1	Solvent-free production of nanostructured CeO <sub>x</sub> /TiO <sub>2</sub> samples for the selective
2	photocatalytic synthesis of benzaldehyde
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12	Abstract
13	An environmentally friendly solvent-free approach was tested using spent coffee as a
14	biomass sacrificial template for the preparation of TiO <sub>2</sub> modified with CeO <sub>x</sub> . The use of
15	coffee as a template pursues the preparation of a nanostructured heterojunction without
16	the need for a solvent. Two variables were optimized in the synthesis process, i.e.
17	calcination temperature and proportion of CeOx. Firstly, bare coffee-template titania was
18	prepared to explore the effect of the calcination temperature, within 500-650 °C. The
19	anatase phase was obtained up to 600 °C. Higher temperatures, i.e. 650 °C, led to the
20	appearance of rutile (10%) and efficient removal of the sacrificial agent (0.6 % residue).
21	The maximum photocatalytic activity in terms of conversion, in the oxidation of benzyl
22	alcohol, was achieved employing the bare coffee-template TiO2 at 650 °C, and it was
23	found comparable to the benchmarked P25. The incorporation of ceria in the solvent-free
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approach considerably improved photocatalytic benzaldehyde production. No changes in 24 the XRD pattern of TiO<sub>2</sub> were appreciated in the presence of ceria due to the low amount 25 added, within 1.5-6.0%, confirmed by XPS as superficial Ce<sup>3+</sup>/Ce<sup>4+</sup>. The UV-visible 26 absorption spectra were considerably redshifted in the presence of Ce, reducing the 27 bandgap values of bare titania. An optimum amount of ceria in the structure within 3-0% 28 was found. In this case, the selectivity towards benzaldehyde was ca. 75%, 3 times higher 29 than the selectivity value registered for the benchmarked P25 or the bare prepared TiO<sub>2</sub>. 30 Ceria-modified samples also showed competitive results in terms of conversion and 31 quantum efficiency. 32

33 Keywords: Green synthesis, solvent-free, coffee-templated, cerium, titania,
34 photocatalysis, benzaldehyde

#### 35 1. INTRODUCTION

The reuse and valorization of household waste are one of the most complex challenges in the current agenda to cross over current unsustainable habits into responsible and greener consumption of natural resources [1–3]. For that reason, the use of waste, such as spent coffee, as a new material resource results in great interest in a circular economy strategy.

The development of functionalized nanomaterials has raised the attention of the 41 research community due to the multiple relevant applications released, such as energy 42 production and storage [4–9], decontamination [10–12], and sensing [13–15], among 43 others [16]. The oxidation of alcohols to aldehydes and ketones is a high-demanded 44 45 chemical reaction in the industrial catalytic sector that generates added-value chemicals. 46 There are diverse already established technologies to carry out that purpose such as catalysis, thermo-catalysis, or electro-catalysis [17–19]. Recently, the use of 47 photocatalysis, as an emerging technique, has been deeply explored for water treatment 48 [20], energy production [21], selective oxidation of alcohols [22] or amines [23] into 49 valuable chemicals at milder conditions with lower energy input compared to the 50 traditional thermo-catalysis [24]. 51

The sacrificial template method has recently been widely reported and demonstrated to be a good strategy to control the morphology and porosity of materials with improved catalytic performance [25]. This green synthetic method, developed in a solid-state medium, is based on the arrangement of a metal precursor onto the surface of the template; followed by the selective elimination of the sacrificial agent through physicochemical treatment, mainly through thermal removal [26]. Although several templates, such as polymers [27] or Metal-Organic Frameworks, [28] have been an object

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of study, recently, the consideration of biomass has gained increased attention since it 59 60 contributes to reducing the costs of the prepared material and at the same time valorizes a waste. Some examples of this strategy for the synthesis of nanostructured titania, which 61 has displayed good results include wood [29], wheat bran [30], orange peels [31], and 62 63 walnut shells [32]. Titanium dioxide has been explored as the photocatalyst used by excellence. However,  $TiO_2$  research continues to focus on two major limitations of this 64 65 semiconductor as avenues for improving catalyst performance: limited absorption due to a wide bandgap, i.e. ca. 3.2 eV; and the high recombination rate of photo-generated 66 primary species [20]. CeO<sub>2</sub> can absorb a larger fraction of the solar spectrum than TiO<sub>2</sub> 67 68 [33], with a bandgap around 3.0-3.4 eV depending on the synthetic method [34]. Nevertheless, the poor thermo-stability [25] and an unappropriated band alignment of 69 CeO<sub>2</sub> limits, its application as an efficient photocatalyst utilizing solar energy [35]. To 70 71 overcome their separate disadvantages, TiO2 and CeO2 can be combined in a heterostructure [34,36–38]. 72

73 To date, there is no previous work dealing with spent coffee powder as a template for 74 the preparation of titania-based materials. Only coffee husk extract has been reported in previous work [39]. This work explores the use of a solvent-free route using coffee as the 75 76 sacrificial template for the synthesis of ceria-modified nanostructured titania, namely c-CeO<sub>x</sub>/TiO<sub>2</sub> applied to the selective oxidation of benzyl alcohol to the more added-valued 77 78 benzaldehyde. The influence of the calcination temperature on the sacrificial agent removal and the crystalline phases were explored, as well as the ceria amount added to 79 80 the heterostructure. A complete characterization including thermogravimetry, N<sub>2</sub> 81 physisorption, XRD, XPS, DRS UV-visible, and photoluminescence technique was applied to assess the benefits of the coffee-templated ceria modified titania, and the 82 photocatalytic activity observed. The nanostructured coffee-template CeOx/TiO2 83

- 84 displayed higher selectivity compared to the bare coffee-template  $TiO_2$  or the
- 85 benchmarked P25.

#### 86 2. EXPERIMENTAL

#### 87 **2.1.** Chemicals

Cerium (III) nitrate hexahydrate (Merck $\mathbb{R}$ , >99.99%), titanium (IV) isopropoxide (Merck $\mathbb{R}$ , >97%), and spent coffee were used for the synthesis of the photocatalytic materials. Analytical grade benzyl alcohol (BA, Merck $\mathbb{R}$ , >99%) and benzaldehyde (BD, Merck $\mathbb{R}$ , >99%) standards were used for calibration curves and the photocatalytic experiments. HPLC grade acetonitrile and methanol were used. Ultrapure water (resistivity, 18.2 M $\Omega$ ·cm) from a Direct-Q $\mathbb{R}$ -UV system (Millipore $\mathbb{R}$ ) was used in all the solutions preparation.

## 95 2.2. Solvent-free coffee-templated synthesis of CeO<sub>x</sub>/TiO<sub>2</sub> and characterization

The coffee-templated cerium titania nanostructures were prepared by an 96 97 environmentally friendly solvent-free solid-state approach. Spent coffee powder was used as a biomass sacrificial template for the synthesis of the photocatalytic materials 98 following an impregnation method. Briefly, the coffee residue was dried overnight at 100 99 °C to control the moisture content in the biomass residue and ground in a mortar. Then, 100 the proper amount of titanium (IV) isopropoxide was dropwise added to the powder 101 coffee using a mass ratio of 1:1. The resultant solid was calcined within 500-650 °C under 102 an air atmosphere (20 mL min<sup>-1</sup>) with a heating rate of 5 °C min<sup>-1</sup>, kept at the selected 103 temperature for 2 h and thereafter cooled naturally to room temperature. The as-obtained 104 sample was named c-TiO<sub>2</sub>-x where x stands for the selected calcination temperature. The 105 CeO<sub>x</sub>-TiO<sub>2</sub> heterostructures were prepared following a similar procedure, but mixing a 106 selected amount of cerium (III) nitrate hexahydrate with the spent powder coffee, mixed, 107 108 and ground in a mortar. The cerium nitrate-coffee mixture was impregnated then with a titanium (IV) isopropoxide solution as previously described. The calcination temperature 109

110 was set at 600 °C. Different molar Ce amounts within 1.5-6.0% concerning the total solid 111 were selected. The obtained samples were labeled as  $CeO_x/TiO_2$ -y where y stands for the 112 molar Ce percentage.

The thermal stability of the samples was assessed by thermogravimetric analysis in a 113 PerkinElmer® thermobalance, model STA 6000. A constant heating rate of 20 °C min<sup>-1</sup> 114 was used under an O<sub>2</sub> atmosphere (flow rate, 20 mL/min) from 30 °C to 850 °C. The 115 formation of crystalline phases was evaluated by X-Ray Diffraction (XRD) in the D8 116 Advance diffractometer of Bruker® AXS, using the X-Ray source of the Cu Ka radiation, 117 coupled to a Lynxeye detector, and monitoring the  $2\theta$  within 8-80° at a rate of 0.08° min<sup>-</sup> 118 <sup>1</sup>. Scan Transmission Electron Microscopy (STEM) was used to study morphology and 119 120 the distribution of elemental composition with High-Angle Annular Dark Field (HAADF) 121 detection and Electron Disperse X-Ray (EDX) analysis in a Thermo Fisher Scientific TALOS F200X device. The surface chemical composition was studied by X-ray 122 Photoelectron Spectroscopy (XPS) in a Specs<sup>TM</sup> device (Specs<sup>®</sup> GmbH) working with 123 an X-ray source from Al Ka. The XPS spectra were referenced to the C1s peak of 124 adventitious carbon to 284.6 eV. The software CasaXPS© was used for the peaks 125 deconvolution, considering a Shirley background correction. The textural properties, i.e. 126 surface area, the volume of the pore, and pore size were determined from N<sub>2</sub> physisorption 127 at 77 K, performed in an ASAP 2000 equipment from Micromeritics<sup>®</sup>. The optical 128 properties were analyzed by Diffuse Reflectance Spectroscopy (DRS) in the UV-visible 129 range in a LAMBDA<sup>TM</sup> 365 UV-vis spectrophotometer of PerkinElmer® equipped with 130 an integrating sphere device. The Kubelka-Munk function and the Tauc plot method were 131 considered for the evaluation of the bandgap values [40]. Photoluminescence (PL) 132 analysis was carried out in a Varian Cary Eclipse fluorescence spectrophotometer of 133

Agilent® at an excitation wavelength of 365 nm as an indirect evaluation of therecombination rate of the photogenerated charges.

## 136 **2.3.** Photocatalytic production of benzaldehyde

The photocatalytic oxidation of benzyl alcohol (BA) to benzaldehyde (BD) was 137 assessed in a discontinuous type annular photoreactor in which the liquid mixture was 138 pumped at the annular space and the radiation source (Sylvania® F11W T5 BL368 lamp, 139 emitting at 365 nm, 11 W) located in the center, see details of the setup and the 140 photoreactor in Fig. 1. The solution temperature was kept constant at 30 °C by 141 recirculating the mixture to a jacketed stirring tank equipped with cooling water. An 142 oxidant environment was generated by bubbling excess air (25 mL min<sup>-1</sup>) in the stirring 143 tank. The initial concentration of BA was 1.5 mM and the catalyst dose was 1 g L<sup>-1</sup> using 144 145 acetonitrile as the reaction media. At certain times, ca. 1.0 mL of samples were extracted and the photocatalyst removed by centrifugation. The importance of holes in the 146 photocatalytic mechanism was assessed by adding oxalic acid 10 mM whereas the 147 contribution of superoxide radical was studied by purging O<sub>2</sub> with N<sub>2</sub> bubbling, both 148 before catalyst addition and irradiation. The sequential reusing tests were carried out by 149 recovering the photocatalyst by filtration in cellulose papers (0.45 µm) and dried 150 151 overnight at 105 °C. The volume of reaction was readjusted to fit the photocatalyst concentration due to the slight solid loss between cycles. Experiments were carried out 152 153 in triplicate and the relative standard deviation error was minor to 5%.



The radiation intensity of the lamp was quantified by an in-situ chemical actinometry 156 based on the photoreduction of the ferrioxalate combined with a polyoxometalate 157  $(Na_2SiW_{12}O_6)$  to monitor the temporal depletion of the ferrioxalate complex [41]. The 158 experimental conditions included oxalic acid 60 mM, FeCl<sub>3</sub> 5 mM, and SiW<sub>12</sub>O<sub>40</sub><sup>4-</sup> 1 mM. 159 The pH was adjusted to 4.5 with HCl and NaOH to avoid self-decomposition of the 160 polyoxometalate complex. The intensity of radiation at 365 nm was found as 161  $I_0 = (2.2 \pm 0.1) \cdot 10^{-4}$  Einstein  $\cdot L^{-1} \cdot min^{-1}$  considering a quantum yield for the oxidation of 162  $SiW_{12}O_{40}^{4-}$  to  $SiW_{12}O_{40}^{5-}$  at 365 ± 10 nm of 0.18 mol·Einstein<sup>-1</sup> [41]. 163

164 The concentration of BA and BD were quantified by High-Performance Liquid 165 Chromatography (HPLC) in a Water device with a Model 590 pump equipped with a dual 166 absorbance detector (Waters 2487). The stationary phase was a SunFire<sup>TM</sup> C18 column 167 (100Å,  $3.5 \mu m$ ,  $4.6 \times 150 mm$ ). The mobile phase consisted of a mixture of ultrapure water 168 (acidified with  $0.1\% v/v H_3PO_4$ , A), acetonitrile (B), and methanol (C). An isocratic elution program with a mixture of A: B: C was set at 77.5:20:2.5 and continuously
pumped at a rate of 1 mL·min<sup>-1</sup>. The BA was quantified at 215 nm and the BD at 248 nm.

# 171 2.4. LVRPA modeling and quantum efficiency calculation

The quantum efficiency  $(Q_E)$  was calculated according to Eq. 1, according to the IUPAC recommendations [42–44], which defines the  $Q_E$  as the ratio of the number of molecules reacting (reaction rate) and photon absorbed by the sample under used illumination condition (photon rate) [45]:

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$$Q_E(\%) = \frac{r_{BA_0} \,(\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1})}{e^{a,v} \,(\text{Einstein} \cdot \text{m}^{-3} \cdot \text{s}^{-1})} \cdot 100$$
[1]

The initial BA degradation rate  $(r_{BA,0})$  was determined from the slope of the temporal evolution of the  $C_{BA}$  at the initial time while the denominator of Eq. 1 was obtained from the radiative transfer equation solved for our reactor configuration, see a full description of the mathematical modeling in the supporting information.

## 181 **3. RESULTS AND DISCUSSION**

#### 182 **3.1.** Characterization of the coffee-template TiO<sub>2</sub> and CeO<sub>x</sub>/TiO<sub>2</sub> nanostructures

183 The use of organic wastes as sacrificial templates during the synthesis of photocatalytic materials has resulted to be an efficient strategy to improve the morphological structure 184 and activity of active semiconductors [25,46]. The applied thermal treatment pursues the 185 186 complete removal of the organic content to lead to the formation of a porous structure [29,39]. To explore the minimum temperature required for that purpose, thermal analysis 187 was carried out for the spent coffee used as a sacrificial template. As depicted in Fig. S1, 188 189 different stages can be observed during the thermal combustion of spent coffee. Firstly, a slight weight loss was monitored as a result of the dehydration of the sample. If the 190 temperature is raised, the highest mass loss stage is observed, at ~300 °C, where the 191

depolymerization and decomposition of polysaccharides and some oils present in the 192 193 coffee sample occur [47]. Two more secondary mass changes were monitored at 370 °C and 475 °C which are associated with the decomposition of the sample. After roughly 500 194 195 °C (2% of residue), it can be assumed that the coffee template is completely calcined with no appreciable residues. Based on these results, a calcination temperature above 500 °C 196 was set for the template synthesis of c-TiO<sub>2</sub>-x. The range was selected within 500 and 197 650 °C to promote the formation of the anatase phase, as higher temperatures may 198 substantially favor the formation of the less photocatalytic activite rutile phase [48]. 199 Furthermore, temperatures higher than 600 °C may favor particles growth and 200 agglomerates that result in detrimental radiation absorption in aqueous media [49,50]. 201

The crystal structure and arrangement of the prepared photocatalytic materials were investigated by XRD. **Fig. 2** depicts the obtained diffractograms and **Table 1** summarizes the quantitative XRD analysis of TiO<sub>2</sub> phases, i.e. anatase and rutile. Williamson–Hall formalism [51] was employed to determine the crystal size and cell parameters.



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Figure 2. XRD diffraction patterns of the c-TiO<sub>2</sub>-x and c-CeO<sub>x</sub>/TiO<sub>2</sub>-y samples with the detected crystal planes of anatase (A) and rutile (R)

Table 1. XRD quantitative analysis and crystallographic properties of anatase (A) and
rutile (R) phases of c-TiO<sub>2</sub>-x and c-CeO<sub>x</sub>/TiO<sub>2</sub>-y samples

Sample	Phases content (%)		Crystal Size (nm)		A cell parameters (Å)		R cell parameters (Å)	
	Α	R	Α	R	a=b	c	a=b	c
c-TiO <sub>2</sub> -500	100	-	18.6	-	3.784	9.496	-	-
c-TiO <sub>2</sub> -550	100	-	18.5	-	3.786	9.498	-	-
c-TiO <sub>2</sub> -600	100	-	19.7	-	3.782	9.496	-	-
c-TiO <sub>2</sub> -650	90	10	26.5	32.2	3.784	9.491	4.603	2.951
c-CeO <sub>x</sub> /TiO <sub>2</sub> -1.5	91	9	20.1	30.1	3.785	9.494	4.606	2.952
c- CeO <sub>x</sub> /TiO <sub>2</sub> -3.0	92	8	20.5	30.6	3.786	9.491	4.604	2.953

	c- CeO <sub>x</sub> /TiO <sub>2</sub> -6.0	93	7	20.2	30.4	3.785	9.493	4.601	2.951
211	All of the sample	es displag	yed the j	presence o	of several	l signals	located a	at 25.0°,	38.1°,
212	47.9°, 54.3°, 55.0°, a	and 63.1°	, respect	tively attri	buted to	(101), (0	04), (200	), (105),	(211),
213	and (204) crystallog	raphic pl	anes of	anatase Ti	O <sub>2</sub> (PDF	21-1272	l, space g	group I4	l/amd)
214	Moreover, for the s	ample c-	TiO <sub>2</sub> -65	0, an addi	itional po	eak arou	nd 27.6°	was obs	served,
215	being attributed to t	he (110)	crystallo	ographic p	lane of r	utile TiC	D <sub>2</sub> (PDF )	21-1276,	, space
216	group P42/mnm). Q	uantitativ	ve analys	is revealed	d 10% of	rutile co	ntent in t	he c-TiC	D <sub>2</sub> -650.
217	The samples c-CeO	x∕TiO₂-y,	all calc	ined at 60	0 °C, also	o describ	ed the m	nentioned	l rutile
218	peak, no observed a	at this ter	nperatur	e for the j	pure c-T	iO <sub>2</sub> -600	which sl	ightly de	ecrease
219	with the higher conte	ent of cer	ium fron	n 9% in c-0	CeO <sub>x</sub> /TiO	$D_2$ -1.5 to	7% in th	e c-CeO <sub>x</sub>	/TiO <sub>2</sub> -
220	6.0 sample. Furthe	rmore, n	nost like	ely due to	o the lo	w conce	entration	employ	ed, no
221	significant XRD sig	nals relat	ed to Ce	entities w	ere obsei	ved. Fur	thermore	, no chai	nges in
222	the cell parameters	were regi	stered at	fter Ce ado	lition wh	ich prov	ides evid	lence tha	t Ce is
223	primarily at the su	rface and	d not do	ping the	anatase	structure	[36]. It	is also	worth
224	mentioning that the	depositio	n strateg	y did not c	considera	bly influ	ence the	arrangen	nent or
225	crystallinity of the s	amples. A	As observ	ved, the sa	mples dis	splay rela	atively hi	gh crysta	allinity
226	and there is negligib	le variati	on withi	n the serie	es, hence	confirmi	ng that n	o alterat	ions of
227	the titania phases are	e taking p	place due	e to the de	position	strategy.			

The textural properties were analyzed by N<sub>2</sub> physisorption at 77 K. **Table 2** shows the results of specific BET surface area, pore volume, and pore size. As observed, all the nanostructures displayed a very similar BET area, an average value of  $41.8 \pm 0.8 \text{ m}^2 \cdot \text{g}^{-1}$ . The pore volume and size were also very uniform, with average values respectively, 0.104  $\pm 0.001 \text{ cm}^3 \cdot \text{g}^{-1}$  and  $7.6 \pm 0.1 \text{ nm}$ . These results support that the presence of CeO<sub>2</sub> species does significantly change the textural properties of TiO<sub>2</sub>, especially for the specific surface area as reported in previous works [38]. The low developed porosity and low 13 crystal size suggest that it is reasonable to assume that the powder dispersion of these
materials can be illuminated without internal shading from pores [52], which is expected
to be beneficial during the photocatalytic process.

Sample	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	pore volume (cm <sup>3</sup> g <sup>-1</sup> )	pore size (nm)	bandgap (eV)
c-TiO <sub>2</sub> -500	42.8	0.102	7.80	3.1
c-TiO <sub>2</sub> -550	42.4	0.102	7.56	3.1
c-TiO <sub>2</sub> -600	41.8	0.104	7.45	3.1
c-TiO <sub>2</sub> -650	42.3	0.105	7.70	3.1
c-CeO <sub>x</sub> /TiO <sub>2</sub> -1.5	40.2	0.106	7.76	2.7
c-CeO <sub>x</sub> /TiO <sub>2</sub> -3.0	41.5	0.107	7.65	2.7
c-CeO <sub>x</sub> /TiO <sub>2</sub> -6.0	41.6	0.105	7.68	2.6

**Table 2.** Textural and optical properties of  $c-TiO_2$ -x and  $c-CeO_x/TiO_2$ -y samples

The morphology and element distribution was studied by STEM-EDX technique. Some micrographs and EDX analysis of the c-CeO<sub>x</sub>/TiO<sub>2</sub>-3.0 sample are depicted in **Fig. 3**. The STEM images show particles at nanosize scale, around 20 nm, aggregated in bigger aggrupation reaching the micrometer scale. It has been observed in the majority some internal space around them, responsible for the porosity created, probably promoted after the template removal by calcination. The mapping of Ce and Ti in the HAAF image, see **Fig. 3E**, confirmed the homogeneous distribution of cerium over the titania particles.





Figure 3. STEM pictures at different amplification (A-C), HAAF image (D), Ce and Ti
mapping (E), and EDX analysis (F-G) of the c-CeO<sub>x</sub>/TiO<sub>2</sub>-3.0 sample.

The chemical composition of the surface of the samples was analyzed by the XPS 249 technique. Fig. 3 displays the XPS spectra of Ti 2p, O 1s, and Ce 3d peaks of C-TiO<sub>2</sub>-250 500, c-TiO<sub>2</sub>-600, and c-CeOx/TiO<sub>2</sub>-y samples. No great differences in binding energy for 251 the Ti  $2p_{3/2}$  peak were registered, e.g.  $458.6 \pm 0.1$  eV, characteristic of Ti<sup>4+</sup> species. Ce 252 3d region displayed well separated spin-orbit components (3d<sub>3/2</sub> and 3d<sub>5/2</sub>), as shown in 253 Fig. 3D, which are further split by multiple contributions. The Ce 3d peak was 254 255 deconvoluted into four contributions [36,52,53]. As an example, Fig. S2 illustrates the representative contributions following the procedure described previously by Paparazzo 256 [53] in which peaks labeled as u and v were attributed to  $3d_{3/2}$  and  $3d_{5/2}$  spin-orbit states, 257

respectively. A quantitative analysis of  $Ce^{3+}$  and  $Ce^{4+}$  oxidation states is available in 258 **Table S1** by assigning the binding energies expected in the  $3d_{5/2}$  peak to Ce<sup>3+</sup> or Ce<sup>4+</sup> 259 [36]. As detected during the XPS analysis, the presence of surface  $Ce^{3+}$  is considerable, 260 which is frequently reported in the literature for the edge positions of ceria nanoparticles 261 [54]. This aspect strongly impacts oxygen and electron mobility due to the presence of 262 surface defects, reduced states of  $Ce^{3+}$  or oxygen vacancies in the  $CeO_x$  structure [52] 263 since promotes the reversible transition of  $Ce^{3+}/Ce^{4+}$  [34]. The formation of  $Ce^{3+}$  on the 264 surface can be promoted due to the presence of a Ce-Ti interface [55], which acts as a 265 stabilization effect produced at the edge of the interface of the oxides. It has been 266 suggested that the Ce<sup>3+</sup> content is a clear fingerprint for measuring the degree of contact 267 between CeO<sub>x</sub> and TiO<sub>2</sub> [36]. The O 1s spectra, see Fig. 4, was divided into two 268 contributions [37], oxygen in the lattice of oxide<sup>-</sup> bonds (~529.9 eV) and superficial 269 270 hydroxyl groups or oxygen vacancies on the surface (~531.5 eV). As observed in Fig. 5, the proportion of surface -OH is decreased due to the presence of  $CeO_x$ . 271



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Figure 4. High resolution of XPS survey spectra of O 1s, Ti 2p, and Ce 3d regions.

The optical properties of the nanostructures were analyzed by DRS-UV-visible. **Fig.** 5 depicts the absorption spectra of the different samples and the Tauc plot for the estimation of the bandgap values of the semiconductors, see **Table 2**. All the c-TiO<sub>2</sub>-x samples displayed a bandgap of ~3.1 eV. The presence of CeO<sub>x</sub> in the structure displayed a redshift in the optical absorption and, therefore, decreased the bandgap value as the Ce ratio was increased, e.g. from 3.09 eV (c-TiO<sub>2</sub>-600) to 2.62 eV (c-CeO<sub>x</sub>-TiO<sub>2</sub>-6.0).



Figure 5. DRS-UV-visible absorption spectra of c-TiO<sub>2</sub>-x and c-CeO<sub>x</sub>/TiO<sub>2</sub>-y samples
(A), and their Tauc plot for bandgap determination (B).

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Fig. 6D depicts the LVRPA absorption profiles, for the samples CeO<sub>x</sub>/TiO<sub>2</sub>-6.0 and 283 284 TiO<sub>2</sub>-600, respectively (see the profile for all the samples in the Supporting Information (Fig. S5). In Fig.6A-C is also schematically described the two-dimensional, two-285 directional model approach used (see details in the Supporting Information) [56]. In both 286 cases, and also for the results included in the Supporting Information, absorption behavior 287 was nearly identical (Fig. S5). Considering that the reactions were carried out under UV-288 289 irradiation, it is hence expected that CeOx/TiO2-6.0 and TiO2-600 exhibit similar absorption profiles under the investigated conditions. In this sense, it should be pointed 290 out that the incorporation of cerium entities has a clear influence on the optical properties, 291 292 increasing the absorption under visible light irradiation, as was also evidenced in Fig. 6. However, the enhancement of the light absorption in this range does not provide a 293 measurable catalytic activity. The samples were tested under visible illumination 294

conditions (Sylvania® F6W T5 Daylight lamp) with a null catalytic response (data notincluded).





**Figure 6.** (A) Representation of the r and z spatial mesh discretization of the photoreactor, (B) Directional mesh for Quadrant I, and (C) representation of quadrants of directions as a function of the direction cosines ( $\mu$ ,  $\eta$ ) concerning r and z-axis in a cross-section of the spatial cell. (D, E) LVRPA of the sample TiO<sub>2</sub>-600 and (F, G) LVRPA of the sample c-CeO<sub>x</sub>/TiO<sub>2</sub>-6.0.

## **303 3.2.** Photocatalytic benzaldehyde production

The photocatalytic activity of the solids prepared was assessed for the selective 304 oxidation of benzyl alcohol into benzaldehyde. The BA conversion and selectivity to BD 305 306 results are depicted in Fig. 7. Also, for comparison purposes, the benchmarked 307 Aeroxide® titania P25 was included. The coffee templated titania samples prepared at 500 and 550 °C displayed the lowest BA conversion, both ca. 14% in 4 h. The c-TiO<sub>2</sub>-x 308 samples prepared at over 600 °C reached a higher value, close to the obtained value of 309 commercial P25. The still appreciable residual content of spent coffee, within 2 to 1 %, 310 in the samples calcined at 500 - 550 °C may explain the lower photocatalytic conversion 311 if compared to those prepared at higher temperatures in which the removal of the coffee 312 313 template was more extensive. This is the reason why a calcination temperature of 600 °C 314 was set for the c-CeO<sub>x</sub>/TiO<sub>2</sub>-y samples as well as a well-defined formation of the anatase phase. 315



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Figure 7. Photocatalytic oxidation of benzyl alcohol to benzaldehyde: benzyl alcohol conversion and quantum yield (A), and selectivity to benzaldehyde (B). *Experimental conditions:* V=350 mL; T=30 °C;  $C_{BA,0}=1.5 \text{ mM}$ ;  $C_{CAT}=1 \text{ g } L^{-1}$ .

The cerium-modified samples improved the photocatalytic conversion and slightly 320 overtook the P25 result. Greater differences were observed in terms of selectivity of BA 321 to BD, see Fig. 8B. There was no registered tendency with calcination temperature, an 322 average of ~25%. The coffee template titania softly improved the selectivity towards BD 323 if compared to P25 (~22%). Nevertheless, the modification of the photocatalysts with the 324 presence of CeO<sub>x</sub> resulted in a high enhancement in the selectivity values. An addition of 325 1.5% CeO<sub>x</sub> raised the selectivity to almost 58%, i.e. two folded concerning bare c-TiO<sub>2</sub>-326 327 600. Higher CeO<sub>x</sub> amounts, 3.0 and 6.0%, almost three folded the value corresponding to the prepared bare c-TiO<sub>2</sub>-600, both catalysts average  $\sim$ 75% of selectivity. From the results 328 of reaction rate and selectivity, the sample c-CeO<sub>x</sub>/TiO<sub>2</sub>-3.0 led to the best results. The 329 330 conversion and selectivity values reached are very competitive if compared with other titania-based materials in the literature (see Table S2). 331

The differences registered in the photocatalytic performance were tentatively 332 correlated with the recombination effect of the photo-generated charges by the 333 photoluminescence technique. Fig. 8 depicts the PL profiles within 420-450 nm. As 334 335 observed, all the samples displayed a maximum located at 430-321 nm. A raise in the calcination temperature of the c-TiO<sub>2</sub>-x samples reduced the PL intensity peak, which 336 means a lesser recombination rate. This aspect explains the lower activity of the samples 337 338 treated at 500 and 550°C. The benchmarked P25 displayed a PL profile very close to c-TiO<sub>2</sub>-600. Regarding the presence of CeO<sub>x</sub>, it is observed a decrease in the PL peak if 339 compared to the bare  $c-TiO_2$  samples. The presence of  $CeO_x$  helps to delocalize the 340 photogenerated electron-hole pairs, minimizing therefore the recombination rate [57,58]. 341

Furthermore, the Ce content is important and according to the intensity of the PL peaks, there is an optimum of the lowest recombination peak, i.e. lower PL peak, for the sample  $c-CeO_x/TiO_2-3.0$ . This optimum Ce content is in good agreement with the photocatalytic activity in terms of either reaction rate or selectivity.



Figure 8. PL intensity of c-TiO<sub>2</sub>-x and c-CeO<sub>x</sub>/TiO<sub>2</sub>-y samples (A), and correlation of
the maximum PL peak value with calcination temperature if c-TiO<sub>2</sub>-x or Ce percentage
in c-CeO<sub>x</sub>/TiO<sub>2</sub>-y (B).

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The role played by the different oxidation species involved in the process of 350 photocatalytic oxidation of benzyl alcohol over the sample c-CeO<sub>x</sub>/TiO<sub>2</sub>-3.0 was studied 351 by adding chemical scavengers (see Fig. 9A). As the photocatalytic activation has been 352 conducted using acetonitrile as solvent and air has been bubbling in the suspension, the 353 354 plausible oxidizing agents responsible for the oxidation of benzyl alcohol are expected to be the photo-generated holes  $(h^+)$  and the superoxide radical  $(O_2^{-})$ . Oxalic acid has been 355 356 reported as a useful h<sup>+</sup> scavenger in photocatalytic reactions since hastily reacts after being adsorbed on the surface of the photocatalyst to trigger the formation of CO<sub>2</sub> [22,59– 357

61]. The reaction with the photogenerated electrons, although feasible, is slow (k= 358  $3.5 \times 10^7$  M<sup>-1</sup> s<sup>-1</sup> [62]). Accordingly, a test in the presence of oxalic acid was conducted, 359 leading to an important decrease in the BA conversion if compared to the blank, which 360 highlights the importance of  $h^+$  in the process. The role played by  $O_2^{\bullet-}$  was assessed by 361 purging the dissolved O<sub>2</sub>, and replacing the air bubbling with N<sub>2</sub> [63,64]. In the presence 362 of N<sub>2</sub> bubbling, partial inhibition of BA oxidation was observed; therefore, the 363 contribution of  $O_2^{\bullet-}$  cannot be discharged. Both  $h^+$  and  $O_2^{\bullet-}$  contribute to the overall 364 photo-degradation process. A plausible mechanism is provided in Fig. 9B. The sample c-365  $CeO_x/TiO_2$  is a heterojunction of  $CeO_x$  and  $TiO_2$  in which the second is the majority 366 367 compound. The energy level of the conduction band of ceria is more negative than titania [65], -0.31 vs -0.2 V [66]. Taking into account the bandgap values for both 368 semiconductors, the bands' alignment responds to a type II heterojunction. The 369 370 photocatalytic activation would start with the excitation of electrons of the electrons of TiO<sub>2</sub> from the valence band to the conduction band. CeO<sub>x</sub> could be also photo-excited 371 372 although at minor importance. The electrons of the conduction band of TiO<sub>2</sub> could be transferred to the Ce<sup>3+</sup> vacancies present in CeO<sub>x</sub>. This process supposes a partial 373 relaxation of the electrons that would avoid the undesirable recombination effect. This 374 phenomenon is not only proposed by the presence of  $Ce^{3+}$  in XPS but also by the minor 375 recombination effect suggested by the photoluminescence assays. The holes from TiO<sub>2</sub> 376 could inject their positive charge into the valence band of CeO<sub>x</sub>, promoting an enhanced 377 378 photo-charge separation. The oxidation of BA to BD, according to the scavenging test, is mainly produced by  $h^+$  and in lesser extent by  $O_2^{\bullet-}$ . 379



**Figure 9.** Photocatalytic oxidation of benzyl alcohol to benzaldehyde in the presence of chemical scavengers with c-CeO<sub>x</sub>/TiO<sub>2</sub>-3.0 (A). *Experimental conditions: V=350 mL;*  $T=30 \ ^{\circ}C; C_{BA,0}=1.5 \ mM; C_{CAT}=1 \ g \ L^{-1}; C_{Oxalic \ acid}=10 \ mM$ . Photocatalytic mechanism of c-CeO<sub>x</sub>/TiO<sub>2</sub> (B).

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The stability of the c-CeO<sub>x</sub>/TiO<sub>2</sub>-3.0 sample was studied in terms of photocatalytic 385 activity in sequential reusing tests. As shown in Fig. 10A, a slight decrease in the 386 photocatalytic BA conversion is observed but stabilized after the first run c-CeO<sub>x</sub>/TiO<sub>2</sub>-387 3.0 sample can be therefore considered stable after 5 reusing cycles. Moreover, the 388 389 photocatalyst after the final run was characterized by XPS and STEM and compared to the fresh sample. The XPS spectra of the spent catalyst (Fig. 10B and C) confirm no 390 change in the titanium oxidation state of titania whereas the cerium kept the contribution 391 392 of the 3+ and 4+ oxidation states with a very comparable to the profile of the fresh sample. STEM mapping confirmed the homogeneous distribution of cerium over titania particles 393 as similarly observed in the fresh sample. 394



Figure 10. Photocatalytic oxidation of benzyl alcohol to benzaldehyde in the presence of chemical scavengers with c-CeO<sub>x</sub>/TiO<sub>2</sub>-3.0 (A). *Experimental conditions: V=350 mL;*  $T=30 \ ^{\circ}C; C_{BA,0}=1.5 \ mM; C_{CAT}=1 \ g \ L^{-1}$ . High resolution of XPS survey spectra of Ce 3d (B) and Ti 2p (C) regions of fresh and used (5<sup>th</sup> run) c-CeO<sub>x</sub>/TiO<sub>2</sub>-3.0 sample (B). STEM picture (D), HAAF image (E), Ce and Ti mapping (F) of c-CeO<sub>x</sub>/TiO<sub>2</sub>-3.0 sample.

# 401 4. CONCLUSIONS

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A route for biomass valorization has been explored using spent coffee powder as a novel biomass sacrificial template to generate nanostructured  $TiO_2$  and  $CeO_x/TiO_2$ . Calcination temperatures as high as 600 °C were required for efficient removal of the coffee residue without negative impact on the photocatalytic activity if compared to the commercial  $TiO_2$ -P25, understood as benzyl alcohol conversion. The template  $TiO_2$ samples prepared over 600 °C, displayed a comparable P25 benzyl alcohol conversion and slightly higher selectivity to benzaldehyde. The characterization results suggested that the crystalline phase at a temperature below 600 °C was exclusively anatase, while at
650 °C the rutile phase started to be considerable (10%).

411 The presence of a low concentration of ceria (from 1.5 to 6.0 %), i.e. undetectable in the XRD patterns, led to the formation of superficial  $Ce^{3+}$  which resulted in benefits for 412 an improved electronic migration in the edges of the CeO<sub>x</sub>/TiO<sub>2</sub> heterostructure. The 413 optical properties were considerably improved and the absorption of radiation redshifted, 414 reducing consequently their bandgap values. Regarding the photocatalytic activity, the 415 incorporation of  $CeO_x$  on the TiO<sub>2</sub> in the coffee-templated approach did not considerably 416 impact the conversion of the alcohol. Nonetheless, and most importantly, the presence of 417 CeO<sub>x</sub> greatly enhanced the selectivity values observing a positive rising effect with ceria 418 content. Amounts of CeO<sub>x</sub> as high as 3.0-6.0% performed the highest selectivity values, 419 ca. 75%, which was almost the 3-folded value registered for the bare TiO<sub>2</sub> template or the 420 benchmarked P25. According to PL results, the sample c-CeO<sub>x</sub>/TiO<sub>2</sub>-3.0 displayed the 421 422 lowest recombination rate.

This work demonstrates that the environmentally friendly solvent-free template approach using biomass wastes as a sacrificial agent, such as spent coffee powder, is a feasible and attractive route to develop novel photocatalytic materials.

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