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Electronic Supplementary Information

Tuning the Photocatalytic Activity of Bismuth Wolframate: Towards Selective Oxidations for the Biorefinery Driven by Solar-Light

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1. Catalyst Preparation

The Bi_2WO_6 photocatalyst was prepared as described in Ref.7. Two 10 wt% sol-gel entrapped Silia*Sun* catalysts were prepared using TEOS (tetraethoxysilane) alone or TEOS and MTES (methyltriethoxysilane) as silica precursors. In the preparation of 10% methyl-modified silica catalyst, a pre-hydrolysed sol was obtained by adding TEOS (4.77 mL, 22.1 mmol) and MTES (0.45 mL, 2.21 mmol) with HCl 0.05N (1.97 mL) and stirring the reaction mixture in the bottom rounded flask for 60 min. The resulting sol was added to a suspension of 150 mg of flower-like Bi_2WO_6 in H_2O (1 mL). After 30 min of further stirring, an aliquot of NaOH 1 N (0.1 mL) was added to the suspension. The alcogel resulting from quick gelation was left in a closed vessel for 24 h after which it was opened and left to dry for 3 days at room temperature and pressure. The doped organosilica glass monolith thereby obtained was powdered in a mortar and used as such in the catalytic reactions. A similar procedure was used to obtain the silica catalyst starting from TEOS (5.68 mL, 25.62 mmol) as unique silica precursor. The resulting embedded methylated and not methylated photocatalysts were labelled Silia*Sun* Me10% and Silia*Sun* Me0%, respectively.

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2. Catalyst Characterization

The catalysts were characterized by X-ray diffraction (XRD) measured on an Empyrean Diffractometer using the Ni-filtered Cu Kα radiation; and by photoluminescence (PL) measured on an Edinburgh FL/FS 900 Spectrofotometer. Diffuse Reflectance Spectroscopy have been performed by means of a Cary-500 spectrophotometer with $BaSO_4$ as the internal reflectance standard. The morphology was investigated by a field-emission scanning electron microscope (FESEM, FEI Nova NANOSEM 230), and by transmission electron microscopy (TEM) carried out using a JEOL model JEM 2010 EX microscope at an accelerating voltage of 200 kV. The Brunauer-Emmett-Teller (BET) surface area, pore size distribution, and pore volume of the photocatalysts were determined by using a Micromeritics ASAP 2020 apparatus by N_2 adsorption at -196°C. All samples were degassed below 1.3 Pa at 200°C prior to the measurement. Specific surface area (SSA) values were calculated by the BET equation in the p/p_0 = 0.05-0.33 range. The pore size distribution was each time calculated by using the Barrett-Joyner-Halenda (BJH) methodology applied both to adsorption and desorption branches of the isotherms.

3. Photocatalytic reactions and TOC Analysis

The photocatalytic reactions were performed in a tight close reaction tube. In a typical reaction, the tube was added with 10 mL of an aqueous substrate solution (0.5 mM) and 1.5 g/L of catalyst, either as such or sol-gel entrapped. The tube was thus placed in a water bath and the bath inserted in a Solar Box (CO.FO.ME.GRA., Milan), namely a solar light simulator equipped with a Xenon lamp (1500 W) irradiating the reaction mixture with simulated solar light (no UV filter was applied). The air cooled Xenon Lamp in the Solar Box replicates the total spectrum of the sun and not just the short UV wavelengths. The light was switched on and the reaction mixture kept under vigorous magnetic stirring during irradiation. The temperature of the water bath quickly reached 60 °C, but did not further change until the lamp was on. The reaction progress was monitored by HPLC by withdrawing a 1.5 mL sample from the reaction mixture. Samples withdrawn from the reaction mixture were filtered off through a nylon filter (0.2 μm) prior to HPLC analysis. In order to desorb any product and substrate molecules adsorbed on the photocatalyst surface, an aliquot (400 μL) of aqueous NaOH (5 M) was added to the reaction sample prior to filtration and injection of 20 μL analyte solution for the HPLC analysis. Solvents of HPLC grade were degassed prior to analysis. Total Organic Carbon (TOC) analysis was conducted with a Shimadzu TOC-5000A analyzer.

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4. Supplementary Figures

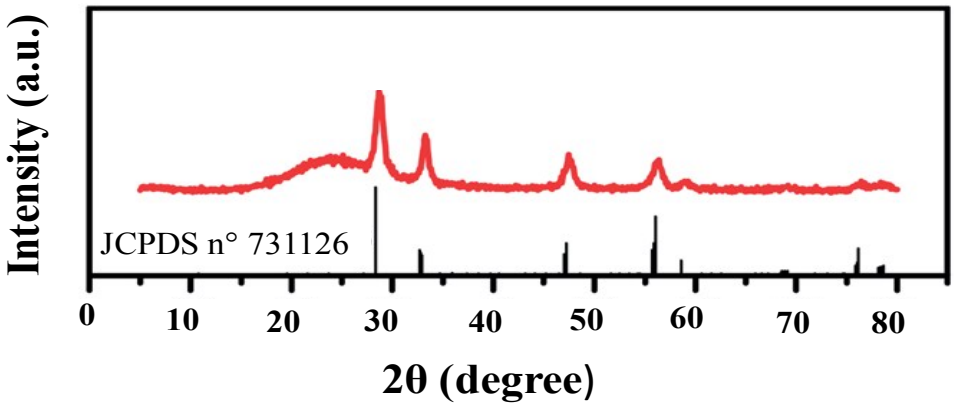

Figure S1: XRD patterns of Silia*Sun* Me0% along with those of pure Bi_2WO_6 according to JCPDS nº 731126. Encapsulation within the silica matrix does not alter the crystallinity of the Bi_2WO_6 phase. The XRD patterns of the Silia*Sun* Me10% sample were similar to those of Silia*Sun* Me0%.

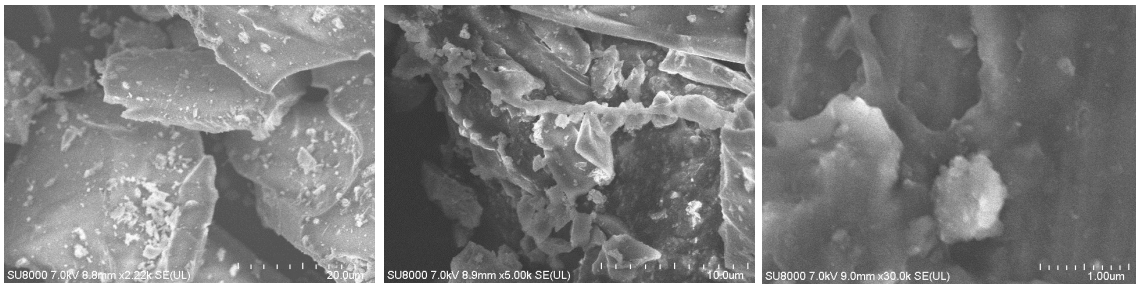

Figure S2: SEM pictures of Silia*Sun* Me0% at different magnification degrees. The pictures of the Silia*Sun* Me10% sample were similar to those of Silia*Sun* Me0%.

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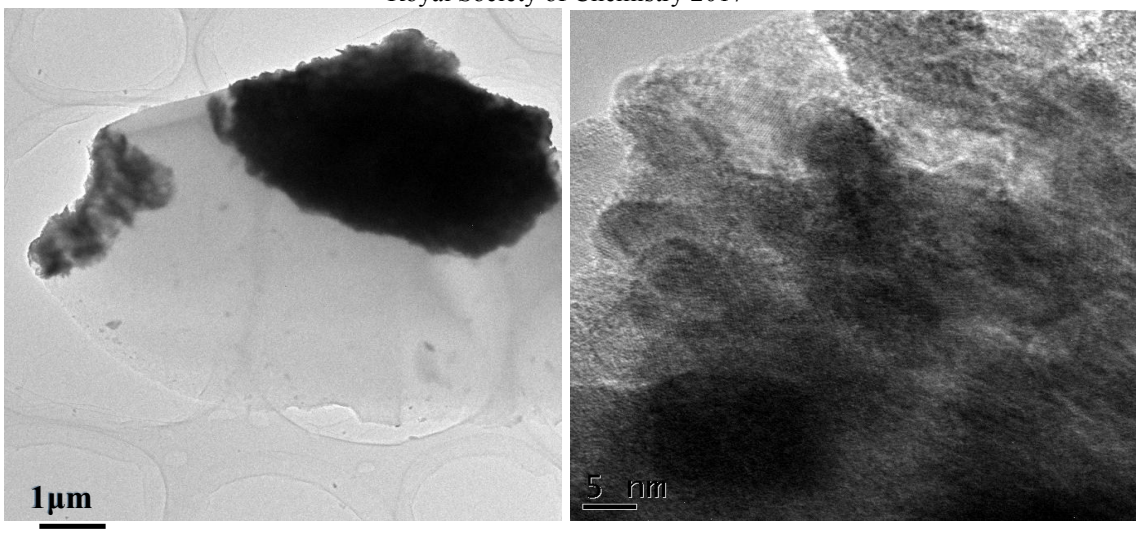

Figure S3: TEM pictures of Silia*Sun* Me0% at different magnification degrees. The pictures of the Silia*Sun* Me10% sample were similar to those of Silia*Sun* Me0%.

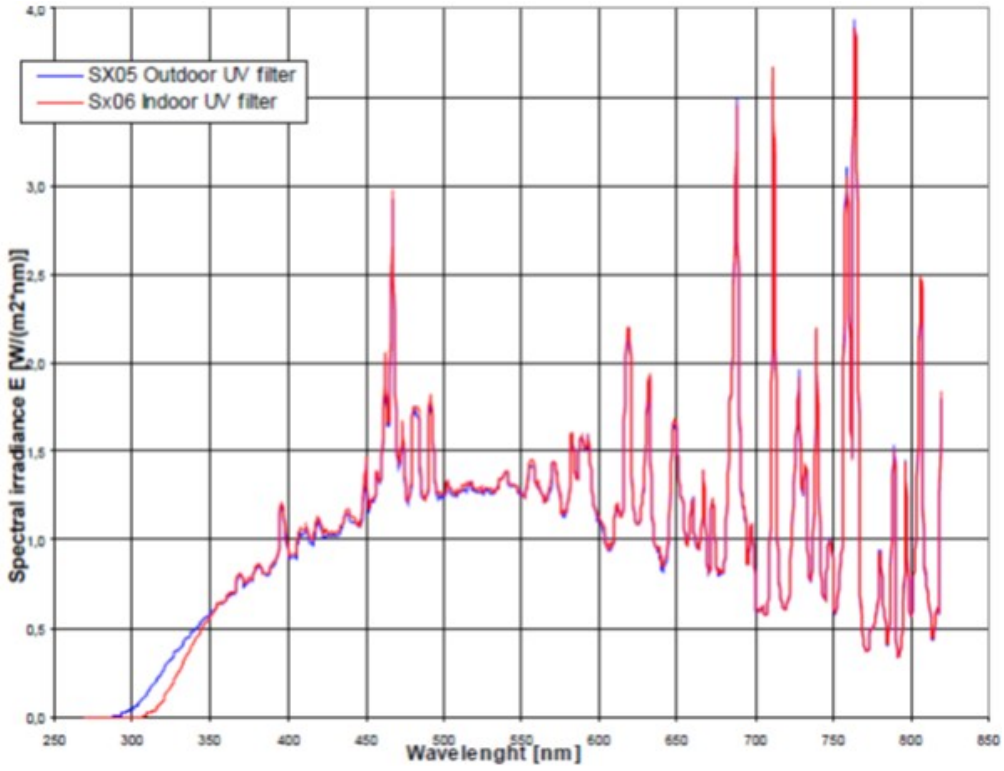

Figure S4: Emission of the Solar Box Xenon lamp with and without UV-filter. The photocatalytic experiments were performed without UV filter.

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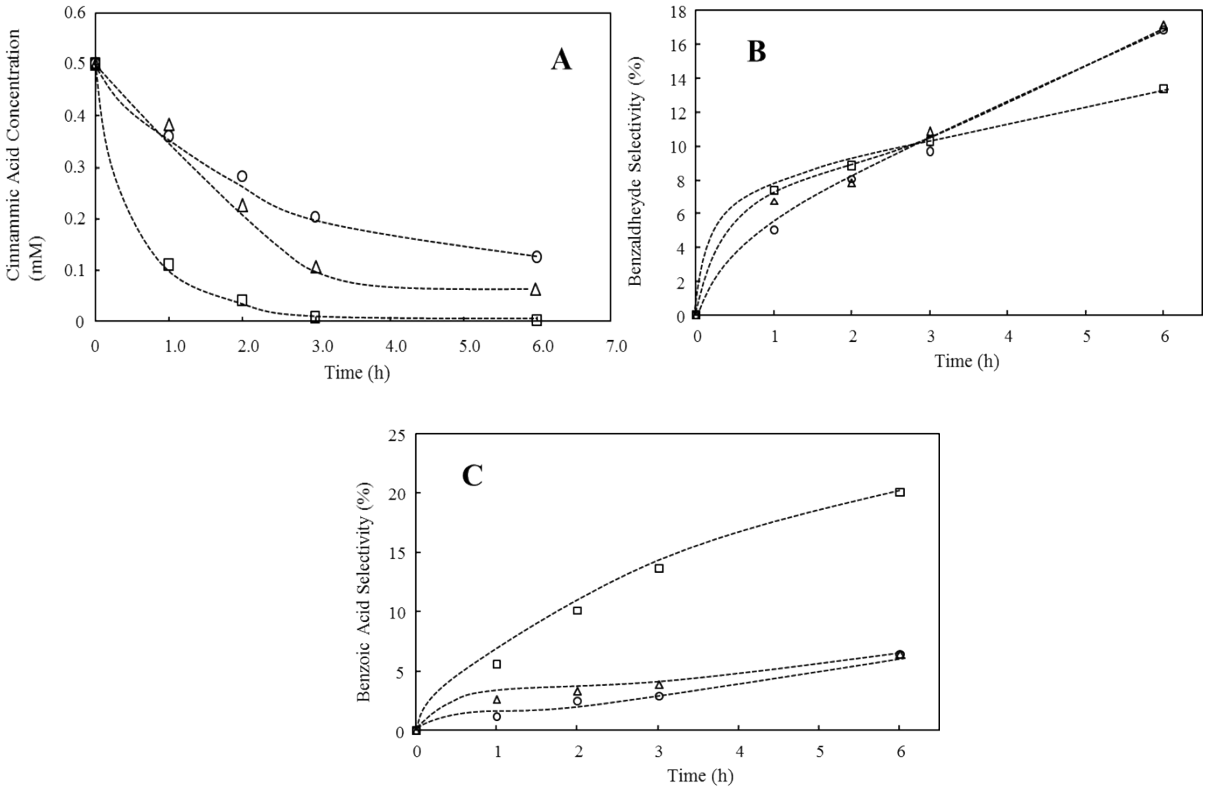

Figure S5: Concentration of cinnamic acid (A) during irradiation and correspondent selectivity values towards benzaldehyde (B) and benzoic acid (C) for pure Bi_2WO_6 (□), Silia*Sun* Me0% (○), and Silia*Sun* Me10% (Δ) photocatalysts in representative runs.

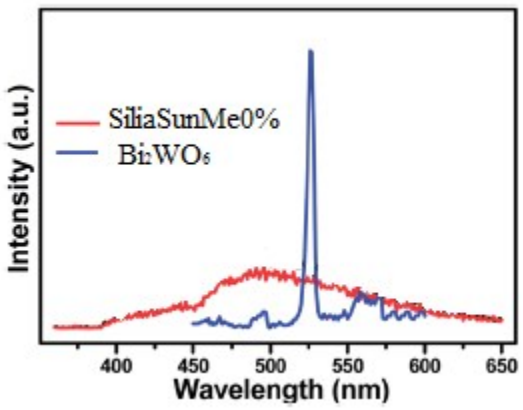

Figure S6: The PL spectra of the bare Bi_2WO_6 and Silia*Sun* Me0% with an excitation wavelength of 340 nm

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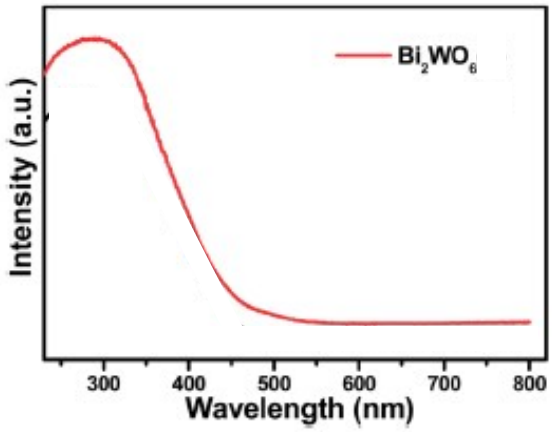

Figure S7: Diffuse reflectance spectrum of bare Bi_2WO_6 evidencing its ability to absorb in the visible light range.

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5. Supplementary Tables

Table S1: Reaction yield of benzaldehyde, benzoic acid, vanillin and vanillic acid over different photocatalysts under visible light irradiation in air.

Catalyst	Reaction Time (h)	Benzaldehyde Yield (%)	Benzoic Acid Yield (%)	Vanillin Yield (%)	Vanillic Acid Yield (%)
Bi_2WO_6	1	5.7	4.3	1.1	0.0
	2	7.8	7.8	3.2	11.0
	3	10.0	13.4	3.6	12.0
	6	13.4	20.7	4.8	13.5
Silia*Sun* Me0%	1	1.0	0.3	0.2	0.0
	2	3.0	1.0	0.4	11.1
	3	5.7	1.7	0.6	11.9
	6	12.2	4.7	1.3	15.3
Silia*Sun* Me10%	1	2.9	0.7	0.2	0.0
	2	4.2	1.5	0.6	11.9
	3	8.5	1.8	1.4	12.9
	6	13.9	5.2	2.5	18.9
TiO_2	1	4.4	1.5	1.1	0
	2	6.0	1.9	1.9	0
	3	6.9	2.4	2.1	0.2

Table S2: Reaction yield of benzaldehyde, benzoic acid, vanillin and vanillic acid over different photocatalysts at similar substrates conversion.

Catalyst	Cinnammic Acid				Ferulic Acid			
	Conversion (%))	Time (h)	Benzaldehyde Yield (%)	Benzoic Acid Yield (%)	Conversion (%)	Time (h)	Vanillin Yield (%)	Vanillic Acid Yield (%)
Bi_2WO_6	78	1	5.7	4.3	78	3	12.0	3.6
Silia*Sun* Me0%	73	6	12.2	4.7	59	6	1.3	15.3
Silia*Sun* Me10%	78	3	8.5	1.8	61	6	2.5	18.9
TiO_2	87	1	4.4	1.5	93	1	1.1	0.0

Table S3: Selectivity towards benzaldehyde, benzoic acid, vanillin and vanillic acid over different photocatalysts at similar substrates conversion.

Catalyst	Cinnammic Acid				Ferulic Acid			
	Conversion (%))	Time (h)	Benzaldehyde Selectivity (%)	Benzoic Acid Selectivity (%)	Conversion (%)	Time (h)	Vanillin Selectivity (%)	Vanillic Acid Selectivity (%)
Bi_2WO_6	78	1	7.4	5.5	78	3	4.5	15.2
Silia*Sun* Me0%	73	6	16.7	6.5	59	6	2.2	26.0
Silia*Sun* Me10%	78	3	10.8	2.3	61	6	4.1	30.9
TiO_2	87	1	5.1	1.7	93	1	1.2	0.0