Understanding activity trends in electrochemical water oxidation to form hydrogen peroxide

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Electrochemical production of hydrogen peroxide ($\text{H}_2\text{O}_2$) from water oxidation could provide a very attractive route to locally produce a chemically valuable product from an abundant resource. Herein using density functional theory calculations, we predict trends in activity for water oxidation towards $\text{H}_2\text{O}_2$ evolution on four different metal oxides, i.e., WO$_3$, SnO$_2$, TiO$_2$ and BiVO$_4$. The density functional theory predicted trend for $\text{H}_2\text{O}_2$ evolution is further confirmed by our experimental measurements. Moreover, we identify that BiVO$_4$ has the best $\text{H}_2\text{O}_2$ generation amount of those oxides and can achieve a Faraday efficiency of about 98% for $\text{H}_2\text{O}_2$ production.
Hydrogen peroxide (H$_2$O$_2$) is an important chemical with a wide range of applications in industry, such as paper and textile manufacturing and environmental protection for detoxification and color removal of wastewater. Currently, H$_2$O$_2$ is produced indirectly via the anthraquinone oxidation process, which is an energy-demanding multi-electron process and requires large plants. Moreover, transportation of H$_2$O$_2$ to the place of use adds additional challenges due to safety concerns. Broader usage of H$_2$O$_2$ could benefit from the capability of direct on-site production. Electrochemical synthesis of H$_2$O$_2$ provides a straightforward route for on-site production and ideally solves the issues associated with the indirect anthraquinone route. Among all these four oxides, BiVO$_4$ is shown to be the best catalyst for the two-electron water oxidation (Eq. 1)\textsuperscript{10,11}. We only focus on the (111) surface, which has been shown theoretically to be stable and exposed in the BiVO$_4$ crystal structure. In addition, we have taken the OH*, O* and OOH* free energies for WO$_3$(100), TiO$_2$(110) and SnO$_2$(110) from reported DFT calculations (Supplementary Note 1, Supplementary Fig. 1 and Supplementary Tables 1, 2)\textsuperscript{13,38,40}. We use the computational hydrogen electrode (CHE) model, which exploits the chemical potential of a proton-electron pair equal to gas-phase H$_2$ at standard conditions. The electrode potential is taken into account by shifting the electron energy by $-\varepsilon U$, where $\varepsilon$ and $U$ are the elementary charge and the electrode potential, respectively. The limiting potential for the electrochemical reaction to occur is defined as the lowest potential, at which all the reaction steps are downhill in free energy following the previous report\textsuperscript{13}. Figure 1 shows the activity volcano plots based on the calculated limiting potentials as a function of the calculated free energy of OH* ($\Delta G_{\text{OH}^*}$) for both two-electron (black) and four-electron (blue) oxidation reactions.

**Results**

**Theoretical analyses.** As discussed above, H$_2$O$_2$ synthesis from water oxidation is a challenging reaction. This is due to the fact that selectivity and activity of the materials are largely limited by several criteria imposed by the thermodynamics of the competing reactions\textsuperscript{3}. The adsorption free energies of relevant intermediates of the one- (Eq. 5), two- (Eq. 1) and four-electron (Eq. 4) water oxidation reactions, i.e., OH*, O* and OOH* can be calculated using density functional theory (DFT). We show here that the free energies of OH* and O* are key parameters determining the selectivity and activity towards different oxidation products, O$_2$ (Eq. 4), OH radical (Eq. 5) or H$_2$O$_2$ (Eq. 1)\textsuperscript{13}. Using DFT, we calculated the free energies of OH*, O* and OOH* on BiVO$_4$ (details of calculations in Supplementary Note 1). We only focus on the (111) surface, which has been shown theoretically to be stable and exposed in the BiVO$_4$ crystal structure. In addition, we have taken the OH*, O* and OOH* free energies for WO$_3$(100), TiO$_2$(110) and SnO$_2$(110) from reported DFT calculations (Supplementary Note 1, Supplementary Fig. 1 and Supplementary Tables 1, 2)\textsuperscript{13,38,40}. We use the computational hydrogen electrode (CHE) model, which exploits the chemical potential of a proton-electron pair equal to gas-phase H$_2$ at standard conditions. The electrode potential is taken into account by shifting the electron energy by $-\varepsilon U$, where $\varepsilon$ and $U$ are the elementary charge and the electrode potential, respectively. The limiting potential for the electrochemical reaction to occur is defined as the lowest potential, at which all the reaction steps are downhill in free energy following the previous report\textsuperscript{13}. Figure 1 shows the activity volcano plots based on the calculated limiting potentials as a function of the calculated free energy of OH* ($\Delta G_{\text{OH}^*}$) for both two-electron (black) and four-electron (blue) oxidation reactions.

**Fig. 1** Activity volcano plots. It is based on calculated limiting potentials as a function of calculated adsorption energies of OH* ($\Delta G_{\text{OH}^*}$) for the two-electron oxidation of water to hydrogen peroxide evolution (black) and the four-electron oxidation to oxygen evolution (blue). The corresponding equilibrium potentials for each reaction have been shown in dashed lines.

Identified as the best catalyst for the two-electron water oxidation in dark and under illumination, and this result is consistent with previous studies on comparing different metal oxides for H$_2$O$_2$ production\textsuperscript{14,33}. Importantly, we identify the optimal bias range for BiVO$_4$ to produce H$_2$O$_2$ in dark (~2.9–3.3 V vs RHE) and under illumination (~1.7 V–2.3 V vs RHE). As such, BiVO$_4$ achieves a high faraday efficiency (FE) of 70% in dark and 98% under 1 sun illumination.
The corresponding equilibrium potentials for each reaction have been shown in dashed lines.

From the thermodynamic point of view, materials with strong OH adsorption energy (shaded in blue in Fig. 1) will further oxidize OH* to O* and OHOH*, following the complete four-electron oxidation reaction (Eq. 4) to evolve oxygen. Therefore, electrocatalysts with weak OH* free energy will have low selectivity towards the four-electron pathway but high preference towards the two-electron route. At the same time, the OH* free energy should be strong enough to dissociate the water molecule and provide a good thermodynamic driving force, for the two-electron pathway towards H2O2. The free energy for H2O2 formation is ~3.5 eV, twice of the equilibrium potential for Eq. 1, so the electrocatalyst should have ΔGOH, > 3.5 eV. Given the fact that the *O and *OH energies are generally found to scale (ΔGOH, = 2ΔGOH, + 0.28)39, this sets a lower limit for OH* free energy, i.e., ΔGOH, > 3.5 – 0.28 ~ 1.6 eV. The upper limit for ΔGOH, is set by the free energy of OH radical formation in the solution (Eq. 5), since too weak OH* free energy with ΔGOH, > ~2.4 eV drives the reaction towards OH radical formation (pink shaded area in Fig. 1). Hence, the combined thermodynamic criteria and scaling relation indicates a selective catalyst for H2O2 evolution should have ΔGOH, from ~1.6 to 2.4 eV. This thermodynamic analysis suggests that WO3, SnO2, BiVO4 and TiO2 should be able to generate H2O2 within certain values of the OH* free energy (shaded in green in Fig. 1). To increase the selectivity region for H2O2 evolution, we need to identify catalyst materials that largely deviate from the O* and OH* scaling relation42.

Aside from the high selectivity, the two-electron oxidation reaction (Eq. 1) ideally should also have high activity with low overpotential. The theoretical overpotential is defined as the difference between the limiting potential and equilibrium potential (1.76 V for the two-electron path). The overpotential is governed by the binding of OH* to the catalyst surface, so controlling the overpotential is a matter of tuning the free energy of OH*41. An OH* free energy (ΔGOH,) of 1.76 eV, when calculated at zero potential and relative to liquid water, will give zero overpotential. The calculated theoretical limiting potential for BiVO4 is 1.95 V, hence it has a theoretical overpotential of ~0.2 V for the two-electron oxidation reaction. The activity of BiVO4 can be further improved with different doped metals such as Sr and Ru (Supplementary Note 2, Supplementary Fig. 2 and Supplementary Table 3). The calculated limiting potentials for WO3, SnO2 and TiO2 are 1.82, 2.02 and 2.27 V, respectively. In the following, we show that the trend in theoretical limiting potentials for WO3, BiVO4, SnO2 and TiO2 is in very good agreement with experimental measurements.

Materials fabrication. Experimentally, we evaluate the H2O2 evolution performance of four oxides: WO3, BiVO4, SnO2 and TiO2 by determining their onset potentials, faraday efficiencies and production rates of H2O2 per geometric area of electrodes. All the oxides were synthesized on transparent and conductive fluorine-doped tin oxide (FTO) substrates. The WO3 was synthesized by flame vapor deposition (FVD). BiVO4, SnO2, and TiO2 were synthesized by a sol–gel process (see Methods and Supplementary Note 3). Since the electrochemical performance of each oxide is affected by its loading, each oxide film was individually optimized to yield the highest FE for the dark electrochemical measurement before taken for comparison. For example, Supplementary Fig. 3 shows that the measured FE for H2O2 production varies with the BiVO4 loading, which was controlled by varying the precursor concentration during the spin coating process (Supplementary Fig. 4). The low loading results in low BiVO4 coverage and exposed FTO, leading to a low H2O2 production. On the other hand, the high coverage results in high film resistance that impedes the charge transport process. Hence, for each oxide investigated, its loading on FTO was individually optimized to yield the highest FE for the dark electrochemical measurement.

H2O2 production comparison under dark conditions. Next, we measured the current–voltage (J–V) curves for the four oxides (WO3, BiVO4, SnO2 and TiO2) without illumination (Fig. 2a). The J–V onset, as well as the experimental measured H2O2 evolution onset potentials (defined as the potential at which the H2O2 concentration reaches 1 ppm), are compared with the calculated theoretical potentials in Fig. 2b. It can be seen that both the measured current onset potential (hollow symbols) and the onset potential for H2O2 generation (solid symbols) increase in the order of WO3 < BiVO4 < SnO2 < TiO2, which agrees with the theoretical predication, supporting the validity of using ΔGOH, as a descriptor to analyze the H2O2 evolution onset (Fig. 1). The measured onset potentials are higher than the calculated values, which is likely due to the additional kinetic barriers to be overcome in the actual experiments.

We further quantified the FE and the amount of H2O2 generated from the oxides as functions of the applied biases. As shown in Fig. 3a, all the metal oxides investigated share the
similar FE trend with increasing applied bias: the FE first increases to a maximum value and then decreases. Or equivalently, for each metal oxide, there is an optimal potential increase to a maximum value and then decreases. Or

in NaHCO₃ shows best performance for H₂O₂ production

Discussion

In the present work, we utilized DFT calculations in conjunction with experimental measurements to study the activity of two-electron water oxidation towards H₂O₂ evolution over four metal oxides, namely WO₃, BiVO₄, SnO₂, and TiO₂. Both the calculated and measured onset potentials for H₂O₂ production increase in the sequence of WO₃, BiVO₄, SnO₂, and TiO₂. Among all these four oxides, BiVO₄ produces the highest faraday efficiency (~70%) and largest amount for H₂O₂ under dark. The peak faraday efficiency BiVO₄ is further increased to 98% by adding illumination, optimizing electrolyte and optimizing the thickness of BiVO₄. Those optimizations also lower the onset potential from 2.2 V to <1.1 V. These results suggest that BiVO₄ is an excellent photoanode candidate for electrochemical and photocatalytic water oxidation. The theoretical simulation and experimental demonstration illustrated in this work have furthered the understanding of the activity and selectivity of water oxidation to H₂O₂ on metal oxide surfaces. Our result has opened an avenue for novel photocatalytic device designs with
fundamental mechanism study that utilize solar energy and water to produce an oxidative product with higher value beyond O₂.

Methods

Fabrication of various metal oxides on FTO. The BiVO₄ precursor solution was prepared by a mixture of a bismuth nitrate hexahydrate (Bi(NO₃)₃.6H₂O, 99.99%; Aldrich) and vanadyl acetylacetonate (C₅H₇O₇V, 98%; Aldrich), which were added to a solution of acetylacetonate (C₅H₇O₇H₂, 99.9%; Aldrich) and acetic acid (CH₃COOH, 99.70%; Fisher) with a ratio of 1.0:1.2, followed by sonication for 10 min. After sonication, a dark green solution was obtained and the solution is usually used within a day after the preparation. For the one named 1-layer, the mole concentration of Bi was varied from 0.08 M, and 0.04 M, 0.02 M, to 0.01 M. For a typical spin coating, 100 µl of the BiVO₄ precursor solution was dropped on a pre-cleaned FTO glass followed by spin coating (500 r.p.m. for 5 s and 1500 r.p.m. for 30 s). The samples were then annealed at 100 °C for 10 min, and 300, 400, and 500 °C for 5 h, respectively. Similar step-wise annealing process was commonly used for metal oxide fabrication, and the purpose is to slowly evaporate the solvent to achieve a better film morphology. For spin coating multiple layers, the same process above was repeated for multiple times. Finally, the coated FTO was annealed in a box furnace at 500 °C for 2 h.

SnO₂ was fabricated by using a sol–gel process similar with BiVO₄. Firstly, the precursor solution was made by dissolving 0.1932 g tin chloride in 10 ml 2-methoxyethanol (CH₃OCH₂CH₂OH, 99.8%; Aldrich) and 0.2 ml acetylacetone (CH₃COCH₂COCH₃, ≥99.3%; Aldrich) as the best condition, and sonicated for 30 min. After that the solution was put in a fume hood with aging for one night. The solution was spin coated on top of cleaned FTO with first 5 s, 500 r.p.m. and second 35 s, 2000 r.p.m. steps. Annealing process was carried out by using step by step method (100 °C for 5 min, 300 °C for 5 min and finally 455 °C for 30 min).

TiO₂ was fabricated from a paste making and coating process. About 9.5 ml ethanol and 0.5 ml water were mixed and 0.3 g polyethylene glycol (Aldrich) was added to a mixture and sonicated for 30 min. Then 0.25 g Ti(OBu)₄ (Aldrich) as the best condition was added and the suspension was sonicated for another 10 min. Then the suspension was put on a hot plate and heated at 120 °C until the total volume reached 5 ml to get the TiO₂ paste. The paste was used to spin coat or blade coat on top of FTO glass, followed by the annealing process at 400 °C for 2 h.

WO₃ was synthesized by FVD method, for which a W wire (0.5 mm in diameter; Aldrich) was oxidized by flame as the WOₓ vapor source. Those WOₓ vapor further deposited on FTO as WₓOₓOₙ nanowires. The optimized FVD condition followed the one used in Rao et al.’s work, with 18.4SLPM:12.5SLPM CH₄ to air flow ratio and a substrate temperature 550 °C for 10 min of deposition (Supplementary Table 4). WₓOₓOₙ nanowires were further converted to WO₃ nanowires by annealing at 500 °C in a box furnace for 1 h.

Characterizations. The H₂O₂ production from various anodes was detected by using the potentiostat with the three-electrode system, in which the Ag/AgCl electrode was used as a reference electrode and Ti foil as the counter electrode. Silver paste and Teflon tape were used to make metal contact and to define area when necessary. The measurements under illumination were obtained under 1 Sun at AM 1.5 G. The amount of generated H₂O₂ was detected by using the standard H₂O₂ strips (Indigo Instruments). In addition, the generated H₂O₂ concentration was further confirmed with a titration process by using potassium permanganate (KMnO₄, Aldrich). The permanganate ion has a dark purple color, and the color disappears during titration when the MnO₄⁻ is totally consumed based on the following equation:

\[
2\text{MnO}_4^- + 5\text{H}_2\text{O}_2 + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{O}_2 + 8\text{H}_2\text{O}
\]

In this work, the sulfuric acid (H₂SO₄, Acros Organics) was used as the H⁺ source. We measured the theoretical generated H₂O₂ mol after the 10 min measurement for each condition. The FE of H₂O₂ is calculated based on the accumulated amount of H₂O₂ after the 10 min measurement for each condition.

\[
\text{FE} = \frac{\text{Amount of generated H}_2\text{O}_2(\text{mol})}{\text{theoretical generated H}_2\text{O}_2} \times 100
\]

where the theoretical amount of H₂O₂ is equal to the total number of electrons divided by two (in mol). The FE of H₂O₂ is calculated based on the accumulated amount of H₂O₂ after the 10 min measurement for each condition. The FE for H₂ and O₂ are calculated in a similar way, in which the theoretical amount of H₂ is also equal to the total amount of electrons divided by two (in mol), while the theoretical amount of O₂ is equal to the total amount of electrons divided by four (in mol), respectively.

Computational details. Density functional theory calculations are done using the projector-augmented wave method and a plane-wave basis set as implemented in the Vienna Ab Initio Simulation Package (VASP). The valence configurations are treated as a 3s²3p⁶4s² for Bi, 3d⁵4s² for V, 2s²2p⁴ for O and 1s² for H. The cutoff energy for plane-wave basis functions is 400 eV. The bulk and surface properties of BiVO₄ are optimized within GGA-PBE. For a more accurate description, the calculations are done within GGA-rPBE for the adsorption energies of OH⁺, O²⁻ and OOOH⁺ species on the BiVO₄(111) surface. The reference energies of the pristine slab, H₂O and O₂ molecules are also carefully treated within GGA-rPBE. For periodic slab calculations, slabs of six metal-oxygen layers are separated by at least 12 Å of vacuum. The atomic positions within the top two layers of the slabs were allowed to relax with the force convergence of 0.02 eV per Å. Spin polarization is considered in all the calculations.

Data availability. Data supporting the findings of this study are available within the article and its supplementary information files, and from the corresponding author upon reasonable request.

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References

1. Campos-Martín, J. M., Blanco-Brieva, G. & Fierro, J. I. G. Hydrogen peroxide synthesis: an outlook beyond the aanthaquinone process. Angew. Chem. Int. Ed. Engl. 45, 6962–6964 (2006).
2. Siahrostami, S. et al. Enabling direct H₂O₂ production through rational electrolyt catalyst design. Nat. Mater. 12, 1137–1143 (2013).
3. Verdaguer-Casadevall, A. et al. Trends in the electrochemical synthesis of H₂O₂: enhancing activity and selectivity by electrocatalytic site engineering. Nano Lett. 14, 1603–1608 (2014).
4. Fellinger, T.-P., Hasch, F., Strasser, P. & Antonietti, M. Mesoporous nitrogen-doped carbon for the electrocatalytic synthesis of hydrogen peroxide. J. Am. Chem. Soc. 134, 4072–4075 (2012).
5. Choi, C. H. et al. Hydrogen peroxide synthesis via enhanced two-electron oxygen reduction pathway on carbon-coated Pt surface. J. Phys. Chem. C 118, 30063–30070 (2014).
6. Park, J., Nabae, Y., Hayakawa, T. & Kakimoto, M. Highly selective two-electron oxygen reduction catalyzed by mesoporous nitrogen-doped carbon. ACS Catal. 4, 3749–3754 (2014).
7. Choi, C. H. et al. Tuning selectivity of electrochemical reactions by atomically dispersed platinum catalyst. Nat. Commun. 7, 10922 (2016).
8. Mase, K., Yoneda, M., Yamada, Y., Fukuzumi, S. & Kloo, D. R. Seawater usable for production and consumption of hydrogen peroxide as a solar fuel. Nat. Commun. 7, 11470 (2016).
9. Mase, K., Yoneda, M., Yamada, Y. & Fukuzumi, S. Efficient photocatalytic production of hydrogen peroxide from water and dioxygen with bismuth vanadate and a Cobalt(II) chloride complex. ACS Energy Lett. 1, 913–919 (2016).
10. Izgorodin, A., Izgorodina, E. & MacFarlane, D. R. Low overpotential water oxidation to hydrogen peroxide on a MnOx catalyst. Energy Environ. Sci. 5, 9496 (2012).
11. McDonnell-Worth, C. & MacFarlane, D. R. Ion effects in water oxidation to hydrogen peroxide. RSC Adv. 4, 30551 (2014).
12. Bard, A. J., Roger, P., Hordan, J. Standard Potentials in Aqueous Solution (M. Dekker, 1985).
13. Viswanathan, V., Hansen, H. A. & Norskov, J. K. Selective electrochemical generation of hydrogen peroxide from water oxidation. J. Phys. Chem. Lett. 6, 4224–4228 (2015).
14. Fuku, K. et al. Efficient oxidative hydrogen peroxide production and accumulation in photoelectrochemical water splitting using a tungsten trioxide/bismuth vanadate photoanode. Chem. Commun. 52, 5406–5409 (2016).
15. Burke, M. S., Enman, L., Batchelor, A. S., Zou, S. & Boettcher, S. W. Oxygen evolution reaction electrocatalysis on transition metal oxides and (Oxy)hydrides: activity trends and design principles. Chem. Mater. 27, 7549–7558 (2015).
16. Reier, T., Oezaslan, M. & Strasser, P. Electrocatalytic oxygen evolution reaction (OER) on Ru, Ir, and Pt catalysts: a comparative study of nanoparticles and bulk materials. ACS Catal. 2, 1765–1772 (2012).
17. Cheng, Y. & Jiang, S. P. Advances in electrocatalysts for oxygen evolution reaction of water electrolysis—from metal oxides to carbon nanotubes. Prog. Nat. Sci. Mater. Int. 25, 545–553 (2015).
18. Diaz-Morales, O., Ledezma-Yanez, I., Koper, M. T. M. & Calle-Vallejo, F. Guideline for the rational design of Ni-based double hydroxide electrocatalysts for the oxygen evolution reaction. ACS Catal. 5, 5380–5387 (2015).

19. Fabbri, E., Habeder, A., Waltar, K., Kötz, R. & Schmidt, T. J. Developments and perspectives of oxide-based catalysts for the oxygen evolution reaction. Catal. Sci. Technol. 4, 3800–3821 (2014).

20. Gong, M. & Dai, H. A mini review of NiFe-based materials as highly active oxygen evolution reaction catalysts. Nano Res. 8, 23–39 (2014).

21. Diaz-Morales, O. et al. Iridium-based double perovskites for efficient water oxidation in acidic media. Nat. Commun. 7, 12363 (2016).

22. Lee, Y., Suntivich, J., May, K. J., Perry, E. E. & Shao-Horn, Y. Synthesis and activities of rutile IrO2 and RuO2 nanoparticles for oxygen evolution in acid and alkaline solutions. J. Phys. Chem. Lett. 3, 399–404 (2012).

23. Dionigi, F. & Strasser, P. NiFe-based (oxy)hydroxide catalysts for oxygen evolution reaction in non-acidic electrolytes. Adv. Energy Mater. 6, 1600621 (2016).

24. Reier, T., Nong, H. N., Teschner, D., Schlögl, R. & Strasser, P. Electrocatalytic oxygen evolution reaction in acidic environments - reaction mechanisms and catalysts. Adv. Energy Mater. 7, 1601275 (2016).

25. Spoerri, C., Kwan, J. T. H., Bonakdarpour, A., Wilkinson, D. & Strasser, P. The stability challenges of oxygen evolving catalysts: towards a common fundamental understanding and mitigation of catalyst degradation. Angew. Chem. 56, 5994–6021 (2017).

26. Han, B. et al. Activity and stability trends of perovskite oxides for oxygen evolution catalysis at neutral pH. Phys. Chem. Chem. Phys. 17, 22576–22580 (2015).

27. Hong, W. T., Welsch, R. E. & Shao-Horn, Y. Descriptors of oxygen-evolution activity for oxides: a statistical evaluation. J. Phys. Chem. C 120, 78–86 (2016).

28. Sou, Z. et al. Fe (oxy)hydroxide oxygen evolution reaction electrocatalysis: intrinsic activity and the roles of electrical conductivity, substrate, and dissolution. Chem. Asian J. 12, 1111–1119 (2017).

29. Burke, M. S. et al. Revised oxygen evolution reaction activity trends for first-row transition-metal (oxy)hydroxides in alkaline media. J. Phys. Chem. Lett. 6, 3737–3742 (2015).

30. Fukushima, K. et al. Photocatalytic hydrogen peroxide production from water on a WO3/BiVO4 photoanode and from O3 on an Au cathode without external bias. Chem. Asian J. 12, 1111–1119 (2017).

31. Fukushima, K., Miyase, Y., Miseki, Y., Gunji, T. & Sayama, K. Enhanced oxidative hydrogen peroxide production on conducting glass anodes modified with metal oxides. ChemistrySelect 1, 5721–5726 (2016).

32. Goto, H. Quantitative analysis of superoxide ion and hydrogen peroxide produced from molecular oxygen on photoradiated TiO2 particles. J. Catal. 225, 223–229 (2004).

33. Hirakawa, T., Yawata, K. & Nosaka, Y. Photocatalytic reactivity for O2− and OH radical formation in anatase and rutile TiO2 suspension as the effect of H2O2 addition. Appl. Catal. A Gen. 325, 105–111 (2007).

34. Cai, R., Kubota, Y. & Fujishima, A. Effect of copper ions on the formation of hydrogen peroxide from photocatalytic titanium dioxide particles. J. Catal. 219, 214–218 (2003).

35. Zhang, J. & Nosaka, Y. Quantitative determination of OH radicals for investigating the reaction mechanism of various visible-light TiO2 photocatalysts in aqueous suspension. J. Phys. Chem. C 117, 1383–1391 (2013).

36. Sánchez-Quiles, D. & Tovar-Sánchez, A. Sunscreens as a source of hydrogen peroxide production in coastal waters. Environ. Sci. Technol. 48, 9037–9042 (2014).

37. Li, G.-L. et al. First-principles investigation of the surface properties of fergusonite-type monoclinic BiVO4 photocatalyst. RSC Adv. 7, 9130–9140 (2017).

38. Man, I. C. et al. Universality in oxygen evolution electrocatalysis on oxide surfaces. ChemCatChem 3, 1159–1165 (2011).

39. Siahrostami, S., Björketun, M. E., Strasser, P., Greeley, I. & Rossmeis, J. Tandem cathode for proton exchange membrane fuel cells. Phys. Chem. Chem. Phys. 15, 9326–9334 (2013).

40. Montoya, J. H., García-Mota, M., Nørskov, J. K. & Vojvodic, A. Theoretical evaluation of the surface electrochemistry of perovskites with promising photon absorption properties for solar water splitting. Phys. Chem. Chem. Phys. 17, 2634–2640 (2015).

41. Nørskov, J. K. et al. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. J. Phys. Chem. B 108, 17886–17892 (2004).

42. Siahrostami, S., Li, G.-L., Viswanathan, V. & Nørskov, J. K. One- or two-electron water oxidation, hydroxyl radical, or H2O2 evolution. J. Phys. Chem. Lett. 8, 1157–1160 (2017).

43. Walsh, A., Yan, Y., Huda, M. N., Al-Jassim, M. & Wei, S.-H. Band edge electronic structure of BiVO4 elucidating the role of the Bi s and V d orbitals. Chem. Mater. 21, 547–551 (2009).

44. Sayama, K. et al. Photoelectrochemical decomposition of water on nanocrystalline BiVO4 film electrodes under visible light. Chem. Commun. 365, 2908 (2003).

45. Rzhikova, E. A. & Ariga, K. (eds) From Molecules to Materials: Pathways to Artificial Photosynthesis (Springer International Publishing, 2016).

46. Rao, P. M. et al. Simultaneously efficient light absorption and charge separation in WO3/BiVO4 Core/Shell nanowire photocathode for photoelectrochemical water oxidation. Nano Lett. 14, 1099–1105 (2014).

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Author contribution

J.K.N. and S.S. conceived and designed the DFT calculations. X.Z. conceived and performed the experiment. All authors discussed the results and commented on the manuscript.

Additional information

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