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6 Tuning the Photocatalytic Activity of Bismuth Wolframate:

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- 7 Towards Selective Oxidations for the Biorefinery Driven by Solar-
- 8 Light
- 3 DOI: 10.1039/x0xx00000x

Received 00th January 20xx,

Accepted 00th January 20xx

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- 4 www.rsc.org/

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10 The sol-gel entrapment of nanostructured Bi₂WO₆ enhances the 33 11 acitivity and the selectivity of the short-gap semiconductor in the 34 12 sunlight-driven photo-oxidation of trans-ferulic and trans- 35 13 cinnamic acid dissolved in water with air as primary oxidant. 36 14 Valuable products such as vanillin, benzaldehyde, benzoic acid 37 15 and vanillic acid are obtained. This provides the proof of concept 38 16 that photocatalysis could be a promising technology in 39 17 40 tomorrow's solar biorefineries. 18 41

19 The aerobic oxidation of trans-ferulic acid (3-(4-hydroxy-3-42 20 methoxyphenyl)-2-propenoic acid) (1, Figure 1) dissolved in 43 21 water at room temperature in the presence of a suspension of 44 22 catalytic amounts of nanostructured Bi₂WO₆ in the absence of 45 23 light, affords vanillic acid (4-hydroxy-3-methoxybenzoic acid) (3,46 24 Figure 1) in high yield (60%).¹ Vanillic acid is a valued fragrance 47 and flavoring agent with several beneficial effects due to its48 25 26 chemopreventive, hepatoprotective and cardioprotective 49 activity, $^{2}\,$ and a global market in various application areas $50\,$ 27 28 exceeding $$200 \text{ million}^3$. The reaction is important because the 51 29 acid is a precursor of vanillin, one of the most important and 52 30 expensive flavour compound in the world (about \$2,400 per

- 31 kilogram for the natural product).⁴ Due to its small bandgap (2.7
- $32\,$ eV), Bi_2WO_6 photocatalytically mediates the synthesis of

chemicals and fuels under visible light, often with remarkable selectivity.⁵ When light is excluded, the adsorbed *trans*-ferulic acid molecules react with the W=O active catalytic centres, whose concentration, among all possible bismuth tungstates, reaches its maximum in Bi_2WO_6 phase.¹ However, when the visible-light conversion of *trans*-ferulic acid dissolved in water is carried out in O₂ saturated atmosphere using the same flower-like Bi_2WO_6 , the former biophenol abundant in plants where it exerts numerous biological activities,⁶ is first converted in small yield (ca. 1%) into vanillin (after 1 h) and then entirely mineralized into CO_2 .

Following promising findings applied to the conversion of glycerol into dihydroxyacetone,⁷ and aiming at finding a way to enhance the Bi_2WO_6 selectivity in the partial oxidation of phenolics of relevance to the bioeconomy, we entrapped flower-like Bi_2WO_6 in two different silica-based ceramic matrices. The resulting photocatalysts were used in the oxidation of *trans*-ferulic and *trans*-cinnamic acid (2, Figure 1) under visible light and in the presence of different O_2 concentrations (0%, 20%, and 100% in the headspace).



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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Figure 1. Chemical structures of *trans*-ferulic acid (1), *trans*-cinnamic acid (2),
 vanillin (3, Y=H), vanillic acid (3, Y=OH), benzaldehyde (4, Y=H), and benzoic acid
 (4, Y= OH).

57 All reactants, except the catalysts, were purchased from Sigma-58 Aldrich and used as received. Bi_2WO_6 was synthesized from 59 $Bi(NO_3)_3$ -5H₂O and Na_2WO_4 -2H₂O via a well known hydrothermal

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60 route in which careful control of reaction time (8 h) affords the 94

required flower-like ${\sf Bi}_2{\sf WO}_6$ microparticles. 8 The XRD analysis 95 61

62 (Figure S1 in ESI) confirmed formation of crystalline Bi₂WO₆ with the main patterns at 2ϑ = 28°, 33°, 47°, and 56°. SEM and TEM 63 64 analysis pictures revealed formation of the flower-like 65 nanostructures¹. The sol-gel entrapped Bi₂WO₆ catalysts were 66 prepared using TEOS (tetraethylorthosilicate) and MTES 67 (methyltriethoxysilane) as silica precursors (see ESI). SEM and 68 TEM analyses of the resulting embedded methylated (SiliaSun Me10%) and non methylated (SiliaSun Me0%) photocatalysts 96 69

(see Figure S2 and S3 in ESI) confirm that even though the 97 70 flower-like superstructure of original Bi₂WO₆ is destroyed, 99 99 71 crystalline Bi_2WO_6 is entrapped in amorphous glassy silica or $\frac{90}{99}$ 72 73 organosilica matrix, encapsulating shell clearly distinguished.

60 0.02 40 Quantity ore 0.0 20 0.4 0.6 0.8 500 750 1000 1250 1500 0.2 1.0 1.2 0.0 Relative Pressure (p/p⁰) Pore Width (Å) 250 0.04 В B (cm³/g STP) 200 0.03 150 dsorbe 0.02 100 ore 0.01 Ouantit 50 0.2 0.4 0.6 0.8 1.0 1.2 50 150 2000 100 Relative Pressure (p/p⁰) Pore Width (Å) 250 0.04 С \mathbf{C}^{*} (cm³/g STP) 200 0.03 cm3/g) 150 Adsorbed 0.02 ore Volume 100 0.0 Ouantity 0.2 0.4 0.6 0.8 1.0 50 100 150 2000 0.0 1.2 Relative Pressure (p/p⁰) Pore Width (Å)

74 Figure 2. N2 adsorption-desorption isotherms (A, B, C), pore size distribution (A', 75 B', C') of the samples: pure Bi_2WO_6 (A, A'), SiliaSun Me0% (B, B'), and SiliaSun 76 Me10% (C, C').

77 The nitrogen adsorption-desorption isotherms at -196 °C and 28 the pore size distribution for all of samples are displayed in129 78 79 Figure 2. The type IV isotherm of pure Bi_2WO_6 , according to the 30 80 De Boer classification⁹, is associated with capillary condensation131 81 taking place in mesopores (see the Bi_2WO_6 average pore size of 32 82 15.5 nm, Table 1). The initial segment of the isotherm at low 33 83 relative pressure values may be attributed to monolayer 34 84 multilayer adsorption. Thereafter, the almost linear middle35 85 section indicates that monolayer coverage is complete and 36 86 multilayer adsorption takes place. The shape of the hysteresi \$37 87 loop (type H1) suggests the presence of spherical particles 38 88 arranged in a fairly uniform way with facile pore connectivity139 89 Although the hysteresis takes place at high relative pressure40 90 (between 0.8 and 1.0) confirming the presence of mesopores 41 91 the shape of the adsorption branches at p/p_0 close to 1 is 42 92 somewhat similar to type II isotherm, indicating the presence of 43 macropores, too.^{10,11} 93

Table 1. BET (Brunauer-Emmet-Teller) specific surface area (SSA), particle size, total pore volume (V_p) , average pore diameter (D_p) of the used samples.

	SSA		Vp	Dp	
	[m²⋅g⁻¹]	[nm]	[cm³·g⁻¹]	[nm]	
Bi ₂ WO ₆	48.2	124.4	0.187	15.5	
SiliaSun Me0%	538.2	11.1	0.326	2.4	
SiliaSun Me10%	560.2	10.7	0.318	2.3	

Indeed, the pore size distribution curve shows a broad distribution up to 1000 Å centered at about 500 Å, with average particle size 124.4 nm (Table 1). The isotherms of the SiliaSun catalysts are very similar and may be associated to type I isotherm typical for microporous solids. The pore diameter indeed is slightly higher than 2 nm for both SiliaSun samples with a relatively small external surface, and large inner surface area typical of silica sol-gels which is 11-12 times higher than that of Bi₂WO₆ with correspondingly smaller average particle size (Table 1). Although the reported pore size of the SiliaSun samples is at the upper limit of the size reported in the literature for micropores, the shape of the isotherms in Figure 2B and Figure 2C is ascribed to microporous solids. The presence of a small, almost horizontal hysteresis loop associated with H4 type isotherm, indicates the presence of narrow slit-like pores and particles with internal voids of irregular shape. For both solgel entrapped catalysts, the pore size distribution curves show a narrow distribution up to 50 Å centered at about 25 Å.

The oxidation reactions were carried out in a tight close reaction tube added with 10 mL of an aqueous solution (0.5 mM) of substrate and 1.5 g·L⁻¹ of catalyst, either as such or sol-gel entrapped. The tube placed in a water bath was inserted in an air cooled solar light simulator (Solar Box, CO.FO.ME.GRA., Milan, Figure S4 in ESI) equipped with a 1500 W Xenon lamp irradiating the reaction mixture with simulated solar light (no UV filter). The temperature of the water bath reached 60 °C and did not further change until the light was kept on. Samples withdrawn from the reaction mixture were filtered off through a nylon filter (0.2 µm) prior to HPLC analysis. Solvents of HPLC grade were degassed prior to analysis. Total Organic Carbon (TOC) analysis was conducted with a Shimadzu TOC-5000A analyzer.

Preliminary experiments, in the presence of the SiliaSun samples, were performed in O2 atmosphere under otherwise similar experimental conditions. In this case, the conversion of the substrates was almost complete (above 90%) after 3 h irradiation, but the selectivity towards the compounds of interest was unsatisfactory (ca. 3% for vanillic acid and ca. 2% for vanillin by starting from ferulic acid; and ca. 6% for benzaldehyde and ca. 4% for benzoic acid by starting from cinnamic acid) with CO₂ being the main oxidation product with both susbstrates. Notably, negligible conversion of the substrate was obtained under N₂ saturated atmosphere even after 6 h, confirming the central role played by O_2 in this kind of oxidation. Blank tests in the absence of light under the same experimental conditions did not show any activity after the same reaction time. The results in Table 2 were obtained carrying out the reaction in the presence of air.



DOI: 10.1039/C7CC04242F

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- 144 Table 2. Conversion of ferulic acid in air under visible light over free and sol-gel
- $145 \qquad \text{entrapped } Bi_2 WO_6. \ \text{Figures are the average of results obtained in three}$

146 independent runs carried out under the same experimental conditions.

Catalyst	Reaction Time (h)	Ferulic acid Conversion (%)	Vanillic acid Selectivity (%)	Vanillin Selectivity (%)
	1	42	5.0	2.7
Bi₂WO ₆	2	78	13.7	4.1
	3	80	15.3	4.5
	6	86	15.6	4.9
Silia <i>Sun</i>	1	21	10.0	1.1
	2	36	30.0	1.2
Me0%	3	37	32.8	1.8
	6	59	26.0	2.0
	1	21	12.0	0.8
Silia <i>Sun</i>	2	31	38.5	2.1
Me10%	3	35	33.7	3.6
	6	61	31.0	4.1
TiO ₂	1	93	-	1.2
	3	99	0.2	2.1

147 The latter results (see also Tables S1, S2, and S3 in ESI) show 148 that, in each case, switching from O_2 to air significantly reduces 149 mineralization while affording formation of vanillic acid and 150 vanillin. The sol-gel entrapment of Bi₂WO₆ in the non photo-151 active silica matrix reduces the overall conversion but doubles 152 the selectivity to vanillic acid with respect to bare Bi₂WO₆ by 153 dispersing the active Bi₂WO₆ phase and lowering the overall86 154 oxidative capability of the photocatalysts. This trend is generall \$87 observed for similar systems.¹² Highlighting the remarkable 88 155 156 effect of Bi_2WO_6 sol-gel encapsulation, the activity per mass of 89 157 Bi_2WO_6 is higher in the embedded samples with respect to th**\underline{490}** 158 bare photocatalyst. Indeed, the active Bi₂WO₆ phase constitute **191** 159 only 10% in weight of the SiliaSun samples. It is worth td92 160 mention that comparable selectivity values to vanillic acid were93 161 obtained in the dark in the presence of bare Bi₂WO₆.¹ However 194 162 while in the dark almost 90 h were required, under solar light95 163 irradiation the same selectivity and yield values are obtained in196 164 3 h. Figure 3A and Figure 3B show the concentration of trans197 165 ferulic acid during irradiation and the corresponding selectivit 198 166 towards vanillic acid over pure Bi_2WO_6 and over the SiliaSun199 167 photocatalysts. Notably, the reduced conversion obtained for 168

the embedded photocatalysts with respect to Bi₂WO₆ (Figure 3A) translates into twice higher selectivity values (Figure 3B). 200 169 170 is evident from Figure 3B that the selectivity reaches $\frac{201}{2}$ maximum and then decreases after a critical reaction time. Thi202 171 general trend is due to the competition for oxidation betwee 203 172 173 the formed target compounds and the substrate molecules. Fo204 174 the sake of comparison, the oxidation of *trans*-ferulic acid wa205 175 performed under the same experimental conditions in the 206 176 presence of TiO₂ P25 (Evonik, Germany). In this case th207177 substrate is almost completely oxidized after 1 h irradiation an208the selectivity towards the desired products is very poor, thu209 178 179 demonstrating the superior synthetic performance of the 10 180 Bi_2WO_6 photocatalysts. Indeed, differently from TiO₂ mediate 211181 photooxidations, Bi_2WO_6 induced photocatalytic oxidatio²₄12 182 processes do not proceed through OH radicals but via direc 213 183 holes and via more selective peroxidic species including

184 activated oxygen (e.g., $O_2^{\cdot-}$).¹³⁻¹⁵



DOI: 10.1039/C7CC04242F

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Figure 3. Concentration of ferulic acid during irradiation time (A) and correspondent selectivity values towards vanillic acid (B) for pure Bi_2WO_6 (\Box), SiliaSunMe0% (o), and SiliaSunMe10% (Δ) photocatalysts in representative runs.

The commercial value of both vanillin and vanillic acid is so high that the hereby reported selectivity values are of practical interest. Notably, ferulic acid partial oxidation has been reported in the presence of TiO_2 in water under UV^{16} or visible light¹⁷ irradiation. In the latter case, selective permeation of vanillin through a membrane strongly enhanced the selectivity of the process by continuously separating the product from the reaction medium, thereby efficiently preventing its further oxidation.¹⁸ This system allows both to completely retain the photocatalytic powder into the reaction unit and to afford downstream highly pure (99.98 %) crystals of vanillin.¹⁹ The application of the latter integrated system to the Silia*Sun*, which affords significantly higher yields of vanillic acid when compared to TiO_2 , is therefore promising.

The same selectivity trend was observed also in the oxidation of trans-cinnamic acid (Table 3 and Figure S5 in ESI). Hence, while reaction over a suspension of Bi₂WO₆ under O₂ resulted in complete mineralization after 3 h, the replacement of O2 with air afforded complete photocatalytic conversion into a mixture of benzoic acid and benzaldehyde in 6 h, with predominance of benzoic acid (see Tables S1, S2, and S3 in ESI). Again, replacing Bi₂WO₆ with the SiliaSun catalysts alters both the activity and the selectivity of bismuth tungstate. Now, after 6 h a large amount of benzaldehyde is obtained along with unreacted substrate both in the original trans configuration, and isomerized into the cis form. Indeed, upon irradiation with visible light trans-cinnamic acid dissolved in water photochemically isomerizes into *cis*-cinnamic acid.²⁰

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 Table 3. Conversion of trans-cinnamic acid under visible light over free and sol-gel

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 entrapped Bi₂WO₆. Figures are the average of results obtained in three

216 independent runs carried out under the same experimental conditions.

Catalyst	Reaction Time (h)	Cinnamic Acid Conversion (%)	Benzoic Acid Selectivity (%)	Benzaldehyde Selectivity (%)	2 2 2
	1	77	5.5	7.4	2
Bi₂WO ₆	2	92	8.5	8.5	2
	3	98	13.6	10.3	2
	6	100	20.1	13.4	2
	1	28	1.2	3.7	2
Silia <i>Sun</i>	2	37.7	1.5	8.0	2
Me0%	3	59.5	2.9	9.7	2
	6	73	6.5	16.7	2
	1	23	2.7	6.0	2
Silia <i>Sun</i>	2	55	2.8	8.0	2
Me10%	3	79	2.9	11.0	2
	6	82	6.4	17.1	2
TiO₂	1	87	4.4	1.50	2
	3	99	3.8	2.4	2

276 217 Again, similarly to what observed with trans-ferulic acid, using77 218 the 10%-methylated SiliaSun catalyst slightly enhances th278 219 selectivity towards the aldehyde (by considering the figures a279 the various reaction times), which now becomes th $\frac{280}{2}$ 220 predominant reaction product (Table 3 and Figure S4 in ESI $\frac{281}{22}$ 221 82 222 Indeed, the silica entrapment addressed the reaction selectivity 83 to the aldehyde or the acid depending on the affinity with the $\frac{33}{84}$ 223 224 used substrate. For all of the runs TOC analysis confirmed $\overline{985}$ 225 satisfactory carbon mass balance, indicating that no other86 226 intermediates were produced during reaction with th@87 227 exception of CO2 and the species detected by HPLC. Finally, t288 228 check for possible leaching of active Bi_2WO_6 reaction centres id 89 229 solution, the solid catalyst was removed by filtration using 290 0.20 μm nylon filter after 90 min (50% of total conversion). Th $\underline{291}$ 230 filtrate monitored for activity within subsequent 2 h showed n_{222}^{292} 231 further reaction, indicating that no catalytically active species 232 were present in the filtrate. Moreover, the filtrate analyzed b $\frac{5}{95}$ 233 ICP-MS showed no presence of bismuth or tungsten, thereb $\overline{296}$ 234 235 excluding leaching of the insoluble Bi2WO6 or its derivatives 236 Further pointing to no changes in the catalyst structure upo298 237 reaction, the XRD analysis of the used photocatalysts reveale 299 238 that in each case the crystal structure was not affected by the 300 239 photocatalytic reaction. Furthermore, the conversion an301selectivity values remained virtually unchanged after thre 240 reaction runs performed with the same catalyst filtered, washe 3^{03} 241 with distilled water and reused as such in a subsequent reaction 305 04 242 run. All these evidences indicate the catalytic nature of the 0.6243 reaction and the recyclability of the catalysts. In analogy $t\tilde{307}$ 244 245 silica-supported TiO2 in which formation of Ti-O-Si linkage induces remarkable optical modification ascribed to electronig 0.9246 semiconductor support interaction,^{21,22} we make the hypothesi**3**10 247 248 that the sol-gel encapsulation of Bi_2WO_6 likely induces formatio $\mathbf{311}$ 249 of oxygen bridges between Si and W with different intermediat **3**12 energy states. Indeed, the photoluminescence spectra of th $^{313}_{114}$ Silia*Sun* Me0% catalyst^{7,23} displays much lower intensity with $^{314}_{115}$ 250 251 respect to bare Bi_2WO_6 , (see Figure S6 in ESI) suggesting a 15 252 interaction between silica and Bi_2WO_6 that markedly influence 317 253 the spatial electron and hole transfer kinetics. This hypothesi318254

255 may justify the observed high activity of the embedded samples 256 even if they contain only 10% in weight of optically active 257 Bi_2WO_6 phase (See Figure S7 in ESI).

In conclusion, we have discovered that trans-ferulic acid and trans-cinnamic acid dissolved in water can be selectively oxidized with significant yield into a mixture of valued acid and aldehyde derivatives (vanillic acid and vanillin, and benzoic acid and benzaldehyde, respectively) under simulated solar light irradiation over flower-like nanostructured Bi₂WO₆ and, even better, over the SiliaSun sol-gel entrapped forms. The sol-gel encapsulation of the photocatalyst significantly enhanced the selectivity towards the aldehyde or the acid, depending on the nature of the substrate. These findings could be relevant from both scientific and technology viewpoints. From the application viewpoint, in light of the forthcoming broad utilization of solar photocatalysis to chemical synthesis,¹⁷ the robustness, low cost and highly porous nature of the sol-gel glassy catalyst make it ideally suited for continuous practical applications. Further experiments are ongoing on different substrates and different SiliaSun catalysts.

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