

### Photocatalytic Water Splitting

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

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Abstract: For overall water-splitting systems, it is essential to establish  $O_2$ -insensitive cathodes that allow cogeneration of  $H_2$ and O2. An acid-tolerant electrocatalyst is described, which employs a Mo-coating on a metal surface to achieve selective  $H_2$  evolution in the presence of  $O_2$ . In operando X-ray absorption spectroscopy identified reduced Pt covered with an amorphous molybdenum oxyhydroxide hydrate with a local structural order composed of polyanionic trimeric units of molybdenum(IV). The Mo layer likely hinders  $O_2$  gas permeation, impeding contact with active Pt. Photocatalytic overall water splitting proceeded using MoO<sub>x</sub>/Pt/SrTiO<sub>3</sub> with inhibited water formation from  $H_2$  and  $O_2$ , which is the prevailing back reaction on the bare Pt/SrTiO<sub>3</sub> photocatalyst. The Mo coating was stable in acidic media for multiple hours of overall water splitting by membraneless electrolysis and photocatalysis.

arvesting solar energy in chemical bonds will ultimately disrupt our dependency on fossil fuels and, consequently, our susceptibility to climate change.<sup>[1]</sup> In this regard, H<sub>2</sub> is considered one of the most promising energy carriers.<sup>[2]</sup> If H<sub>2</sub> is generated from H<sub>2</sub>O using renewable energy (for example, photocatalytic overall water splitting), it is possible to obtain a sustainable fuel without any carbon footprint.<sup>[3]</sup> One of the significant issues associated with water splitting is the facile reverse reaction; that is, the catalyst for the hydrogen evolution reaction (HER) is also active in undesired water-formation reactions, such as the oxygen reduction reaction (ORR),<sup>[4-6]</sup> or the thermal reaction of H<sub>2</sub> and O<sub>2</sub>. Therefore, inhibition of these back reactions is of paramount importance for photocatalytic water splitting.

Successful visible-light-driven photocatalytic overall water splitting was achieved by employing a  $(Ga_{1-x}Zn_x)$ - $(N_{1-x}O_x)$  solid-solution semiconductor decorated with a CrOx/Rh HER electrocatalyst.<sup>[7,8]</sup> Electrochemical protocols using model electrodes suggested that a  $CrO_x$  layer protects the noble metal (that is, Pt or Rh) from contacting the locally generated O<sub>2</sub> while minimally impacting the intrinsic electrocatalytic HER performance of the noble metal.<sup>[9]</sup> Nevertheless, the Cr species are not stable in acidic media, in which improved HER kinetics prevail. Acidtolerant tungsten carbide nanoparticles were reported to exhibit reasonable activity (yet to be improved) for the HER, while being insensitive towards the water-forming backreaction.<sup>[10]</sup> Noble metal poisoning with chemisorbed CO (Rh, Pt, Pd),<sup>[11]</sup> and surface coatings with some amorphous metal oxyhydroxide layers<sup>[12,13]</sup> (Ti, Nb, Ta, and so forth) were also reported to have similar functions to the Cr-based modifier, but the structural and mechanistic elucidation of such functional materials is yet to be explored. In this contribution, we report the structural and electrochemical properties of a Mo-coated Pt HER catalyst that is highly active, oxygen-insensitive, and stable in acidic media for overall water splitting. In operando X-ray absorption spectroscopy (XAS) at relevant potential shifts was used to characterize the working electrode. To our best knowledge, the Mo-based modifier developed in this study is the only acid-tolerant material to date that can selectively prevent the water-forming back reaction.

One of the key factors for the successful fabrication of Mo was selecting the appropriate acidity of the synthesis solution (1.1 < pH < 4.9). In a typical case, Mo species were deposited

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on a Pt rotating disk electrode (RDE) in mildly acidic conditions ( $-282 \ \mu A \ cm^{-2}$ , 169 C cm<sup>-2</sup>, 10 mM H<sub>2</sub>MoO<sub>4</sub>, 60 mM KClO<sub>4</sub>, pH 2.8, H<sub>2</sub> atmosphere, 298 K; see the Supporting Information, Section 2, for further details). Figure 1 shows cyclic voltammograms (CV) of the unmodified



**Figure 1.** CVs of Pt and MoO<sub>4</sub>/Pt RDEs under a) Ar at 3600 rpm, b) O<sub>2</sub>, and c) H<sub>2</sub> saturation conditions with varying rotation rates. d) Comparison of the CV polarization of MoO<sub>4</sub>/Pt under different gas atmospheres at 3600 rpm (electrodeposition:  $-282 \ \mu A cm^{-2}$  for 10 min, 0.1  $\mbox{M}$  KClO<sub>4</sub>, 0.01  $\mbox{M}$  H<sub>2</sub>MoO<sub>4</sub>, pH 2.8; reaction: 50 mVs<sup>-1</sup>, 0.1  $\mbox{M}$  KClO<sub>4</sub>, pH 1.8, 298 K).

and Mo-modified Pt RDEs (denoted MoOx/Pt) under Ar (pH 1.8, 0.1 M KClO<sub>4</sub>). The CV of pristine Pt in Ar (Figure 1 a) was consistent with the literature.<sup>[6]</sup> The MoO<sub>x</sub>/Pt (Figure 1a) gave an approximate 100 mV shift in the peak maximum of the reduction of oxidized Pt (from 0.81 to 0.72  $V_{RHE}$ ). A clear redox pair ascribed to the Mo<sup>4+</sup>/Mo<sup>6+</sup> cycle was observed at 0.32 (cathodic scan) and 0.48 V<sub>RHE</sub> (anodic scan).<sup>[14]</sup> Figure 1 b presents cathodic scans for bare Pt and the MoO<sub>x</sub>/Pt CV in saturated O2. For the Pt RDE, potential-independent cathodic currents were observed below  $0.6 V_{RHE}$ , demonstrating ORR limiting diffusion currents. Negative potentials below  $0 V_{RHE}$  resulted in the evolution of additional reduction currents ascribed to HER.<sup>[15]</sup> In contrast, ORR currents were negligible for  $MoO_x/Pt$  irrespective of the disk rotation speed. A similar ORR inhibition was reported in the literature using Cu surfaces in the presence of molybdates in solution.<sup>[16]</sup> Noticeably, MoO<sub>x</sub>/Pt catalyzed HER currents with an onset potential very similar to that of bare Pt in the presence of saturated  $O_2$  (Figure 1b).

Figure 1 c presents anodic scans with bare Pt and the CV of  $MoO_x/Pt$  under saturated H<sub>2</sub> at different rotation rates. Ptgenerated potential-independent hydrogen oxidation reaction (HOR) currents, indicative of the diffusion-limiting behavior of H<sub>2</sub>. Diminished HOR currents were observed for  $MoO_x/Pt.^{[17-19]}$  Further investigations using glassy carbon (GC) and Au revealed that the deposited Mo itself was inactive towards the ORR and HER (Supporting Information, Figure S3). A H<sub>2</sub> Faradaic efficiency (FE) of  $94 \pm 6\%$  at  $-0.18 V_{RHE}$  was confirmed by on-line gas chromatography for  $MoO_x/Pt$ , while  $42 \pm 4\%$  FE was observed for pristine Pt saturated by O<sub>2</sub>; the FE loss was associated with the competitive reduction of O<sub>2</sub> molecules. The MoO<sub>x</sub>/Pt electrode gave a slightly larger Tafel slope compared to the bare Pt electrode (Supporting Information, Figure S4), but was stable for more than 15 h under cathodic conditions and exhibited constant H<sub>2</sub> evolution (Supporting Information, Figure S5). To visualize the impact of various gas atmospheres, the CVs in H<sub>2</sub>, Ar, and O<sub>2</sub> for the MoO<sub>x</sub>/Pt electrode are compared in Figure 1d. It was corroborated that minor but apparent HOR/ORR currents might exist for MoO<sub>x</sub>/Pt in H<sub>2</sub>/O<sub>2</sub> atmospheres, respectively, without significantly affecting the HER onset potential of the bare Pt catalysts. The observed diminution in the limiting diffusion currents suggest that the Mo layer works as a membrane to block gaseous species  $(H_2 \text{ and } O_2)$  dissolved in the aqueous phase from reaching the metal surfaces underneath.

The in operando XAS measurements were conducted at the Mo K-edge using custom-made, thin-film multilayer electrodes fabricated on 120 µm glass substrates to lessen X-ray attenuation (for detailed characterization see the Supporting Information, Figures S6–S12). The Mo K-edge X-ray absorption near-edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) spectra of the MoO<sub>y</sub>/Pt samples were recorded successively at open circuit potential  $(0.95 V_{RHE})$ , then at HER potential  $(-0.15 V_{RHE})$ , and then with increasing oxidative potentials (from 0.2 to 1.2 V<sub>RHE</sub>) in O<sub>2</sub>-saturated electrolytes (pH 1.8, 0.1M KClO<sub>4</sub>). In Figure 2a the Mo K-edge shifted from 20011.3 to 20011.7 eV when the applied potential on  $MoO_x/$ Pt was varied from -0.15 to  $1.2 V_{\text{RHE}}$ . The position of the absorption edge energies of MoO<sub>2</sub> (20010.4 eV) and MoO<sub>3</sub> (20016 eV) references suggested a mixture of Mo<sup>IV</sup> and Mo<sup>VI</sup> oxidation states under all the applied potentials with a predominant presence of Mo<sup>IV</sup><sup>[20-22]</sup> The ex situ XPS study supports this scenario (Supporting Information, Figures S11 and S12). The pre-edge feature in Figure 2a is ascribed to the 1s to 4d-5p dipolar transition, and its intensity depends on the degree of distortion of the MoO<sub>6</sub> octahedra (that is, largest in MoO<sub>3</sub> and lowest in MoO<sub>2</sub>; Supporting Information, Figure S13).<sup>[22]</sup> See the Supporting Information, Section 4, for further XAS details.

Figure 2b shows the experimental Fourier transforms (FT) EXAFS at the Mo K-edge of  $MoO_x/Pt$  compared under varying potentials against the experimental  $MoO_2$  reference. The parameters extracted from the fits of all EXAFS data are summarized in Table S1 and Figure S15 (Supporting Information). The FT-EXAFS of  $MoO_2$  exhibited peaks at 2.2 Å and 2.7 Å attributed to Mo–Mo scattering from distorted edge-sharing octahedra. The peak at 3.3 Å was attributed to Mo–Mo scattering from corner-sharing octahedra (Figure 2b,  $MoO_2$ ). Interestingly, the FT-EXAFS spectra of  $MoO_x/Pt$  showed only one sharp peak at 2.2 Å (2.55 Å with phase correction), ascribed to Mo–Mo scattering with a negligible contribution from other scatterers at longer distances; possibly related to the amorphous nature of

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Figure 2. a) Mo K-edge XANES spectra of the MoO<sub>x</sub>/Pt electrode at various potentials (0.1 M KClO<sub>4</sub>, pH 1.8, 298 K) along with MoO<sub>2</sub> and MoO<sub>3</sub> references. b) Fourier transforms of EXAFS (without phase correction) for MoO<sub>2</sub>/Pt at various potentials along with a MoO<sub>2</sub> reference. The open symbols represent experimental data, and the full lines indicate spherical wave theory. c) Theoretical XANES spectra of the dimeric and trimeric motifs that represent the experimental Mo K-edge XANES spectra under HER conditions. The normalized spectra of the  $[Mo_2O_{10}]^{12-}$  and  $[Mo_3O_{13}]^{14-}$  isopolymolybdates were obtained by ab initio calculations with FDMNES code. The computations are shown along with the experimental spectrum measured at -0.15 V (vs. RHE, 0.1  ${\rm M}$  KClO4, pH 1.8, 298 K). d) Pt  $L_3\text{-edge}$  high-energy resolution fluorescence detection (HERFD)-XANES spectra of MoO<sub>x</sub>/Pt on GC under potential control for electrolysis under O<sub>2</sub> saturation (0.1 M KClO₄, pH 1.8, 298 K). The spectrum obtained from bare Pt is included for comparison.

the material, as observed by high-resolution transmission electron microscopy (HRTEM) (Supporting Information, Figure S6). The first shell was fitted using two Mo-O scattering paths, resulting in Mo-O bond distances of approximately 1.7 and 2.0 Å for all applied potentials (Figure 2b). EXAFS quantitatively supported the qualitative XANES observations of the symmetrization of the MoO<sub>6</sub> octahedra at -0.15 V (vs. RHE; see N(Mo-O<sub>1</sub>) variations in the Supporting Information, Table S1). Second shell analysis provided a range of degeneration (coordination number) of the Mo–Mo scattering path ( $R = 2.55 \pm 0.01$  Å) between  $1.3 \pm$ 0.6 at 1.2  $V_{\text{RHE}}$  and 2.8  $\pm$  0.8 at  $-0.15 \: V_{\text{RHE}}$  (Supporting Information, Table S1). A coordination number of 1 is indicative of a dimeric structural motif, whereas 2 suggests a trimeric structure. Ab initio calculations of the Mo K-edge XANES spectra of  $[Mo_2O_{10}]^{12-}$  and  $[Mo_3O_{13}]^{14-}$  anions in Figure 2c showed that the trimeric motif closely reproduced the main features of the Mo K-edge XANES spectrum taken at  $-0.15 V_{RHE}$  in  $O_2$ -saturated electrolytes ( $[Mo_3O_{13}]^{14-}$  in Figure 2c). The combination of XANES and EXAFS suggested a local structural order in the form of a Mo<sub>3</sub> triangular arrangement (most likely as [Mo<sub>3</sub>O<sub>13</sub>]<sup>14-</sup> polyanions) within the Mo coating under HER conditions. In operando XANES at the Pt L<sub>3</sub>-edge under varying potentials suggested that Pt is mostly in a metallic state (Figures 2d; Supporting Information, Figure S17).

A selective HER catalyst should function as a cocatalyst for photocatalytic overall water splitting. As a proof of concept, a 0.3 wt % Pt/SrTiO<sub>3</sub> model photocatalyst was decorated with Mo (see Methods section in the Supporting Information for details). Figure 3 shows a comparison of the



*Figure 3.* a) Photocatalytic water splitting for 0.3 wt% Pt/SrTiO<sub>3</sub> with and without Mo under UV-light irradiation ( $300 < \lambda < 800$  nm, 50 mg, in Milli-Q water). b) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) of the MoO<sub>x</sub>/Pt/SrTiO<sub>3</sub> photocatalyst after photocatalytic water splitting and c) elemental mappings built with the absorption edges extracted from EELS. Scale bar: 2 nm.

photocatalytic water-splitting activity for both Pt/SrTiO<sub>3</sub> and MoO<sub>x</sub>/Pt/SrTiO<sub>3</sub> in pure water. The reaction was conducted using a recirculating batch reactor,<sup>[23]</sup> and the irradiation source was turned off after 24 h of continuous water splitting to examine the effects of the water-formation back reaction. Pt/SrTiO<sub>3</sub> evolved H<sub>2</sub> and O<sub>2</sub> at a 2 to 1 ratio for the first 10 h until a plateau was observed; indicating an equilibrium between the forward rate of gas evolution and the reverse reaction to form water. When the light was turned off, the amount of H<sub>2</sub> and O<sub>2</sub> in the system decreased, showing that Pt/SrTiO<sub>3</sub> suffered from the back reaction where  $H_2$  and  $O_2$ recombined back into H<sub>2</sub>O. MoO<sub>x</sub>/Pt/SrTiO<sub>3</sub> steadily and continuously split water for 24 h, exhibiting negligible gas decay during the subsequent dark conditions of the experiment (6 h). The apparent quantum efficiency calculated at 350 nm was  $14\pm2\%$  (without Mo) and  $9\pm1\%$  (with Mo) after the first hour of photocatalytic H<sub>2</sub> generation (see photon flux spectra in the Supporting Information, Figure S18). The lesser H<sub>2</sub> production rates for MoO<sub>x</sub>/Pt/SrTiO<sub>3</sub> compared with Pt/SrTiO<sub>3</sub> were consistent with the decreased HER activity observed electrocatalytically (Figure 1; Supporting Information, Figure S4). Nonetheless, MoO<sub>x</sub> was an effective modifier of the Pt HER electrocatalyst to achieve photocatalytic evolution of stoichiometric amounts of H<sub>2</sub> and O2 from H2O without introducing water-forming dark reactions. Figures 3b and c present the Cs-corrected dark-field HRTEM and electron energy loss spectroscopy (EELS) characterizations of two locations of the Mo-modified 0.3 wt% Pt/SrTiO<sub>3</sub> photocatalyst for two representative regions. The EELS elemental mapping confirmed that Pt

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and Mo were present in the same location, indicating successful decoration of Pt with Mo species (Figure 3c). Additionally, the TEM results indicated that Mo was randomly distributed on the surface of the  $SrTiO_3$  photocatalyst (Supporting Information, Figure S19), which is considered to be kinetically silent.

The  $MoO_x$  may function as a gas membrane that selectively hinders HOR and ORR. In our experiments, the ORR and HOR did not exhibit classical rotation-dependent Levich behavior (Figures 1b and c); hence, electrocatalysis was not apparently limited by mass transport of the dissolved gases in solution.<sup>[24,25]</sup> The analytical solution of the mass-transport model for a solute reacting in a membrane-covered rotating electrode indicates that the measured limiting diffusion current would be independent of the rotation rate at high rates (and when the permeability of the membrane is much lower than that in the solution, Figure 1).<sup>[25]</sup> A detailed description of the theory for a membrane-covered rotating disk electrode is shown in Section 6 of the Supporting Information.

The local structure of the Mo<sup>IV</sup> species under HER conditions was suggested to be a polyanionic [Mo<sub>3</sub>O<sub>13</sub>]<sup>14-</sup> trimer by in operando XANES and EXAFS at the Mo K-edge (Figure 2). Such a trimeric unit is most likely distributed within the amorphous Mo-based hydrated oxyhydroxide phase, trapping a microporous network filled with water.<sup>[9]</sup> Such a highly hydrated inorganic layer is expected to be utilized for transport of H<sub>2</sub>O and H<sup>+</sup>, which are reactants for the HER.<sup>[26]</sup> Therefore, HER can occur on the Pt surface, causing substantial H<sub>2</sub> accumulation at the Pt-Mo interface (supersaturated condition). This creates a large chemical potential gradient that allows H<sub>2</sub> to diffuse through the amorphous hydrated microchannels within the  $MoO_x$  film. In contrast, concentrations of the gases are low for ORR/HOR in the bulk of the solution ( $O_2 = 1.27 \text{ mmol } L^{-1}$ ;  $H_2 =$ 0.78 mmol L<sup>-1</sup>). Because of the low concentration gradient,  $H_2$  or  $O_2$  cannot reach the Pt surface through the Mo layer, resulting in lessened local fugacity of the reactive gases near the active Pt sites, which is consistent with universal ORR suppression as observed with an Au electrode (Supporting Information, Figure S3).

In conclusion, the results show that adequate modification of a Pt electrode with  $Mo^{IV}$  polyanionic species render the electrode insensitive towards ORR and HOR while preserving high HER performance. The inhibition of water-forming reactions and the superior selectivity towards H<sub>2</sub> generation in the presence of O<sub>2</sub> may originate because the Mo coating likely acts as a membrane, confining the availability of O<sub>2</sub> and H<sub>2</sub> near Pt. Indeed, this electrocatalytic concept was reflected in photocatalysis, as overall water splitting proceeded without the back reaction for MoO<sub>x</sub>/Pt/SrTiO<sub>3</sub>. We propose a Mo modifier that is stable in acidic to near-neutral pH conditions to create a selective O<sub>2</sub>-insensitive H<sub>2</sub>-evolving electrocatalyst for water splitting with application in electrolysis and photocatalysis.

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#### **Conflict of interest**

The authors declare no conflict of interest.

Keywords: electrocatalysis  $\cdot$  hydrogen evolution  $\cdot$  in operando XAS  $\cdot$  photocatalysis  $\cdot$  water splitting

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# Communications



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



Oxygen-tolerant hydrogen evolution: Molybdenum species inhibit water-forming reactions on platinum and other metal catalysts. Hydrogen was selectively produced by electro- and photocatalytic water splitting in the presence of competing oxygen. In operando characterization revealed an amorphous oxyhydroxide hydrated structure of polyanionic trimeric molybdenum(IV) protecting metallic platinum.

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