

Electronic Supporting Information

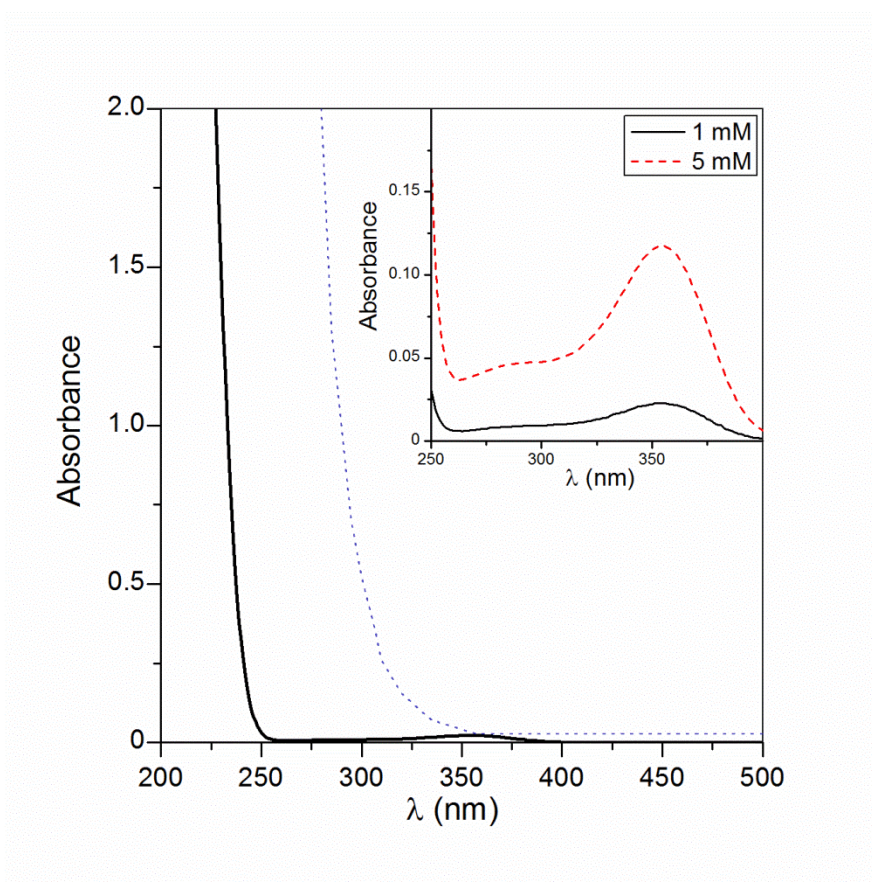


Figure S1. UV-vis spectra of aqueous NaNO_2 solutions. The blue dotted-line corresponds to the absorbance spectra of a 7740-Pyrex well of 2 mm wall thickness.

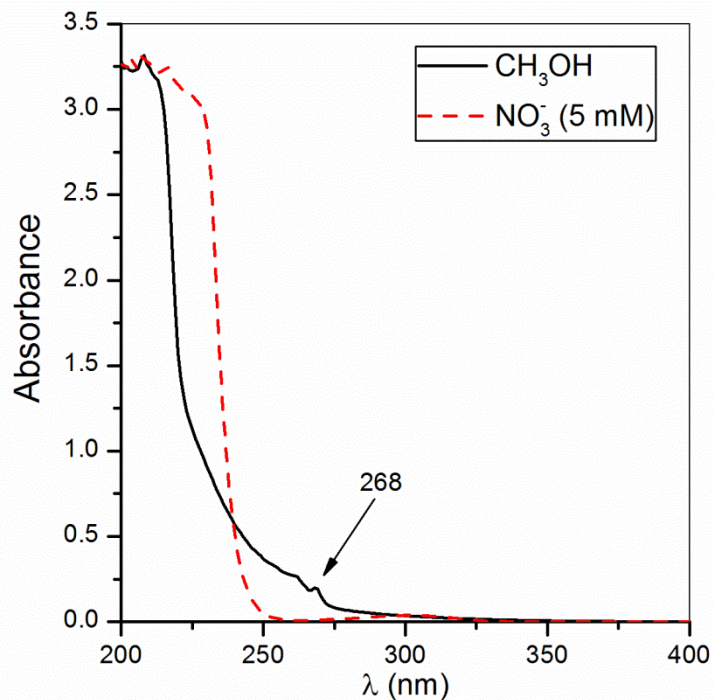


Figure S2. UV-vis spectra of KNO₃ (5mM) and CH₃OH solutions.

Experimental conditions

BiVO₄ was prepared through hydrothermal synthesis. Bi(NO₃)₃·5H₂O and NaVO₃ were used as Bi and V precursors. Two solutions, one of Bi precursor in 5 mL of glacial acetic acid and other of V in 45 mL of Milli-Q water were mixed in stoichiometric proportion to obtain a yellow suspension that was kept under stirring for 1h, after which was transferred to a Teflon autoclave where it was submitted to hydrothermal treatment at 140°C for 20h. The obtained powder was filtered, washed and further calcined at 300°C for 4 h.

For the photocatalytic oxidation of methane to methanol, a commercial photochemical reactor (Ace Glass) was used. This set-up was equipped with an immersion medium-pressure mercury lamp (450W, Ace Glass) with UVC-visible radiation. Cold water was continuously recirculated through the inner jacket of the reactor, in order to control both the temperatures of the lamp and of the reaction system (~55°C). The outlet gas tube was connected to a six port valve with a loop, used to allow the sample injection to a gas chromatography instrument (Shimadzu GC-2010, equipped with an Agilent J&W HP-PLOT Q column and TCD and FID detectors), in which the gas composition was analysed.

During each test, a suspension of Milli-Q water (300 mL) with the corresponding amount of catalyst (1g/L) was added to the reactor and kept in suspension by mechanical stirring. A calibrated gas mixture of CH₄ in He (20%) was continuously sparged (~22.4 mL/min) through the reactor in dark for 30 min, after which the illumination was turned on and a periodical injection of the outlet gas was made for the analysis of products.

In the case of the tests with nitrite ions, solutions of NaNO₂ in Milli-Q water were prepared, after which the corresponding amount of catalyst was added and the same experimental procedure was followed for carrying out

the photocatalytic test. Aliquots of 10 mL were extracted from the liquid phase at the end of the tests, filtered through a Millipore syringe filter and analyzed by UV-vis spectrophotometry.

Characterization of BiVO₄

The crystalline phase was determined by X-ray diffraction (XRD), using a Bruker D8 Advance diffractometer equipped with a Cu K α radiation source, a LYNXEYE super speed detector and a Ni filter. The XRD measurements indicate that only the monoclinic phase of BiVO₄ (JCPDS 14-0688) was obtained as shown in Figure S2.

The band gap was determined by UV-vis spectrophotometry from the calculation of the tauc function $[F(R) \cdot h\nu]^n$ and considering that BiVO₄ has an indirect gap. The spectrum is also shown in Figure S2, with the obtained value of 2.4 eV.

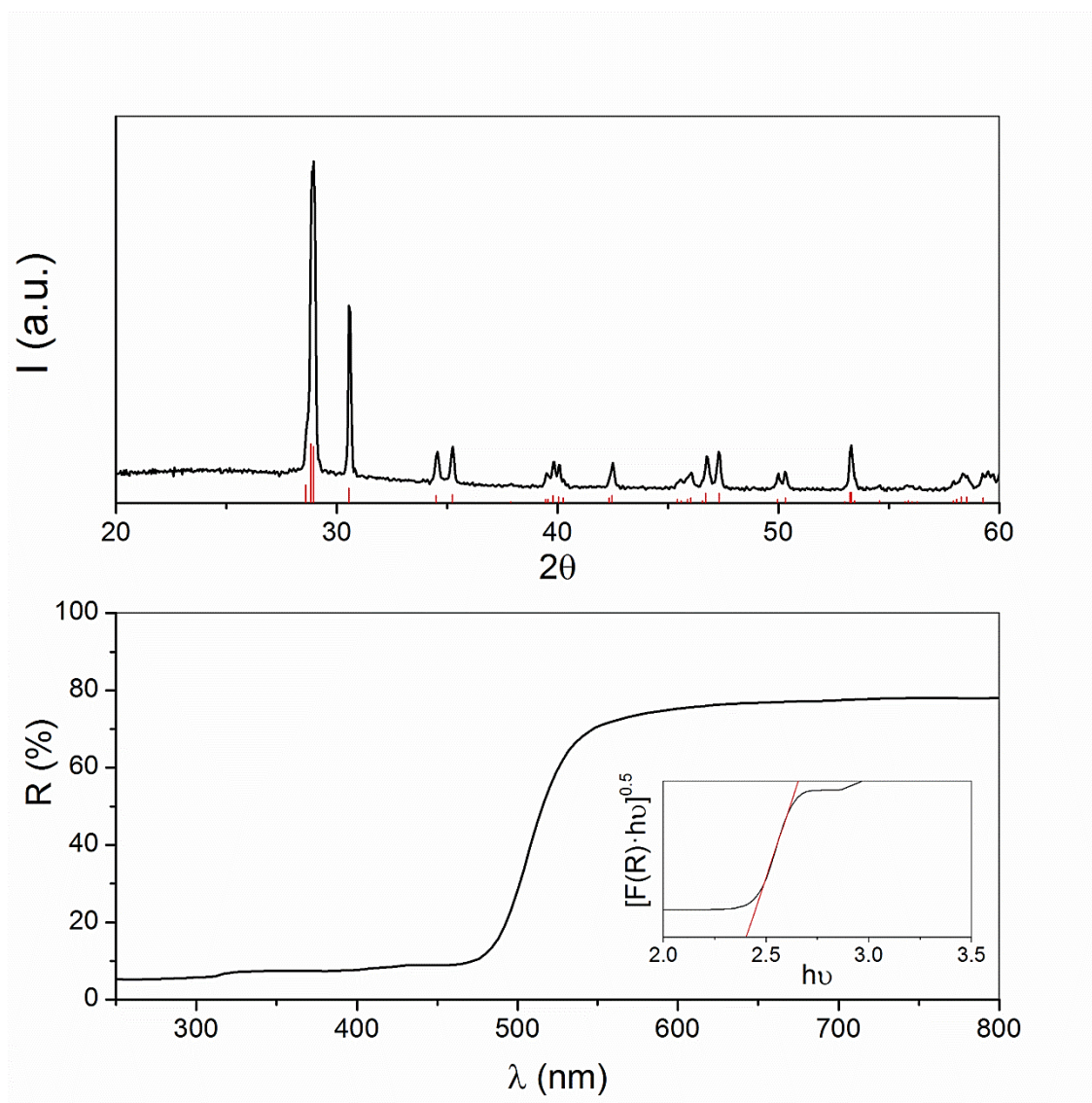


Figure S3. XRD pattern and UV-vis spectra (as %R) of the BiVO₄ sample.

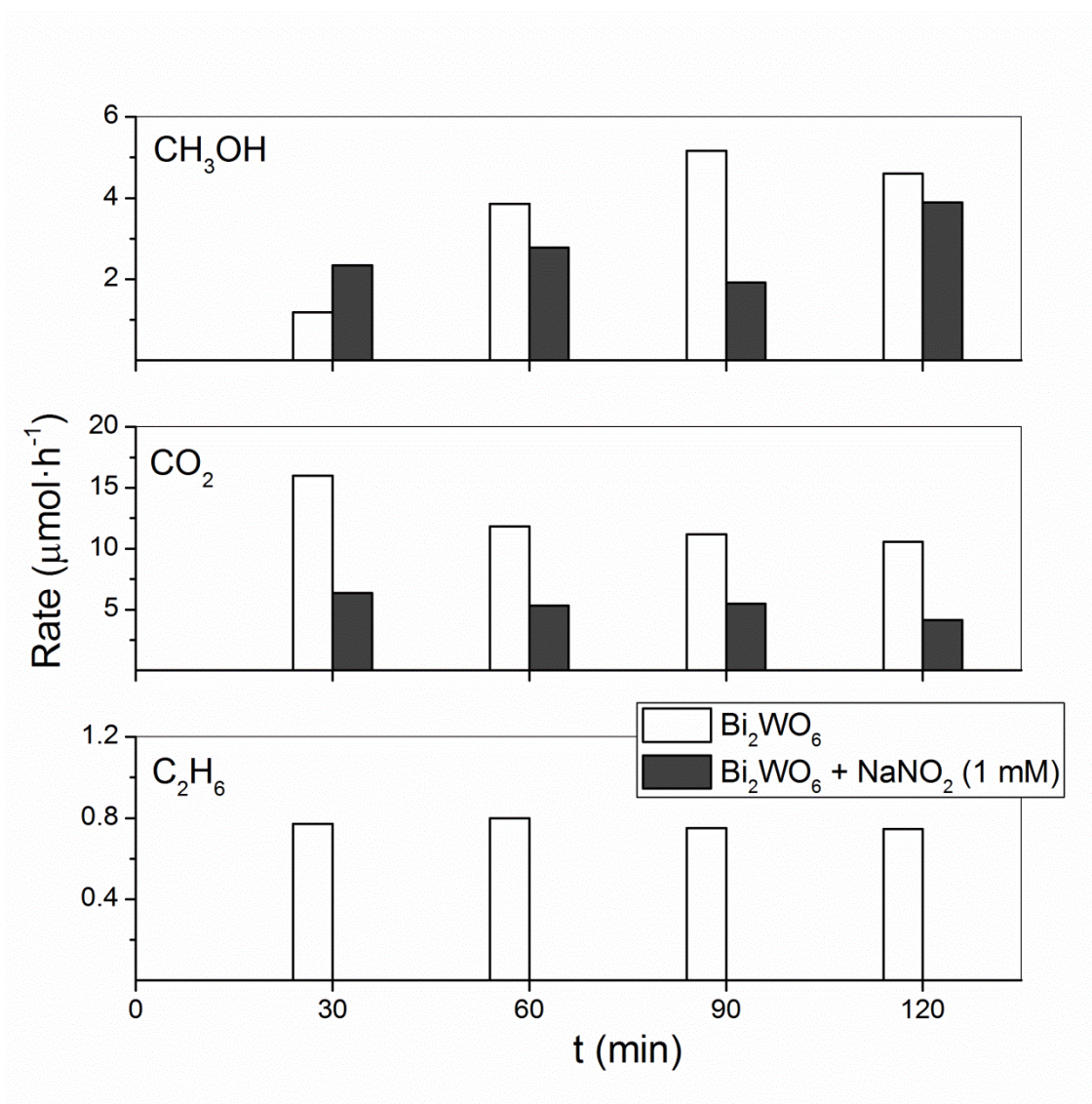
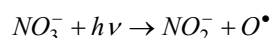
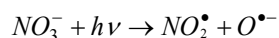


Figure S4. Rate of products in the tests with NaNO_2 (1 mM) in presence of the Bi_2WO_6 photocatalyst.

Table S1. Obtained values for methanol selectivity and methane conversion during the tests in presence of Bi_2WO_6 without and with a solution of KNO_3 (1mM) as additive.

Time (min)	Bi_2WO_6		$\text{Bi}_2\text{WO}_6 + \text{NaNO}_3$ (1mM)	
	$S_{\text{CH}_3\text{OH}}$ (%)	X_{CH_4} (%)	$S_{\text{CH}_3\text{OH}}$ (%)	X_{CH_4} (%)
30	6	1.6	4	9.9
60	22	1.4	11	4.5
120	28	1.4	4	1.6

Photolysis of nitrate (NO_3^-) is a very complex process¹. The formation of hydroxyl radicals ($\bullet\text{OH}$) has been identified in literature as a primary reaction, while NO_2^- species and O_2 have also been found to be formed as stable products under specific media conditions.^{1,2} These processes are illustrated in the next equations:



Unlike NO_2^- , NO_3^- ion is a poor $\bullet\text{OH}$ scavenger. Moreover, the formation of NO_2^- during NO_3^- photolysis greatly depends on the pH value, as it pass through the peroxyxynitrite (ONOO^-) decomposition which could lead instead to ONOOH and NO_3^- at acidic conditions.² In this sense, a basic media would be necessary in order to favor nitrite (which might scavenge $\bullet\text{OH}$ radicals) over nitrate formation.

These points explain the overall role that nitrate species could play over methane oxidation. Under our present irradiation conditions, which are described in the Experimental conditions section, $\bullet\text{OH}$ concentration increases through the NO_3^- photolysis in which $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands at around 200 and 302 nm (Figure S2) are excited. Thus, very high initial values of CO_2 productivity ($\sim 113 \mu\text{mol}\cdot\text{h}^{-1}$) and methane conversion are obtained, in comparison to the photocatalytic test with only Bi_2WO_6 . Accordingly, CH_3OH yield drops, as the system becomes highly oxidizing. These results are comparable to the previously obtained ones in presence of Fe^{3+} species as electron scavengers, which have proved to have a detrimental effect on the selectivity.

1. J. Mack and J. R. Bolton, *Journal of Photochemistry and Photobiology A: Chemistry*, 1999, 128, 1-13.
2. S. Goldstein and J. Rabani, *Journal of the American Chemical Society*, 2007, 129, 10597-10601.