

Supporting Information for

Direct observation of the chemical transformations in BiVO₄ photoanodes upon prolonged light-aging treatments

Ramón Arcas,^[a] Drialys Cardenas-Morcoso,^[b] Maria Chiara Spadaro,^[c] Miguel García-Tecedor,^[d] Camilo A. Mesa,^{*[a]} Jordi Arbiol,^[c,e] Francisco Fabregat-Santiago,^[a] Sixto Giménez,^{*[a]} and Elena Mas-Marzá,^{*[a]}

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- [a] R.Arcas, C.A.Mesa, S.Giménez, F.Fabregat-Santiago, E.Mas-Marzá
Institute of Advanced Materials (INAM) Universitat Jaume I
Av. Sos Baynat, s/n, 12006, Castelló, (Spain)
E-mail: cmesa@uji.es, sjulia@uji.es, emas@uji.es
- [b] D. Cardenas-Morcoso
Material Research and Technology (MRT) Department
Luxembourg Institute of Science and Technology (LIST)
41 Rue du Brill L-4422 Belvaux, (Luxembourg)
- [c] M.C.Spadaro, J.Arbiol
Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST
Campus UAB, Bellaterra, Barcelona, Catalonia, 08193, (Spain)
- [d] M.García-Tecedor
Unidad de Procesos Fotoactivados
Instituto IMDEA Energía
Avda. Ramón de la Sagra, 3 Parque Tecnológico de Móstoles E-28935 Móstoles, Madrid, (Spain)
- [e] J.Arbiol
ICREA
Pg. Lluís Companys 23, 08010 Barcelona, Catalonia, (Spain).

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1. Experimental section

Preparation of Zr doped BiVO₄ photoanodes

All reagents and solvents employed were purchased and used as received, without extra purification. Bismuth(III) nitrate pentahydrate ($\geq 98.0\%$), zirconyl chloride octahydrate (98.0%), Vanadium(IV)-oxy acetylacetonate (98.0%), Sodium hydroxide (pellets for analysis), Tetrabutylammonium perchlorate ($\geq 99.0\%$ electrochemical degree), Benzyl alcohol (anhydrous 99.8%), Ferrocene (98.0%), and Dimethylsulfoxide (anhydrous) were purchased from Sigma Aldrich; Acetonitrile (HPLC) were purchased from Scharlab. Fluorine-doped tin oxide (FTO)-coated glass slides were purchased from Hartford glass (sheet resistance 15 Ω/cm^2).

The synthesis and fabrication of 2.5 % zirconium doped BiVO₄ electrodes over fluorine-doped tin oxide (FTO) coated glass substrates were performed following a reported procedure.^[1] This method consists of electrodeposition of a Bi(NO₃)₃·5H₂O (20mM) and ZrCl₂O·8H₂O (0.5 mM) solution in ethylene glycol followed by drop-casting of a solution of VO(acac)₂ (0.15 M) in DMSO. The electrodes were calcined at 500°C for 2 h with a heating rate of 2 °C·min⁻¹. Finally, the excess of V₂O₅ was removed by immersing the electrodes in a KOH 1 M solution for 20-30 min.

Prolonged light-aging treatments.

The BiVO₄ photoelectrodes were illuminated for 48 h directly using an ozone-free 300 W Xenon (Xe) lamp under ambient conditions. Note that, during the light-aging treatment the photoelectrode is exposed to ambient conditions, without being in contact to the electrolyte. We termed this process as Light-Aging treatment (LA). The power of the lamp was calibrated to 100 mW·cm⁻² or 300 mW·cm⁻², corresponding to 1 sun (1LA-BiVO₄) and 3 sun (3LA-BiVO₄) irradiated samples, respectively.

Morphological and structural characterization.

Field Emission Scanning Electron Microscopy (SEM) was performed with a JSM-7000F JEL FEG-SEM system (Tokyo, Japan) equipped with an INCA 400 Oxford EDS analyzer (Oxford, U.K.) and operating at 25 kV. Raman spectroscopy was carried out with a WiTec apyron system, equipped with a 300 mm focal length UHTS 300 spectrometer system. The scanned area of combined spectra was 40 x 24 μm^2 with a laser power of 2 mW and an integration time of 0.5 s. The crystalline structure of BiVO₄ was assessed by X-ray diffraction (XRD) collected on a Rigaku Miniflex 600, (Rigaku Corporation, Tokyo, Japan) with copper K α radiation ($\lambda = 1.5418 \text{ \AA}$) operating at a grazing incidence of 1°, at a scan rate of 3° min⁻¹. High-resolution transmission electron microscopy (HRTEM) together with scanning transmission electron microscopy (STEM) investigation was performed on a field emission gun FEI Tecnai F20 microscope at 200 kV with a point-to-point resolution of 0.19 nm. High angle annular dark-field (HAADF) STEM was combined with electron energy loss spectroscopy (EELS) in the Tecnai F20 microscope by using a GATAN QUANTUM energy filter. To prepare the TEM samples, a BiVO₄ photoanode was scratched and the obtained powder was deposited on a TEM grid. After deposition, the grid was illuminated at 1 sun following the same procedure to perform the light treatment in 1LA-BiVO₄.

(Photo)electrochemical characterization.

Cyclic voltammetry (CV) and Impedance Spectroscopy (IS) measurements were performed on a PGSTAT302N potentiostat (Metrohm-Autolab, The Netherlands). The photoelectrochemical cell consisted of a one-compartment, three-electrode configuration quartz cell. Non-aqueous Ag/AgNO₃ electrode (ALS, Japan) and a platinum foil (25x25 mm, 0.1 mm thick, Alfa Aesar) were employed as reference and counter electrodes respectively, while a 0.1 M tetrabutylammonium perchlorate (TBAClO₄) in CH₃CN solution served as non-aqueous electrolyte. An ozone-free 300 W Xenon (Xe) lamp calibrated with a thermopile to 100 mW·cm⁻² was used for the photoelectrochemical experiments. CV measurements were carried out at 50 mV·s⁻¹. IS measurements were performed at selected applied bias with a sinusoidal perturbation of 20 mV and a frequency range from 100 kHz to 50 mHz. We have homogenized all potentials against NHE when measurements are performed in an organic electrolyte and against RHE when measurements are performed in water. For this purpose, we estimate the $E_{1/2}$ of the Ferrocene/Ferrocinium couple redox peak (see Figure S1) in our experimental conditions (in organic electrolytes) and compare with the reported $E_{1/2}$ (0.4V vs NHE).^[2,3] Finally, the Nernst equation was employed to normalize aqueous systems following equation 1.

$$V_{RHE} = V_{Ag/AgCl} + V_{Ag/AgCl}^0 + 0.059 \cdot pH \quad \text{Eq.1}$$

Infra-red (IR) photoelectrochemical characterization.

Chronoamperometry measurements under IR were performed using a mobile PalmSens3 potentiostat (Compact electrochemical interfaces). For these measurements, identical experimental conditions as those described above were employed. An infrared diode laser (MDL-III-980-2W) from Roithner LaserTechnik (980 nm ± 5 nm, 2 W cw, stability < 5%, beam aperture of 5 x 8 mm²) was employed to illuminate the BiVO₄ photoanodes, focusing the beam as close as possible to the photoanode. Manual chopping was carried out.

2. Cyclic voltammetries measurements

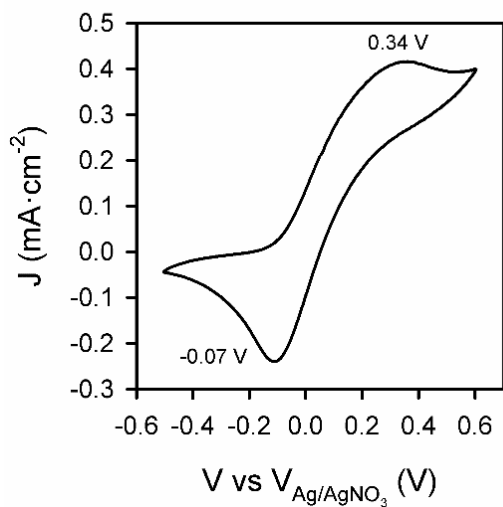


Figure S1. Cyclic voltammetry peak of Ferrocene/Ferrocenium (Fc/Fc⁺). 1.9 mM of ferrocene was used to calibrate the applied voltage to the normal hydrogen electrode (NHE). Conditions: 100 mM of benzyl alcohol, in 0.1 M TBAClO₄ in CH₃CN, using BiVO₄ as WE, Pt film as CE, and Ag/AgNO₃ as RE.

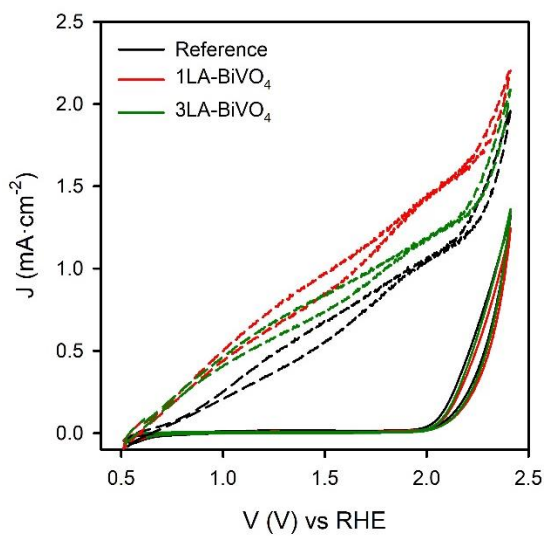


Figure S2. CV of Reference (black) and 1LA-BiVO₄ (red) measured at scan rates of 20 mV·s⁻¹ in a 0.1M KPi buffered aqueous solution (pH 7.8) in the dark (solid lines) and under 100 mW·cm⁻² illumination (dashed lines).

3. Morphological and structural characterisation data (SEM, DRX, TEM, SAED and STEM-EELS)

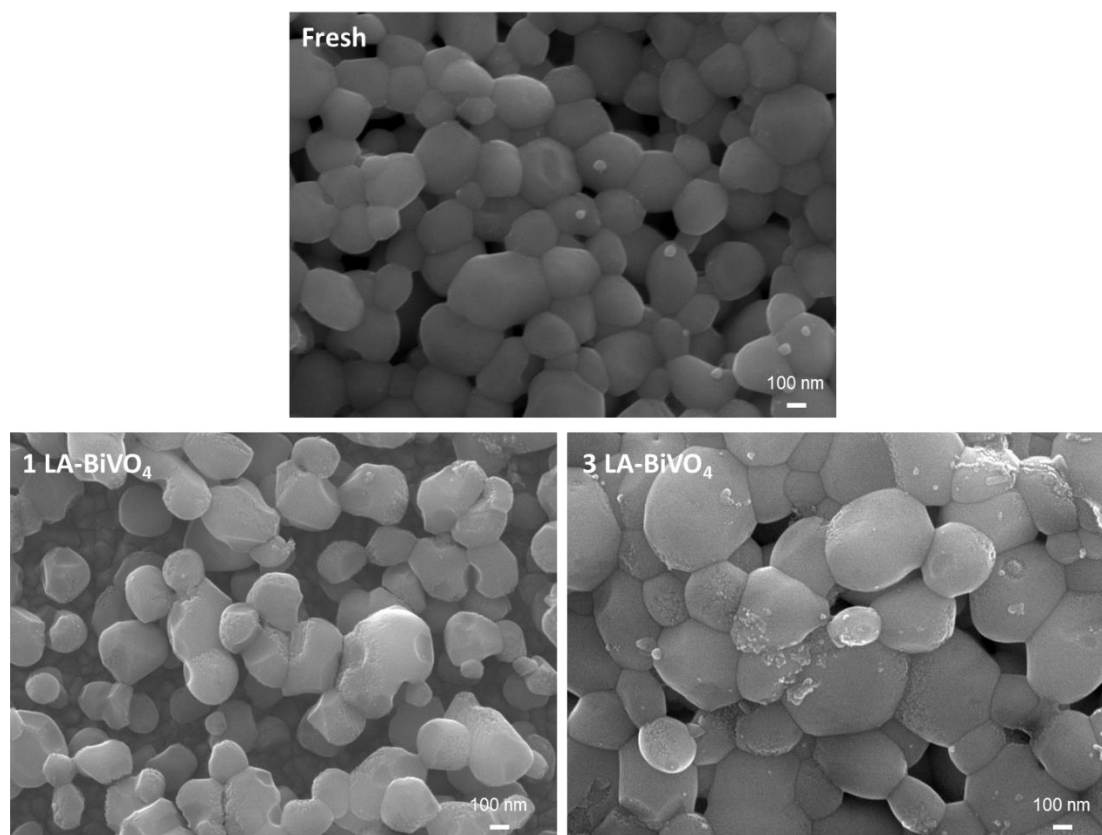


Figure S3. Top-view SEM images of Reference, 1LA-BiVO₄ and 3LA-BiVO₄ samples.

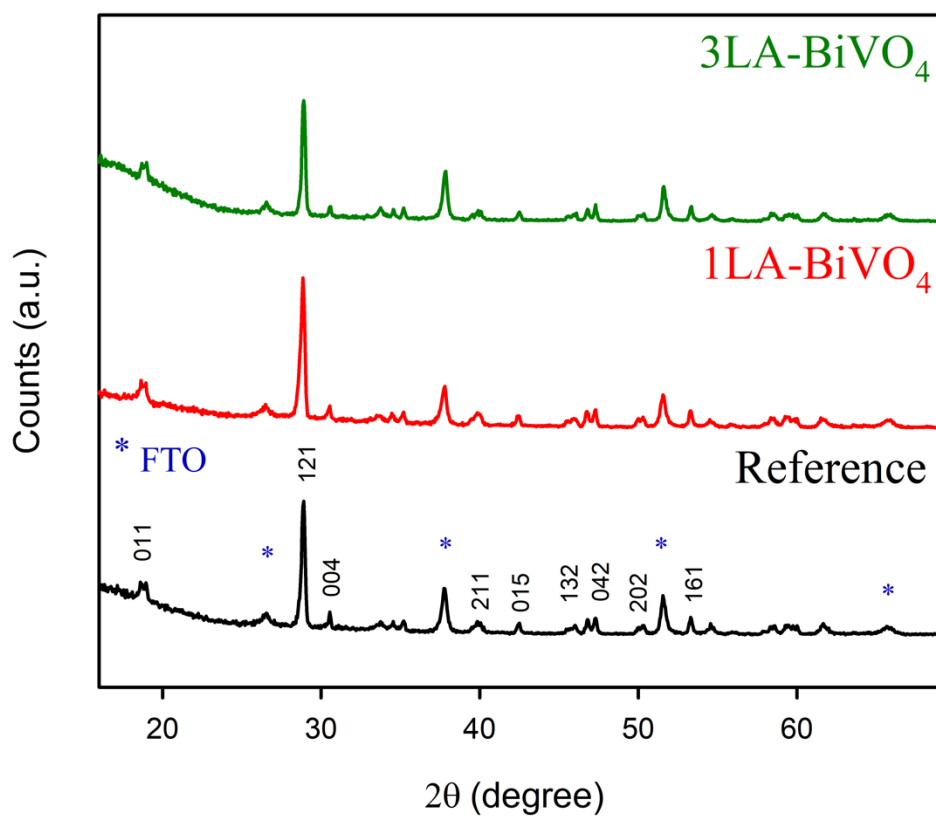


Figure S4. XRD spectra for Reference (black), 1LA-BiVO₄ (red) and 3LA-BiVO₄ (green) photoanodes.

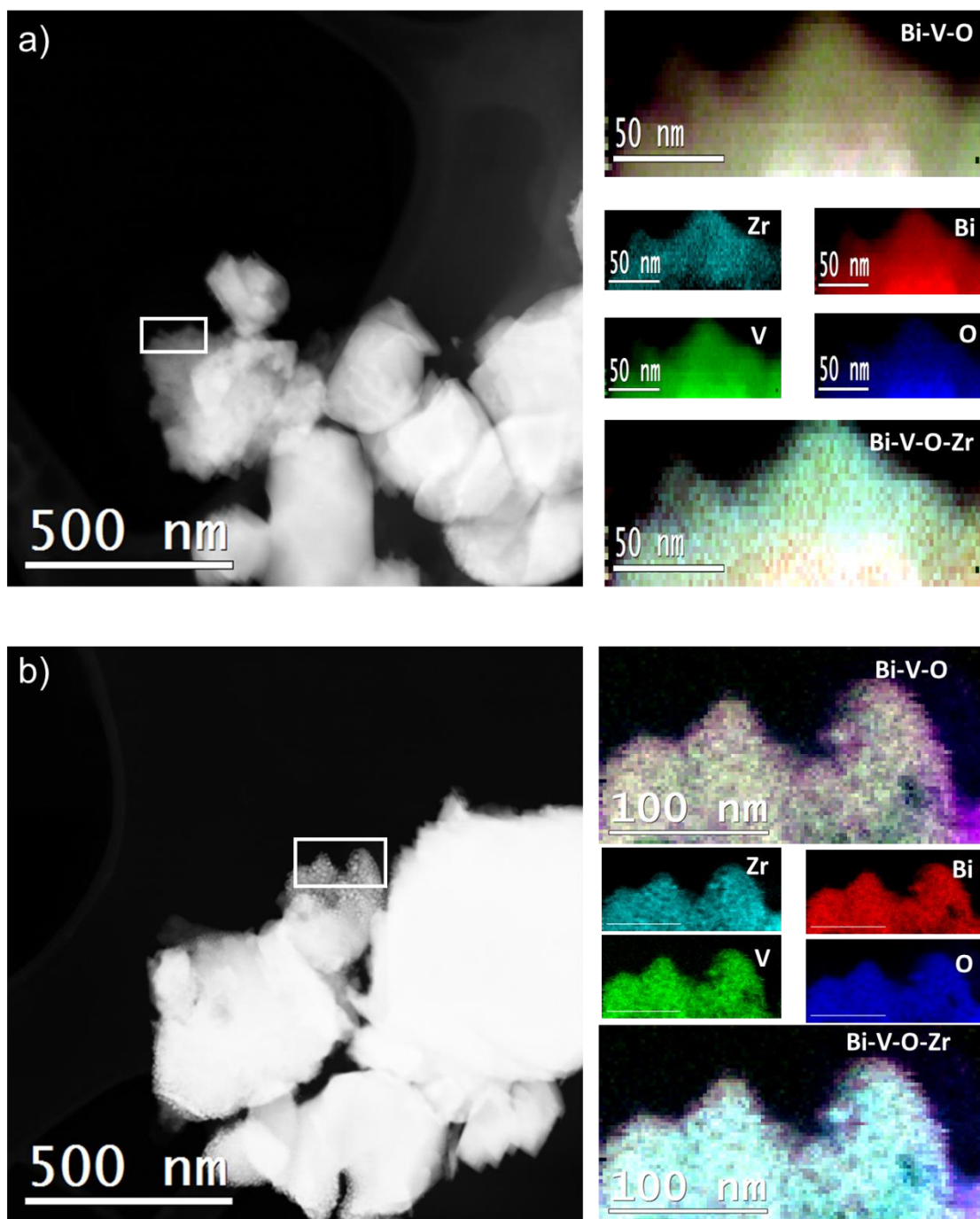


Figure S5. STEM-EELS measurements of Zr, Bi, V and O of a BiVO_4 section in (a) Reference and (b) 1LA- BiVO_4 samples.

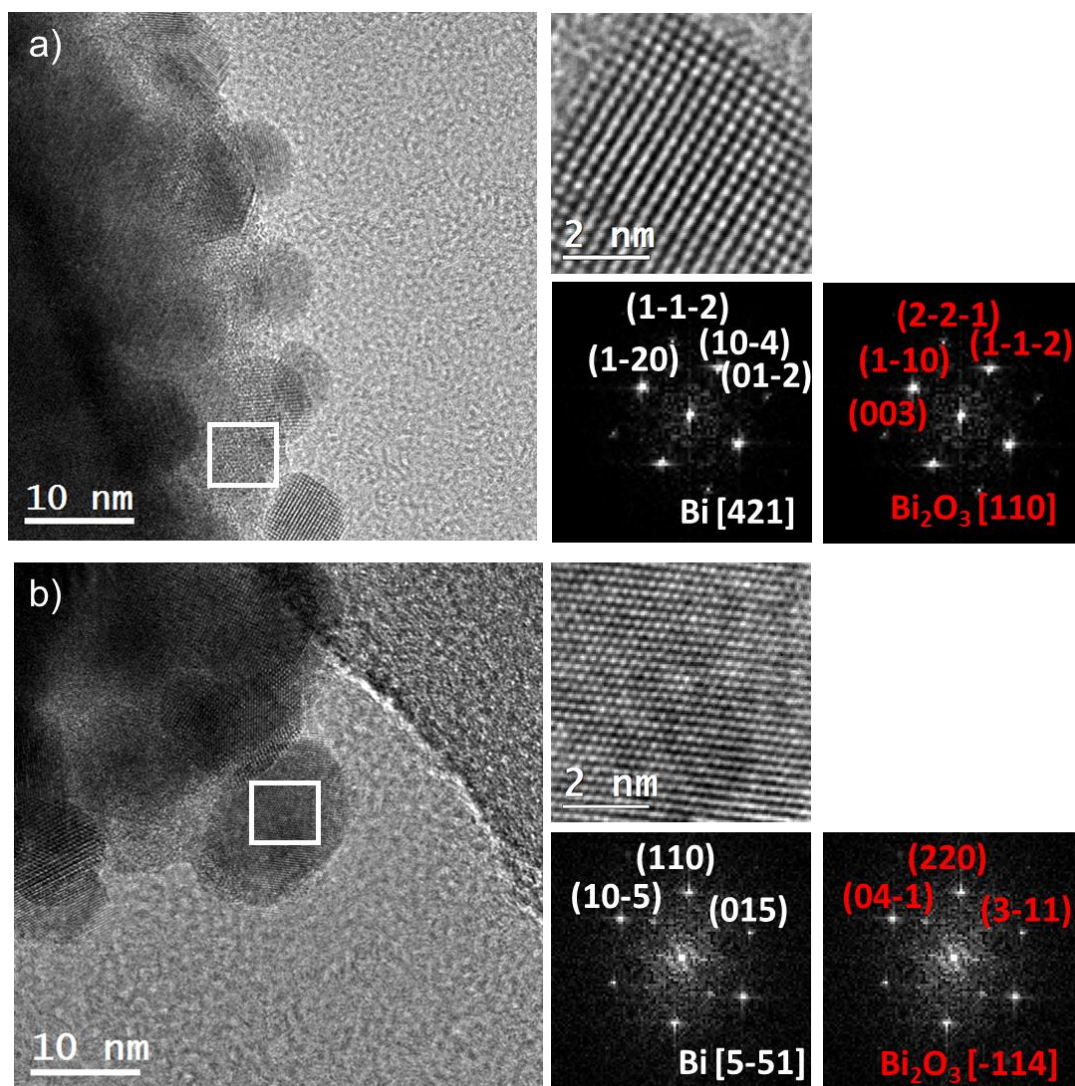


Figure S6. HRTEM images evidencing the particle segregation after electron beam irradiation of BiVO_4 samples. The power spectra analysis confirms that two possible structures consisting of metallic Bi or Bi_2O_3 could be possible and compatible with the structural indexation of the power spectra obtained on the HRTEM image.

The migration of atomic species from the bulk forming new particles at the surface of the BiVO_4 can be visualized at [10.5281/zenodo.5643642](https://zenodo.org/doi/10.5281/zenodo.5643642).

4. Electrochemical characterisation by impedance spectroscopy

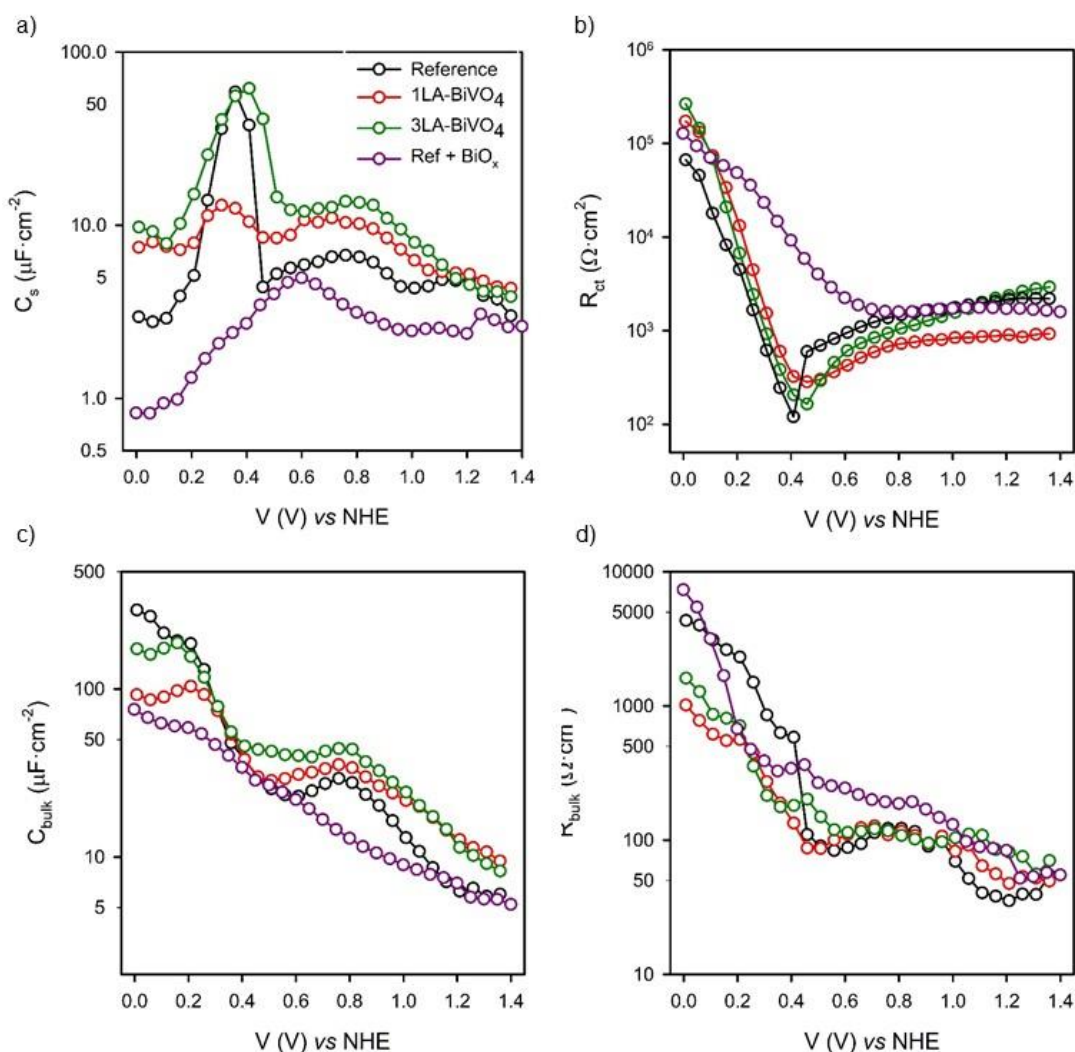


Figure S7. Impedance spectroscopy parameters extracted from fitting the experimental data with the selected equivalent circuit showed in Figure 3, (a) surface capacitance, C_s (b) charge transfer resistance, R_{ct} (c) bulk capacitance, C_{bulk} and (d) bulk resistance, R_{bulk} in BiVO_4 as a function of the light intensity during LA. Reference (Black), 1LA- BiVO_4 (Red), 3LA- BiVO_4 (Green), Reference with electrodeposited BiO_x on top (purple). Measurements were performed under illumination at 0.1 M benzyl alcohol oxidation conditions

Coating the fresh BiVO_4 with electrodeposited bismuth species yields to the suppression of surface states associated to charge transfer Figure S7a and to an increase in R_{ct} in Figure S7b. The Bi coating seems to hinder the contribution of OV_s to C_{bulk} in Figure S6c.

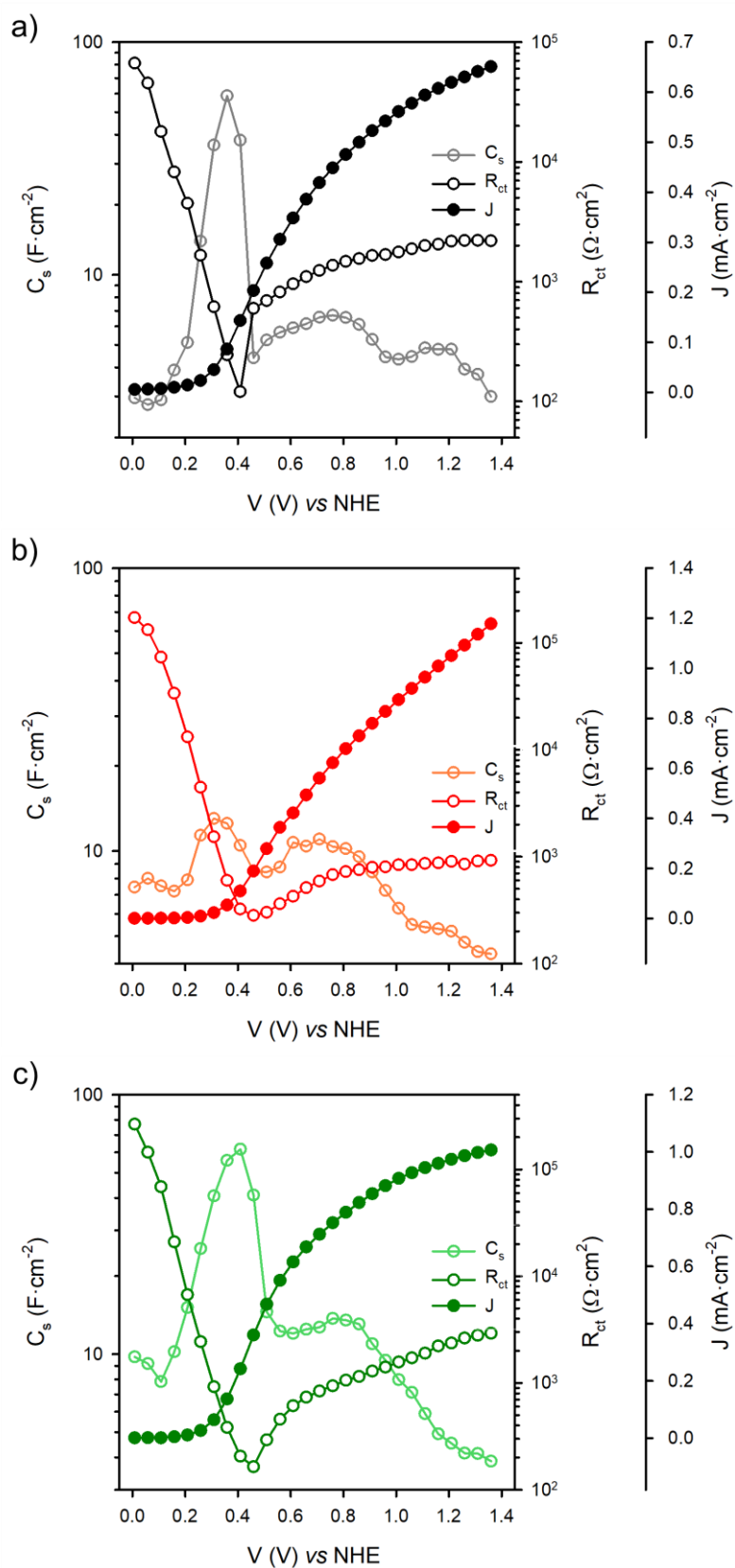


Figure S8. Comparison of C_s , R_{ct} and the J-V as a function of the applied potential for (a) Reference (Black), (b) 1LA-BiVO₄ (red) and 3LA-BiVO₄ (green). Measurements were performed under illumination at 0.1 M benzyl alcohol oxidation conditions.

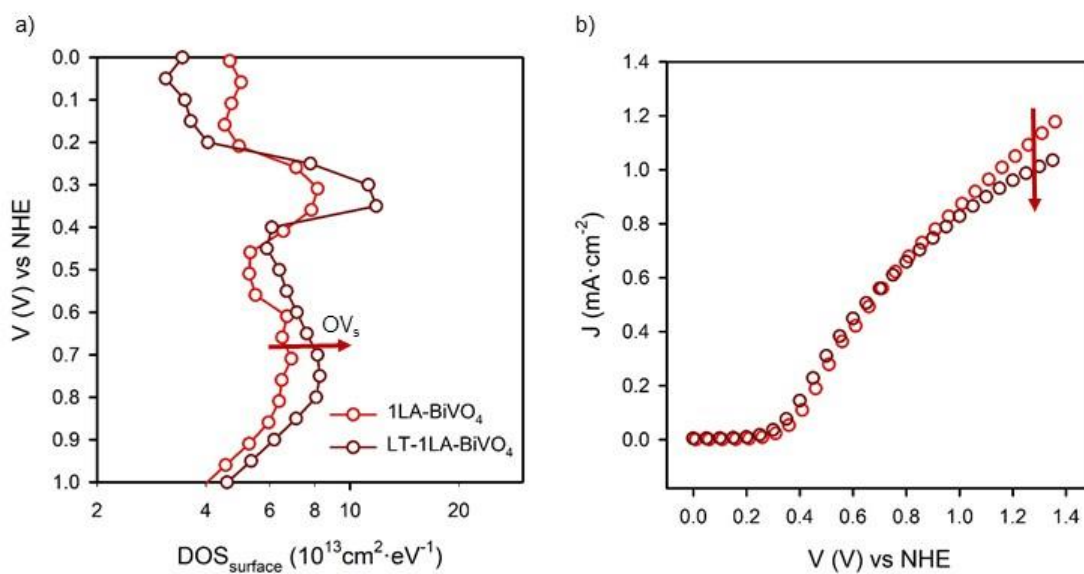


Figure S9. (a) Density of surface states and (b) Steady-state photocurrent as a function of applied potential. 1LA-BiVO₄ (Red) and LT-1LA-BiVO₄ (Maroon)

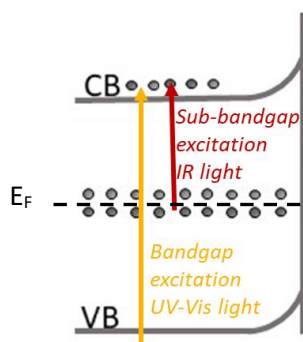


Figure S10. Schematic representation of the light-induced processes in a semiconductor upon bandgap excitation (yellow) using UV-Vis radiation, compared to sub-bandgap excitation (red) upon IR irradiation.

5. References

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- [2] V. V Pavlishchuk, A. W. Addison, *Inorganica Chim. Acta* **2000**, 298, 97–102.
- [3] A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, **2009**.