

## Supplementary Information

### Intensity Modulated Photocurrent Spectroscopy for solar energy conversion devices. What does negative value mean?

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#### **Experimental details:**

##### *BiVO<sub>4</sub> photoelectrodes synthesis*

BiVO<sub>4</sub> photoanodes were prepared by a two-step method previously reported in Ref.<sup>1</sup>, consisting in the electrodeposition on fluorine doped tin oxide (FTO) coated glass of metallic Bi from a Bi<sup>3+</sup> plating bath (20 mM Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (Sigma-Aldrich) in ethylene glycol), followed by deposition by drop casting of VO(acac)<sub>2</sub> (Sigma-Aldrich) in DMSO as vanadium precursor. The electrodeposition was carried out by passing a total charge of 0.32 C cm<sup>-2</sup>. The samples were annealed at 500°C for 2h and finally, the electrode was cleaned by soaking in a 1M NaOH solution for 30 min under vigorous stirring.

##### *Photoelectrochemical measurements:*

The photoelectrochemical measurements was performed on a three-electrode cell connected to a Autolab Potentiostat/Galvanostat PGSTAT302; were the BiVO<sub>4</sub>/FTO was the working electrode, an Ag/AgCl in 3 M KCl electrode and a Pt wire were used as reference and counter electrode respectively, and a 0.1 M potassium phosphate buffer at pH 7.5 was used as electrolyte. The applied potentials were referred to the Reversible Hydrogen Electrode (RHE) using the Nernst equation:  $V_{RHE} = V_{Ag/AgCl} + V_{Ag/AgCl}^0 + 0.059 \cdot pH$ . For measurements with constant and modulated illumination, a monochromatic LED ( $\lambda=470$  nm) from Philips LUMILEDS and controlled by a LED driver module coupled to the potentiostat, was used. The extracted photocurrent,  $j_e$ , was recorded from chronopotentiometry measurements for 60 seconds for each dc light illumination,  $j_\phi$ . For light intensities below 10 mA cm<sup>-2</sup>, the measurement was extended to 120 s. A Si photodiode was used to calibrate the range of dc light intensities, as well as the ac perturbation for modulated measurements, which in all cases was the 10% of the dc light intensity. IMPS measurements were carried out between 20 kHz and 0.01 Hz.

**Table S1.**  $EQE_{diff}$  values extracted from IMPS measurements at -0.05 V vs RHE and from the slope of steady-state values at the same voltage.

$j_{\phi}$	4.4 mA cm <sup>-2</sup>	36 mA cm <sup>-2</sup>
$EQE_{diff-IMPS}$	-0.00075	-0.00065
$EQE_{diff}$	-0.0015	-0.00073

## References

1. Safshekan, S.; Herraiz-Cardona, I.; Cardenas-Morcoso, D.; Ojani, R.; Haro, M.; Gimenez, S. Solar Energy Storage by a Heterostructured BiVO<sub>4</sub>-PbO<sub>x</sub> Photocapacitive Device. *ACS Energy Letters* 2017, 2 (2), 469-475.