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Well-known semiconductor gains renewed interest for green hydrogen generation

Bismuth vanadate (BiVO4), a semiconductor material with several outstanding physical and chemical properties, was once seen as an ideal photoanode for hydrogen generation via sunlight-assisted photoelectrochemical water splitting. However, scientists soon realized that the electric current produced by this reaction -directly proportional to the amount of hydrogen generated- was insufficient to meet the worldwide demands for green energy. As a result, interest in this semiconductor gradually declined, and many research groups started to focus on alternative materials to be employed as photoanodes for the water-splitting reaction. Nevertheless, some institutes, including ICFO, have kept investigating ways of unlocking the full potential of BiVO4. In an ACS Energy Letters publication, ICFO researchers have now demonstrated a new route to exploit this material for hydrogen generation. By targeting lower solar energies, where light absorption was previously considered too weak to promote the water-splitting reaction, they have succeeded in generating and detecting photocurrents by increasing the optical path of the light inside the semiconductor material.
Departing from this finding, the team has shown how novel designs relying on an optimal management of light propagation within the BiVO4 could lead to even higher photocurrent levels than what was previously thought possible. More importantly, they have reinforced the idea that BiVO4 is a worth-considering material for green hydrogen generation.

September 03, 2025

In the context of climate and energy crisis, scientists are tirelessly working to find sustainable fuels. Hydrogen, which can be produced from water-splitting reaction powered by solar light, has emerged as a promising candidate. The challenge now is to make the conversion process green, efficient and cost-effective. To achieve such a goal, it is crucial to wisely choose the materials to employ as electrodes (photoanode and photocathode) in the water-splitting reaction. A good or a bad choice can make the difference between a successful and a failed hydrogen generation set-up. ?

A few years ago, a semiconductor called **bismuth vanadate (BiVO4)** attracted the attention of the scientific community as a possible photoanode for its appealing physical properties, which include **non-toxicity, low-cost preparation and high stability**. However, the excitement didn't last long. It turned out that the maximum photocurrent driven solely by solar photons with energies higher than the bandgap of the BiVO4 (2.4 eV), for which the semiconductor best absorbs light, was not sufficient for industrial applications.

Now, ICFO researchers **Dr. Catarina G. Ferreira**, **Dr. Carles Ros**, **Dr. Mingyu Zhang**, **Valentina Gacha**, **Dr. Dimitros Raptis**, led by **ICFO and UPC Prof. Jordi Martorell**, in collaboration with the Technical University of Munich, have tackled the problem from a different perspective. Instead of focusing on this i¿½high-energyi¿½ regime, they have explored lower s
lar energies, right below the bandgap of Bi4O.i¿½Previous studies pointed to the material
s ability to absorb -at least, to some extent- lower energy photons, but the contributions
o photocurrent generation were never explicitly addressed before,i¿½ share the authors
In fact, in this regime the absorption is so low that trying to generate photocurrent se
med almost pointl
ss. ICFO's proposal has, for the first time in a long while, brought some hope to the field. In an ACS Energy Letters publication, the team has reported an alternative approach to increase the optical path of the light inside the BiVO4 by introducing a reflective mirror on the rear interface of the photoanode. In this way, the light entering the material is reflected back before leaving, passing through the semiconductor one more time and, therefore, boosting the chances of absorption. Despite its simplicity, **the researchers have demonstrated the effectiveness of this strategy to generate photocurrent for incoming energies lower than the bandgap of the material**, regardless of how the device was fabricated. In addition, they have developed a theoretical model to estimate the maximum photocurrent that could ideally be generated by optimally tailoring the light propagating inside the bismuth vanadate, ultimately **showing that the commonly reported limit may be greatly exceeded**.

Most importantly, by showing how innovative design strategies can make a decisive difference, the study revives the interest for BiVO4 photoanodes in the race for hydrogen generation.

Reference:

Catarina G. Ferreira, Carles Ros, Mingyu Zhang, Guanda Zhou, Valentina Gacha, Dimitrios Raptis, Ian D. Sharp, and Jordi Martorell, Sub-Bandgap Photon-to-Current Conversion in Bismuth Vanadate Photoanodes and Its Impact on the Maximum Photocurrent Density Achievable for Water Splitting, ACS Energy Letters 0, 10 (2025).
DOI: 10.1021/acsenergylett.5c01894

Acknowledgements:

The authors acknowledge the financial support by the European Commission through the LICROX project (grant 951843). The work also had the support of the Department of Research and Universities, the Department of Climate Action, Food and Rural Agenda, and the Climate Fund of the Government of Catalonia through SolarComb (grant 2023 CLIMA 00036). In addition, the work was partially funded by Ministerio de Ciencia e Innovacion (grant CEX2019-000910-S), Fundacio Cellex, Fundacio Mir-Puig, and Generalitat de Catalunya through Centres de Recerca de Catalunya, as well as by the German Research Foundation under e-conversion Germany's Excellence Strategy ? EXC2089-390776260 and TUM.solar in the context of the Bavarian Collaborative Research Project Solar Technologies Go Hybrid (SolTech). C.R. acknowledges support from the Ministerio de Ciencia e Innovacion/Agencia Estatal de Investigacion (grant FJC2020-043223-I) and the Severo Ochoa Excellence Postdoctoral Fellowship (grant CEX2019-000910-S).

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Sample of $BiVO_4$ photoanode used in the study. Source: ICFO.