SUPPORTING INFORMATION

Unravelling the bulk and interfacial charge transfer effects of molybdenum doping in BiVO₄ photoanodes

Annalisa Polo[a], Ivan Grigioni[a], Mirko Magni[b], Anna Facibeni[c], Maria Vittoria Dozzi[a,*], Elena Selli[a]

[a] *Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, I-20133 Milano, Italy*

[b] *Dipartimento di Scienze e Politiche Ambientali, Università degli Studi di Milano, via Celoria 2, I-20133, Milano, Italy*

[c] *Dipartimento di Energia, Politecnico di Milano, Via Ponzio 34/3, I-20133 Milano, Italy*

*E-mail address: mariavittoria.dozzi@unimi.it

1. Structural characterization of the films
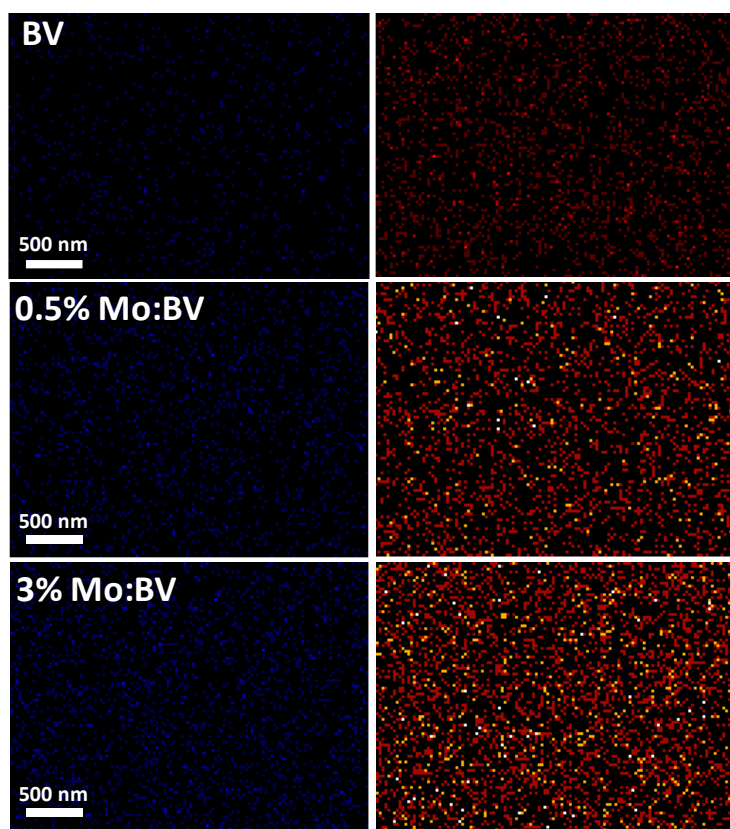
Energy-dispersive X-ray spectroscopy (EDX)

Figure S1. *Energy-dispersive X-ray spectroscopy (EDX) images of pure, 0.5 at% and 3 at% Mo⁶⁺ doped BiVO₄ films. Red, Blue and yellow colours refer to Bi, V and Mo elements, respectively.*

2. Electrochemical characterization of the films

Electrochemical active surface area

Many parameters describing the performance of electrodes (including the PEC performance) are referred to the geometric area of the irradiated spot of the electrode in contact with the electrolyte. Nevertheless, the geometric area (A_g) is simply the projection on a plane (parallel to the macroscopic phase boundary of the electrode) of the real surface area (A) actually involved in any PEC process. These two entities are related each other by the linear relationship $A = A_g \cdot f_r$, where f_r is the roughness factor [1].

Especially when comparing the activities of electrodes exhibiting substantial differences in morphology or structure, as it is the case for the examined Mo^{6+} doped $BiVO_4$ (BV) photoanodes, the calculation of the real surface area is necessary for a correct interpretation of the observed results. An effective *in situ* approach to estimate the real surface area of the films is provided by the electrochemical active surface area (ECSA) obtainable from the capacitive current (*i.e.*, the non Faradic one) associated with the charging and discharging of the double layer built at the electrode/electrolyte interface [1–3].

A valuable way to measure the capacitive current is through cyclic voltammetry (CV) [1], by properly selecting a narrow potential window (a few tens of millivolt), centred around the open circuit potential (OCP) of the investigated system, in which no Faradic process can take place. Under this hypothesis, the recorded current is only capacitive (I_c) and it depends linearly on the potential sweep rate (v) according to $I_c = C_{DL} \cdot v$, where C_{DL} represents the double layer capacitance of the interface and corresponds to the ECSA$\cdot C_s$ product, with C_s being the intrinsic specific capacitance of the semiconductor material (typically in the 15-130 $\mu F\ cm^{-2}$ range [2]).

Specifically, such measurements were performed with the investigated electrodes in the dark, using the same cell configuration with a geometric area of 0.7 cm^2. For each of the tested electrodes, four consecutive CV traces, centred around the OCP and spanned over a narrow potential window (between

–0.05 V and +0.05 V *vs.* OCP) were recorded at six different potential scan rates, ranging from 0.005 to 0.075 V s^{-1}, as shown in Figure S2 for the pure BiVO$_4$ sample.
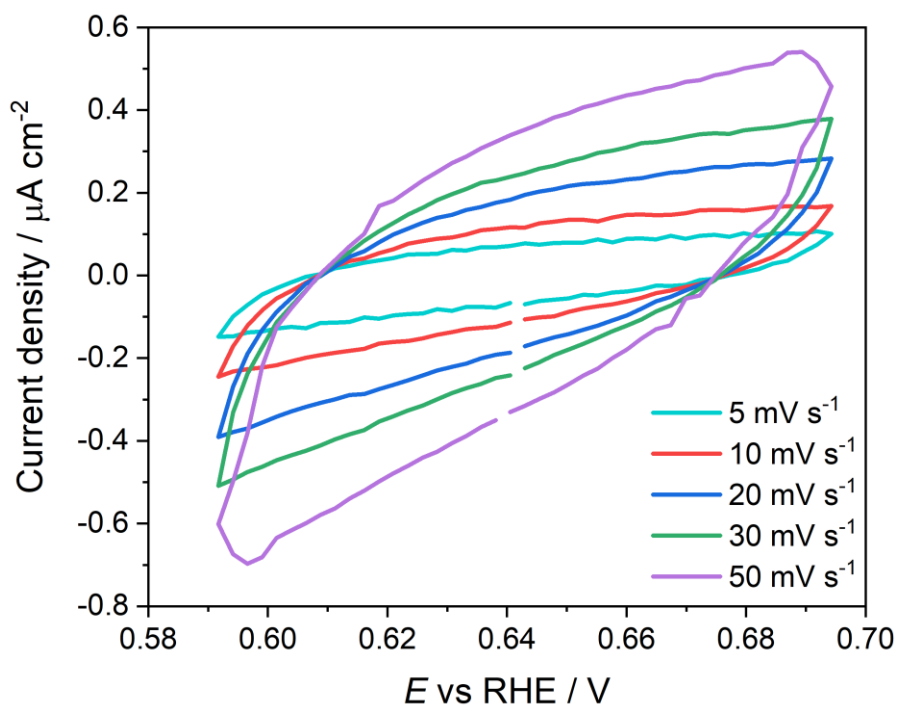

Figure S2. *Cyclic voltammetry relative to the pure BiVO$_4$ electrode recorded in the range between –0.05 and +0.05 V vs. OCP, at different potential scan rates (ranging from 5 to 50 mV s^{-1}).*

Unfortunately, the specific capacitance for BiVO$_4$ is not known in the open literature. Moreover, by considering that pretty low f_r can be obtained from these measurements by using a C_s value of 60 μF cm^{-2} (as generally reported for metal oxides-based materials [4]) and that the actual determination of the absolute ECSA value for each electrode is out of our scope, *relative* ECSA values were determined for an internal comparison purpose, assuming that the small amount of added Mo^{6+} does not significantly affect the charging mechanism of the oxide material.
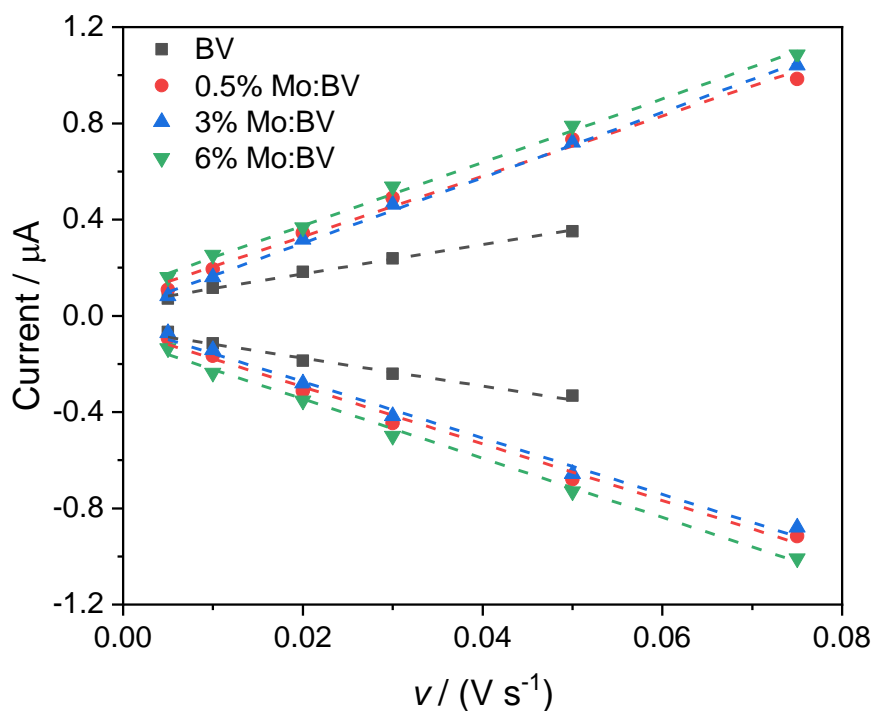
Figure S3. *Capacitive anodic and cathodic current values recorded with the pure, 0.5 at%, 3 at% and 6 at% Mo^{6+} doped BV electrodes in a N$_2$-purged 0.5 M Na$_2$SO$_4$ solution, as a function of the potential scan rates (ranging from 0.005 to 0.075 V s^{-1}). The reported current values were extrapolated at the open circuit potential (OCP) value from the corresponding cyclic voltammetry scans recorded in the range between –0.05 and +0.05 V vs. OCP.*

In particular, relative ECSA values were thus obtained by evaluating the ratio between the C_{DL} slope attained for each investigated sample respect to pure BiVO$_4$. Such C_{DL} parameter is obtained as an average of the slopes (expressed as absolute value) obtained for the anodic and cathodic branches of the straight lines interpolating the recorded I_c values as a function of v, with I_c read in the middle of the CV potential window on the anodic and cathodic scan, respectively (see Figure S3). The so obtained relative electrochemical active surface area values (ECSA$_{rel}$) are collected in Figure 1c of the main text.

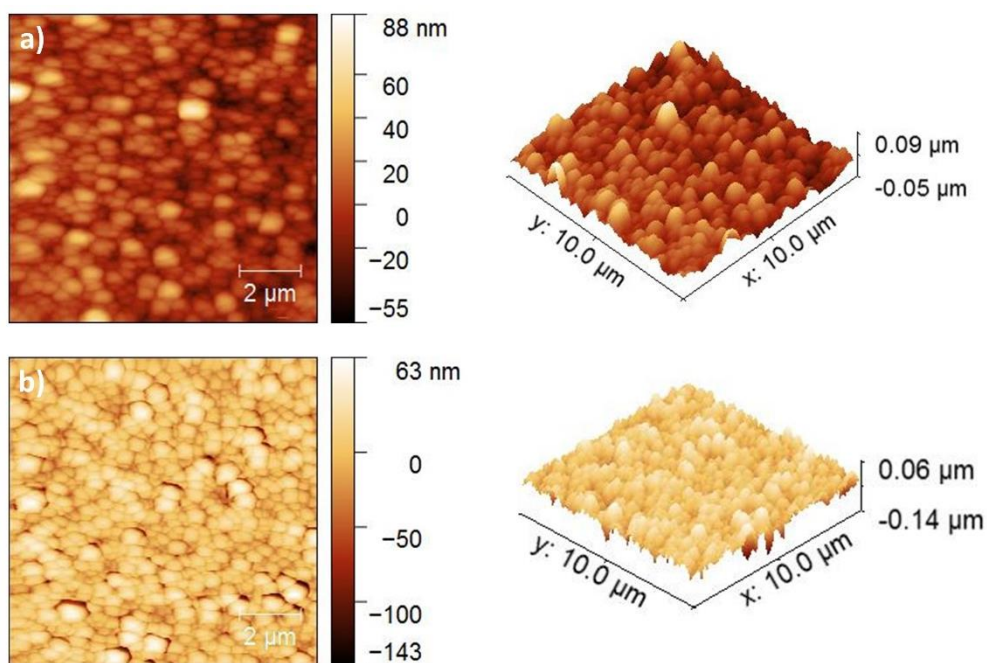# 3. Morphological characterization of the films

Atomic force microscopy

Figure S4. *Atomic force microscopy (AFM) surface topography of the (a) pure BV and (b) 6% Mo:BV films.*

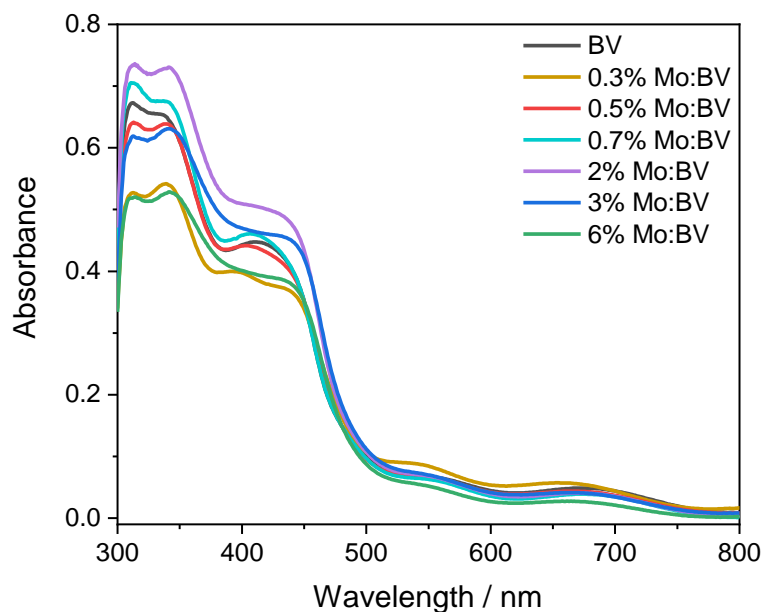# 4. Optical characterization of the films

UV-vis absorption spectra

Figure S5. *UV-vis absorption spectra of all synthesized films recorded in the transmittance mode.*

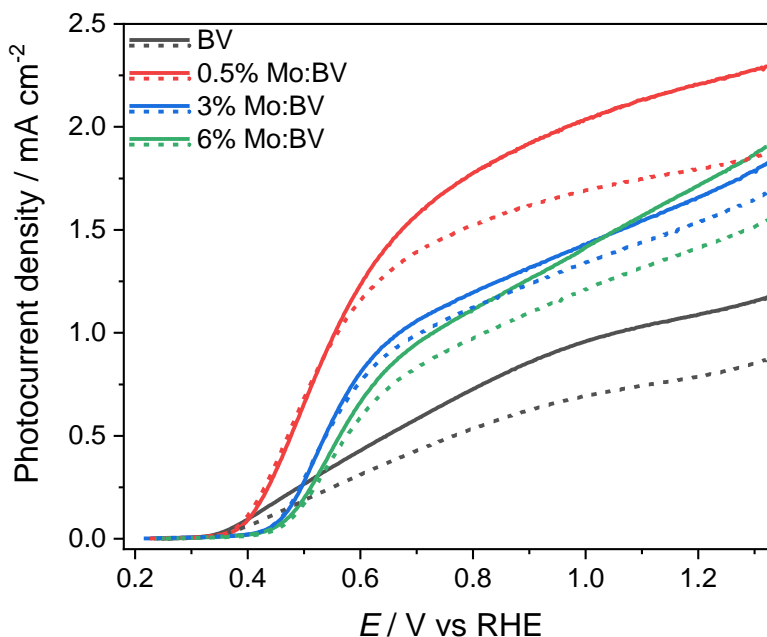# 5. Photoelectrochemical performance

Sulfite oxidation

Figure S6. *Comparison between the LSV curves recorded under back- (continuous lines) and front-side (dashed lines) irradiation with selected electrodes, in 0.5 M Na₂SO₃ solution buffered at pH 7 with 0.5 M potassium phosphate.*
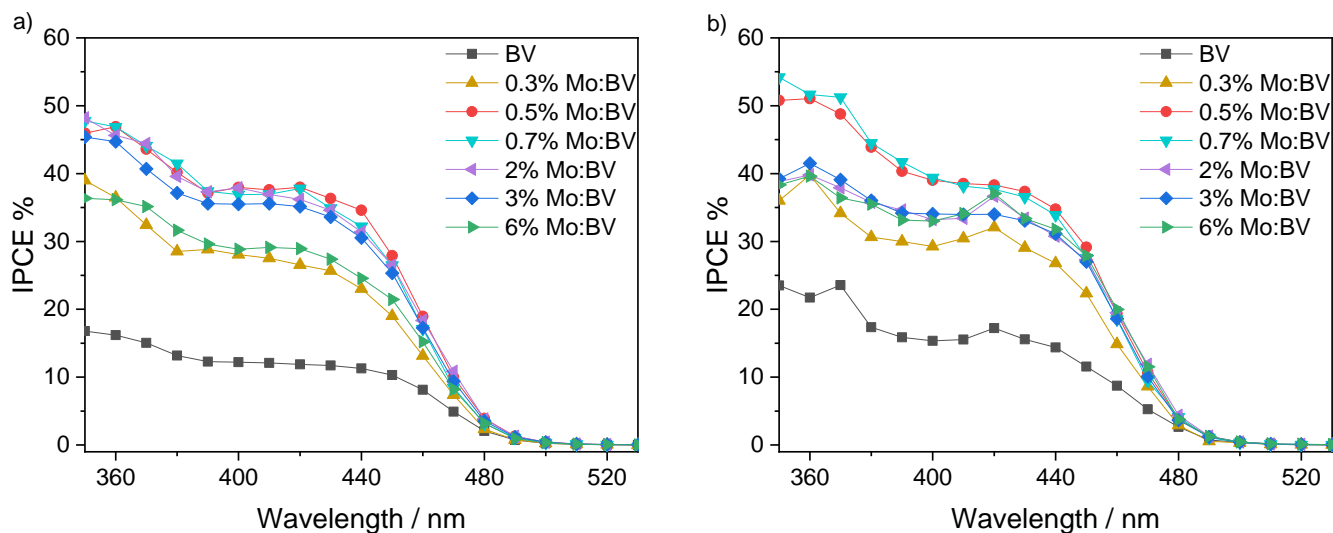

Figure S7. *Incident photon to current efficiency (IPCE) analyses recorded at 1.0 V vs. RHE under (a) front-side and (b) back-side irradiation with all investigated electrodes in 0.5 M Na₂SO₃ solution buffered at pH 7 with 0.5 M potassium phosphate.*
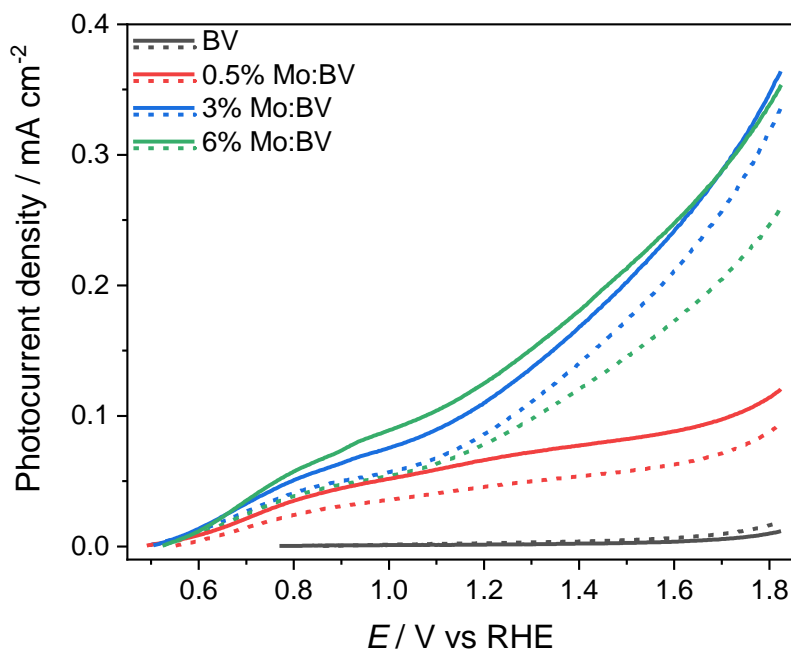
Water oxidation

Figure S8. *Comparison between the LSV curves recorded under back- (continuous lines) and front-side (dashed lines) irradiation with selected electrodes, in 0.5 M Na_2SO_4 solution (pH 7).*

References

[1] S. Trasatti, O.A. Petrii, Real surface area measurements in electrochemistry, Pure Appl. Chem. 63 (1991) 711–734. https://doi.org/10.1351/pac199163050711.

[2] C.C.L. McCrory, S. Jung, J.C. Peters, T.F. Jaramillo, Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction, J. Am. Chem. Soc. 135 (2013) 16977–16987. https://doi.org/10.1021/ja407115p.

[3] G.L. Chiarello, M. Bernareggi, M. Pedroni, M. Magni, S.M. Pietralunga, A. Tagliaferri, E. Vassallo, E. Selli, Enhanced photopromoted electron transfer over a bilayer WO_3 n–n heterojunction prepared by RF diode sputtering, J. Mater. Chem. A 5 (2017) 12977–12989. https://doi.org/10.1039/C7TA03887A.

[4] Q. Shi, S. Murcia-López, P. Tang, C. Flox, J.R. Morante, Z. Bian, H. Wang, T. Andreu, Role of Tungsten Doping on the Surface States in $BiVO_4$ Photoanodes for Water Oxidation: Tuning the Electron Trapping Process, ACS Catal. 8 (2018) 3331–3342. https://doi.org/10.1021/acscatal.7b04277.