



An Oxygen-insensitive Hydrogen Evolution Catalyst Coated by a Molybdenum-based Layer for Overall Water Splitting

Harvesting solar energy in chemical bonds will ultimately disrupt dependency on fossil fuels and, consequently, susceptibility to climate change. In this regard, H₂ is considered one of the most promising energy carriers. If H₂ is generated from H₂O using renewable energy (for example, photocatalytic overall water splitting), it is possible to obtain a sustainable fuel without any carbon footprint. 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), or the thermal reaction of H₂ and O₂. Therefore, inhibition of these back reactions is of paramount importance for photocatalytic water splitting.

An international research team, including scientists from the King Abdullah University of Science and Technology (KAUST) in Saudi Arabia and SSRL, has developed a new hydrogen evolution catalyst with a molybdenum coating that prevents this problematic back reaction and works well in realistic operating conditions.

In a new study, featured in *Angewandte Chemie*, the research team reports 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. By using SSRL Beam Lines 6-2 and 4-1, *operando* high-resolution x-ray absorption spectroscopy (BL6-2) and EXAFS (BL4-3) studies characterized the working electrode in action. 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 H₂ generation in the presence of O₂ seems to originate because the Mo coating likely acts as a membrane, confining the availability of O₂ and H₂ near Pt.

Indeed, this electrocatalytic concept was reflected in photocatalysis experiments, as overall water splitting proceeded without the back reaction for MoO_x/Pt/SrTiO₃. The Mo-based modifier developed and characterized in this study is the only acid-tolerant material to date that can selectively prevent the water-forming back reaction.

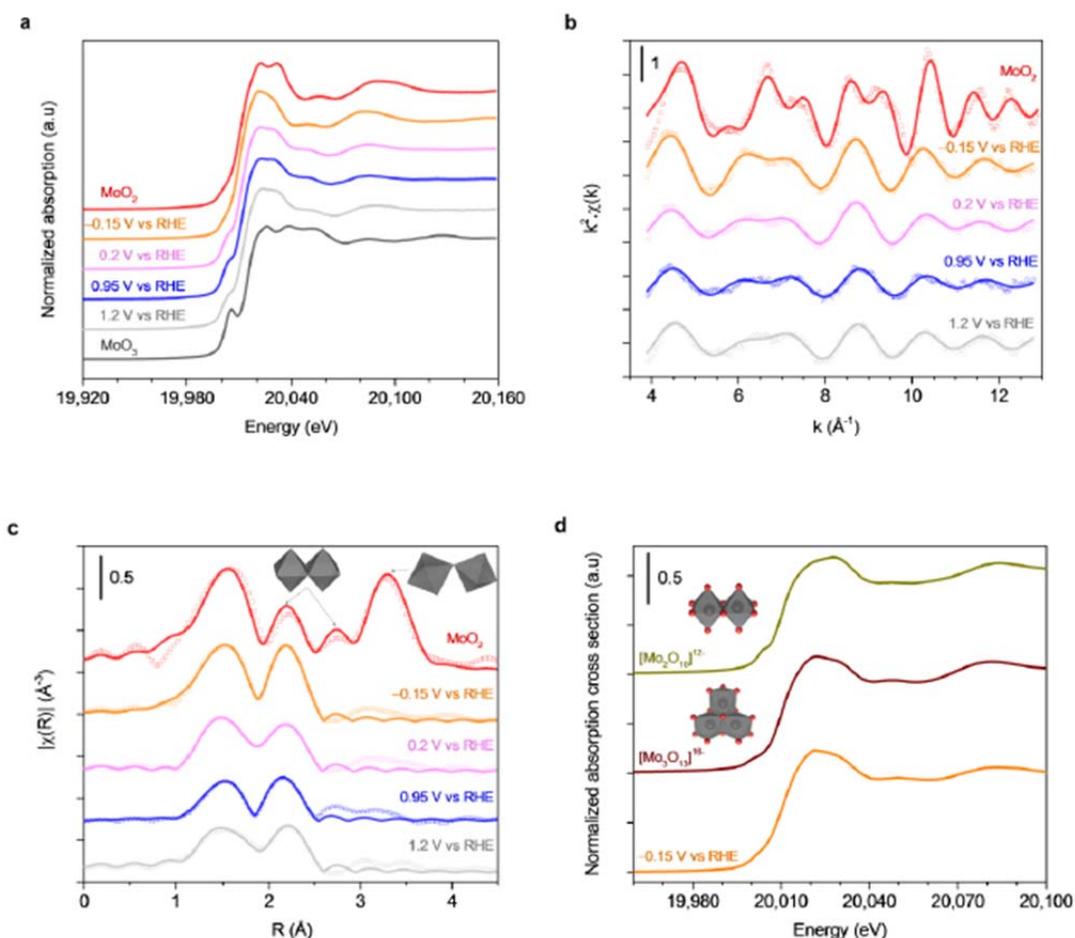
Primary Citation

A. T. Garcia-Esparza, T. Shinagawa, S. Ould-Chikh, M. Qureshi, X. Peng, N. Wei, D. H. Anjum, A. Clo, T.-C. Weng, D. Nordlund, D. Sokaras, J. Kubota, K. Domen and K. Takanabe, "An Oxygen-insensitive Hydrogen Evolution Catalyst Coated by a Molybdenum-based Layer for Overall Water Splitting", *Angew. Chem.* **56**, 5780 (2017) doi: 10.1002/ange.201701861

Contacts

Dimosthenis Sokaras, Stanford Synchrotron Radiation Lightsource

Angel Garcia-Esparza and Kazuhiro Takanabe, KAUST



In-operando Mo-K edge XAS measurements and *ab initio* simulations. (a) Mo K-edge XANES spectra of the MoO_x/P electrode taken at various potentials (0.1 M KClO₄, pH 1.8, 298 K) along with MoO₂ and MoO₃ references. (b, c) In-operando EXAFS measurements. (b) EXAFS $k^2 \cdot \chi(k)$ functions at Mo K-edge and (c) corresponding Fourier transforms (without phase correction) for the MoO_x/P electrode taken at various potentials (0.1 M KClO₄, pH 1.8, 298 K) along with the MoO₂ reference. The open symbols represent experimental data, and the full lines indicate spherical wave theory. (d) The theoretical XANES spectra of the dimeric and trimeric structural motifs that best represents the experimental Mo-K edge XANES spectra under H₂ production conditions. The normalized (with respect to the experimental spectrum) Mo K-edge XANES spectra of the [Mo₂O₁₀]¹²⁻ and [Mo₃O₁₆]¹⁶⁻ isopolymolybdates was obtained via *ab initio* calculations with the FDMNES code. The computations are shown together with the experimental spectrum measured with an applied potential of -0.15 V vs. RHE (0.1 M KClO₄, pH 1.8, 298 K).

SSRL is primarily supported by the DOE Offices of Basic Energy Sciences and Biological and Environmental Research, with additional support from the National Institutes of Health, National Institute of General Medical Sciences.