(H_2(sol)-H_2O) = 4.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  against  $D_e(H_2(sol)-H_2O \text{ in } MoO_x.)$ ~  $10^{-12} \text{ m}^2 \text{ s}^{-1}$ 

Compare diffusion  $D(O_2(sol)-H_2O) = 2.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  against  $D_e(O_2(sol)-H_2O \text{ in } MoO_x.)$ ~  $10^{-13} \text{ m}^2 \text{ s}^{-1}$ 

To summarize, the Mo membrane porosity is expected to be very low as shown by the ratio of D/De in the range of 1000 (H<sub>2</sub>) and 10000 (O<sub>2</sub>).

Three major observations can be emphasized from the electrochemical study: (a) ORR and HOR did not apparently occurred on the MoO<sub>x</sub>/Pt and MoO<sub>x</sub>/Au electrodes; hence, O<sub>2</sub> and H<sub>2</sub> cannot permeate through the Mo film from the bulk of the electrolyte to the electrified substrate; (b) The HER clearly proceeded and was stable for many hours indicating that H<sub>2</sub> may diffuse in the Mo membrane from the electrode to the bulk of the solution; and (c) The non-Faradaic response of the substrate was not significantly altered by the presence of MoO<sub>x</sub>; hence, no major changes in the double layer capacitance indicate a similar surface area when compared to the bare noble metal polished electrode. The Mo membrane was characterized mostly as an amorphous hydrated oxyhydroxide material most likely trapping a microporous network of water; thus, H<sub>2</sub>O and H<sup>+</sup> transport is possible as the reactants for the HER. Under the HER cathodic conditions, H<sub>2</sub> gas accumulates at the confined substrate-membrane interface generating large concentration gradients. Under steady-state conditions, assuming for example –10 mA cm<sup>-2</sup>, and confinement at the interface of 1 nm (i.e. typical double layer thickness in a 0.1 M electrolyte) we can estimate that the local activity can be orders of magnitude larger than in the membrane-solution boundary (e.g.,  $5.2 \times 10^5$  mmol L<sup>-1</sup> s<sup>-1</sup> of H<sub>2</sub> at any given time in comparison to the solubility of H<sub>2</sub> in the bulk of 0.78 mmol L<sup>-1</sup>). Although this is a highly-simplified assumption, it is clear that such scenario may generate the required driving force for H<sub>2</sub> permeation in a membrane.

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