

Watching active sites switch gears: hole-density-gated water oxidation on a single BiVO₄ particle

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Water oxidation is the kinetic bottleneck of artificial photosynthesis, yet the catalytic surface on which this bottleneck unfolds is far from uniform. Facets, terminations, defects and local electric fields generate a nanoscale landscape in which photogenerated holes, adsorbed intermediates and O-O bond formation are coupled but rarely observed together. Conventional ensemble measurements average away this heterogeneity; many local probes, in turn, visualize either charge transport or chemical conversion, but not their operative correlation under reaction conditions [1-4]. In a recent work published in *Nature Nanotechnology*, Nie and co-workers addressed this challenge by integrating electrochemical shell-isolated nanoparticle-enhanced Raman spectroscopy (EC-SHINERS) with atomic force microscopy-scanning electrochemical microscopy (AFM-SECM) on individual faceted BiVO₄ particles [5]. The resulting correlative operando platform links three quantities that are usually measured separately: surface-reaching hole flux, OER intermediate evolution and nanoscale reaction current. Its central message is that an active site is more than a static atomic arrangement; it is a charge-density-dependent structural motif whose catalytic identity can change during operation.

The authors first mapped the distribution of photogenerated holes that successfully reach the particle surface. In sample generation-tip collection mode, a Pt nanoelectrode positioned at the apex of an

AFM tip detected the oxidation of [Fe(CN)₆]⁴⁻ to [Fe(CN)₆]³⁻, an outer-sphere redox process that reports surface hole flux without involving catalytic bond making (Fig. 1 a, b). Finite-element modelling was used to deconvolute inter-facet diffusion and improve the effective spatial resolution to approximately 25 nm. The (110) facet generated larger redox currents than the (010) facet across the examined conditions, in agreement with stronger band bending and preferential hole accumulation indicated by KPFM and surface photovoltage measurements. Moreover, the linear relationship between the nanoelectrode current and calculated surface hole density supports the use of this approach as a quantitative measure of the holes available for interfacial chemistry.

When the experiment was shifted from hole mapping to direct OER imaging, a less intuitive picture emerged. At lower applied potentials, oxygen evolution initiated near inter-facet edges and spread mainly across the (110) facet, consistent with its higher hole accumulation. As the potential increased, however, the dominant OER current migrates to the (010) facet even though the (110) facet still displays a higher charge-transfer current (Fig. 1c). This inversion decouples hole availability from catalytic output. Showing that local hole density is necessary, but insufficient, to predict activity; the decisive factor is how each facet converts accumulated holes into specific intermediates and O-O forming configurations. Operando EC-SHINERS

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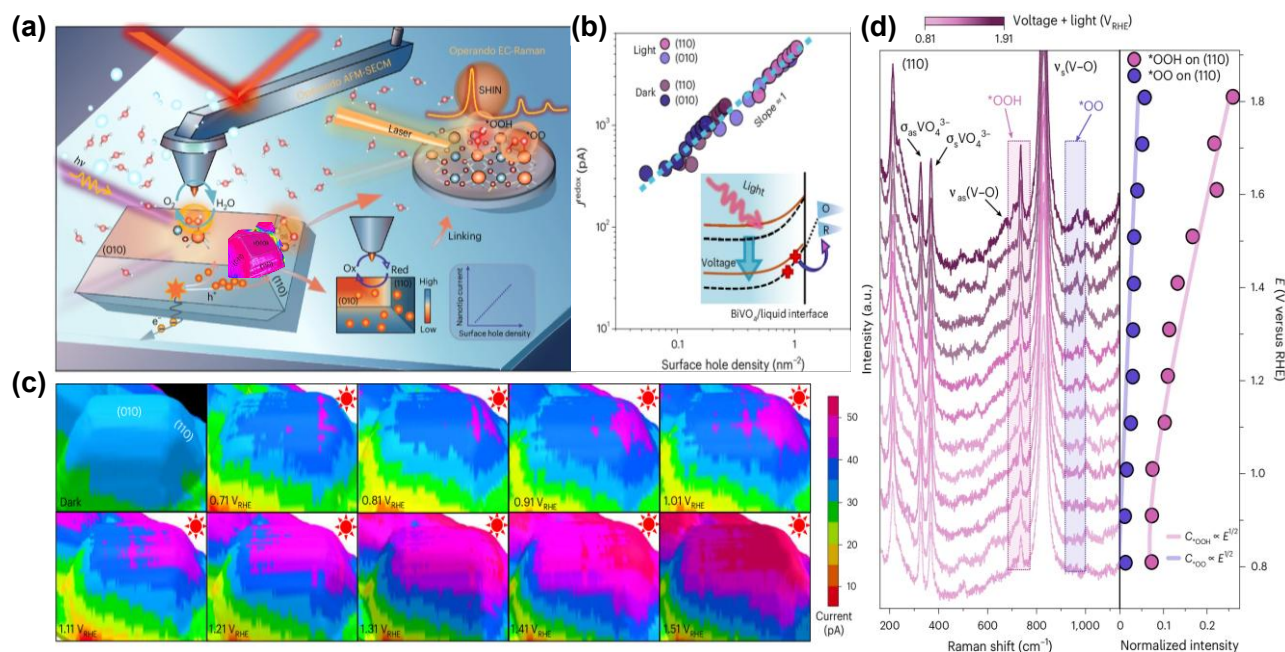


Figure 1. (a) Schematic of the AFM-SECM/EC-SHINERS platform. (b) Relationship between the charge-transfer current measured by the Pt nanoelectrode on the (110) and (010) facets and the calculated surface hole density under varying bias. (c) Nanoscale water oxidation imaging on faceted BiVO₄ under photoelectrochemical conditions. (d) In situ EC-Raman spectra of the (110) facet under 450 nm illumination.

provided the missing chemical dimension. Potential-dependent Raman bands at approximately 737 and 963 cm⁻¹ were assigned to *OOH and *OO species, respectively, with the isotope response in D₂O supporting the O-H character of the former (Fig. 1d). The normalized intensities of these bands scaled with $E^{1/2}$, the same dependence observed for the OER photocurrent, indicating that surface hole density rather than bias alone, governs the population of reactive intermediates. Both facets show a transition from *OOH-rich chemistry at low hole density to increased *OO character at higher hole density, but the trajectories diverge sharply, pointing to distinct O-O forming routes.

By correlating decoupled OER currents with facet-specific surface hole densities, the study reveals a biphasic kinetic scaling law (Fig. 2a). Below a critical surface hole density of about 0.67 nm⁻², both facets exhibit an apparent first-order dependence, consistent with a single-hole-limited proton-coupled electron-transfer step. Above this threshold, the kinetic behavior diverges: the (110) facet transitions towards second-order kinetics, whereas the (010) facet approaches third-order behavior. Interestingly, the facet requiring a greater number of oxidizing equivalents ((010)) becomes more active at elevated hole densities. These

observations suggest that multihole accumulation need not represent a kinetic limitation. Instead, when oxidizing equivalents can be accumulated and delivered cooperatively, it may provide access to a more favorable catalytic pathway.

The intermediate evolution and modelling analysis help explain why the two facets respond differently. On the (010) facet, *OOH first increases and then decreases as *OO becomes dominant at high hole density (Fig. 2b). In the same regime, a Raman feature near 607 cm⁻¹ appears, resembling BiO_x vibrations reported for bismuth oxide phases and in reconstructed BiVO₄(010) models [6–8]. This behavior points to a dynamic reorganization of the Bi-O-V surface core under multihole accumulation rather than a fixed adsorption site undergoing a simple sequence of elementary steps. Microkinetic modelling connects this spectroscopic picture into a possible structural mechanism (Fig. 2c). On the (010) facet, terminal and two-fold-coordinated hydroxyl groups undergo sequential oxidation to oxo species, which then couple into a peroxo-bridged configuration. Bridging oxygen atoms in the Bi-O-V core can act as multielectron storage elements, allowing oxidizing equivalents to accumulate within a cooperative cluster. The third hole enables nucleophilic water attack and

intramolecular proton-coupled electron transfer, thereby completing O-O bond formation through a peroxo-mediated route. In this sense, the Bi-O(H)-V motif resembles an inorganic multihole reservoir, echoing the functional logic of the Mn_4CaO_5 cluster in

photosystem II [9]. On the (110) facet, two-hole injection can generate adjacent oxo centers for intramolecular coupling, but weaker cooperativity and the absence of a third stored oxidizing equivalent lead to a higher energetic demand.

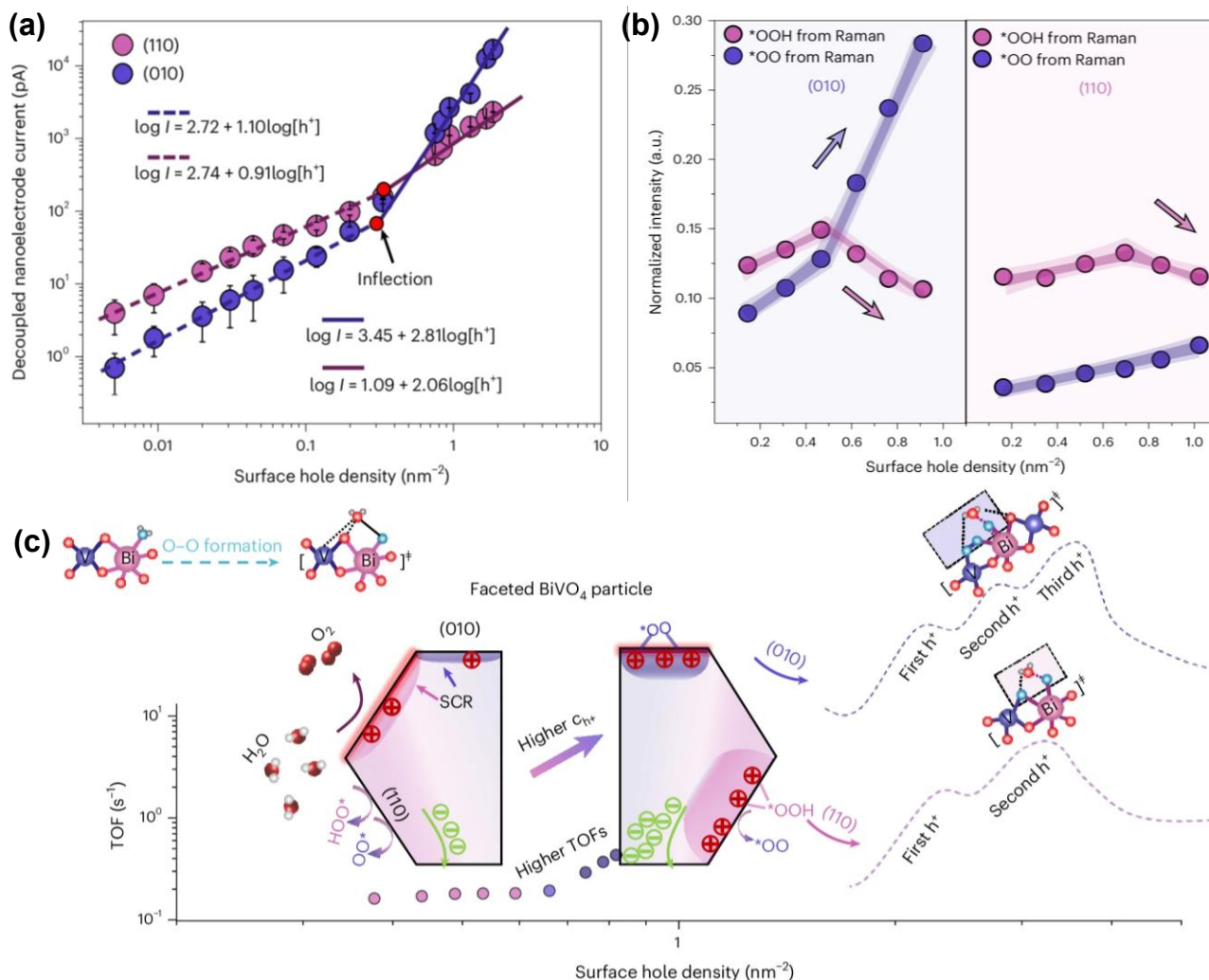


Figure 2. (a) Correlation between decoupled nanoelectrode current (I) and surface hole density ($[h^+]$) on the (110) and (010) facets. (b) Extracted Raman peak intensities of *OOH and *OO intermediates on the (010) and (110) facets, normalized to the main Ag vibrational peak, as a function of surface hole density. (c) Schematic illustration of hole-density-dependent water oxidation pathways at the BiVO_4 /electrolyte interface.

A major strength of this work lies in the direct correlation of charge transfer, intermediate evolution and local catalytic current on the same BiVO_4 particle. This approach makes it possible to examine spatial heterogeneity as part of the reaction mechanism rather than as an averaged surface property. The results show that a high surface hole density alone does not guarantee high OER activity. The response also depends on whether the surface can accommodate

several oxidizing equivalents and direct them towards O-O bond formation. This interpretation places greater emphasis on multihole accumulation and surface restructuring in the analysis of photoelectrocatalytic activity. For BiVO_4 , the findings suggest that activity may be improved by stabilizing the Bi-O-V framework, modifying the electronic structure through Mo or W substitution, or controlling facet termination and surface reconstruction. These strategies could affect the

hole density required to access the cooperative pathway identified on the (010) facet.

The work also leaves several questions open. It remains to be established whether comparable kinetic transitions occur on other oxide photoanodes, including Fe_2O_3 , WO_3 and TiO_2 . Defects, inter-facet junctions, local pH and co-catalyst layers may also alter the critical hole density and the associated surface chemistry. Extending the same spatially resolved measurements from isolated particles to photoelectrode films will be important for determining how these effects operate in practical materials. Overall, the work links local hole accumulation to changes in reaction intermediates and water-oxidation kinetics. It shows that the catalytic response of an oxide surface depends on how the accumulated holes are used, as well as on how many holes reach the surface.

References

- [1] Nathan S. Lewis, Daniel G. Nocera. Powering the planet: chemical challenges in solar energy utilization. *Proceedings of the National Academy of Sciences of the United States of America*, 2006, 103, 15729–15735. <https://doi.org/10.1073/pnas.0603395103>.
- [2] Camilo A. Mesa, Laia Francàs, Ke R. Yang, Pablo Garrido-Barros, Ernest Pastor, Yimeng Ma, Andreas Kafizas, Timothy E. Rosser, Matthew T. Mayer, Erwin Reisner, Michael Grätzel, Victor S. Batista, James R. Durrant. Multihole water oxidation catalysis on haematite photoanodes revealed by operando spectroelectrochemistry and DFT. *Nature Chemistry*, 2020, 12, 82–89. <https://doi.org/10.1038/s41557-019-0347-1>.
- [3] Florian Le Formal, Ernest Pastor, Camilo A. Mesa, Stephanie R. Pendlebury, Michael Grätzel, James R. Durrant. Rate law analysis of water oxidation on a hematite surface. *Journal of the American Chemical Society*, 2015, 137(20), 6629–6637. <https://doi.org/10.1021/jacs.5b02576>.
- [4] Sacha Corby, Reshma R. Rao, Ludmilla Steier, James R. Durrant. The kinetics of metal oxide photoanodes from charge generation to catalysis. *Nature Reviews Materials*, 2021, 6, 1136–1155. <https://doi.org/10.1038/s41578-021-00343-7>.
- [5] Wei Nie, Hong-Jia Wang, Yuying Gao, Deng Li, Yu Jin, Shisheng Zheng, Qian Li, Ziyuan Wang, Jian-Feng Li, Fengtao Fan, Can Li. Spatial imaging of water oxidation on single-particle catalysts. *Nature Nanotechnology*, 2026, In Press. <https://doi.org/10.1038/s41565-026-02184-3>.
- [6] Osmar Depablos-Rivera, Ana Martinez, Sandra E. Rodil. Interpretation of the Raman spectra of bismuth oxide thin films presenting different crystallographic phases. *Journal of Alloys and Compounds*, 2021, 853, 157245. <https://doi.org/10.1016/j.jallcom.2020.157245>.
- [7] C. Díaz-Guerra, P. Almodóvar, M. Camacho-López, S. Camacho-López, J. Piqueras. Formation of $\beta\text{-Bi}_2\text{O}_3$ and $\delta\text{-Bi}_2\text{O}_3$ during laser irradiation of Bi films studied in-situ by spatially resolved Raman spectroscopy. *Journal of Alloys and Compounds*, 2017, 723, 520–526. <https://doi.org/10.1016/j.jallcom.2017.06.263>.
- [8] Yonghyuk Lee, Taehun Lee. Machine-learning-accelerated surface exploration of reconstructed $\text{BiVO}_4(010)$ and characterization of their aqueous interfaces. *Journal of the American Chemical Society*, 2025, 147(9), 7799–7808. <https://doi.org/10.1021/jacs.4c17739>.
- [9] Michihiro Suga, Fusamichi Akita, Keitaro Yamashita, Yoshiaki Nakajima, Go Ueno, Hongjie Li, Takahiro Yamane, Kunio Hirata, Yasufumi Umena, Shinichiro Yonekura, Long-Jiang Yu, Hironori Murakami, Takashi Nomura, Tetsunari Kimura, Minoru Kubo, Seiki Baba, Takashi Kumasaka, Kensuke Tono, Makina Yabashi, Hiroshi Isobe, Kizashi Yamaguchi, Masaki Yamamoto, Hideo Ago, Jian-Ren Shen. An oxyl/oxo mechanism for oxygen-oxygen coupling in PSII revealed by an x-ray free-electron laser. *Science*, 2019, 366, 334–338. <https://doi.org/10.1126/science.aax6998>.
- [10] Rengui Li, Fuxiang Zhang, Donge Wang, Jingxiu Yang, Mingrun Li, Jian Zhu, Xin Zhou, Hongxian Han, Can Li. Spatial separation of photogenerated electrons and holes among {010} and {110} crystal facets of BiVO_4 . *Nature Communications*, 2013, 4, 1432. <https://doi.org/10.1038/ncomms2401>.