

Supplementary Information

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

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Experimental details:

BiVO₄ photoelectrodes synthesis

BiVO₄ photoanodes were prepared by a two-step method previously reported in Ref.¹, consisting in the electrodeposition on fluorine doped tin oxide (FTO) coated glass of metallic Bi from a Bi³⁺ plating bath (20 mM Bi(NO₃)₃·5H₂O (Sigma-Aldrich) in ethylene glycol), followed by deposition by drop casting of VO(acac)₂ (Sigma-Aldrich) in DMSO as vanadium precursor. The electrodeposition was carried out by passing a total charge of 0.32 C cm⁻². 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 BiVO₄/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_ϕ . For light intensities below 10 mA cm⁻², 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_{ϕ}	4.4 mA cm ⁻²	36 mA cm ⁻²
$EQE_{diff-IMPS}$	-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 BiVO₄-PbO_x Photocapacitive Device. *ACS Energy Letters* 2017, 2 (2), 469-475.