

SUPPORTING MATERIALS

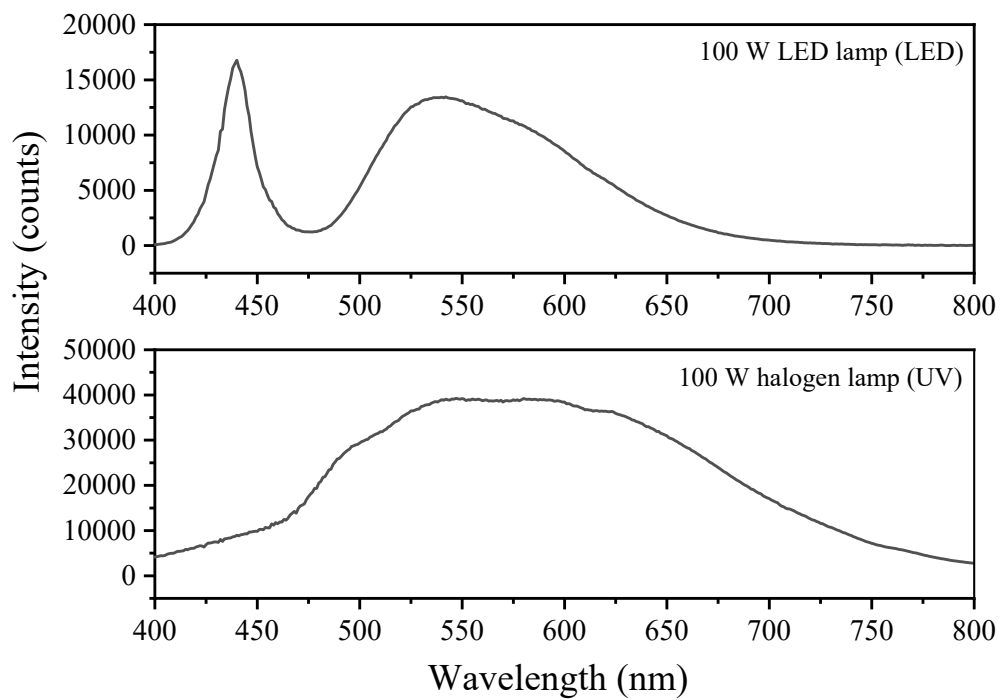


Figure S1. Spectra of the light sources (LED and UV) used in the trials.

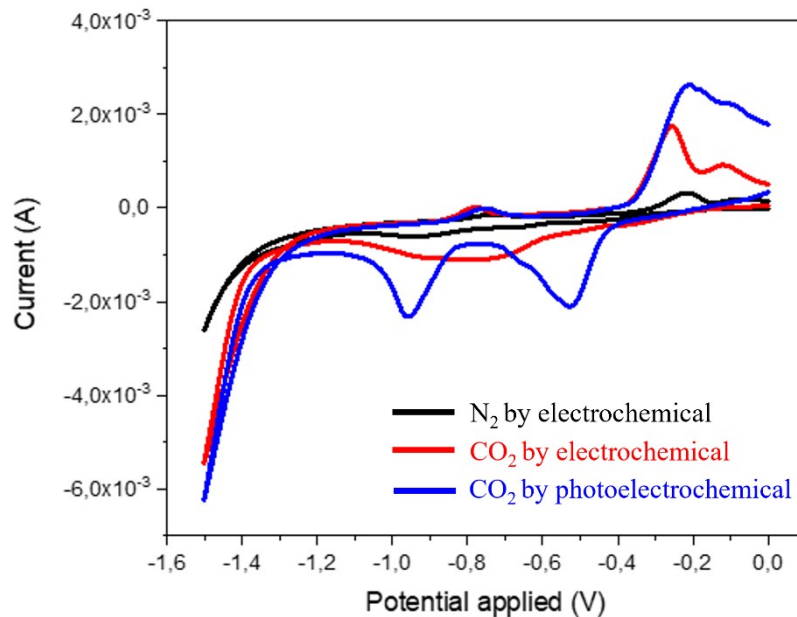


Figure S2. Cyclic voltammetry profiles of the as-synthesized $BiVO_4$ applying a potential window from 0.1 to -1.5 V vs Ag/AgCl at a sweep rate of 20 $mV s^{-1}$. The measurements were conducted under two different conditions: under N_2 (black line) and CO_2 saturation (red line). Additionally, the experiment was repeated, keeping the aforementioned conditions, under CO_2 saturation and LED illumination, as an irradiation source (blue line).

Cyclic voltammetry was performed under the conditions mentioned in section 2.4. flow cell configuration, applying a potential window from 0.1 to -1.5 V vs Ag/AgCl at a sweep rate of 20 $mV s^{-1}$ with LED illumination, as an irradiation source. We underscore that a reduction mechanism is observed in cyclic voltammetry for the electrochemical process, centered at -0.8 V vs Ag/AgCl. This suggests that it may be a convolution of two other mechanisms with a maximum near -0.85 and -0.7 V vs Ag/AgCl. Hence, the peaks observed in the photoelectrochemical cyclic voltammetry can be attributed to a shift of these mechanisms, related to a distinct adsorption mechanism of CO_2 induced by light, as well as to an increased frequency of electron transitions, also stirred by light. Although the cyclic voltammetry typically maintains its profile with peaks increasing when the light is on – comparing electrochemical and photoelectrochemical methods –, there can be changes in the cyclic voltammetry profile when turning the light on or off¹. The peak at -0.5 V vs Ag/AgCl is associated with the first steps of CO_2 reduction, possibly carbon monoxide (CO)². We assume that this is a reaction intermediate, as noticed by other similar experiments³.

Regarding the peak around -1.0 V, it can be attributed to the quasi-reversible redox process, $\text{Bi}^{3+} \leftrightarrow \text{Bi-metal}^4$, which leads to the formation of Bi– BiVO_4 heterojunctions.

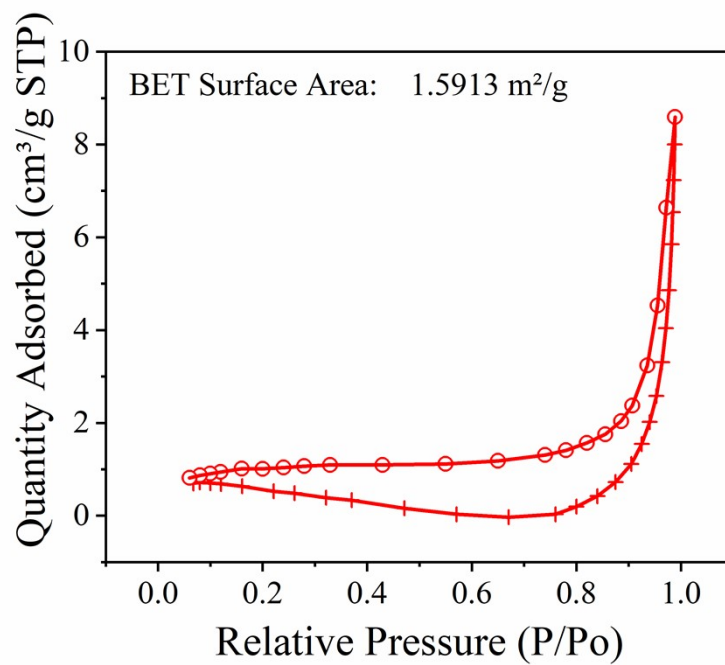


Figure S3. BET measure of as-synthesized BiVO_4 .

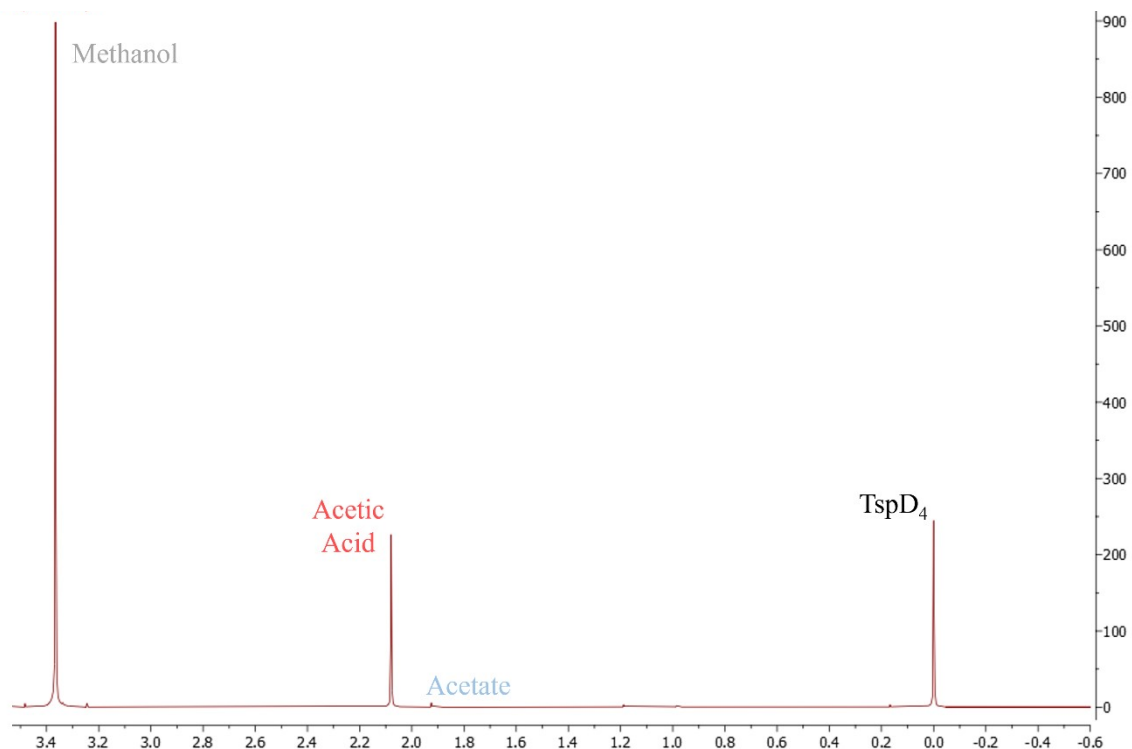


Figure S4. ¹H NMR spectrum of liquid chemicals from CO₂R of as-synthesized BiVO₄ induced by photoelectrochemical powered by LED illumination. The reactions were made in 0.5M Na₂HCO₃ at pH 8 for 6 h. Priorly to the reactions, the electrolyte was purged with CO₂ gas. A 100W LED lamp and chronoamperometric measurements (at -1.0 V vs Ag/AgCl) source were applied for photoelectron reactions. All experiments were performed with recirculation through the reservoir. More details are found in section 2.4 flow cell configuration.

References

1. P. B. Pati, R. Wang, E. Boutin, S. Diring, S. Jobic, N. Barreau, F. Odobel and M. Robert, *Nat. Commun.*, 2020, **11**, 3499.
2. E. H. Dias, G. T. S. T. Da Silva, J. C. Da Cruz and C. Ribeiro, *ChemElectroChem*, 2022, **9**(11), e202200206.
3. G. O. Larrazábal, A. J. Martín and J. Pérez-Ramírez, *J. Phys. Chem. Lett.*, 2017, **8**, 3933–3944.
4. Y. Arora, S. Battu, S. Haram and D. Khushalani, *Sci. Rep.*, 2018, **8**, 12752.