Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting information

Unveiling the contribution of singlet oxygen in the photoelectrochemical oxidation of benzyl alcohol

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1. Zr decorated $BiVO_4$ photoanodes characterization

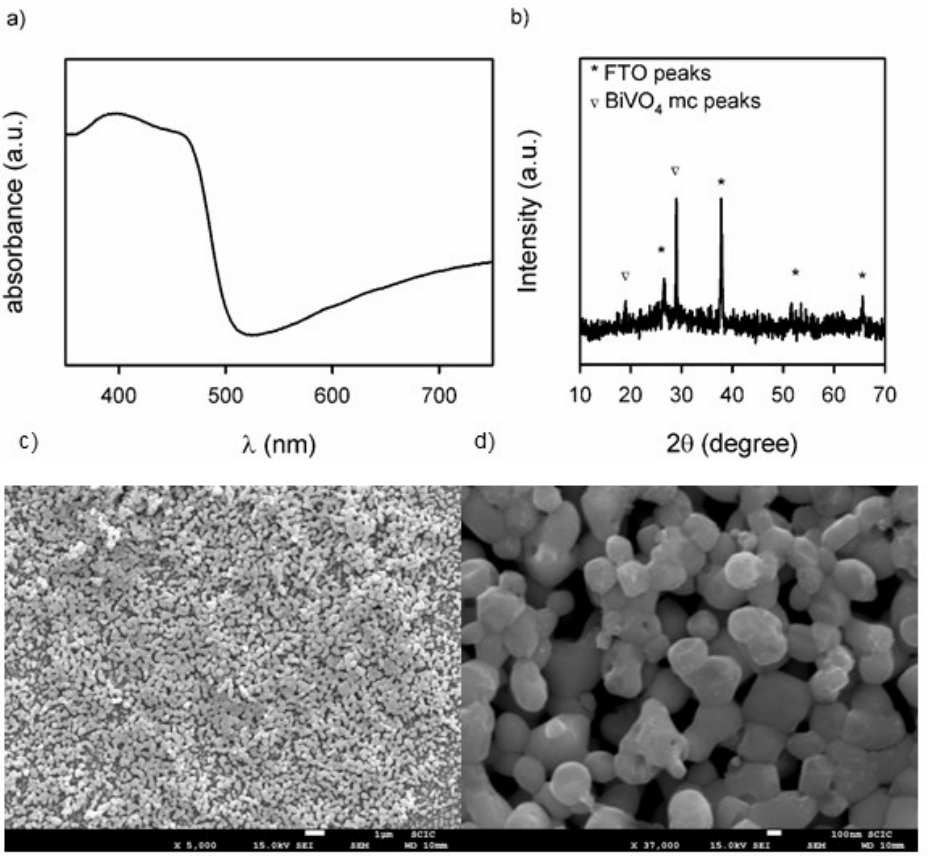


Figure S1. Optical and structural characterization of Zr decorated $BiVO_4$ photoanodes. a) UV-vis Absorption. b) XRD data. c) and d) SEM images.

2. Ferrocene/Ferrocenium (Fc/Fc^+) couple used as an internal reference

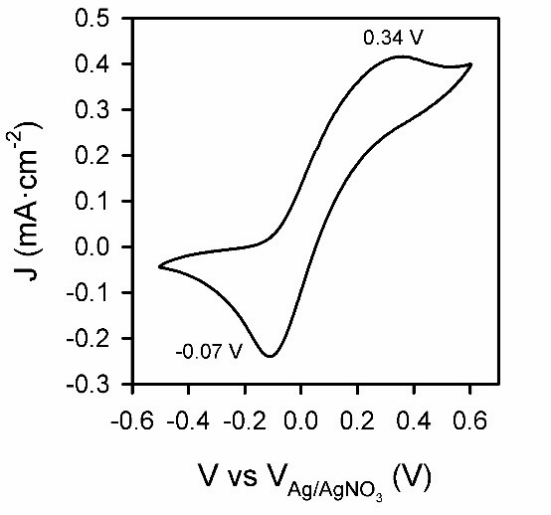


Figure S2. Cyclic voltammetry peak of Ferrocene/Ferrocenium (Fc/Fc^+). 2mM of ferrocene was used to calibrate the voltage of the reference electrode. Conditions: 100 mM of benzyl alcohol (**1**), in 0.1 M $TBAClO_4$ in CH_3CN, using Zr decorated BiVO4 as WE, Pt film as CE, and $Ag/AgNO_3$ as RE.

3. Effect of water in photoelectrochemical measurements

The effect of water in the CV measurements is shown in Figure S3. Experimental conditions: cyclic voltammetry in 0.1 M $TBAClO_4$ CH_3CN solution, Zr decorated $BiVO_4$ as WE, Pt as CE and $Ag/AgNO_3$ as RE, illumination with an ozone-free Xe lamp 100 $mW \cdot cm^{-2}$. In dry condition the solvent was dried, $TBAClO_4$ was dried by heating at 80ºC for 2 days and Zr decorated $BiVO_4$ was pre-heated at 300ºC for 6 days. In not dried condition, the solvent and $TBAClO_4$ were obtained from ambient conditions, without previous treatment, and the Zr decorated $BiVO_4$ was the same sample used previously under dry condition. In not dried conditions there is an increase of the photocurrent due to the oxidation of water.

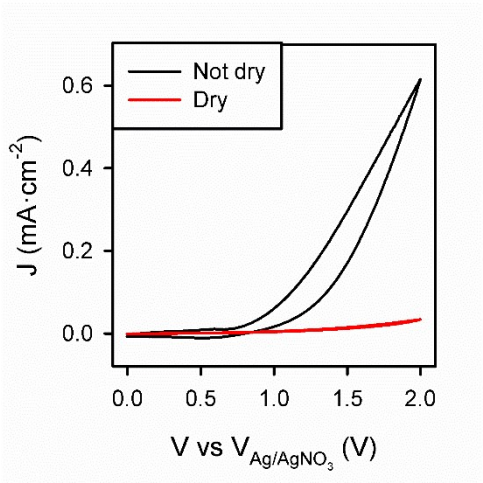


Figure S3. Cyclic voltammetry measurements, humid and dried electrolyte (black and red line, respectively).

4. Electrocatalytic oxidation of benzyl alcohol (1) with Pt and $BiVO_4$ electrodes in dark

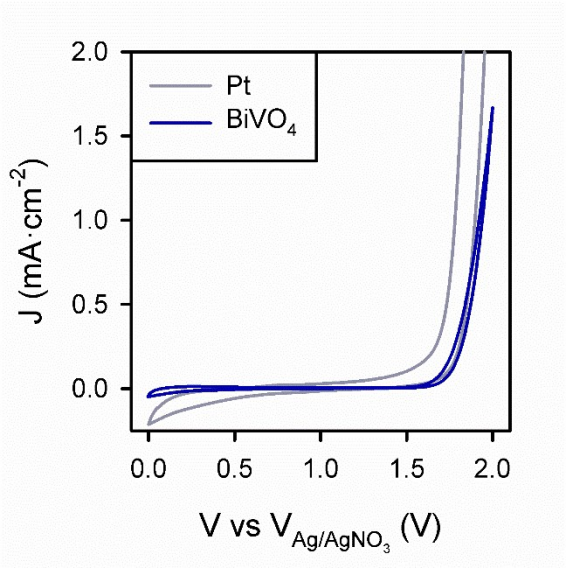
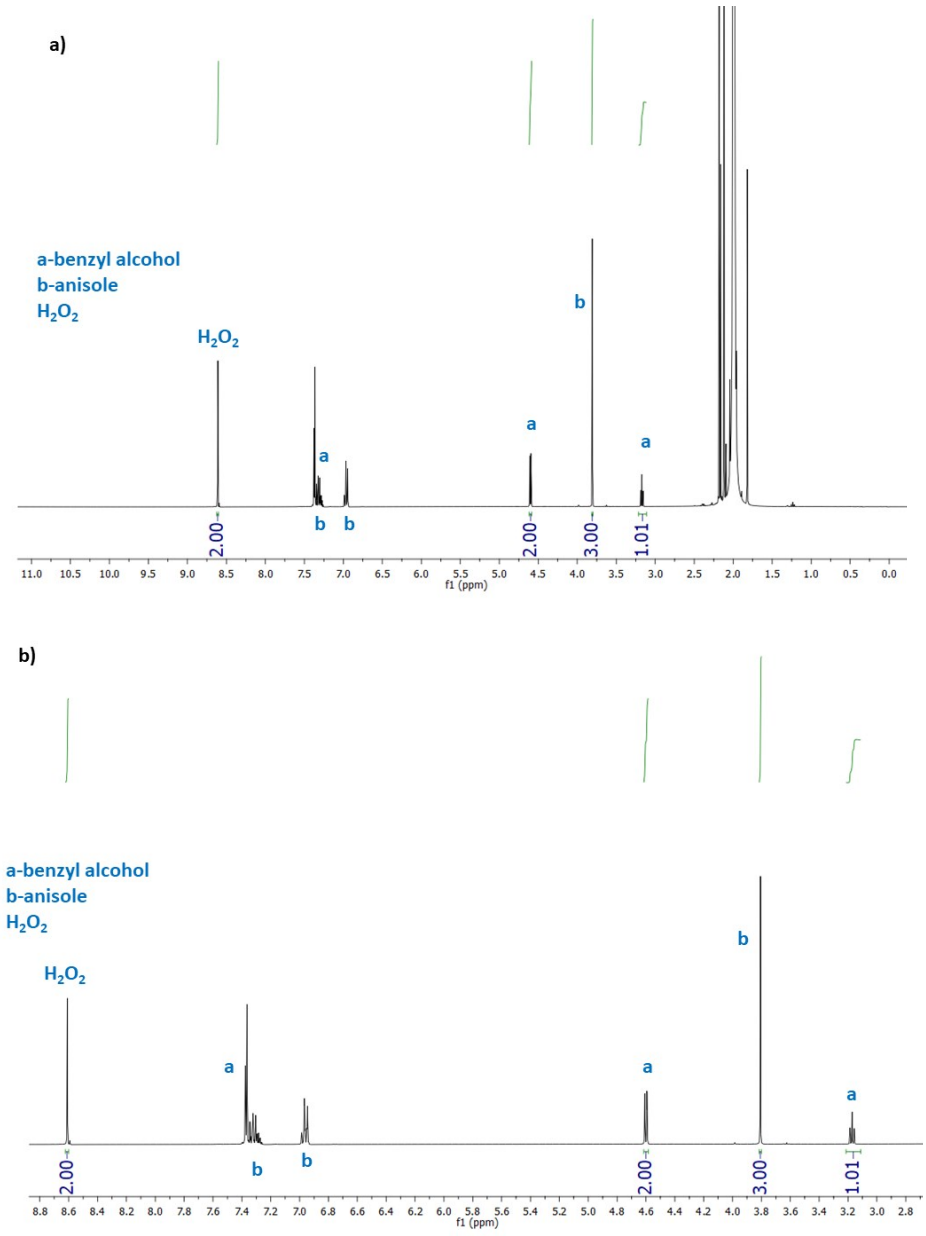


Figure S4. Cyclic voltammetry, of (**1**), using Pt (grey) or Zr decorated $BiVO_4$ (blue) as WE electrodes in the dark. The photoelectrode response for the oxidation of **1** is not so far from the one obtained using Pt as WE. Conditions: 100 mM of **1**, in 0.1 M $TBAClO_4$ in CH_3CN, using Pt film as CE and $Ag/AgNO_3$ as RE.

5. Detection and quantification of H_2O_2

Detection and quantification of H_2O_2 were done by ^1H NMR. The signal of H_2O_2 in the ^1H NMR spectrum of the chronoamperometry experiments was assigned by comparison with the signal of pure H_2O_2 in the same deuterated solvent. The quantification was done using anisole as an integration reference standard.



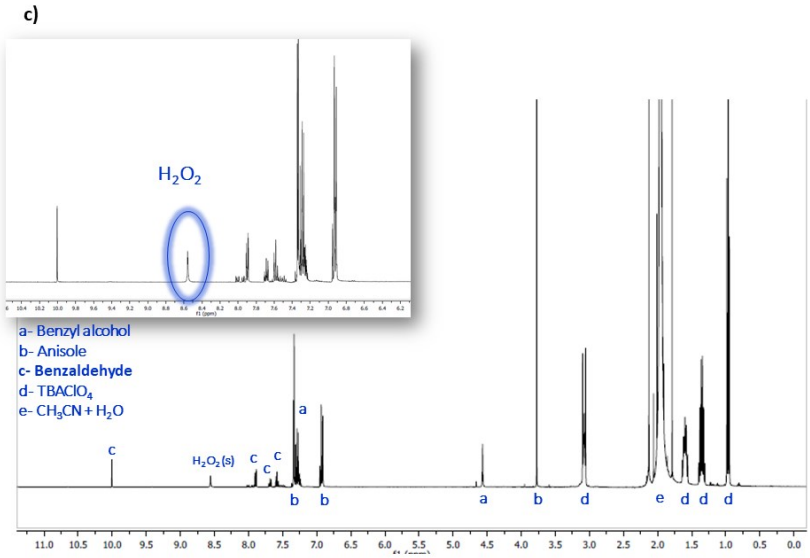


Figure S5. a) and b)[1]H NMR of H_2O_2, benzyl alcohol and anisole, in a molar ratio 1:1:1, in CD_3CN. From this data, it can clearly be observed the signal for H_2O_2, and its integration using anisole as an integration reference standard; c) [1]H NMR of a chronoamperometry experiment at V_{oc}, where H_2O_2 can be detected and quantified.

6. Cyclic voltammetry of benzyl alcohol (1) using Zr decorated BiVO4 as WE under visible light

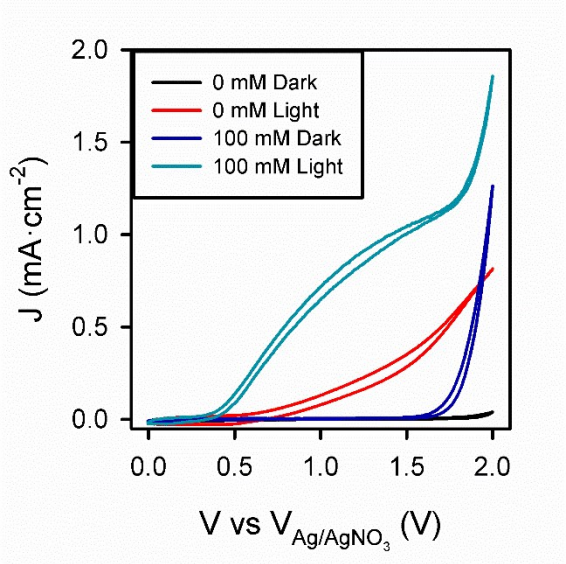


Figure S6 Cyclic voltammetry in dark or illuminating only with visible light, in the absence or presence of **1** (100 mM), in 0.1 M $TBAClO_4$ in CH_3CN, using Zr decorated $BiVO_4$ as WE, Pt film as CE and $Ag/AgNO_3$ as RE,

7. Effect of atmosphere, light and DABCO, a $^1O_2$ quencher, in anthracene and 1 solution under illumination

Solutions of anthracene or **1** illuminated with different light conditions under different atmospheres, in the presence or absence of DABCO as $^1O_2$ quencher. The reactions do not occur in the absence of UV light, O_2 or under the presence of DABCO.

Table S1. The reaction of solutions of anthracene or **1** under different conditions

Entry	Substrate	Light conditions	Atmosphere	DABCO	Conversion[a]
1	**anthracene**	UV	O_2	×	✓
2	**anthracene**	vis	O_2	×	very low
3	**anthracene**	UV	N_2	×	×
4	**anthracene**	UV	O_2	✓	×
5[b]	**1**	UV	N_2	×	×
6[b]	**1**	vis	O_2	×	×
7[b]	**1**	UV	O_2	✓	×

Reaction conditions: 3 mM of the substrate in 2 mL of CD_3CN, during 30 min. DABCO added in a 1:1 molar ratio with respect to the substrate. [a]^{1}H NMR conversion. [b]100 mM of the substrate in 15 mL of CH_3CN.