

Reverse micelle strategy for effective substitutional Fe-doping in small-sized CeO<sub>2</sub> nanocrystals: Assessment of adsorption and photodegradation efficiency of ibuprofen under

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1 **Reverse micelle strategy for effective substitutional Fe-doping in small-**  
2 **sized CeO<sub>2</sub> nanocrystals: assessment of adsorption and**  
3 **photodegradation efficiency of ibuprofen under visible light**

4  
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27 **Abstract**

28 Reverse micelle nanoreactors were successfully designed to synthesize small-sized ceria nanocrystals  
29 (3.5-4.2 nm) with a sizeable amount of substitutional iron. Undoped and doped CeO<sub>2</sub> catalysts with  
30 an iron content (0.50-10 mol %) compliant with the nominal value were prepared and tested for the  
31 first time for the removal of ibuprofen both in the dark and under UV or visible light irradiation.

32 The effective inclusion and distribution of iron in the ceria lattice were ascertained through in-depth  
33 physicochemical characterization. In particular, X-ray diffraction suggested the formation of an F-  
34 type crystal structure, ruling out the formation of separate iron-containing crystalline phases. On the  
35 other hand, substitutional doping of CeO<sub>2</sub> with Fe atoms favoured the formation of Ce<sup>3+</sup> defects and  
36 vacancy sites (VOs) with a maximum for the sample with 2.5 mol % iron (Fe2.5), as evidenced by  
37 X-ray photoelectron spectroscopy (XPS) measurements and Raman spectroscopy. UV-Vis  
38 spectroscopy showed that the optical properties were successfully modified by the presence of iron,  
39 which causes a gradual decrease in band gap as iron content increases. The experimental evidence  
40 was further verified and supported by density functional theory calculations. DFT calculations also  
41 revealed that the surface iron and oxygen vacancies are the preferential sites for ibuprofen adsorption.  
42 Nevertheless, it was found under dark conditions that adsorption capacity does not monotonically  
43 increase with iron content, revealing contrasting roles of surface characteristics. Indeed, catalytic  
44 experiments have identified a trade-off between adsorption and photodegradation, identifying Fe2.5  
45 as the best-performing catalyst for ibuprofen removal under visible light irradiation. These results  
46 were discussed by considering the key properties of the catalysts as well as their different surface  
47 charge determined by  $\zeta$  potential measurements. The best catalyst was tested through reuse  
48 experiments that proved its stability over 4 cycles. Finally, an attempt was made to identify the  
49 photodegradation by-products, allowing the detection of 1-ethenyl-4-(2-methylpropyl)benzene as the  
50 main by-product.

51

52 **Keywords:** Substitutional Fe doped CeO<sub>2</sub>, Reverse micelle, Ibuprofen, Photodegradation, DFT.

53

54

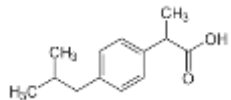
55

56 **1. Introduction**

57 Pharmaceuticals are considered emerging environmental pollutants due to the increase in their  
 58 consumption and consequent accumulation in water [1]. Ibuprofen (IBU) (Table 1), is among the  
 59 most widespread non-steroidal anti-inflammatory drugs (NSAIDs) in the world, whose presence in  
 60 wastewater is a serious concern because it is not biodegradable [2]. The detected concentrations for  
 61 ibuprofen in wastewater treatment plants are in the ranges of 55–69  $\mu\text{g}\cdot\text{L}^{-1}$  [3]. Over the last few  
 62 years, to address this environmental concern, several chemical, physical and biological methods have  
 63 been proposed [4]. Chemical methods include advanced oxidation processes (AOPs), coagulation-  
 64 flocculation, electrocoagulation, chemical oxidation, and ion exchange [4]. Among those, AOPs can  
 65 degrade recalcitrant pollutants with a rapid reaction rate and high removal efficiency due to the  
 66 generation of reactive free radicals [5].

67

68 **Table 1** - Structure and properties of ibuprofen

Compound	IUPAC name	Molecular formula	Molecular weight	Solubility in water	Structure
IBU	2-[4-(2-methyl propyl) phenyl]propanoic acid	$\text{C}_{13}\text{H}_{18}\text{O}_2$	206.28 g/mol	21 mg/L (at 25 °C)	

69

70 The use of semiconductors has broadened AOPs to heterogeneous photocatalysis, a process operating  
 71 at room temperature and atmospheric pressure [5–8]. Moreover, the combination, through the design  
 72 of an appropriate catalyst, with solar reactors makes this method stand out from others in terms of  
 73 environmental friendliness and cost-effectiveness through the use of renewable energy [9–11].  
 74 Indeed, nowadays, new photocatalysts active in the visible range are attracting increasing interest  
 75 among the scientific community [9].

76 Although some formulations for the catalytic photodegradation of ibuprofen under visible light were  
 77 explored, the proposed solutions suffer from the complicated design of the photocatalyst [12–17], and  
 78 typically the experiments are conducted in harsh reaction conditions (e.g., powerful lamps, highly  
 79 concentrated systems [14,15]). The challenge is therefore to design simple, inexpensive, high-  
 80 performance catalysts for optimal degradation of ibuprofen under visible light irradiation.

81 Cerium oxide was selected for its many trade-offs between reactivity, photochemical stability, cost-  
 82 effectiveness, and the environmentally friendly nature of  $\text{CeO}_2$  nanoparticles ( $\text{CeO}_2$ -NPs) [18–21].

83 The photocatalytic activity of cerium oxide can be enhanced, increasing the photo-absorption  
 84 capability, by replacing a small fraction of  $\text{Ce}^{4+}$  with a different cation [22,23]. Among heteroatom  
 85 dopants, transition metals are particularly appealing as they can create defect states in the band gap  
 86 or introduce energy levels into it. In this regard, iron is considered one of the most attractive  
 87 candidates on account of its environmental compatibility, abundance, and low cost [24]. One of the  
 88 most intriguing features of using  $\text{Fe}^{3+}$  as a dopant is the possibility of further promoting the generation  
 89 of oxygen vacancies (VOs) and the reversible conversion between the  $\text{Ce}^{4+}/\text{Ce}^{3+}$  valence state.  
 90 [25,26]. Oxygen vacancies not only extend the absorption edge but are reported to delay the electron–

91 hole recombination rates, thus increasing the separation efficiency of carriers for enhanced  
92 photocatalytic performances [27,28].

93 In conclusion, the introduction of Fe trivalent ions can be considered a powerful tool for rational  
94 defect engineering. Indeed, the beneficial effect of iron doping is reported by a certain number of  
95 papers for the photodegradation of model dye molecules under visible irradiation, recently reviewed  
96 [22]. Nevertheless, it must be considered that the influence of metal dopant and VOs on the ceria  
97 properties is interrelated to the concentration, distribution or position of Fe and defects in the ceria  
98 lattice [29]. In particular, the extent to which these features occur can be strongly impacted by the  
99 preparation method [30].

100 In this scenario, it should be noted that many methods reported in the literature suffer from poor  
101 reproducibility and control of process parameters, often failing to achieve real doping or, on the other  
102 hand, requiring harsh operating conditions [31–36]. The hydrothermal method was exploited by Cai  
103 et al. [32] for preparing Fe-doped ceria materials with different doping amounts. They obtained a  
104 catalyst with a crystallite size of approximately 100 Å and observed that the low Fe<sup>3+</sup> doping could  
105 effectively improve the concentration of Ce<sup>3+</sup>, enhancing the degradation ability of the model dye  
106 Acid Orange 7 (AO7). However, despite the versatility of the hydrothermal approach, it still  
107 represents a “black box” method as is impossible to have strict control over the process. Channei et  
108 al. [36] used flame pyrolysis to produce photocatalysts based on Fe-doped CeO<sub>2</sub> nanoparticles for the  
109 conversion of both formic acid and oxalic acid. This method, such as the aforementioned  
110 hydrothermal method, does not easily allow the control and variation of synthesis parameters  
111 invalidating the simplicity of the experimental setup [37].

112 In this perspective, it is important to have a method that goes beyond the trial-and-error approach and  
113 allows rigorous control of the composition of the catalyst, preserving its homogeneity and promoting  
114 improved optical, structural, and morphological properties.

115 Based on the previous considerations, in our work, we bring the reader's attention to a Fe-doped ceria  
116 system, so far never adopted for the photodegradation of ibuprofen. A further outcome of this research  
117 was the development of a versatile and reliable synthesis protocol, capable of exploiting the  
118 recognised advantages and potential of the one-pot reverse micelle approach. From a practical point  
119 of view, a significant advantage of the method is its scalability, including synthesis in microfluidic  
120 systems, for the production of larger quantities of catalysts [38–44].

121 The homogeneity of the final material is due to atomic-scale mixing, which in turn is ensured by the  
122 presence of a small aqueous core, where the reaction takes place. This mixing allows to easily promote  
123 the presence of the dopant in the oxide lattice. The size and shape of these small water domains can  
124 be controlled by varying the ratio between the liquid phases (water and oil) and selecting the right  
125 surfactant in terms of both type (non-ionic, anionic, cationic and amphoteric) and amount. As a result,  
126 not only the intimate contact of the metal precursor is well confined, but also the relative nucleation  
127 on growth steps can be easily monitored [45].

128 A pure ceria and iron-doped ceria with metal contents of 0.5, 2.5, 5 and 10 mol % Fe were prepared  
129 channelling the reactions that usually take place in aqueous media into the small domains of the  
130 reverse micelles.

131 To assess the physicochemical properties and to understand the structure/composition-activity  
132 relationship of Fe-doped CeO<sub>2</sub> in the photodegradation of ibuprofen, an in-depth characterisation was  
133 conducted. In detail, the prepared catalysts were characterised using various analytical techniques  
134 such as inductively coupled plasma mass spectrometry (ICP-MS), Thermogravimetric analysis  
135 (TGA), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), Field

136 emission scanning electron microscopy (FESEM), Diffuse reflectance spectroscopy (DR/UV-Vis),  
137 Raman spectroscopy, N<sub>2</sub> adsorption/desorption at -196 °C, X-ray photoelectron spectroscopy (XPS)  
138 and ζ-potential measurements.

139 Density Functional Theory (DFT) calculations were performed in order to investigate the stability  
140 and the effects on the electronic and structural properties of the CeO<sub>2</sub>(111) in the presence of  
141 substitutional and interstitial Fe atoms. The calculations suggest that, in a wide range of temperatures  
142 and pressure, the thermodynamically most stable structures are the ones where Fe atoms substitute  
143 Ce sites in the presence or absence of oxygen vacancies in agreement with the experimental  
144 observations. Additional calculations were performed to investigate the interaction between undoped  
145 and Fe-doped ceria surfaces with ibuprofen in order to identify preferential sites for adsorption.

146 The catalysts were tested both in the dark and under either UV or visible irradiation, to compare the  
147 performance of each synthesized material. A preliminary kinetic model was implemented to measure  
148 the activity of each catalyst in terms of both ibuprofen adsorption and related photodegradation. Reuse  
149 experiments were conducted to test the stability of the most active material, further assessed by post-  
150 reaction characterizations. Finally, an attempt was made to determine the photodegradation products  
151 via specific analytical methods (i.e., GC and LC-MS).

152

## 153 2. Materials and methods

154 Cyclohexane (ACS reagent ≥ 99.5%), cerium nitrate hexahydrate, iron chloride (reagent grade 97%),  
155 ammonia (ACS reagent 28-30%), 1-butanol (ACS reagent ≥ 99.4%), polyoxyethylene (10) cetyl ether  
156 (Brij C10) and ethanol (puriss ≥ 99.8%) were purchased by Sigma-Aldrich and used without further  
157 modification. Bi-distilled water has been used for the preparation of salt solution. Ibuprofen solutions  
158 were prepared using 4-isobutyl- $\alpha$ -methylphenylacetic acid, 99% (manufactured by Alfa Aesar).

159

### 160 2.1 Precipitation by reverse micelles

161 In a typical synthesis, adapted from the literature [46,47], the oil/surfactant phase is prepared by  
162 dissolving 8.2 g of surfactant (Brij C10) in 100 mL of cyclohexane under stirring at room temperature.  
163 An aqueous solution is prepared by dissolving the proper amount of cerium and iron precursors in  
164 distillate water to achieve a final concentration of 0.5M. The volume of the aqueous precursor solution  
165 has been selected to obtain a  $w_0$  value of 25 ( $w_0$  is defined as the water-surfactant molar ratio). The  
166 aqueous solution is slowly added dropwise to the oil phase to obtain appropriate water-in-oil (w/o)  
167 micelles. To preserve the optical transparency of the emulsion, avoiding the formation of flocculates,  
168 4 mL of co-surfactant (1-butanol) are also added. The optimised protocol involves alternating the  
169 additions of water and the co-surfactant. Finally, 5.4 mL of precipitating agent, ammonia solution,  
170 are slowly dripped. The mixture is stirred for 1.5h at room temperature. The solid phase is then  
171 collected by centrifugation, washed twice with ethanol and dried under a hood for 2 days. The dried  
172 powder has been manually ground before being calcinated at 120 °C for 6 h. The amounts of cerium  
173 and iron were calculated to obtain a nominal composition expressed as a molar % of iron equal to 0  
174 mol % (CeO<sub>2</sub>), 0.5 mol % (Fe0.5), 2.5 mol % (Fe2.5), 5 mol% (Fe5) and 10 mol % (Fe10). Samples  
175 Fe2.5 after its use as a catalyst for the ibuprofen degradation under visible light was labelled  
176 Fe2.5\_post reaction.

177

## 178 2.2 Structural, morphological and surface characterization

179 Thermogravimetric analysis was performed on Mettler-Toledo TGA/SDTA 851e instrument. The  
180 curves were recorded in air increasing the temperature from 25 to 800 °C at the rate of 10 °C/min.

181 Inductively coupled plasma mass spectrometry (ICP-MS) analysis (ICAPQ Thermo Scientific) was  
182 applied to determine the effective composition of the prepared catalysts, expressed as Fe/Ce molar  
183 ratio. Before analysis, samples are subjected to an extraction process with a hot nitric acid solution to  
184 ensure complete dissolution of the interest elements. The subsequent dilutions method is used to  
185 achieve the concentration range used for calibration curve preparation.

186 X-ray powder diffraction (XRPD) was performed on a Philips X'Pert diffractometer equipped with a  
187 Cu K $\alpha$  radiation ( $2\theta$  range = 5° - 90°; step = 0.02°  $2\theta$ ; time per step = 1 s). Lattice parameters and  
188 cell volumes were determined by UnitCell Software, while the crystallite size (L) has been calculated  
189 by Scherrer formula:  $L = \frac{k\lambda}{\beta\cos\theta}$ , k is a constant equal to 0.90,  $\lambda$  is the X-ray wavelength equal to  
190 0.154 nm,  $\beta$  is the full width at half maximum, and  $\theta$  is the half diffraction angle.

191 The optical properties of the powders were recorded on a UV-Vis Varian Cary 5000  
192 spectrophotometer equipped with a DR integration sphere in the 200–600 nm range. The indirect  
193 band gap values are obtained by applying the Tauc plot method referring to the formula  
194  $(F(R)h\nu)^{1/2} = f(h\nu)$ .

195 The vibrational properties of the samples have been analysed with Raman spectroscopy. Spectra were  
196 collected and recorded at room temperature with a LabRAM HR spectrometer (Jobin Yvon-Horiba),  
197 using a X50 confocal microscope and an excitation wavelength of 532 nm. The excitation power was  
198 kept low to ensure no photodegradation of the samples. The spectra were dispersed with 1800 gr/mm  
199 grating, leading to a 1 cm<sup>-1</sup> accuracy.

200 Transmission Electron Microscopy characterization was carried out with a Thalos F200X instrument  
201 (ThermoFisher) and Energy Dispersive X-ray spectroscopy (EDX) spectra were acquired with four  
202 Silicon drift detectors (SDD). The catalysts as dry powders were dispersed in isopropyl alcohol and  
203 subsequently drop-casted onto Cu holey carbon grids. Before insertion in the TEM column, the  
204 samples were plasma-cleaned in Ar atmosphere. Thermo Scientific Velox software was used for the  
205 analysis of TEM and EDX data. The crystallographic model for cubic CeO<sub>2</sub> (Fm-3m space group) is  
206 provided in the Crystallography Open Database (COD ID: 4343161). To complete the morphological  
207 characterization a field emission scanning electron microscopy (FE-SEM) was used (ZEISS  
208 MERLIN instrument (Oberkochen, Germany)).

209 Textural properties have been evaluated through N<sub>2</sub> physisorption and desorption at 77K  
210 (Quantachrome Autosorb1 Instruments.). Before the measurement, the sample was outgassed under  
211 a high vacuum at 120°C for 3 hours to remove pollutants previously adsorbed. From the isotherm  
212 obtained by nitrogen adsorption, the specific surface area (SSA) of the samples was calculated  
213 according to the BET (Brunauer–Emmet–Teller), total pore volume, V<sub>p</sub>, was determined from the  
214 amount of adsorbed N<sub>2</sub> at p/p°=0.98. BJH pore size distribution was determined by the desorption  
215 branch of isotherms [48,49].

216 X-ray photoelectron spectroscopy (XPS) measurements were carried out in a Prevac spectrometer  
217 using a focused monochromatic Al K $\alpha$  X-ray source (1486.6 eV) with a pass energy of 40 meV for  
218 survey scans and 20 meV for detailed scans. Despite our efforts, sample charging occurred and was  
219 only partially compensated by an electron flood source. Binding energies were then shifted from one  
220 core level to another. To analyse the spectra, the O1s signal was shifted to reach O $\alpha$  at 529 eV, while

221 the Ce3d signal referred to as  $v'''$  was set at 898.4 eV. Some peak broadening may have resulted  
 222 from the residual charge. All the peaks were fitted with a Voigt shape function.

223  $\zeta$ -potential curves were obtained by measuring the electrophoretic mobility as a function of pH at  
 224 30°C with a Litesizer (Anton Paar Instruments, Worcestershire, UK). The samples were prepared  
 225 with a starting concentration of 1 mg/50mL, and subsequently, 0.1 M NaOH or 0.1 M HCl were added  
 226 to varying the pH. The  $\zeta$ -potential measurements were carried out in an Omega cuvette (Anton Paar)  
 227 accessory. The measurements were performed in triplicate.

228 FT-IR 4700LE (JASCO, Tokyo, Japan) using the ATR (attenuated total reflectance) was used to  
 229 obtain Fourier transform infrared (FTIR) spectra, the spectrum was obtained at a resolution of 2 cm<sup>-1</sup>  
 230 over the range of 400-4000 cm<sup>-1</sup>. Firstly, the sample of pristine photocatalyst Fe2.5 was mixed with  
 231 potassium anhydrous bromide (KBr) (m/m, 1:2000), and the mixture was pressed to obtain a pellet.  
 232 KBr was used also as reference material. To identify the interaction between IBU and Fe2.5 catalyst,  
 233 the pellet of Fe2.5 was covered with a drop of saturated IBU solution and dried in an oven at 60°C  
 234 for one hour before the analysis.

235

### 236 2.3 Computational Details

237 Density Functional Theory (DFT) calculations were performed within Periodic Boundary Conditions  
 238 (PBC) using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional based on the  
 239 generalized gradient approximation (GGA) [50] and ultrasoft pseudopotentials [51]. The spin  
 240 polarized Kohn-Sham equations were solved in the planewave pseudopotential framework, with the  
 241 wavefunction basis set and the Fourier representation of the charge density being limited by kinetic  
 242 cutoffs of 60 and 500 Ry, respectively. The Quantum Espresso code [52] was employed for all  
 243 calculations. It is well established that a reliable description of both stoichiometric and reduced ceria-  
 244 based materials can be achieved by adding a Hubbard U term to the GGA energy functional acting  
 245 on the f states of the Ce ions. Therefore, all the calculations reported in this work were performed at  
 246 the DFT+U level, as implemented by Cococcioni and de Gironcoli [53], employing a U value of 4.5  
 247 eV. This is consistent with previous literature reporting values between 4.5 and 5 eV [54–65]. In all  
 248 calculations the Brillouin zone integration was performed on the  $\Gamma$  point only.

249 All the calculations were performed on the (111) termination of CeO<sub>2</sub> (Fig. SI.1), being the most  
 250 stable one and the most present in the experiment (see Fig. 1a). We are aware that this represent a  
 251 simplification of the system prepared from experiments but from a computational point of view is not  
 252 possible to capture the complexity of the real system. The Ibuprofen (IBU) molecule is anionic in  
 253 experimental pH-neutral conditions [66], therefore it was simulated in its deprotonated form when  
 254 adsorbed on the CeO<sub>2</sub>(111) surface. The proton released by the molecule is transferred to O3c (tri-  
 255 coordinated O) atoms of the surface similarly to previous theoretical studies [67–70].

256 The CeO<sub>2</sub> (111) surface was modelled using a (5x4) slab supercell with three O-Ce-O trilayers (180  
 257 atoms) and separated by more than 20 Å of vacuum in the direction perpendicular to the surface.  
 258 During the optimizations, the bottom tri-layer of the slab was fixed to simulate the equilibrium bulk-  
 259 like position, while the upper two tri-layers and the organic ligand were fully relaxed. The O-defective  
 260 systems were modeled by removing O3c and O4c atoms from the surface and subsurface layers of  
 261 the CeO<sub>2</sub> (111) slab (VO<sub>x</sub>). The formation energies of the oxygen vacancies were computed as  
 262  $E_{FORM(VO_x)} = E_{VO_x} - E_{CeO_2} + \frac{1}{2}E_{O_2}$ , where  $E_{CeO_2}$  is the energy of the stoichiometric surface, while  
 263  $E_{VO_x}$  and  $E_{O_2}$  are the energies of the surface with oxygen vacancies and of the gas phase O<sub>2</sub> molecule,  
 264 respectively.

265 The adsorption energy of IBU was computed using the formula  $E_{ads} = E_{CeO_2/IBU} - (E_{CeO_2} +$   
 266  $E_{H-IBU})$ , where  $E_{CeO_2/IBU}$  is the energy of the combined system (namely the surface plus the anionic  
 267 IBU),  $E_{CeO_2}$  is the energy of the stoichiometric and/or O-defective surface ( $E_{VOx}$ ) alone, and  $E_{H-IBU}$   
 268 is the energy of the neutral IBU in gas phase.

269 The substitutional and interstitial Fe-doping effects were evaluated by replacing and adding Ce atoms  
 270 in all considered systems.

271 In order to analyze the thermodynamic stability of different structures in the absence and in the  
 272 presence of i) Fe dopant and ii) oxygen vacancies as a function of temperature and pressure, the  
 273 formalism of approximate *ab initio* thermodynamics was employed [71–74]. According to this  
 274 formalism, the Gibbs energies of the formation of the different ceria systems depend on the  
 275 temperature and pressure through the following expression (Eq.1):

$$276 \quad \Delta G_{ads}(T, p) = \frac{1}{A} \{ E_{tot} - E_{CeO_2} + N_0^V \mu_0(T, p) + N_{Ce}^V [E_{CeO_2}^{bulk} - 2\mu_0(T, p)] - \mu_{Fe} \} \quad (1)$$

277 where  $A$  is the surface area,  $E_{tot}$  and  $E_{CeO_2}$  are the total energies of the considered ceria system and  
 278 stoichiometric ceria surface, respectively. The quantities  $N_O$  and  $N_{Ce}$  represent the number of O and  
 279 Ce vacancies present in the structure under consideration, whereas  $E_{CeO_2}^{bulk}$  is the energy of a formula  
 280 unit of the  $CeO_2$  bulk phase. Finally,  $\mu_{Fe}$  and  $\mu_O$  are the oxygen and iron chemical potentials. The  
 281 chemical potential of Fe,  $\mu_{Fe}$ , is set to be the total energy per atom of the bulk Fe crystal, whereas the  
 282 upper bound of the chemical potential of  $O_2$ ,  $\mu_O(T, p)$ , is given by the total energy of molecular  
 283 oxygen,  $\frac{1}{2} E_{O_2}$ . This upper bound is taken as the zero of our energy scale by using  $\Delta\mu_O(T, p) = \mu_O - \frac{1}{2}$   
 284  $E_{O_2}$ . In addition, assuming that volume and entropy contributions are negligible in  $\Delta G_{ads}(T, p)$  [73],  
 285 the Gibbs energies are approximated by the total energies of our DFT calculations.

286 Electronic properties were investigated only for the most stable systems. In addition, to determine the  
 287 approximate oxidation states of anions and cations the charge analysis was performed following the  
 288 Bader's theory since the charge enclosed within the Bader volume can be considered a good  
 289 approximation of the total electronic charge of an atom [75–77].

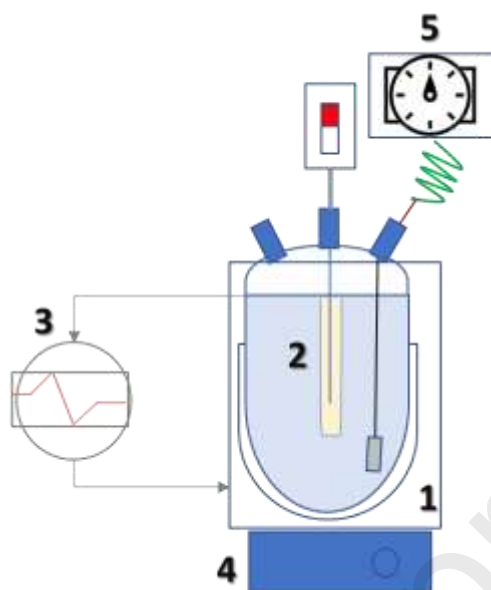
290

## 291 2.4 Catalytic and kinetic tests

292 The photodegradation experiments were conducted in a 1.5 L jacketed glass vessel, closed with a  
 293 three-neck lid, as reported in Scheme 1. The reactions were carried out using a co-axial lamp,  
 294 connected to the reactor through the central neck of the lid. In particular, two different lamps were  
 295 used: a lamp irradiating in the visible region (Sylvania T5, with a power of 4W and a colour  
 296 temperature of 6500 K, solar emission spectrum, potential difference 220V, and geometry 14 cm x  
 297 1.5 cm), or a lamp irradiating in the UV region (Toshiba FL4BLB, with a power of 4W and emission  
 298 at a wavelength of 365 nm, potential difference 220 V, and geometry 15 cm x 1.5 cm). The irradiance

299 of the lamp in the experimental apparatus was estimated to be 510 W/m<sup>2</sup>. One neck of the lid was left  
 300 free for collecting samples during the reaction, while the last neck is used for measuring the solution  
 301 temperature through a dedicated thermocouple. The reaction temperature was controlled using an  
 302 ultra-thermostat while the dispersion agitation was ensured by magnetic stirring. The airflow rate was  
 303 set through an electronic gas flowmeter regulator (supplied by Bronkhorst). Air dispersion was  
 304 enhanced by connecting the outlet of the gas flowmeter regulator to a sintered filter of 50 mesh,

305 immersed in the liquid-solid dispersion. This technical solution allowed it to reach a high gas-liquid  
 306 surface area, minimizing eventual gas-liquid mass transfer limitations.



307  
 308

309 **Scheme 1:** Reaction system sketch. 1 Batch reactor, 2 lamps, 3 ultra-thermostat, 4 stirring plates, 5  
 310 digital flowmeter regulator.

311

312 As ibuprofen is characterized by relatively low solubility in water (21 mg/L, 25 °C) [78], the solutions  
 313 (with an initial concentration,  $C_{IBU,0}$ , of 12.4 mg/L) have been prepared and kept in stirring overnight  
 314 at room temperature and covered with aluminum foil to protect the solution from the light. After the  
 315 total dissolution of ibuprofen, the solution is transferred into the reactor, stirred at 750 rpm and  
 316 warmed up at 30°C. At this point, the catalyst ( $\rho_B=0.07\text{g/L}$ ) was loaded into the reactor. It is important  
 317 to underline that the operation conditions were chosen from preliminary tests to measure the catalytic  
 318 activity of the catalysts synthesized in this work.

319 Three different types of kinetic experiments were conducted: (i) adsorption; (ii) under UV irradiation;  
 320 (iii) under visible irradiation. In the first case, the system was covered with aluminum foils to prevent  
 321 any contact with the solution with the solar light. In the other two cases, a specific lamp was adopted  
 322 as previously stated. Also in the latter cases, the system was covered with aluminum foil. Airflow  
 323 was adjusted using the digital flow meter and was set at a fixed flow (50mL/min), allowing it to reach  
 324 full saturation of oxygen in the water. Of course, no air was fed during the adsorption experiments.  
 325 The reaction was then started by switching on the lamp and prosecuting until a maximum time of 5h.

326 Before any subsequent operation, a first sample was collected to check the initial ibuprofen  
 327 concentration ( $C_{IBU,0}$ ); subsequently, samples were collected every 30 minutes for the first 2 hours of  
 328 reaction, and every hour for the remaining three hours (0, 30, 60, 90, 120, 180, 240 and 300 minutes).  
 329 Each sample was then centrifuged at 3300 rpm for 30 minutes, and the resulting liquid sample was  
 330 analyzed by UV-VIS spectroscopy (UV-Vis Jasco V-550), see Supplementary Information for details  
 331 (Fig. SI.2 and Equation SI-1, i.e., the calibration curve).

332

#### 333 2.4.1 Regeneration experiments

334 The stability of the most active catalyst was tested via reuse experiments, adopting the following  
335 reaction conditions:  $T=30^{\circ}\text{C}$ ,  $C_{\text{IBU},0}=12.4\text{mg/L}$ ,  $\rho_{\text{B}}=0.07\text{ g/L}$ , visible light, Fe<sub>2.5</sub> catalyst. In  
336 particular, the catalyst was recovered after each photodegradation test, by filtering it on a Buchner  
337 funnel. Before reusing it, the catalyst was washed several times on the funnel itself using water, and  
338 then was recovered by filtration and oven-dried for 12 h at  $60^{\circ}\text{C}$ . The procedure was repeated for  
339 four cycles [79].

#### 341 2.4.2 Photodegradation products identification

342 A dedicated kinetic experiment was performed to identify the reaction products. The experiment was  
343 performed using the Fe<sub>2.5</sub> catalyst under visible irradiation, adopting an initial concentration of  
344 ibuprofen of  $12.4\text{ mg/L}$ , a catalyst loading of  $0.07\text{ g/L}$ , a stirring rate of  $750\text{ rpm}$ , and a temperature  
345 of  $30^{\circ}\text{C}$ .

346 LC-MS analysis was performed by an Agilent HPLC system (1260 Series) coupled to an Agilent  
347 6230 TOF mass spectrometer apparatus. The HPLC separation was carried out on a reverse-phase  
348 C18 column (Poroshell 120 EC-C18 3x50 mm 2.7  $\mu\text{m}$  from Agilent Life Sciences) by using water  
349 and acetonitrile as mobile phases A and B, respectively, both acidified with 0.1% formic acid. A  
350 linear gradient was employed by increasing mobile phase B from 50% to 95% over 9 min at a flow  
351 rate of  $0.3\text{ mL min}^{-1}$ . The injection volume of each sample was  $20\text{ }\mu\text{L}$  and the MS source was an  
352 electrospray ionization (ESI) interface in the positive ion mode with a capillary voltage of  $3000\text{ V}$ ,  
353 gas temperature at  $325^{\circ}\text{C}$ , dry gas ( $\text{N}_2$ ) flow at  $5\text{ L min}^{-1}$  and the nebulizer pressure at  $35\text{ psi}$ , the  
354 fragment at  $50\text{ V}$ . The MS spectra were acquired in a mass range of  $50\text{--}1000\text{ m/z}$  with a rate of  
355  $1\text{ spectrum/s}$ , abundance threshold 200 (0.015 relative thresholds).

356 GC-MS analyses were performed on a 5390 MSD quadrupole mass spectrometer (Agilent  
357 Technologies) equipped with a gas chromatograph by using a Polysiloxane DB-5 column ((5%-  
358 Phenyl)-methylpolysiloxane, Agilent Technologies) ( $30\text{m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$ ) from Phenomenex.  
359 The injection temperature was  $250^{\circ}\text{C}$ , the oven temperature was increased and held at  $50^{\circ}\text{C}$  for three  
360 minutes and then increased to  $150^{\circ}\text{C}$  at  $10^{\circ}\text{C/min}$ , increasing to  $230^{\circ}\text{C}$  at  $14^{\circ}\text{C/min}$  and finally to  
361  $280^{\circ}\text{C}$  at  $15^{\circ}\text{C/min}$  held for 7 min. Electron Ionization mass spectra were recorded by continuous  
362 quadrupole scanning at  $70\text{ eV}$  ionization energy, in the mass range of  $m/z\ 40\text{--}550$  analysis. Each  
363 sample was measured in triplicate.

364

365

### 366 3. Results and discussion

367

#### 368 3.1 About the adopted reverse micelle approach

369 Although the co-precipitation-based synthesis method is extensively used, with a very simple set-up,  
370 it suffers from poor control over particle size and homogeneity in mixed oxide systems [80].

371 In this work, the aforementioned drawbacks were overcome by channelling the reactions that  
372 normally take place in aqueous media into the small domains of reverse micelles. Specifically, an  
373 aqueous solution containing the iron and cerium precursor was added to a solution of the non-ionic

374 surfactant, Brij C10, in cyclohexane, generating a water-oil microemulsion. The cage-like  
375 environment provided by the microemulsion with the simultaneous presence of the cerium and iron  
376 precursors, enabled excellent control of the final stoichiometry, resulting in homogeneity and mixing  
377 on an atomic scale, ultimately favouring the effective inclusion of iron heteroatoms in large amounts,  
378 as discussed hereafter [80–84].

379 The synthesis parameters, in particular the type and nature of the surfactant and the water/surfactant  
380 ratio, were optimized after careful variation. The value  $w$ , defined as the water-surfactant molar ratio  
381 ( $[\text{H}_2\text{O}/\text{BrijC10}]$ ), is considered a key parameter for tuning the size of the spherical droplet, affecting  
382 the dynamics of water and defining the spatial confinement of the reaction [85,86]. The occurrence  
383 of chemical reactions was clearly visible through the colour change of the macrosystem, which moved  
384 from a colourless/pale yellow to purple-dense, turning yellow after the fixed reaction time (estimated  
385 at one and a half hours). The formation of the purple slurry was attributed to the generation of  
386 insoluble  $\text{Ce}^{3+}$  species that after the complete oxidation turned to yellow  $\text{Ce}^{4+}$  species [46,87]. The  
387 obtained material was recovered by centrifugation, washed to purify from the oil/surfactant, and left  
388 catalysts to dry under the hood. Then, the dried powders were heat treated at 120 °C for 6h. The  
389 absence of significant quantities of organic residues, confirming the effectiveness of the protocol  
390 without the need to use high calcination temperatures, was revealed by the thermogravimetric analysis  
391 (Fig. SI.3). The thermal behaviour of the material was explained by identifying three regions in the  
392 thermogravimetric curve: (i) from room temperature to 120 °C where the weight loss is due to  
393 physisorbed water, (ii) 200-350 °C related to the removal of chemisorbed water occurs, (iii) 400-800  
394 °C characteristic of combustion of organic compounds [88–90]. The synthesis procedure was  
395 designed to ensure the highest reproducibility. The effective presence of iron species into the ceria  
396 phase was highlighted by the different colour of the powders, changing from light yellow for pure  
397 ceria to a reddish-yellow with increasing in the Fe contents (Fig. SI.4).

398 The results of the quantitative analysis performed by ICP-MS are shown in Table 2. The Fe/Ce ratio  
399 is in excellent agreement with the nominal value, showing that the adopted synthesis protocol  
400 effectively preserves stoichiometry and avoids material losses during the production steps.

401

### 402 3.2 Structural, textural and surface properties

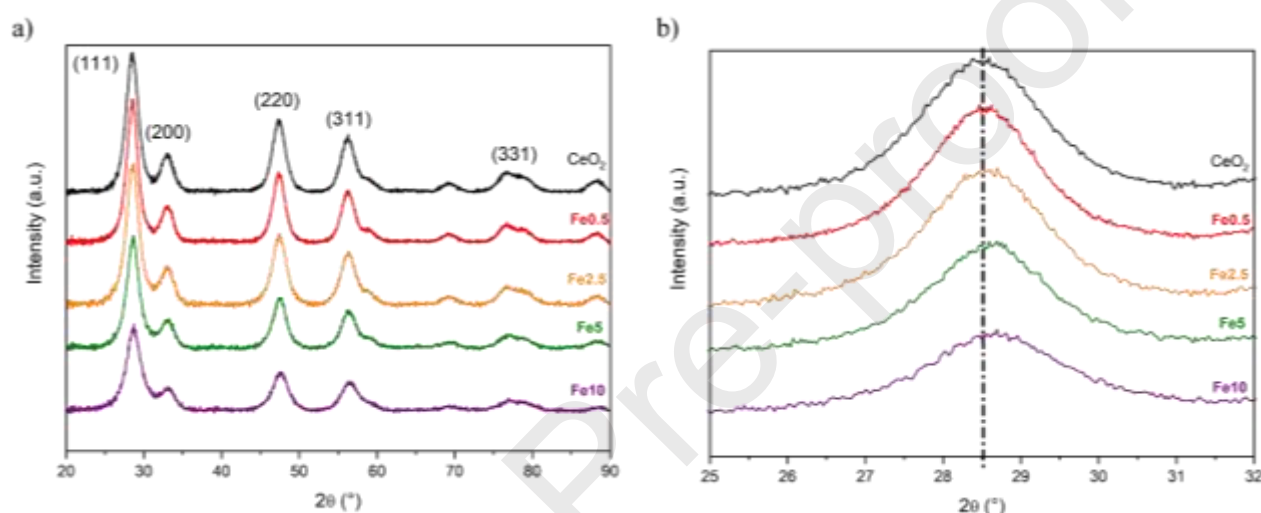
403 Cerium oxide occurs in the fluorite phase where the cerium atoms are organised in a face-  
404 centered cubic lattice structure with 8-fold coordination, while the oxygens are present as  $\text{OCe}_4$  units  
405 [91]. Defect chemistry and the numerous studies conducted on doped and undoped nanometric  $\text{CeO}_2$   
406 crystal structure have unequivocally stated that its reactivity and performance of heterogeneous  
407 catalysis are surprisingly modulable by engineering the defects and surface structure using a flexible  
408 and reliable synthesis procedure [92,93].

409 XRD diffraction patterns of ceria and Fe-containing ceria samples are reported in Fig. 1a. The  
410 pristine ceria shows an XRD profile corresponding to a cubic fluorite structure (JCPDS files 34-  
411 0394), where the peak at 28.5°, 33.3°, 47.1° and 56.1° can be associated with the planes 111, 200,  
412 220, and 311, respectively [46]. Although the diffraction patterns of Fe-containing samples reveal  
413 that the F-type crystalline structure is retained, the diffraction lines show a progressive shift towards  
414 higher 2-teta values, Fig. 1b [46]. As reported by many authors, an isomorphic substitution of  $\text{Ce}^{4+}$   
415 ions (ionic radius 0.97 Å, coordination number CN=8) by smaller  $\text{Fe}^{3+}$  ions (ionic radius 0.78Å,  
416 CN=8) can account for the lattice shrinkage, appearing as a displacement of the diffraction patterns  
417 towards higher angles [25,93]. The observed lattice constraint follows Vegard's law [94] as suggested  
418 by the lattice parameters reported in Table 2 and further evidenced by Fig. SI.5. Substitutional doping  
419 with the formation of oxygen vacancies, one oxygen vacancy paired with two  $\text{M}^{3+}$  for charge

420 neutrality, is a dominant mechanism for ceria doped with aliovalent cations [93,95]. Nevertheless,  
 421 the small size of  $\text{Fe}^{3+}$  also allows for a dopant interstitial compensation mechanism where three  $\text{Fe}^{3+}$   
 422 in substitution sites are coupled to one in interstitial sites. This last mechanism leads to a decrease in  
 423 oxygen vacancy concentration. The further increase in iron content may subsequently promote  
 424 epitaxial growth on the  $\text{CeO}_2$  surface [25,96]. In this scenario, the adopted synthesis method was  
 425 decisive in promoting substitutional doping, limiting the formation of crystalline phases attributable  
 426 to iron oxides. The type of doping was also supported by DFT calculation (*vide infra*).

427 Moreover, the control exerted by the aqueous core during synthesis is successfully reflected in the  
 428 formation of small-sized crystallites (Table 2), compared to the more conventional methods [96–98]

429



430

431

432 **Fig. 1:** a) XRD patterns of the synthesized samples in 2theta range 20°-90° and b) enlarged view of  
 433 (111) diffraction peak.

434

435 **Table 2:** Summary of analytical data: chemical composition calculated from ICP-MS elemental  
 436 analysis and structural parameters obtained from the cell refinement of the XRD patterns.

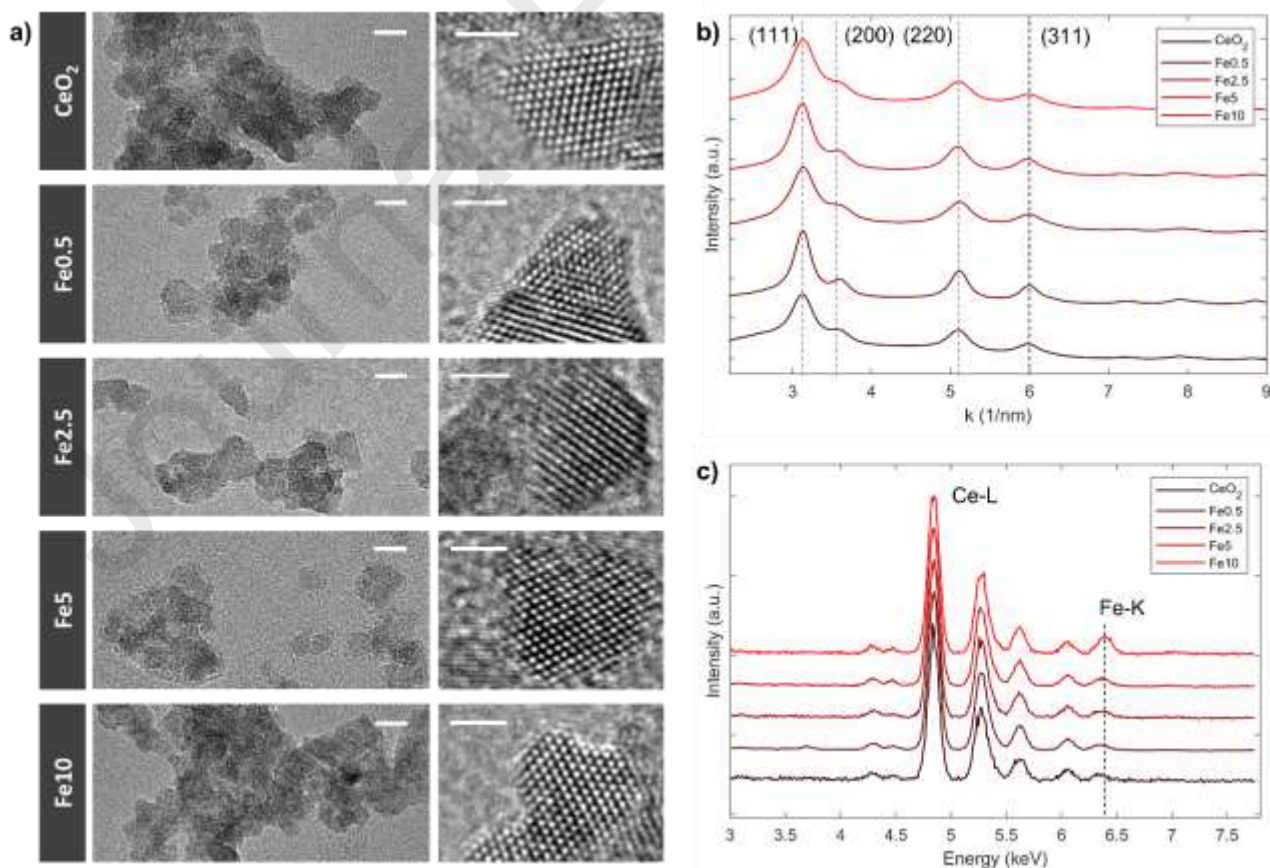
Sample	Nominal ratio Fe/Ce (molar %)	Actual ratio		Lattice Parameter (Å) <sup>a</sup>	Cell Volume (Å <sup>3</sup> )	Crystallite size, L (Å) <sup>b</sup>
		Fe/Ce ICP-MS (molar %)				
$\text{CeO}_2$	-	-		$5.4269 \pm 3 \cdot 10^{-4}$	$159.83 \pm 2 \cdot 10^{-2}$	42

<b>Fe0.5</b>	0.5	0.66	$5.4259 \pm 3 * 10^{-4}$	$159.74 \pm 2 * 10^{-2}$	44
<b>Fe2.5</b>	2.58	2.87	$5.4234 \pm 3 * 10^{-4}$	$159.52 \pm 2 * 10^{-2}$	40
<b>Fe5</b>	5.31	4.3	$5.4162 \pm 3 * 10^{-4}$	$158.89 \pm 2 * 10^{-2}$	40
<b>Fe10</b>	11.2	11.1	$5.4030 \pm 3 * 10^{-4}$	$157.72 \pm 2 * 10^{-2}$	34

437 <sup>a</sup> for fluorite phase; <sup>b</sup> Calculated using Scherrer equation due to (1 1 1) plane

438

439 Further insight into the morphology and structure of the iron-doped ceria catalysts is provided by  
 440 Transmission and Scanning Electron Microscopy (Fig. 2 and Fig.SI.6, respectively). Based on TEM  
 441 images (Fig. 2a), the catalyst powders are constituted of aggregates of approximately spherical  
 442 nanoparticles. Inspection of high-resolution images reveals that the nanoparticles are single  
 443 crystalline, with a crystalline structure corresponding to cubic CeO<sub>2</sub> (Fm-3m space group). It is worth  
 444 pointing out that the characteristic size of the nanoparticles is in the order of 5 nm or lower, in  
 445 accordance with the crystallite size estimation based on the application of the Scherrer formula on  
 446 XRD data.



447

448 **Fig. 2:** a) TEM high-resolution images of the different Fe-doped CeO<sub>2</sub> catalysts (scalebar: left  
 449 column 5 nm, right column 2 nm). Rotationally-averaged selected-area electron diffraction patterns  
 450 are provided in b). Representative EDX spectra are shown in c).

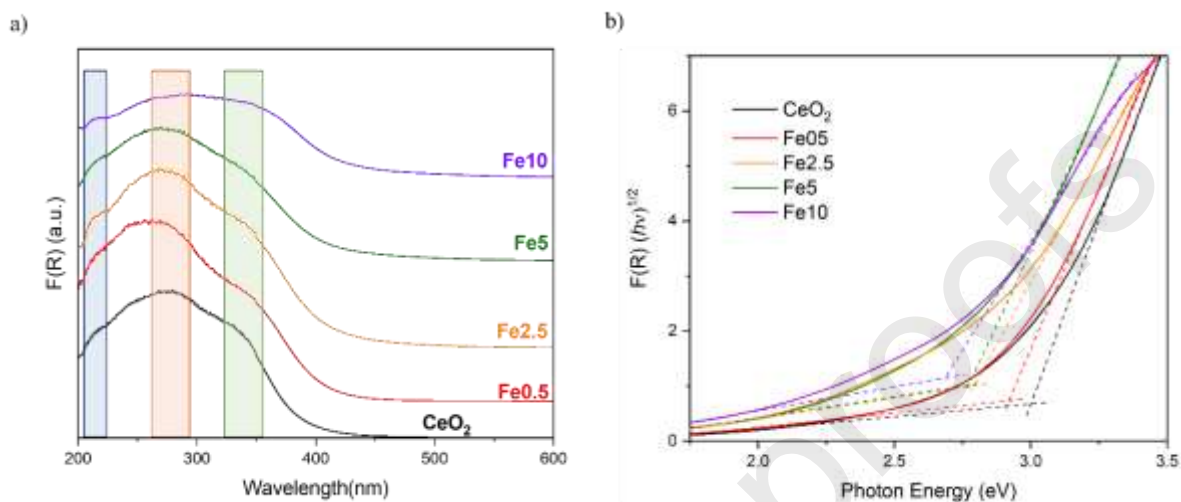
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452 Moreover, from high-resolution images, there is no evidence of secondary iron-containing crystalline  
 453 phases. This is confirmed by rotationally-averaged selected area electron diffraction (SAED) patterns,  
 454 such as the ones provided in Fig. 2b. For each Fe-containing catalyst sample, the diffraction patterns  
 455 only show peaks corresponding to the (111), (200), (220), and (311) family of crystallographic planes  
 456 of cubic CeO<sub>2</sub>, in agreement with the previously discussed XRD results. Finally, EDX spectra of the  
 457 catalysts (Fig. 2c) indicate the presence of Fe in all the samples besides pristine CeO<sub>2</sub>. It is interesting  
 458 to notice that the contribution from the Fe K $\alpha$  line ( $\sim$  6.4 keV) in EDX spectra correlates with the  
 459 nominal increase of Fe in the catalysts, confirming that the crystalline nanoparticles host an increasing  
 460 amount of Fe ions, without significant changes in the F-type crystalline structure of CeO<sub>2</sub>. The SEM  
 461 micrographs (Fig.SI.6) show a quasi-spherical shape of nanoparticles with a uniform distribution, in  
 462 agreement with the morphologies obtained from TEM data. To further confirm the presence of Fe in  
 463 all samples a compositional analysis has been done also by EDS. The atomic ratio Fe/Ce obtained  
 464 (average in 5 spots) is in good accordance with the theoretical molar ratio and experimental ICP data  
 465 (see Table SI.1 for details). The optical properties of the prepared materials were evaluated by UV-  
 466 Vis diffuse reflectance spectroscopy. The D(R) spectra are shown in Fig. 3a. The UV-Vis spectrum  
 467 of pure CeO<sub>2</sub>, black line, consisted of a strong absorption band located in the 200-400 nm range where  
 468 different transitions can be observed. The absorption at low wavelength, one centered at 215 nm and  
 469 the other at around 275 nm (blue rectangle and green rectangle in Fig. 3a, respectively), are generally  
 470 attributed to charge-transfer transitions between O 2p and Ce 4f orbital. In particular, the absorption  
 471 due to Ce<sup>3+</sup>  $\leftarrow$  O<sup>2-</sup> charge transfer is observed at 215 nm while the peak at a higher wavelength is  
 472 ascribed to Ce<sup>4+</sup>  $\leftarrow$  O<sup>2-</sup> transition [97,99]. The shoulder at 340 nm is assigned to interband transitions  
 473 [46]. The reported behaviour is also observed in the spectra of iron-containing samples; however, a  
 474 careful examination reveals some modifications.

475 The shift to the lower wave number of the main peak recorded for the Fe0.5 sample could be caused  
 476 by the isolated Fe<sup>3+</sup> species[100,101]. Indeed, Fe Oh and Td species show the typical transitions in  
 477 the UV range, allowing a not easy assignment due to overlapping absorption range with ceria. The  
 478 absorption at 215 nm appears more prominent when increasing the iron doping percentage up to  
 479 Fe2.5, thus suggesting a more pronounced presence of defective sites [102]. The spectrum recorded  
 480 for the Fe10 sample (purple curve) shows a feature at about 380 nm that is generally assigned to the  
 481 presence of oligomeric hematite-like clusters, as reported by Schwidder et al [42]. However, the  
 482 typical d-d transitions of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, located at 533 nm, are not observed. The lack of stoichiometric iron  
 483 phase is in accordance with the XRD results, whereas the oligomeric clusters are in accordance with  
 484 the Raman results, which evidence a contribution at ( $\sim$  670 cm<sup>-1</sup>) only into the sample at higher iron  
 485 loading (*vide infra*). The spectra of all the iron-doped catalysts show a red shift in the absorption  
 486 edge, indicative of the Ce-Fe interaction.

487 The effect of iron doping on the optical band gap was assessed by Tauc plot relation. In Fig. 3b  
 488  $(F(R)(h\nu)^{1/2})$  is plotted versus the photon energy,  $h\nu$ , and the indirect band gap energy ( $E_g$ ) was  
 489 obtained by applying the double tan approximation [103]. The band gap value of pristine CeO<sub>2</sub> was  
 490 found to be 3.0 eV. The effective inclusion of the Fe species in the ceria lattice results in a decrease  
 491 in  $E_g$ , ascribable to the introduction of vacant 3d orbitals between the valence and conduction bands  
 492 of CeO<sub>2</sub> [104].

493 Table 3 shows that  $E_g$  values decrease monotonically with iron content [36,60]. This trend is also  
 494 observed in the theoretical  $E_g$  values calculated for the undoped and Fe-doped  $\text{CeO}_2$  discussed in the  
 495 following DFT study section. The band gap values obtained in the iron-doped samples reported here  
 496 are somewhat lower than those reported in the literature for the same compositions [36,60,105–107].  
 497 Once again, all the previous features can be attributed to the adopted reverse micelle strategies.



498

499

500 **Fig. 3:** a) DR UV-Vis spectra of synthesized samples plotted as Kubelka-Munk function  $F(R)$ . b)  
 501 The indirect band gap calculation of pristine and Fe-doped porous  $\text{CeO}_2$  based on the Kubelka-  
 502 Munk function by Tauc plot relation using the double tan approximation.  $\text{CeO}_2$  (black curve); Fe0.5  
 503 (red curve), Fe2.5 (orange curve), Fe5 (green curve) and Fe10 (purple curve).

504

505 Significant information on the fate of iron in ceria nanocrystals can be obtained from Raman. The  
 506 spectra corresponding to the iron-doped samples are shown in Fig. 4a along with that of pure  $\text{CeO}_2$   
 507 nanocrystals. Three main contributions are observed. The prominent peak corresponds to the  $F_{2g}$  peak  
 508 and it results from the vibration of the O sublattice. It stands at  $458.5 \text{ cm}^{-1}$  for the pure  $\text{CeO}_2$   
 509 nanocrystals, some  $6.5 \text{ cm}^{-1}$  lower than the position of pristine bulk  $\text{CeO}_2$ . This shift is consistent with  
 510 the reported decrease of peak position with particle size reduction [91] and a Gruneisen parameter  
 511 value of 1.57. For instance, Spanier et al. [108] reported a  $4 \text{ cm}^{-1}$  redshift for 6 nm nanocrystals. The  
 512 peak shows an asymmetry towards low wavenumbers. Such an asymmetry is often seen in nanocrystal  
 513 samples and related to size dispersion [91,109,110].

514 As iron is incorporated into the nanocrystals, the  $F_{2g}$  peak mode is further softened and broadened.  
 515 Such behaviour was previously observed by Popovic et al. [111] for Fe-doped  $\text{CeO}_2$  nanocrystals.  
 516 The trend is not strictly monotonous with the nominal Fe concentration. Fig. 4b shows the correlation  
 517 between the  $F_{2g}$  peak shift ( $\Delta\omega$ ) and the corresponding variation of the peak FWHM (full-width-at-  
 518 half-maximum). The variation is linear as previously observed by Popovic et al. However, the slope  
 519 of our curve is -6.9, slightly higher than that reported in [111], with a value of -5.3. This behaviour  
 520 originates from two causes: grain size and strain effect (causing homogeneous line broadening) and  
 521 charges delocalization in oxygen-deficient ceria. Since all the samples have about the same  
 522 nanocrystal mean size, neither the mode softening nor the line broadening can be attributed to any  
 523 size effect. The observed linear variation thus results from changes in strain within the nanocrystals  
 524 and charge delocalization. The two phenomena are hard to disentangle without further modelling.

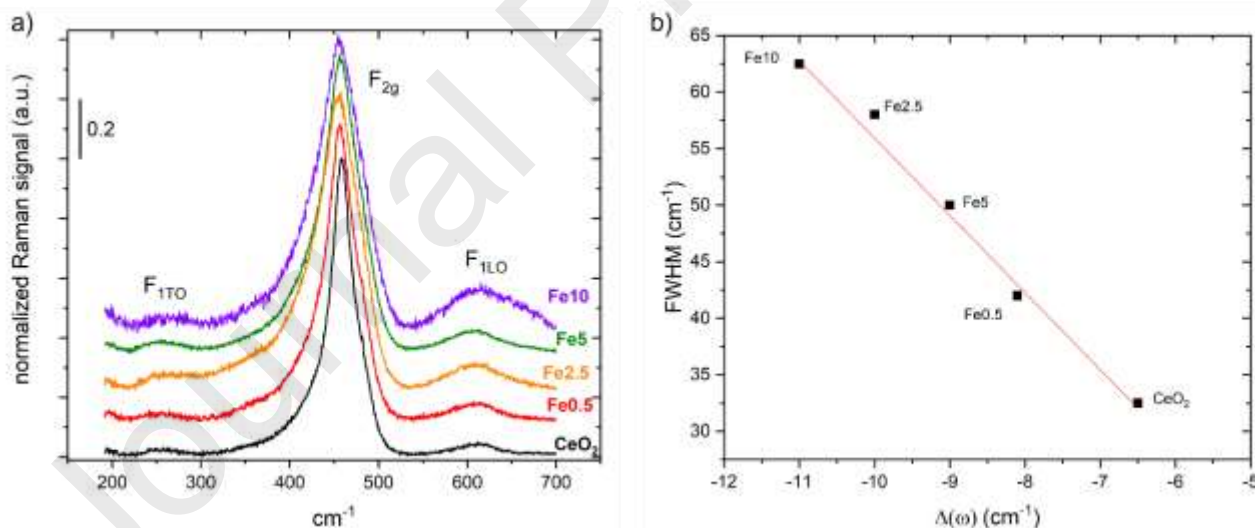
525 However, the actual occurrence of such a variation is the signature that the samples are oxygen  
 526 deficient and that charge delocalization happens for 4f electrons located at Ce(Fe)-VO-Ce(Fe)  
 527 orbitals. This charge delocalization is generally favourable to the photocatalytic activity. This is  
 528 confirmed in our case where the sample Fe2.5 shows both the highest delocalization and the highest  
 529 photocatalytic activity (see Fig. 11). We exclude from our analysis the Fe10 sample that cannot be  
 530 considered as simply doped ceria since it probably contains oligomeric species at its surface,  
 531 detrimental to its catalytic activity.

532 Two supplementary peaks are noticed at  $270\text{ cm}^{-1}$  and  $606\text{ cm}^{-1}$  respectively. They are assigned to  
 533 the  $F_{1TO}$  and  $F_{1LO}$  phonon modes. These vibrations are forbidden in pristine  $\text{CeO}_2$  but are often seen  
 534 in nanocrystal samples as a result of the long-range symmetry breaking of the crystals. The magnitude  
 535 of the  $F_{1LO}$  peak increases with Fe content as evidenced in Fig. SI.7 where the change in the ratio  
 536 between the  $F_{1LO}$  contribution and the  $F_{2g}$  contribution is plotted versus the sample composition.  
 537 The  $F_{1LO}$  feature can be assigned to defects involving dopant cation complexes close to VO [112]. It  
 538 can be clearly observed that moving from sample Fe0.5 to sample Fe2.5 the ratio is almost doubled,  
 539 indicating the increased presence of the aforementioned VO-related complexes.

540 For the Fe10 sample, on top of the  $F_{1LO}$  feature, a second contribution at approximately  $670\text{ cm}^{-1}$   
 541 appears. This contribution cannot be assigned to the presence of VO but rather to the presence of Fe  
 542 at high content [112]. As already mentioned, this sample cannot be considered in the strict sense as  
 543 doped ceria.

544

545



546

547 **Fig. 4:** a) Raman spectra of pristine and Fe-doped  $\text{CeO}_2$  nanocrystals for different doping  
 548 concentrations. All spectra are normalized to the maximum intensity of the  $F_{2g}$  peak. b) Variation of  
 549 the  $F_{2g}$  peak FWHM concerning its position variation as a function of the Fe concentration in  $\text{CeO}_2$   
 550 nanocrystals.  $\Delta\omega$  is referred to the value of pristine  $\text{CeO}_2$ .

551

552 The textural properties were evaluated by  $\text{N}_2$  adsorption at low temperatures ( $-196\text{ }^\circ\text{C}$ ). The  
 553 adsorption/desorption isotherms, Fig. SI.8a, resemble type IV, typical of mesoporous material with a  
 554 hysteresis loop indicating block-neck pores shape (hysteresis type H2). All the studied samples have

555 a BET-specific surface area higher than or equal to  $180 \text{ m}^2 \text{ g}^{-1}$  Table 3, with the exception of the  
 556 sample Fe10 that shows a surface area of  $274 \text{ m}^2 \text{ g}^{-1}$ . Considering that the surface area is interparticle,  
 557 the discordant value of Fe10 can be explained by the smaller particle size, Table 2. The limited  
 558 particle growth observed at high iron contents may be correlated with the presence of iron-containing  
 559 species on the surface [46,93]. The pore size distribution (PSD) evaluated by the BJH method on  
 560 desorption branches, Fig.SI.8b, suggests that the synthetic route is effective for the preparation of  
 561 mesoporous (doped) ceria.

562 The designed reverse micelles synthesis route allows for obtaining a very high surface area compared,  
 563 not only with different methods [33,107,113] but also with similar procedures reported in the  
 564 literature [46,47].

565

566 **Table 3:** Energy of band gap ( $E_g$ ) and textural properties of pristine and Fe-doped  $\text{CeO}_2$  sample

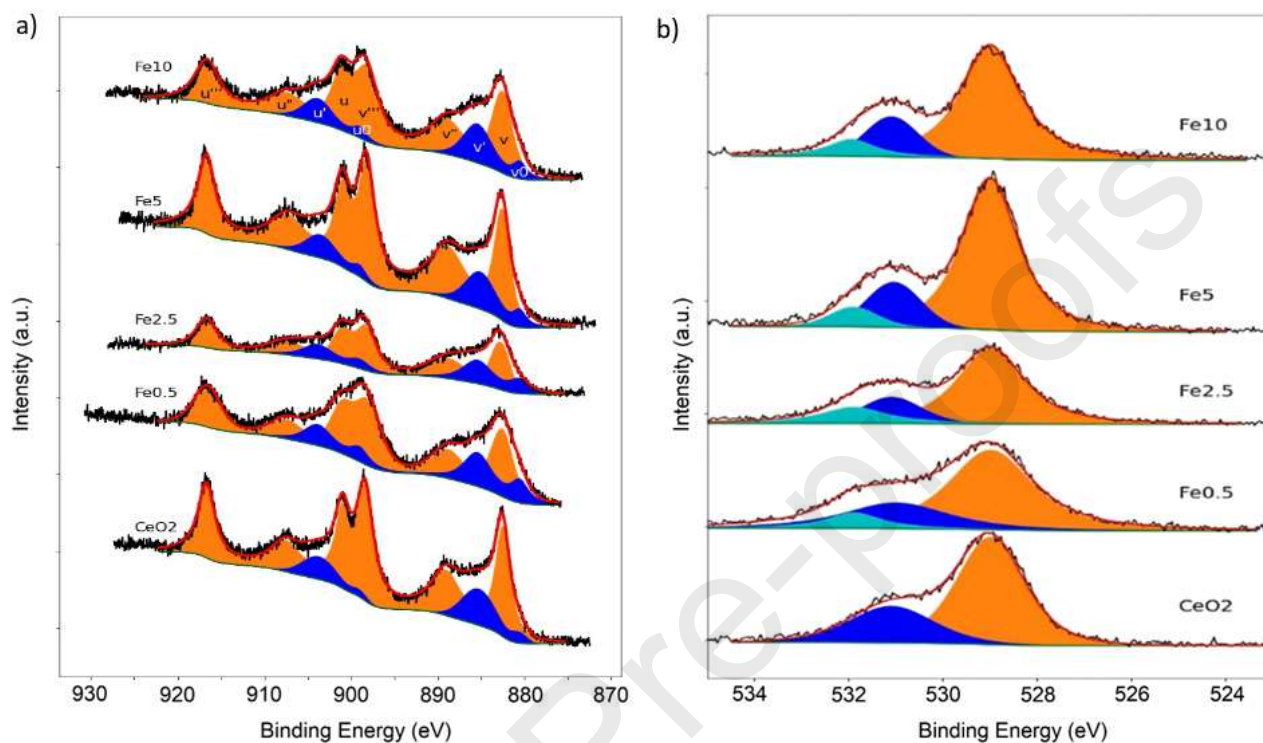
567	Sample	$E_g$ (eV)	BET SSA ( $\text{m}^2 \text{ g}^{-1}$ )	$V_p$ ( $\text{cm}^3 \text{ g}^{-1}$ )
568				
569	$\text{CeO}_2$	3.00	182	0.196
570				
571	Fe0.5	2.91	180	0.184
572				
573	Fe2.5	2.79	191	0.188
574				
575	Fe5	2.77	189	0.192
576				
577	Fe10	2.68	274	0.280

575 In order to have a better  
 576 surface a XPS analysis was  
 577 spectrum, although highly  
 578 deconvoluted with some precautions [114,115]. Here Ce3d XPS spectra, shown in Fig. 5a, were  
 579 solved with five  $3d_{5/2}$  components denoted as  $v_0$  (880.6 eV),  $v$  (882.6 eV),  $v'$  (885.45 eV),  $v''$  (888.85  
 580 eV) and  $v'''$  (898.4 eV) with  $\pm 0.3$  eV resolution and their  $3d_{3/2}$  counterparts (called  $u_x$ ) separated by  
 581 18.45 eV ( $\pm 0.15$  eV) with a ratio  $u_x/v_x$  of 1.5 ( $\pm 0.1$ ). The amount of surface  $\text{Ce}^{3+}$  ion was  
 582 determined using the area of  $v_0$ ,  $u_0$ ,  $v'$  and  $u'$  peaks, while  $v$ ,  $u$ ,  $v''$ ,  $u''$ ,  $v'''$  and  $u'''$  were assigned  
 583 to surface  $\text{Ce}^{4+}$  ion.

584 The two ions appear for different environments of Ce atoms, resulting in different charge transfers.  
 585  $\text{Ce}^{3+}$  is indeed present in  $\text{Ce}_2\text{O}_3$ , while  $\text{CeO}_2$  is made of  $\text{Ce}^{4+}$  ions. Since the O1s core level is sensitive  
 586 to changes in the coordination of the oxygen atoms, its deconvolution should also allow the evaluation  
 587 of the charge transfer between oxygen and cerium atoms. Three components are usually considered  
 588 to resolve XPS spectra of the O1s core level in  $\text{CeO}_2$ . The first one, labeled  $\text{O}\alpha$  at 529 eV, is usually  
 589 associated with lattice oxygen, i.e.  $\text{Ce}^{4+}$  in  $\text{CeO}_2$ . Following [116],  $\text{O}\beta$  feature at 531 eV and  $\text{O}\gamma$   
 590 feature at 532 eV are attributed to surface hydroxyl groups, resulting from the dissociation of  
 591 adsorbed water and irreversibly adsorbed molecular water, respectively. These energies ( $\pm 0.1$  eV)  
 592 were fixed to fit our XPS data, as shown in Fig. 5b. Finally, relative atomic concentration was

593 calculated as the ratio of the normalized intensity of one element with a given valence over the  
 594 normalized intensity of that element (whatever the valence), with a sensitivity factor calculated as the  
 595 product of theoretical inelastic mean free path and cross section.

596



597

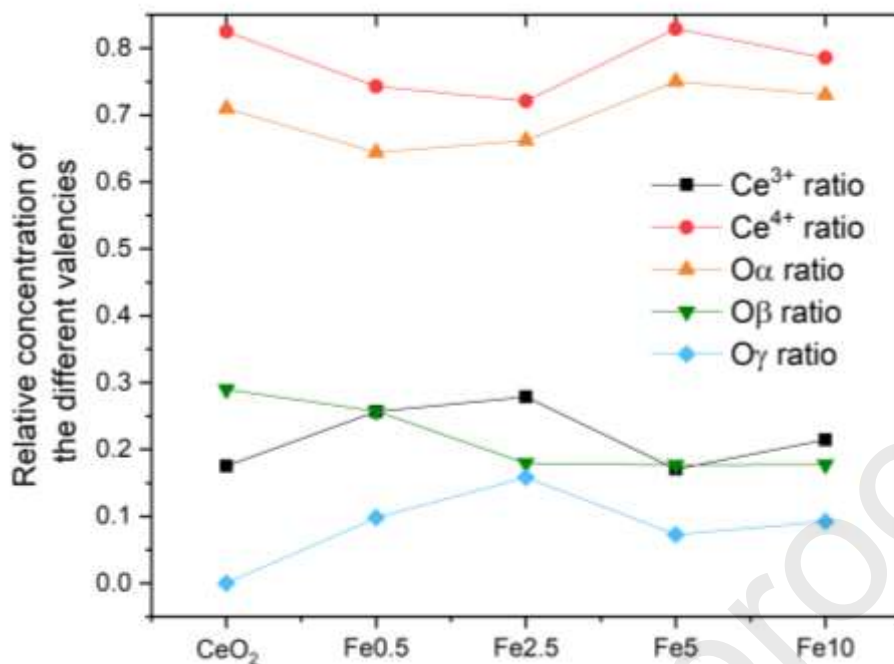
598

599

600 **Fig. 5:** Experimental and fitted XPS spectra. Ce3d (a) and O1s (b) core level spectra as a function  
 601 of the Fe concentration in CeO<sub>2</sub> nanocrystals. Experimental data are in black, Shirley background in  
 602 green. The sum of 5 components of doublets (2 of Ce<sup>3+</sup>, blue area, 3 of Ce<sup>4+</sup>, orange area) are used  
 603 to fit the Ce3d signal (a) or of 3 components (O<sub>α</sub>, O<sub>β</sub> and O<sub>γ</sub>, areas in orange, blue and cyan,  
 604 respectively) to fit O1s signal in red.

605

606



607

608 **Fig. 6:** Relative atomic composition of the synthesized pristine and doped CeO<sub>2</sub> nanocrystals as a  
 609 function of Fe content.

610

611 As shown in Fig. 6, the Ce<sup>4+</sup> relative atomic concentration follows nicely that of O<sub>α</sub>. Both signals  
 612 decrease as the Fe content increases from CeO<sub>2</sub> to Fe<sub>2.5</sub> and next decrease and reach an almost  
 613 constant value. This is consistent since both signals come from the CeO<sub>2</sub> units in the nanocrystal bulk.  
 614 Remarkably, the variation of the Ce<sup>3+</sup> relative atomic concentration is opposite to that of Ce<sup>4+</sup>. This  
 615 reveals that the increase in Fe content from CeO<sub>2</sub> to Fe<sub>2.5</sub> promotes the enrichment of Ce<sup>3+</sup> within  
 616 the Ce. Adding more Fe does not lead to more Ce<sup>3+</sup> ions. On the contrary, it appears that the further  
 617 addition of Fe atoms, beyond Fe<sub>2.5</sub>, is less effective in generating Ce<sup>3+</sup> ions.

618 As demonstrated by DFT calculations (see below), the generation of Ce<sup>3+</sup> ions is related to the  
 619 generation of VOs. The evolution of the oxygen concentration cannot be directly seen in the XPS  
 620 spectra since, as stated above, there is no XPS feature directly related to VOs. Consequently, even  
 621 though the analysis of the Ce<sup>3+</sup> feature remains delicate since the X rays may induce the reduction of  
 622 ceria during the observation [117], its evolution remains a relevant indication of the VOs  
 623 concentration. Interestingly, one can note that the minimum Ce<sup>4+</sup> concentration (thus the maximum  
 624 of Ce<sup>3+</sup> and VOs concentrations) is concomitant with the maximum catalytic activity.

625 To conclude the discussion, the analysis of the Fe2p core level signal would have been highly  
 626 relevant. However, Fe2p signal is very weak, although increasing with doping, and at the same  
 627 energies as the signal of Ce M45N45V Auger electrons (see supplementary Fig. SI.9). From its  
 628 analysis only 3% atomic concentration was found when 10% was expected. As XPS is sensitive to  
 629 the extreme surface (first few nms), it indicates that Fe might be inhomogeneously distributed in the  
 630 nanocrystals.

631

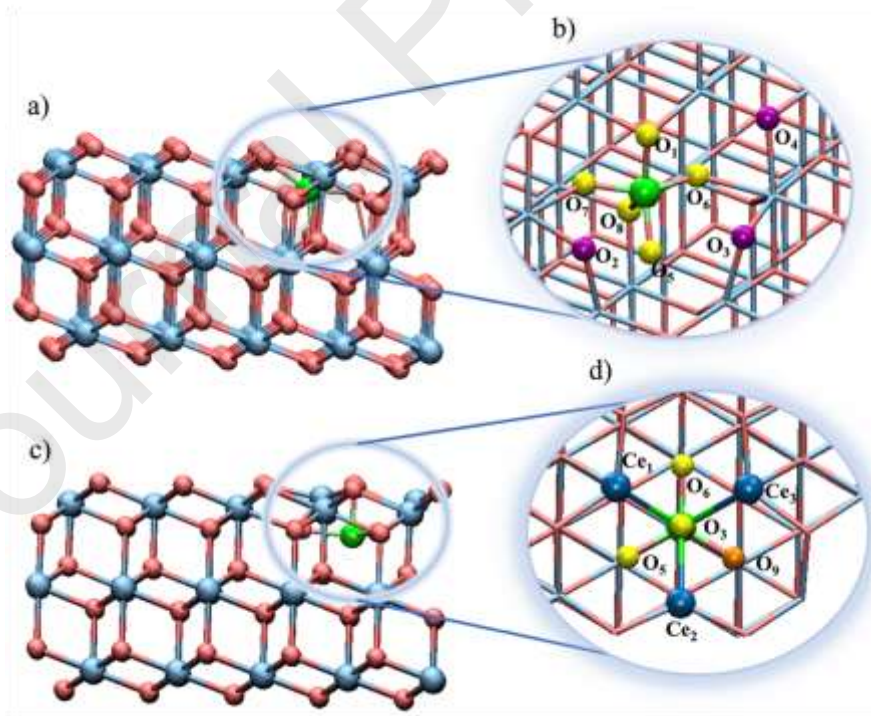
632 3.3 DFT study

633

634 3.3.1. Fe-doped CeO<sub>2</sub> surfaces characterization

635 Density functional theory (DFT) calculations were performed to investigate the effects of Fe-doping  
 636 on the structural and electronic properties of CeO<sub>2</sub> (111) surfaces. We have considered the scenario  
 637 in which iron atoms substitute surface and subsurface Ce sites (Fe@Ce) as well as interstitial doping,  
 638 where Fe atoms occupy interstitial sites in the crystal structure (Fe<sub>Int</sub>).

639 The optimized geometry of the system with surface substitutional Fe doping (Fe@Ce<sub>1</sub>), reported in  
 640 Fig. 7a, results in more stable than the subsurface one (Fe@Ce<sub>2</sub>) by 1.1 eV. The presence of such a  
 641 Fe substitutional point defect induces a rearrangement of the neighboring O atoms. As a result, on the  
 642 doped CeO<sub>2</sub> (111) surface, two non-equivalent O atoms (O<sub>1</sub> and O<sub>4</sub>) and two equivalent (O<sub>2</sub>=O<sub>3</sub>) O  
 643 sites are present, whereas in the subsurface layer all the O atoms (O<sub>5</sub>, O<sub>6</sub> and O<sub>7</sub>) results to be  
 644 equivalent (see Fig. 7b). In this configuration, the Fe atom relaxes inward and binds to an O atom of the  
 645 surface O<sub>1</sub>, to three O atoms of the second layer O<sub>5</sub>, O<sub>6</sub> and O<sub>7</sub>, and to an O atom of the third layer  
 646 O<sub>8</sub> (yellow O in Fig. 7b). The Fe-O bond lengths are found to be in the range of 1.84-2.14 Å, and  
 647 therefore, corresponding to the distances in  $\alpha$ - and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (1.89-2.10 Å) [118]. In addition, the Bader  
 648 charge of the substitutional Fe dopant is 14.28 e<sup>-</sup> similar to those computed for the metal in  $\alpha$ - and  $\gamma$ -  
 649 Fe<sub>2</sub>O<sub>3</sub> (14.34 and 14.49 e<sup>-</sup>). The Fe-O bond lengths of the five-coordinate moiety and the Bader charge  
 650 calculations suggest that in our system the iron atom has an oxidation state of +3. In the doped surface,  
 651 the Bader charges of the Ce atoms (9.6 e<sup>-</sup>) are consistent with the presence of Ce<sup>4+</sup>, indicating that no  
 652 Ce<sup>4+</sup> is reduced to Ce<sup>3+</sup> in presence of the Fe dopant (see PDOS Fig. SI.10a). In the presence of a  
 653 substitutional Fe atom in the CeO<sub>2</sub> system the computed value of the bandgap is 1.7 eV, thus 0.2 eV  
 654 lower with respect to the undoped case, that is 1.9 eV (compare Fig. SI.10a and SI.10b).



655

656 **Fig. 7.** Panel a) optimized structure of Fe@Ce<sub>1</sub> (111). Panel b) First and second coordination spheres  
 657 of the Fe dopant. Ce, O, O<sub>1,5-8</sub>, O<sub>2-4</sub> and Fe surface atoms are represented in balls and sticks and  
 658 depicted in blue, red, yellow, purple and green, respectively. Panel c) optimized structure of Fe<sub>Int</sub>.

659 Panel d) coordination sphere of the interstitial Fe dopant. Ce, O, O<sub>3,5,6</sub>, O<sub>9</sub> and Fe surface atoms are  
 660 represented in balls and sticks and depicted in blue, red, yellow, orange, and green, respectively.

661

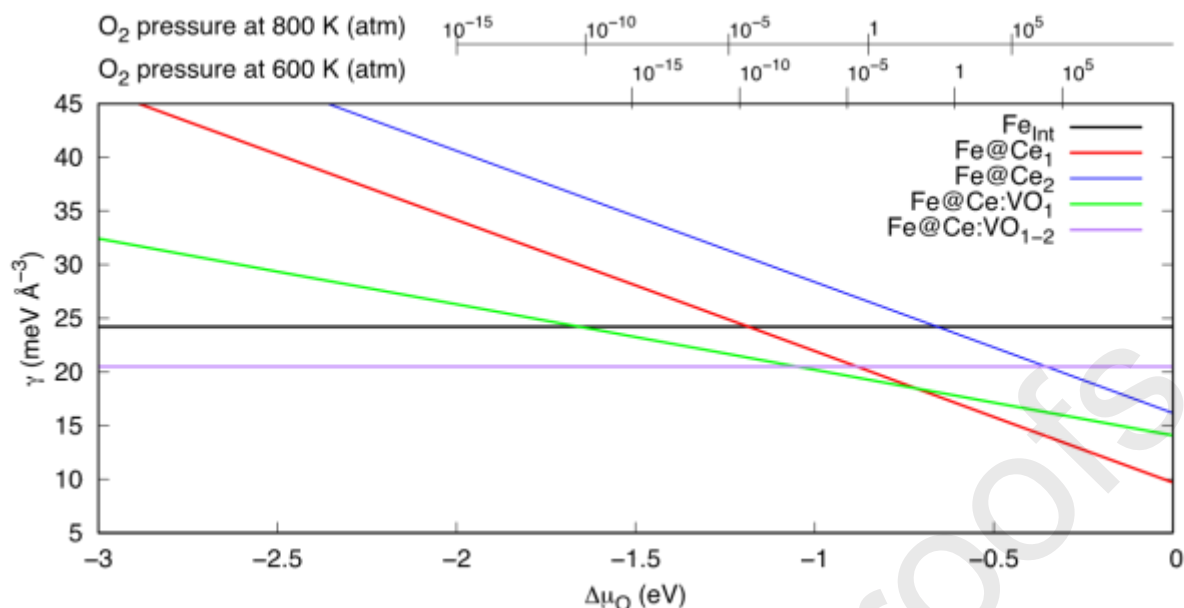
662 Fig. 7.c shows the optimized structure of the Fe<sub>Int</sub> system. Also in this case, the presence of the  
 663 interstitial Fe dopant induces structural distortions on the surface. In fact, the Fe atom relaxes outward  
 664 binding to the surface O<sub>3</sub> atoms and to the three O atoms of the second layer O<sub>5</sub>, O<sub>6</sub> and O<sub>9</sub>, (yellow  
 665 and orange O in Fig. 7d). The formation of these new Fe-O bonds and the breaking of the pre-existing  
 666 Ce-O bonds generates three reduced Ce<sup>3+</sup>. The Bader charges of these Ce atoms (9.9 e<sup>-</sup>) are consistent  
 667 with the presence of Ce<sup>3+</sup>, also confirmed by the formation of two bandgap states below the Fermi  
 668 level (black peaks in Fig. SI.11a of the SI) and by the spin density analysis, where the electron excess  
 669 on the Ce<sup>3+</sup> are indicated with black densities analogously to the colors of the respective bandgap  
 670 peaks (Fig. SI.11c). In Fe<sub>Int</sub> system the computed value of the bandgap is 1.7 eV similar to the  
 671 substitutional Fe doping (compare Fig. SI.10a and SI.11a). For both doping types, the theoretical  $\Delta\Delta E$   
 672 (eV) related to the band gap energy variation of the undoped and doped surfaces is in line with the  
 673 experimentally calculated one and reported in Table 3.

674 Next, we have considered the formation of O vacancies on the most stable Fe@Ce<sub>1</sub> system. The  
 675 presence of a Fe substitutional point defect generates four non-equivalent O atoms, namely O<sub>1</sub>,  
 676 O<sub>2</sub>=O<sub>3</sub>, O<sub>4</sub> in the outermost layer and O<sub>5</sub>=O<sub>6</sub>=O<sub>7</sub> in the subsurface layer, as discussed above (Fig. 7b).  
 677 It is, therefore, possible to create four non-equivalent oxygen vacancies: VO<sub>1</sub>, VO<sub>2=3</sub> and VO<sub>4</sub> in the  
 678 external layer and VO<sub>5=6=7</sub> in the subsurface layer. The computed values of the formation energies  
 679 ( $E_F$ ) of VO<sub>1</sub>, VO<sub>2=3</sub>, VO<sub>4</sub> and VO<sub>5=6=7</sub> are found to be 0.7, 0.8, 2.13 and 1.1 eV, respectively. Our  
 680 results show low formation energies for those oxygen vacancies arising from oxygen atoms directly  
 681 coordinating or close enough to the Fe dopant (see VO<sub>1</sub>, VO<sub>2=3</sub> and VO<sub>5=6=7</sub>) and high  $E_F$  for those  
 682 far from the iron atom. This occurs because the oxygen atoms very close to Fe are more affected by  
 683 the structural distortions generated by the Fe dopant. The formation of a second oxygen vacancy VO<sub>2</sub>  
 684 on the most stable reduced surface VO<sub>1</sub> (Fe@Ce<sub>1</sub>:VO<sub>1-2</sub>) is also favored, with an  $E_F$  of 0.9 eV,  
 685 suggesting that the Fe dopant is likely the center of the oxygen vacancy cluster. A close inspection of  
 686 the Bader charges, PDOS and spin density plots of the most stable Fe@Ce<sub>1</sub>:VO<sub>1</sub> (111) system shows  
 687 that the formation of an O vacancy leads to the reduction of two Ce<sup>4+</sup> atoms that are formally Ce<sup>3+</sup>  
 688 (see Fig. SI.12).

689 To define the relative stability of the Fe-doped systems containing different types and or number of  
 690 atoms depending on pressure and temperature, we have employed the formalism of ab initio  
 691 thermodynamics as detailed described in the Experimental Section.

692 Fig. 8 shows a plot of the Gibbs energies  $\Delta G_{\text{ads}}(T, p)$  of the system discussed above as a function of  
 693 the O chemical potential including a conversion to oxygen partial pressures at several relevant  
 694 temperatures. It is possible to identify three thermodynamically stable phases. The first phase, which  
 695 holds for values of  $\mu_o > -0.7$  eV, corresponds to the system where a Fe atom substitutes a surface Ce  
 696 ion, Fe@Ce<sub>1</sub> (red line). Under O-rich conditions this structure becomes the thermodynamically most  
 697 stable one. The second most stable structure is the one obtained by removing a surface O atom from  
 698 the Fe@Ce<sub>1</sub> system (green line). This structure becomes thermodynamically stable in the range  $-1.05$   
 699  $< \mu_o < -0.7$  eV (purple line). Finally, for  $\mu_o < -1.05$  the Fe@Ce<sub>1</sub> system in the presence of two surface  
 700 O vacancies becomes thermodynamically stable. These findings are in line with the experimental data  
 701 suggesting that in the presence of Fe atoms substituting Ce ions the formation of O vacancies is  
 702 favored. In addition, we predict that subsurface substitutional and interstitial Fe doping are never  
 703 thermodynamically stable (blue and black lines, respectively).

704



705

706 **Fig. 8.** Gibbs energies  $\Delta G_{\text{ads}}(T, p)$  for substitutional, interstitial Fe atom in  $\text{CeO}_2$  (111) and for  
 707 reduced  $\text{Fe@Ce}_1\text{:VO}_1$  and  $\text{Fe@Ce}_1\text{:VO}_{1-2}$  (111) as a function of the oxygen chemical potential  $\Delta\mu_{\text{O}}$   
 708 in eV.

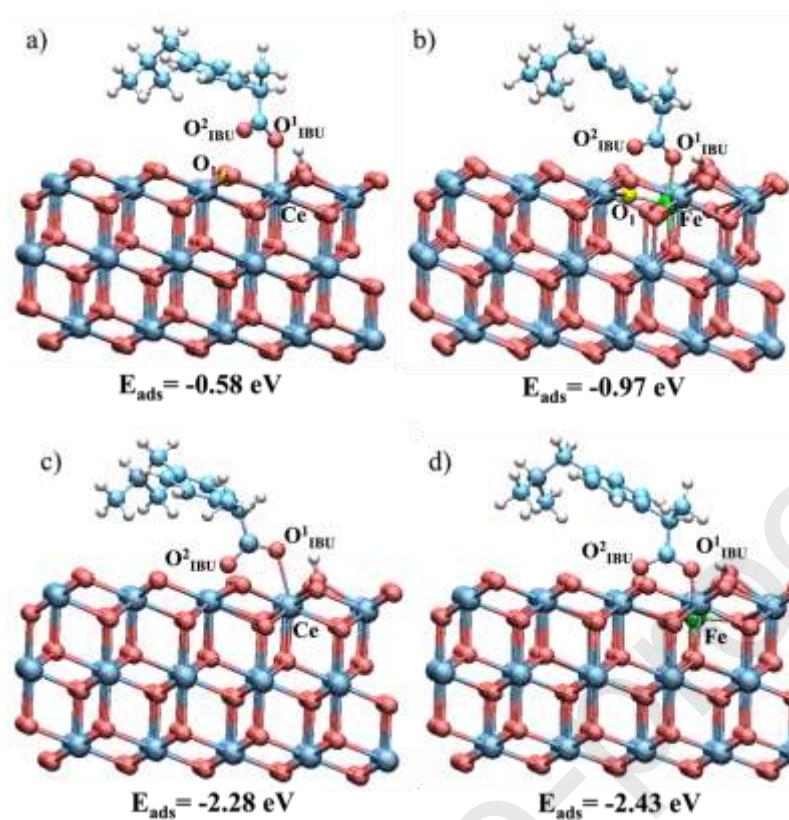
### 709 3.3.2. Ibuprofen absorption on the surfaces

710 The interaction of IBU with stoichiometric (reduced) undoped  $\text{CeO}_2$  (111) and the most stable  
 711  $\text{Fe@Ce}_1$  surfaces was investigated, simulating IBU in its deprotonated form according to the  
 712 experimental conditions.

713 Fig. 9 shows the optimized geometries of the most stable configurations of the IBU adsorbed on  
 714  $\text{CeO}_2(111)$ ,  $\text{Fe@Ce}_1$  (111),  $\text{CeO}_2\text{:VO}_1(111)$ , and  $\text{Fe@Ce}_1\text{:VO}_1(111)$  (panel a-d, respectively).

715 IBU interacts with  $\text{CeO}_2(111)$  through an ionic-like bond between an oxygen atom of its carboxylate  
 716 group ( $\text{O}^1_{\text{IBU}}$ ) and a surface Ce atom of 2.38 Å and an  $E_{\text{ads}}$  of -0.58 eV (Fig. 9a). In  $\text{Fe@Ce}_1$  (111),  
 717 the ligand binds the surface by a covalent-like bond between  $\text{O}^1_{\text{IBU}}$  and the Fe dopant of 2.12 Å and  
 718 an  $E_{\text{ads}}$  of -0.98 (Fig. 9b). In the stoichiometric system, the Fe dopant presence improves the  
 719 adsorption energy of IBU by 0.4 eV due to i) the greater orbital availability of  $\text{Fe}^{3+}$  with respect to  
 720  $\text{Ce}^{4+}$  to host electrons and, thus, form new bonds and to ii) the structural distortions generated by the  
 721 substitutional dopant. In fact, in the presence of Fe, the surface oxygen atom  $\text{O}_1$  goes down towards  
 722 the subsurface oxygen layer allowing a better interaction of the ligand with the  $\text{Fe@Ce}_1$  (111) surface.

723 These energy stabilizations are also reflected in the reduced undoped and Fe-doped systems (Fig. 9c  
 724 and 9d, respectively). The experiments are performed in aqueous solution and, therefore, water  
 725 molecules will fill surface O vacancies of the ceria surface leading to a hydroxylated surface.  
 726 However, if we assume that O vacancies are present on the catalysts, IBU molecules will adsorb on  
 727  $\text{CeO}_2\text{:VO}_1$  (111) and  $\text{Fe@Ce}_1\text{:VO}_1$  (111) through an ionic and covalent bond of 2.56 and 2.10 Å,  
 728 respectively, and with  $E_{\text{ads}}$  of -2.28 and -2.43 eV for the undoped (panel c in Fig.9) and Fe-doped  
 729 (panel d in Fig.9) reduced systems. Therefore, the hypothetical presence of the surface oxygen  
 730 vacancy  $\text{VO}_1$  improves the ligand  $E_{\text{ads}}$  of about 1.5 eV with respect to the stoichiometric surfaces as  
 731  $\text{O}^2_{\text{IBU}}$  tends to occupy the vacant site stabilizing the IBU adsorption.



732

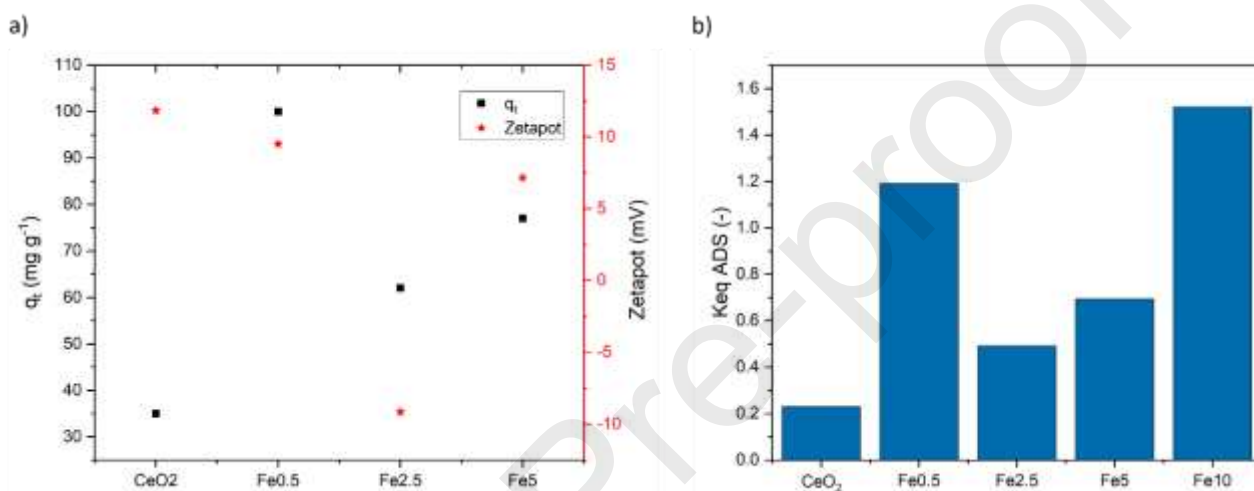
733 **Fig. 9.** Optimized structure of a)  $\text{CeO}_2$  (111), b)  $\text{Fe@Ce}_1$  (111), c)  $\text{CeO}_2@\text{VO}_1$  (111) and d)  
734  $\text{Fe@Ce}_1:\text{VO}_1$  (111) with the corresponding  $E_{\text{ads}}$  (eV). Ce, O and  $\text{O}^{1-2}_{\text{IBU}}$ ,  $\text{O}_1$ , C, H and Fe surface  
735 atoms are represented in balls and sticks and depicted in blue, red, yellow, cyan, white and green,  
736 respectively.

737

738

## 739 3.4 Ibuprofen adsorption and photodegradation activity

740 Adsorption and photodegradation tests were conducted to investigate the performance of each  
 741 synthesized catalyst. An attempt was made to justify the adsorption efficiency with the main  
 742 properties of the catalysts. Except for the Fe10 sample, we do not observe any significant difference  
 743 in terms of SSA and pore size. These findings lead us to speculate that the adsorption behaviour of  
 744 IBU, except for Fe10, should not be determined by textural properties but could reflect differences in  
 745 surface charge [93]. For this reason, the  $\zeta$ -potential values at the pH of ibuprofen solution (pH=4.6),  
 746 extrapolated from the  $\zeta$ -potential curves (Fig. SI.13), were plotted vs the maximum adsorption  
 747 capacity ( $q_t=(C_{IBU,0}-C_{IBU})/\rho_B$ ), measured in dedicated experiments adopting the following  
 748 experimental conditions:  $T=30\text{ }^\circ\text{C}$ ,  $C_{IBU,0}=12.4\text{ mg L}^{-1}$ ,  $\rho_B=0.07\text{ g L}^{-1}$ , reaction time of 300 min (Fig.  
 749 10a).



750

751 **Fig. 10** – a) Potential ( $\zeta$ ) of the pristine and Fe-doped  $\text{CeO}_2$  vs the adsorption capacity. b) Trend of  
 752 the adsorption equilibrium constant. The present experimental conditions were adopted for each  
 753 experiment:  $T=30\text{ }^\circ\text{C}$ ,  $C_{IBU,0}=12.4\text{ mg L}^{-1}$ ,  $\rho_B=0.07\text{ g L}^{-1}$ , reaction time of 300 min.

754

755 From the results shown in Fig. 10a, it is interesting to observe that Fe0.5 and Fe5 samples are  
 756 positively charged at pH=4.6, namely the pH of the ibuprofen solution, while Fe2.5 is negatively  
 757 charged. It is worth mentioning that the surface of both ceria and doped ceria is not “naked” but  
 758 hydroxylated. Thus, being ibuprofen a weak acid (pKa 4.41), in water it is partially dissociated in its  
 759 anionic form. Therefore, the strongest interactions are expected to be with positively charged  
 760 materials. Accordingly, the adsorption efficiency passes through a minimum for the Fe2.5 catalyst  
 761 where the surface is negatively charged, inhibiting the ibuprofen adsorption. The different surface  
 762 charge may be related to the type of hydroxyls exposed by Fe- $\text{CeO}_2$  surfaces, their distribution and  
 763 their location with respect to oxygen vacancies [119,120].

764 The  $\text{CeO}_2$  sample shows an opposite trend showing a very low adsorption efficiency even if the  
 765 surface is positively charged, a finding not explainable by the above-mentioned hypothesis. But it is  
 766 important to remind that from DFT computations (see Fig. 9), the adsorption energy of ibuprofen  
 767 improves when it interacts with Fe rather than Ce, clearly leading to a lower adsorption efficiency  
 768 compared with the samples containing Fe. As previously stated, the Fe10 sample is not included in  
 769 the trend of doped samples discussion, because of its different properties such as very high surface  
 770 area and the presence of surface oligomers (*vide supra*) that may promote higher adsorption  
 771 efficiency. Furthermore, the type of adsorption was further evaluated by FT-IR spectroscopy. The

772 spectra obtained from the Fe2.5 sample and from the same sample after contact with a saturated  
 773 ibuprofen solution are shown in Fig. SI.14. The spectra show a broad band between 3750 and 3000  
 774  $\text{cm}^{-1}$  due to O-H stretching vibration of surface hydroxyl groups and undissociated water  
 775 characterized by its bending mode at  $1630 \text{ cm}^{-1}$  [121,122]. Bands at around  $1364$  and  $1529 \text{ cm}^{-1}$  can  
 776 be attributed to carbonate species, whose presence results from interactions of  $\text{CeO}_2$  with atmospheric  
 777 carbon dioxide [123]. Metal-oxygen vibrations are generally observed at low wavenumbers, below  
 778  $800 \text{ cm}^{-1}$ . The absence of new chemical bonds in the post-saturation sample, inferred from the  
 779 absence of new peaks in the saturated Fe2.5 catalyst, suggests a physisorption mechanism.

780 To measure the relative influence of adsorption and photodegradation contribution, the results were  
 781 interpreted with a simplified kinetic model. The model was written taking into consideration a  
 782 constant volume ideal batch reactor, where at the beginning of the reaction the ibuprofen solution is  
 783 loaded to the vessel and the reaction is considered to occur in isothermal conditions. The rate  
 784 expressions were developed, considering that ibuprofen (IBU) is adsorbed on the surface of the  
 785 photocatalysts (\*) leading to an adsorbed specie (IBU\*), as in Eq. 2.



787 The reversible rate expression reported in Eq. 3 was adopted to describe the adsorption rate.

$$788 \quad r_{\text{ADS}} = k_{\text{ADS}} \left( c_{\text{IBU}} - \frac{1}{K_{\text{eqADS}}} c_{\text{IBU}^*} \right) \quad (3)$$

789 The mentioned rate expression was included in the mass balance equation valid for a batch system,  
 790 see Eq. 4.

$$791 \quad \frac{dc_{\text{IBU}}}{dt} = -r_{\text{ADS}} \cdot \rho_B \quad (4)$$

792 The ordinary differential equation was solved in MATLAB R2023a environment, using *ode45*  
 793 function, and the related adsorption kinetic and equilibrium constants were obtained by parameter  
 794 estimation activity on the adsorption kinetic experiments. In detail, the objective function, defined as  
 795 the square root of the squares of the residuals, was minimized using *lsqnonlin* algorithm. The results  
 796 of the parameter estimation activities are reported in Figs 10b and Table 4.

797 As shown in Fig. 10b, the adsorption equilibrium constants follow the same trend as the adsorption  
 798 capacity ( $q_t$ ), being both quantities related to each other whose trend was previously explained via  $\zeta$   
 799 -potential curves.

800 As adsorption is a physical phenomenon, its velocity depends on the effective diffusivity of ibuprofen  
 801 molecules in the catalyst pores, thus the lumped kinetic constants reported in Table 4 are dependent  
 802 on both the porosity and tortuosity of the catalysts. Being the pore volumes of each material very  
 803 similar (see Table 3), the expected kinetic constants shall fall in the same range, as obtained by  
 804 parameter estimation and reported in Table 4.

805

806 **Table 4** – Adsorption rate, adsorption equilibrium and degradation rate constants values. The  
 807 experimental conditions were adopted for each experiment:  $T=30^\circ\text{C}$ ,  $C_{\text{IBU},0}=12.4 \text{ mg L}^{-1}$ ,  $\rho_B = 0.07 \text{ g}$   
 808  $\text{L}^{-1}$ , reaction time of 300 min.

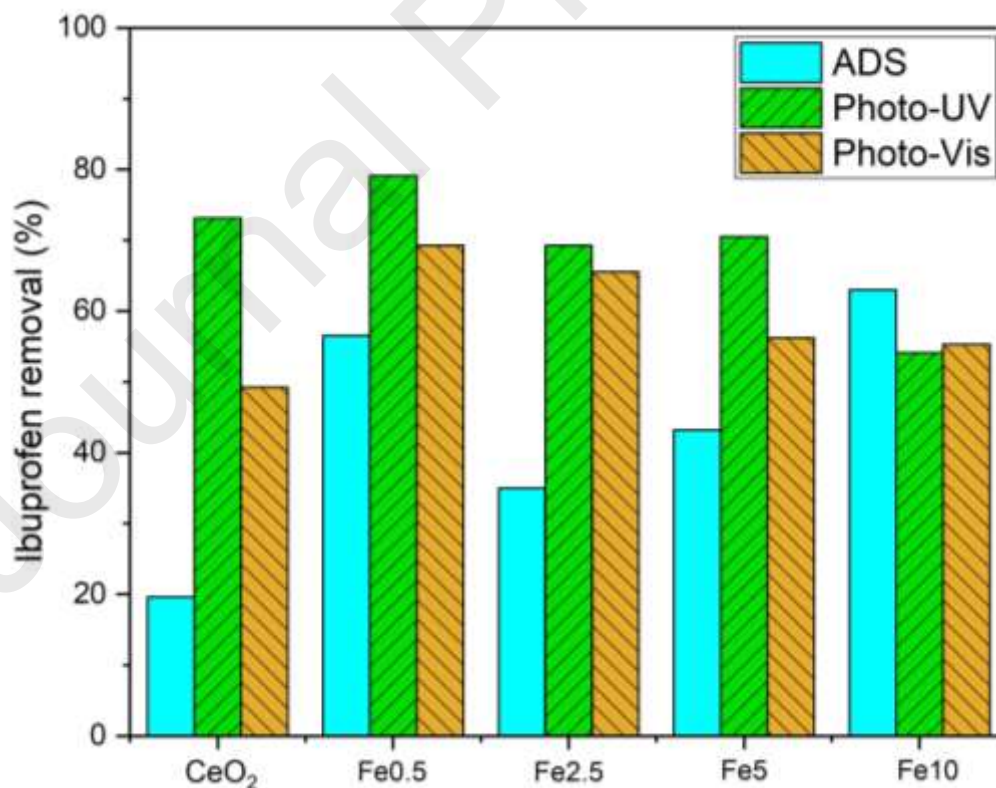
809

810 The  
811 experiments were  
812 the presence of UV  
813 irradiation. The  
814 reported in Fig. 11,  
815 that UV irradiation  
816 efficient than  
817 for all the catalysts.  
818 of pure ceria settles  
819 (see Table 3), which  
820 to mainly exploit  
821 UV light. The  
822 the ceria lattice  
823 onset of absorption  
824 samples. For this  
825 samples can be  
826 visible irradiation.  
827 performance

Sample	$k_{ADS}$ ( $L g^{-1} min^{-1}$ )	$K_{eqADS}$ (-)	$k_{DEG}$ ( $L g^{-1} min^{-1}$ )
<b>CeO<sub>2</sub></b>	0.09 ±0.02	0.23 ±0.01	0.03 ±0.01
<b>Fe0.5</b>	0.25 ± 0.01	1.19 ±0.02	0.03 ±0.01
<b>Fe2.5</b>	0.16 ±0.02	0.49 ±0.02	0.11 ±0.01
<b>Fe5</b>	0.23 ±0.02	0.69 ±0.02	0.04 ±0.01
<b>Fe10</b>	0.37 ±0.02	1.52 ±0.03	0.0010± 0.0003

814 photodegradation  
815 conducted either in  
816 or visible  
817 main results are  
818 where it is evident  
819 is slightly more  
820 visible irradiation  
821 The band gap value  
822 at the value of 3 eV  
823 allows the material  
824 the absorption of  
825 presence of iron in  
826 induces a shift in the  
827 in the studied  
828 reason, the doped  
829 more active under  
830 However,  
831 between UV and

828 visible irradiation is a delicate balance of several factors, including band gap, surface defects and  
829 intra-band gap defect states (that can also act as recombination centres). The performance of the  
830 catalysts under visible irradiation is indeed promising for a scale-up process, considering the low  
831 lamp power and the used dosage of the catalysts.



832

833 **Fig. 11** –Trend of the ibuprofen removal percentage per each catalyst, under either dark or UV or VIS  
834 irradiation. The present experimental conditions were adopted for each experiment:  $T=30^{\circ}C$ ,  $C_{IBU,0}=12.4$  mg  
835  $L^{-1}$ ,  $\rho_B=0.07$  g  $L^{-1}$ , reaction time of 300 min.

836

837 Qualitatively, the best catalyst in terms of the overall removal of ibuprofen under visible irradiation  
 838 is Fe0.5. Nevertheless, it is worth to be mentioned that during the photodegradation experiment, both  
 839 adsorption and chemical reactions occur. For this reason, we have modified the aforementioned  
 840 simplified mode, including a degradation step, described by the following rate expression.

$$841 \quad r_{DEG} = k_{DEG} \cdot c_{IBU^*} \quad (5)$$

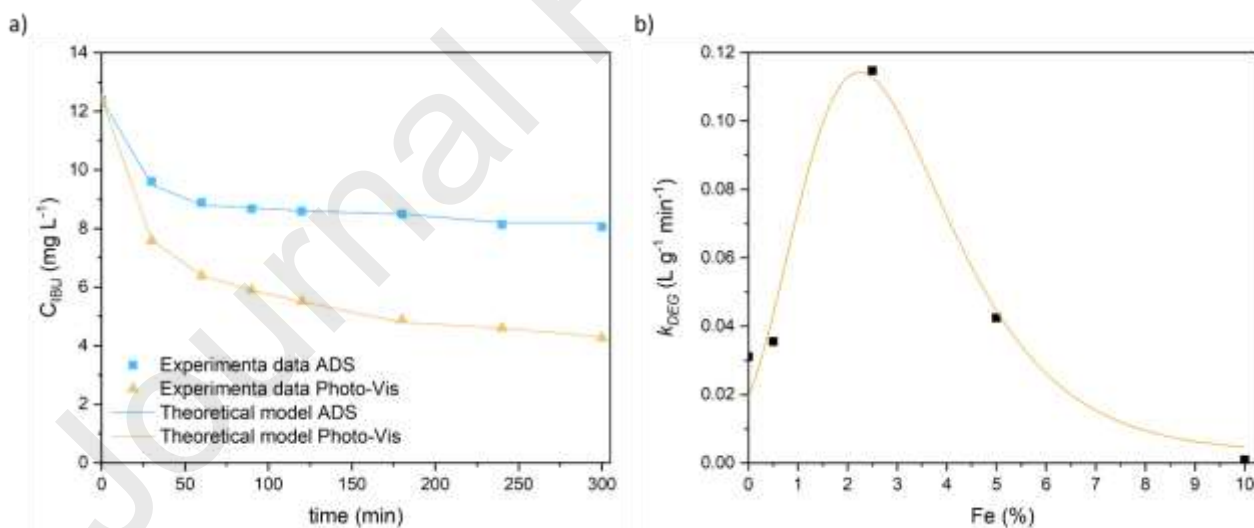
842 It must be pointed out, that we are implicitly assuming that photodegradation occurs in series to the  
 843 adsorption process, while it could occur also in parallel. This simplification can be considered  
 844 reasonable as we are interested in retrieving the order of magnitude of the kinetic constants to compare  
 845 the activity of each catalyst. Further, the ibuprofen photolysis in the absence of the catalyst was  
 846 neglected as proved experimentally [113].

847 Thus, the mass balance equation needs to be further modified, supposing that IBU\* undergoes  
 848 photodegradation, Eq. 6.

$$849 \quad \frac{dc_{IBU^*}}{dt} = (+r_{ADS} - r_{DEG}) \rho_B \quad (6)$$

850 In detail, Fig. 12a shows an example of data fit for the Fe2.5 catalyst: as revealed, a good fit was  
 851 obtained both for adsorption and photodegradation experiments under visible irradiation. The results  
 852 of the parameter estimation activities for all catalysts are reported in Table 4 and Fig. 12b.

853



854

855 **Fig. 12.** a) Example of data fit on the kinetic data measured using the Fe2.5 catalyst for both dark and  
 856 photodegradation experiments under visible irradiation ( $T=30^{\circ}C$ ,  $C_{IBU,0}= 12.4 mg L^{-1}$ ,  $\rho_B= 0.07 g L^{-1}$ ). Symbols represent the experimental data and lines the calculated profiles. b) Plot of the degradation  
 857 constant as a function of Fe loading.  
 858

859

860 Fig. 12b clearly illustrates that Fe2.5 is the best performing photocatalyst as it shows the highest  
 861 degradation constant.

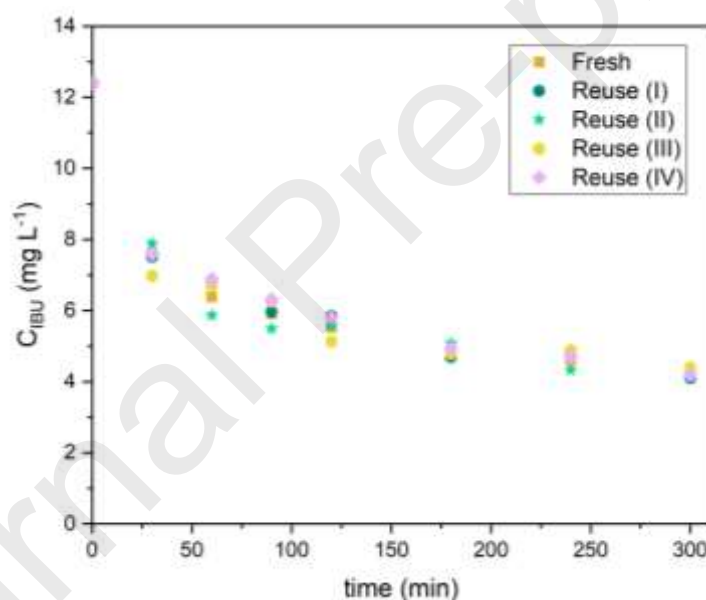
862 Raman and XPS findings revealed (*vide supra*) that Fe2.5 has the highest content of Ce<sup>3+</sup> and defects-  
 863 related oxygen vacancies. Raman results also suggested the highest charge delocalization for Fe2.5  
 864 (Fig. 4).

865 As extensively presented in the literature, the presence of oxygen vacancies can lead to increased  
 866 photo-oxidation performance as they constitute trapping centres for photogenerated electrons,  
 867 effectively limiting the rate of electron-hole recombination [124,125].

868 Finally, by comparing the band gap values with the degradation kinetic constant, it is possible to see  
 869 that the activity passes through a maximum, as classically reported in the literature [126], thus it is  
 870 possible to define an optimal band gap value of 2.79 eV (see Table 3).

871 For the mentioned reasons, it is interesting to further investigate the performance of Fe2.5 in terms  
 872 of stability. Thus, reuse experiments were conducted under visible light irradiation. As reported in  
 873 Fig. 13, the activity of Fe2.5 did not change after four cycles of photodegradation tests, demonstrating  
 874 good stability, thus a potential use in continuous apparatus, allowing the scale-up of the process from  
 875 batch to continuous operation.

876



877

878 **Fig. 13** – Reuse of the photocatalyst Fe2.5 in four photodegradation tests. The present experimental  
 879 conditions were adopted for each experiment:  $T = 30^{\circ}\text{C}$ ,  $C_{\text{IBU},0} = 12.4 \text{ mg L}^{-1}$ ,  $\rho_{\text{B}} = 0.07 \text{ g L}^{-1}$ , reaction  
 880 time of 300 min.

881

882 To further ascertain the stability of the catalyst, some relevant characterizations were conducted on  
 883 the Fe2.5 sample after the reaction. The obtained results clearly showed no substantial changes in the  
 884 nanocatalyst properties after the catalytic test. Indeed, the XRD diffraction pattern of the Fe2.5\_post  
 885 reaction (Fig SI.15a) shows the occurrence of the fluorite phase without any significant distortion of  
 886 the structure.

887 Thermogravimetric analysis (Fig. SI.15b) analysis reports only a small variation on the region of  
 888 chemisorbed water compared with the pristine catalyst, indicating that no organic by-products were  
 889 adsorbed on the catalyst surface.

890 In accordance with XRD analysis, electron diffraction (see figure Fig. SI.15c) confirms that the cubic  
891 fluorite structure of the catalyst is retained after the catalytic tests and that no secondary crystalline  
892 phases are formed. The presence of Fe in the nanostructures is recognized by EDX analysis, with  
893 comparable EDX spectra (Fig. SI.15d) before and after the catalytic reaction. Moreover, based on  
894 HR-TEM images (Fig.SI.15e), it is interesting to notice that the catalytic reaction does not induce  
895 morphological or structural changes on the nanoparticles, which also preserve their characteristic size  
896 of approximately 5 nm.

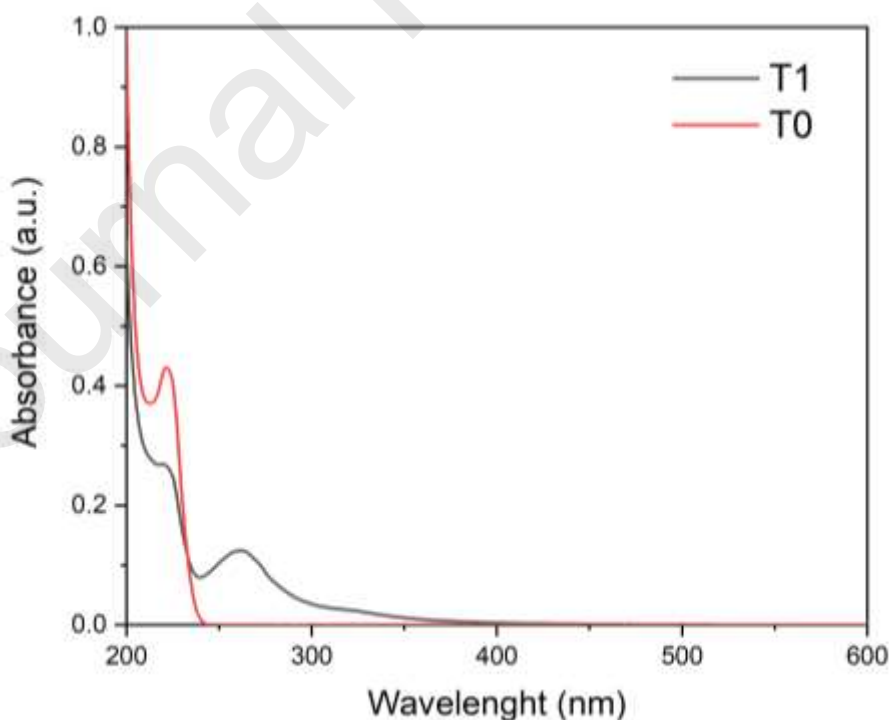
897 Finally, XPS analysis performed on the sample post-catalysis shows first no contamination. Ce3d  
898 spectra obtained before and after photocatalysis are quite similar (Fig. SI.16a). A minor change of the  
899 v component (at 882.6 eV) can be seen, meaning that the  $Ce^{4+}$  contribution may have increased  
900 slightly. However, that variation is so small that it hardly affects its 3d3/2 counterpart. Consequently,  
901 in accordance with the other analyses, the XPS study confirms that the photocatalytic tests did not  
902 induce significant changes in the photocatalyst.

903

### 904 3.4 Identification of degradation by-products

905 A further objective of this work was the identification of possible degradation products.

906 The samples collected during the kinetic experiments were analysed via UV-Vis spectrophotometry  
907 and allowed the identification of an absorbance peak characteristic of an unknown chemical  
908 compound, at the wavelength  $\lambda=260$  nm. Fig. 14 shows an example of the absorbance spectrum  
909 obtained at two different times, collected during a kinetic run conducted imposing the following  
910 reaction conditions: catalyst Fe<sub>2.5</sub>,  $T=30^{\circ}C$ ,  $C_{IBU,0}=12.4mg/L$ ,  $\rho_B=0.07 g/L$ . In particular, the T0 sample  
911 was collected at time=0, while T1 at time = 30 min of reaction time.



912

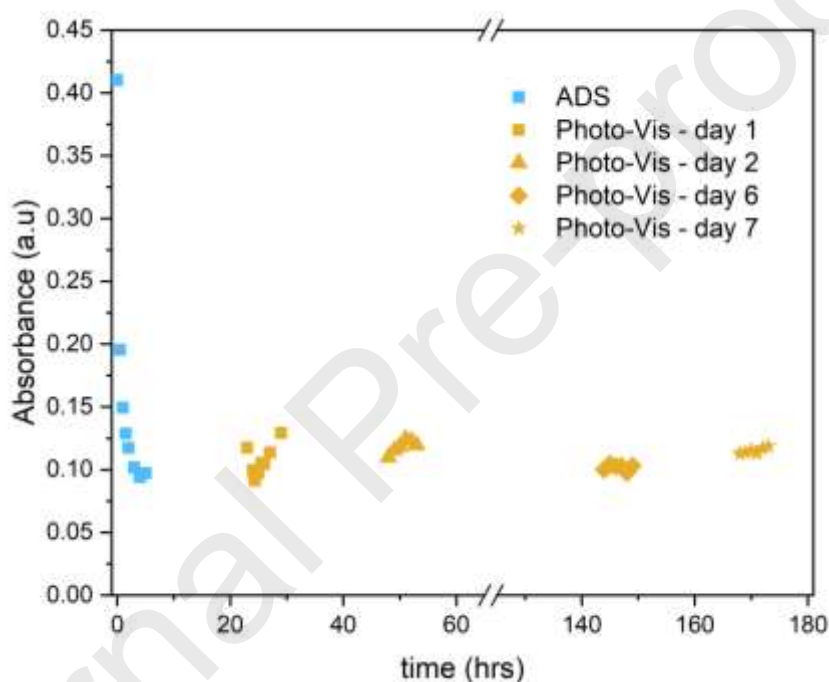
913 **Fig. 14:** Comparison between absorbance spectra of samples T0 (sample collected at time = 0) and T1  
914 (sample collected at time = 30 min), collected during a kinetic run conducted imposing the following  
915 reaction conditions: catalyst Fe<sub>2.5</sub>,  $T=30^{\circ}C$ ,  $C_{IBU,0}=12.4mg L^{-1}$ ,  $\rho_B=0.07 g L^{-1}$ .

916

917 As Fig. 14 reveals, the peak at  $\lambda=260$  nm is not present when analysing ibuprofen in water solution  
 918 (T0). The additional peak was detected in every photodegradation test but with an absorbance variable  
 919 with the experimental time. In particular, the absorbance increases as the reaction proceeds,  
 920 simultaneously with the decrease of the absorbance measured at  $\lambda=220$  nm.

921 Thus, it is important to carry out a more sophisticated analysis to understand the nature of the chemical  
 922 compounds present during the photodegradation tests. The identification of the by-product generated  
 923 by the reaction was conducted by performing an adsorption test and subsequent photodegradation.  
 924 The samples were analysed using a UV-Vis spectrophotometer to monitor the absorbance peaks for  
 925 ibuprofen and the by-products identified, further identified by LC-MS analysis.

926 The results obtained from the spectrophotometer analysis are shown in Fig. 15.



927

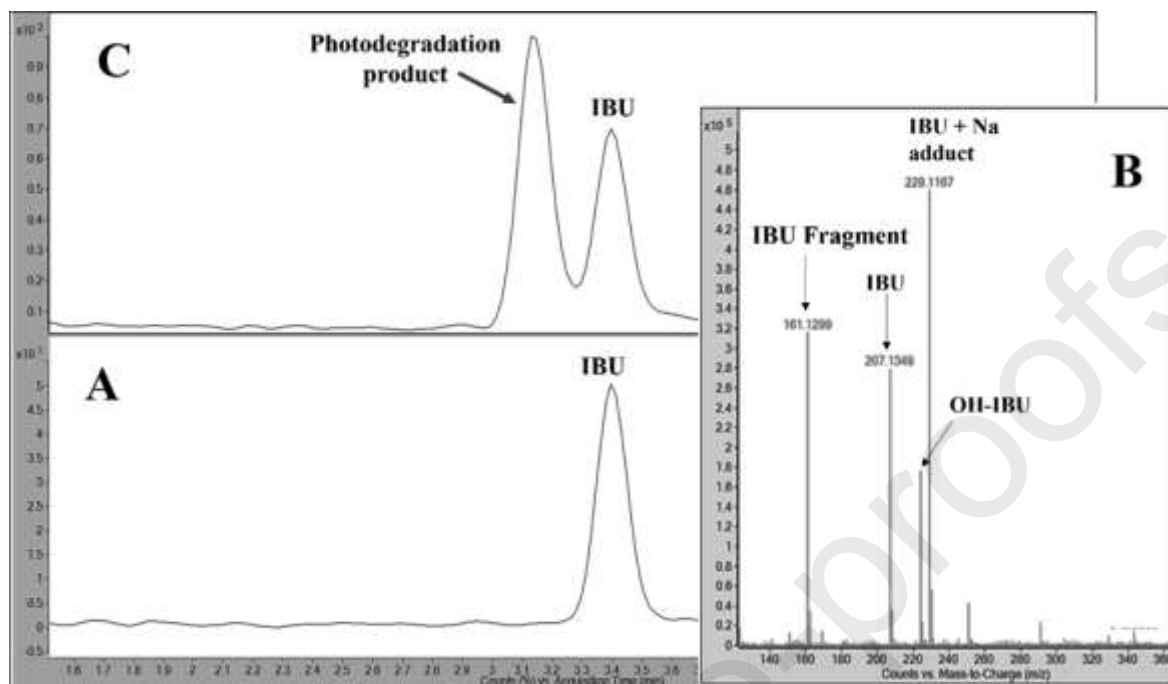
928 **Fig. 15:** Results obtained from spectrophotometer analyses. Experimental conditions: catalyst  
 929  $\text{Fe}_{2.5}$ ,  $T = 30^{\circ}\text{C}$ ,  $C_{\text{IBU},0} = 12.4 \text{ mg L}^{-1}$ ,  $\rho_{\text{B}} = 0.07 \text{ g L}^{-1}$ .

930

931 From the results reported in Fig. 15, it is possible to note that in dark, the absorbance recorded at the  
 932 wavelength of  $\lambda=220$  nm decreases, due to a decrease of ibuprofen concentration in the liquid solution  
 933 due to the related adsorption on the catalyst. Starting from the first day of photodegradation, the  
 934 absorbance measured at  $\lambda=220$  nm remains constant for 7 days of reaction. The observed trend could  
 935 be explained by the formation of by-products, showing an absorption at the same wavelength as  
 936 ibuprofen.

937 The identification of neo-formed by-products obtained from the ibuprofen photodegradation was also  
 938 performed by LC-MS analysis. The MS analysis was preliminarily performed on the standard solution  
 939 (T0) of ibuprofen to set up the chromatographic conditions and MS parameters. The ion current of  
 940 the chromatographic peak (3.4 min, Fig. 16 panel A) detected in the mixture at T0 was assigned to  
 941 the molecular ion ( $\text{M}+\text{H}^+$ ) of ibuprofen (IBU) at 207.1  $\text{m/z}$  in addition to the hydroxylated form

942 (223.1  $m/z$ ) and the sodium adduct species (229.1  $m/z$ ) (Fig. 16, exploded panel B). Interestingly, an  
 943 MS signal at 161.1  $m/z$  was detected in the standard mixture (T0) due to the residue fragmentation  
 944 occurring within the ESI source causing the loss of formic acid from the starting molecule.

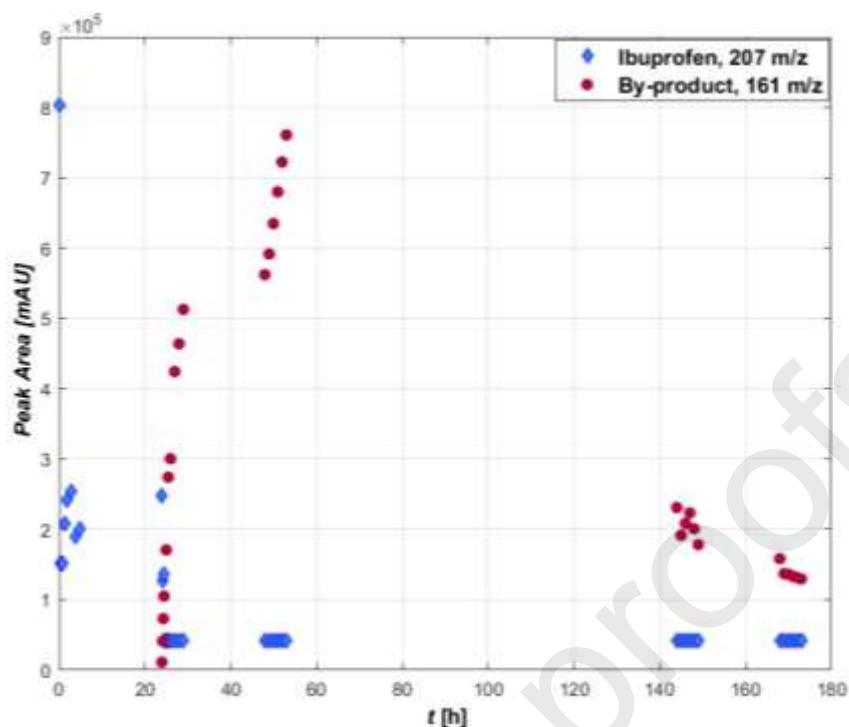


945

946 **Fig. 16:** Total ion current (TIC) chromatogram of the standard mixture (T0) (panel A) and the relative  
 947 MS spectrum of peak at 3.4 min (panel B). TIC chromatogram of the mixture at the reaction time of  
 948 24 h (T10) (panel C).

949

950 Then, each aliquot analysed via UV-VIS spectrophotometry was further analysed via LC-TOF, to  
 951 monitor the formation of the main by-products along the whole photodegradation experiment. The  
 952 results reported in Fig. 17 demonstrated a marked decrease in ibuprofen after the first 30 min of  
 953 reaction time (adsorption phase) followed by small variations of the peak area up to T10, Fig. 16  
 954 panel C, (roughly 24 h of reaction) till reaching a constant value of roughly the 5% of the initial value  
 955 (T0 sample) (Fig. 17).



956

957 **Fig. 17:** Monitoring of kinetics of ibuprofen degradation and formation of by-products by mass  
 958 spectrometry analysis.

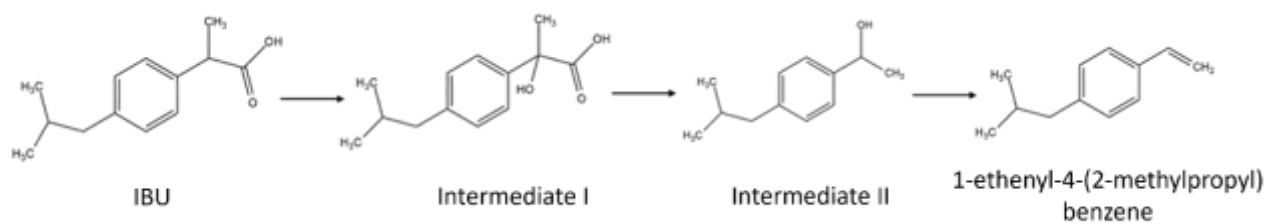
959

960 The occurrence of neo-formed by-product started to appear at T8, corresponding to the start of the  
 961 photodegradation step, displaying a chromatographic peak at a retention time shift of 0.3 min (3.1  
 962 min) from the intact ibuprofen. The identification of by-product at 161 m/z assigned to the 1-ethenyl-  
 963 4-(2-methylpropyl)benzene (C<sub>12</sub>H<sub>16</sub>) was confirmed by GC-MS analysis where the fragments  
 964 originated from the electron impact (IE) source were compared to the NIST database (Fig. SI.17).

965 Furthermore, a significant increase of by-product was observed up T23 (roughly after 2 days) where  
 966 it reached the highest concentration. Then, after the second day, a drastic reduction of the product  
 967 was recorded.

968 The presence of the mentioned by-product was already reported in the literature as possible  
 969 intermediate in a more complex mechanism involving several degradation species. In particular, Rao  
 970 et al., [127], reported that 1-ethenyl-4-(2-methylpropyl)benzene is produced by the dehydration and  
 971 decomposition of two intermediates as described in Scheme 2. In the present work, the mentioned  
 972 two intermediates were not detected, probably because the related reactions of formation and  
 973 disappearance are relatively fast in the presence of Fe<sub>2.5</sub> catalyst.

974



975

976 **Scheme 2:** Possible degradation pathway of IBU with formation of by-product detected in the present  
977 study.

978

979

980

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981 **Conclusions**

982 Meticulous synthesis strategies for the preparation of robust and efficient photocatalysts are at the  
983 forefront of rapidly evolving fields, such as the removal of emerging contaminants in visible light-  
984 activated photocatalytic processes.

985 To avoid a trial and error approach we have selected a reliable and valuable bottom-up approach, the  
986 reverse micelle method, that allows to closely control the crystallographic and electronic properties  
987 of the ceria nanostructured photocatalysts. With controlled precipitation within the micelle nano-  
988 reactors, undoped and iron-substituted (0.50-10 mol %) ceria nanoparticles consisting of single  
989 crystals were successfully prepared. The sample with the highest iron content is the only one that  
990 shows the presence of oligomeric species on the surface while the other samples show an effective  
991 inclusion of substitutional iron in the ceria lattice.

992 The effect of the different iron content in the various samples revealed the role of iron heteroatoms  
993 in the delicate balance between adsorption and relative photodegradation of ibuprofen. Light was  
994 shed on the relationship between composition-structure and activity through numerous catalytic  
995 experiments, conducted both in the dark and under UV or visible irradiation. The results were  
996 supported by a combination of advanced characterisation techniques and DFT calculations, showing  
997 that the doping of the CeO<sub>2</sub>(111) surface with a substitutional Fe atom i) causes a decrease in the  
998 band gap of the system, improving the catalytic performance of the catalyst, ii) favours the formation  
999 of vacant sites (VO<sub>x</sub>) when the oxygen atoms are directly coordinated with the dopant or very close  
1000 to it, iii) favours the IBU adsorption both in the stoichiometric and reduced model. Despite the  
1001 presence of iron and vacancies being beneficial for ibuprofen adsorption, experimentally we find a  
1002 non-linear trend of the adsorption capacity with the iron content. The latter was explained by  
1003 measuring the z-potential of each sample, finding that adsorption is more efficient when the catalyst  
1004 surface is positively charged. The combination of this effect and the non-linear trend of ibuprofen  
1005 adsorption with Fe content leads to the identification of an optimal composition of the photocatalyst,  
1006 namely 2.5 mol% Fe doped CeO<sub>2</sub>. The mentioned material showed good stability along 4 cycles of  
1007 re-use experiments, demonstrating to be a promising material for a future application in flow.

1008 Finally, GC-MS and HPLC-MS analyses were conducted on the samples collected in a dedicated  
1009 experiment conducted with Fe2.5 catalyst under visible irradiation, allowing the identification of 1-  
1010 ethenyl-4-(2-methylpropyl)benzene as the main by-product.

1011

1012

1013 **List of abbreviations**

*IBU*      *Ibuprofen*      1014

(\*)      *Free site*      1015      **List of symbols**

(*IBU*)      *Ibuprofen*

(*IBU*\*)      *Ibuprofen adsorbed into the solid*

*AOPs*      *Advanced oxidation processes*

*NSAIDs*      *Non-steroidal anti-inflammatory drugs*

$C_{IBU,0}$       *ibuprofen initial concentration*      ( $mg L^{-1}$ )

$C_{IBU}$       *concentration of ibuprofen at t time*      ( $mg L^{-1}$ )

$C_{IBU^*}$       *concentration of adsorbed ibuprofen*      ( $mg L^{-1}$ )

$k_{ADS}$       *adsorption kinetic constant*      ( $L (g min)^{-1}$ )

$k_{DEG}$       *desorption kinetic constant*      ( $L (g min)^{-1}$ )

$K_{eqADS}$       *adsorption constant*      (-)

$qt$       *adsorbed amount*      ( $mg g^{-1}$ )

$r_{ADS}$       *adsorption rate*      ( $mg g^{-1} min^{-1}$ )

$r_{DEG}$       *desorption rate*      ( $mg g^{-1} min^{-1}$ )

$t$       *time*      ( $min$ )

$T$       *temperature*      ( $^{\circ}C$ )

1016

1017 ***Greek symbol***

$\rho_B$  sorbent bulk density ( $\text{g L}^{-1}$ )

1018

1019 **Acknowledgments**

1020 Miss Sonia Romano is cordially acknowledged for the experimental and numerical support given for  
1021 the realization of the present study.

1022

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1023 **Reference**

- 1024 1. Shah, A.H.; Rather, M.A.; Shah, A.H.; Rather, M.A. Advances in Nano Research. *Adv Nano Res* **2021**,  
1025 *10*, 397, doi:10.12989/ANR.2021.10.4.397.
- 1026 2. Nath Bhadra, B.; Ahmed, I.; Kim, S.; Jhung, S.H. Adsorptive Removal of Ibuprofen and Diclofenac  
1027 from Water Using Metal-Organic Framework-Derived Porous Carbon.,  
1028 doi:10.1016/j.cej.2016.12.127.
- 1029 3. Madikizela, L.M.; Chimuka, L. Simultaneous Determination of Naproxen, Ibuprofen and Diclofenac in  
1030 Wastewater Using Solid-Phase Extraction with High Performance Liquid Chromatography. *Water SA*  
1031 **2017**, *43*, 264, doi:10.4314/wsa.v43i2.10.
- 1032 4. Oba, S.N.; Ighalo, J.O.; Aniagor, C.O.; Igwegbe, A. Removal of Ibuprofen from Aqueous Media by  
1033 Adsorption: A Comprehensive Review. *Science of the Total Environment* **2021**, *780*, 146608,  
1034 doi:10.1016/j.scitotenv.2021.146608.
- 1035 5. Ohtani, B. Photocatalysis A to Z-What We Know and What We Do Not Know in a Scientific Sense.  
1036 *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **2010**, *11*, 157–178,  
1037 doi:10.1016/j.jphotochemrev.2011.02.001.
- 1038 6. Nan Chong, M.; Jin, B.; Chow, C.W.; Saint, C. Recent Developments in Photocatalytic Water  
1039 Treatment Technology: A Review. *Water Res* **2010**, *44*, 2997–3027,  
1040 doi:10.1016/j.watres.2010.02.039.
- 1041 7. Melchionna, M.; Fornasiero, P. Updates on the Roadmap for Photocatalysis. **2020**,  
1042 doi:10.1021/acscatal.0c01204.
- 1043 8. Mancuso, A.; Morante, N.; De Carluccio, M.; Sacco, O.; Rizzo, L.; Fontana, M.; Esposito, S.; Vaiano, V.;  
1044 Sannino, D. Solar Driven Photocatalysis Using Iron and Chromium Doped TiO<sub>2</sub> Coupled to Moving  
1045 Bed Biofilm Process for Olive Mill Wastewater Treatment. *Chemical Engineering Journal* **2022**, *450*,  
1046 138107, doi:10.1016/j.cej.2022.138107.
- 1047 9. Lou, L.; Wang, J.; Joon Lee, Y.; Ramkumar, S.S.; Lou, L.; Ramkumar, S.S.; Wang, J.; Lee, Y.J. Visible  
1048 Light Photocatalytic Functional TiO<sub>2</sub>/PVDF Nanofibers for Dye Pollutant Degradation. *Particle &*  
1049 *Particle Systems Characterization* **2019**, *36*, 1900091, doi:10.1002/PPSC.201900091.
- 1050 10. Iervolino, G.; Zammit, I.; Vaiano, V.; Rizzo, L. Limitations and Prospects for Wastewater Treatment by  
1051 UV and Visible-Light-Active Heterogeneous Photocatalysis: A Critical Review. *Top Curr Chem* **2020**,  
1052 *378*, 7, doi:10.1007/s41061-019-0272-1.
- 1053 11. Tamaro, O.; Morante, N.; Marocco, A.; Fontana, M.; Castellino, M.; Barrera, G.; Allia, P.; Tiberto,  
1054 P.; Arletti, R.; Fantini, R.; et al. The Beneficial Role of Nano-Sized Fe<sub>3</sub>O<sub>4</sub> Entrapped in Ultra-Stable Y  
1055 Zeolite for the Complete Mineralization of Phenol by Heterogeneous Photo-Fenton under Solar  
1056 Light. *Chemosphere* **2023**, *345*, 140400, doi:10.1016/j.chemosphere.2023.140400.
- 1057 12. El-Sheikh, S.M.; Khedr, T.M.; Hakki, A.; Ismail, A.A.; Badawy, W.A.; Bahnemann, D.W. Visible Light  
1058 Activated Carbon and Nitrogen Co-Doped Mesoporous TiO<sub>2</sub> as Efficient Photocatalyst for  
1059 Degradation of Ibuprofen. *Sep Purif Technol* **2017**, *173*, 258–268,  
1060 doi:10.1016/J.SEPPUR.2016.09.034.
- 1061 13. Liu, N.; Wang, J.; Wu, J.; Li, Z.; Huang, W.; Zheng, Y.; Lei, J.; Zhang, X.; Tang, L. Magnetic Fe<sub>3</sub>O<sub>4</sub>  
1062 @MIL-53(Fe) Nanocomposites Derived from MIL-53(Fe) for the Photocatalytic Degradation of  
1063 Ibuprofen under Visible Light Irradiation. **2020**, doi:10.1016/j.materresbull.2020.111000.

- 1064 14. Sarafraz, M.; Amini, M.M.; Adiban, M.; Eslami, A. Facile Synthesis of Mesoporous Black N–TiO<sub>2</sub>  
1065 Photocatalyst for Efficient Charge Separation and the Visible-Driven Photocatalytic Mechanism of  
1066 Ibuprofen Degradation. *Mater Sci Semicond Process* **2020**, *120*, 105258,  
1067 doi:10.1016/J.MSSP.2020.105258.
- 1068 15. Liu, N.; Fei, F.; Dai, W.; Lei, J.; Bi, F.; Wang, B.; Quan, G.; Zhang, X.; Tang, L. Visible-Light-Assisted  
1069 Persulfate Activation by SnS<sub>2</sub>/MIL-88B(Fe) Z-Scheme Heterojunction for Enhanced Degradation of  
1070 Ibuprofen. *J Colloid Interface Sci* **2022**, *625*, 965–977, doi:10.1016/J.JCIS.2022.06.099.
- 1071 16. Liu, N.; Wu, J.; Fei, F.; Lei, J.; Shi, W.; Quan, G.; Zeng, S.; Zhang, X.; Tang, L. Ibuprofen Degradation by  
1072 a Synergism of Facet-Controlled MIL-88B(Fe) and Persulfate under Simulated Visible Light.,  
1073 doi:10.1016/j.jcis.2021.12.142.
- 1074 17. Chaker, H.; Fourmentin, S.; Chérif-Aouali, L. Efficient Photocatalytic Degradation of Ibuprofen under  
1075 Visible Light Irradiation Using Silver and Cerium Co-Doped Mesoporous TiO<sub>2</sub>. *ChemistrySelect* **2020**,  
1076 *5*, 11787–11796, doi:10.1002/slct.202002730.
- 1077 18. Montini, T.; Melchionna, M.; Monai, M.; Fornasiero, P. Fundamentals and Catalytic Applications of  
1078 CeO<sub>2</sub>-Based Materials. **2016**, doi:10.1021/acs.chemrev.5b00603.
- 1079 19. Mansingh, S.; Padhi, D.K.; Parida, K.M. Enhanced Photocatalytic Activity of Nanostructured Fe Doped  
1080 CeO<sub>2</sub> for Hydrogen Production under Visible Light Irradiation. *Int J Hydrogen Energy* **2016**, *41*,  
1081 14133–14146, doi:10.1016/j.ijhydene.2016.05.191.
- 1082 20. Corma, A.; Atienzar, P.; García, H.; Chane-Ching, J.-Y. Hierarchically Mesostructured Doped CeO<sub>2</sub>  
1083 with Potential for Solar-Cell Use. *Nat Mater* **2004**, *3*, 394–397, doi:10.1038/nmat1129.
- 1084 21. Kusmierek, E. A CeO<sub>2</sub> Semiconductor as a Photocatalytic and Photoelectrocatalytic Material for the  
1085 Remediation of Pollutants in Industrial Wastewater: A Review. *Catalysts* **2020**, *10*, 1435,  
1086 doi:10.3390/catal10121435.
- 1087 22. Ma, R.; Zhang, S.; Wen, T.; Gu, P.; Li, L.; Zhao, G.; Niu, F.; Huang, Q.; Tang, Z.; Wang, X. A Critical  
1088 Review on Visible-Light-Response CeO<sub>2</sub>-Based Photocatalysts with Enhanced Photooxidation of  
1089 Organic Pollutants. *Catal Today* **2019**, *335*, 20–30, doi:10.1016/J.CATTOD.2018.11.016.
- 1090 23. Atran, A.A.; Hamdy, M.S. Improving the Photocatalytic Performance of Porous Ceria under Visible  
1091 Light Illumination via Mn Incorporation. *Catalysts* **2023**, *13*, 523, doi:10.3390/catal13030523.
- 1092 24. Tsoncheva, T.; Rosmini, C.; Dimitrov, M.; Issa, G.; Henych, J.; Němečková, Z.; Kovacheva, D.; Velinov,  
1093 N.; Atanasova, G.; Spassova, I. Formation of Catalytic Active Sites in Hydrothermally Obtained Binary  
1094 Ceria-Iron Oxides: Composition and Preparation Effects. *ACS Appl Mater Interfaces* **2021**, *13*, 1838–  
1095 1852, doi:10.1021/ACSAMI.0C16326/ASSET/IMAGES/LARGE/AM0C16326\_0011.JPEG.
- 1096 25. Liu, B.; Yan, Z.; Xu, T.; Li, C.; Gao, R.; Hao, H.; Bai, J. Co-Construction of Oxygen Vacancies and  
1097 Heterojunctions on CeO<sub>2</sub> via One-Step Fe Doping for Enhanced Photocatalytic Activity in Suzuki  
1098 Reaction. *Chemical Engineering Journal* **2022**, *442*, 136226, doi:10.1016/J.CEJ.2022.136226.
- 1099 26. *Cerium Oxide (CeO<sub>2</sub>): Synthesis, Properties and Applications*; Elsevier, 2020; ISBN 9780128156612.
- 1100 27. Younis, A.; Chu, D.; Kaneti, Y.V.; Li, S. Tuning the Surface Oxygen Concentration of {111} Surrounded  
1101 Ceria Nanocrystals for Enhanced Photocatalytic Activities. *Nanoscale* **2015**, *8*, 378–387,  
1102 doi:10.1039/C5NR06588G.

- 1103 28. Choudhury, B.; Chetri, P.; Choudhury, A. Oxygen Defects and Formation of Ce<sup>3+</sup> Affecting the  
1104 Photocatalytic Performance of CeO<sub>2</sub> Nanoparticles. *RSC Adv* **2013**, *4*, 4663–4671,  
1105 doi:10.1039/C3RA44603D.
- 1106 29. Trovarelli, A. Structural and Oxygen Storage/Release Properties of CeO<sub>2</sub>-Based Solid Solutions.  
1107 *Comments on Inorganic Chemistry* **1999**, *20*, 263–284, doi:10.1080/02603599908021446.
- 1108 30. TROVARELLI, A. Catalytic Properties of Ceria and CeO<sub>2</sub>-Containing Materials. *Catalysis Reviews*  
1109 **1996**, *38*, 439–520, doi:10.1080/01614949608006464.
- 1110 31. Zhang, F.; Zhao, L.; Chen, H.; He, Y.; Tian, P.; Zeng, X. Synthesis of Mesoporous Fe/h-CeO<sub>2</sub> Hollow  
1111 Micro-Spheres with Enhanced Visible Light Photocatalytic Activity. *Mater Res Express* **2019**, *6*,  
1112 095516, doi:10.1088/2053-1591/ab3015.
- 1113 32. Cai, W.; Chen, F.; Shen, X.; Chen, L.; Zhang, J. Enhanced Catalytic Degradation of AO7 in the CeO<sub>2</sub>-  
1114 H<sub>2</sub>O<sub>2</sub> System with Fe<sup>3+</sup> Doping. *Appl Catal B* **2010**, *101*, 160–168,  
1115 doi:10.1016/j.apcatb.2010.09.031.
- 1116 33. Channei, D.; Inceesungvorn, B.; Wetchakun, N.; Ukritnukun, S.; Nattestad, A.; Chen, J.;  
1117 Phanichphant, S. Photocatalytic Degradation of Methyl Orange by CeO<sub>2</sub> and Fe-Doped CeO<sub>2</sub> Films  
1118 under Visible Light Irradiation. *Sci Rep* **2014**, *4*, 5757, doi:10.1038/srep05757.
- 1119 34. Zhao, B.; Shao, Q.; Hao, L.; Zhang, L.; Liu, Z.; Zhang, B.; Ge, S.; Guo, Z. Yeast-Template Synthesized  
1120 Fe-Doped Cerium Oxide Hollow Microspheres for Visible Photodegradation of Acid Orange 7. *J*  
1121 *Colloid Interface Sci* **2018**, *511*, 39–47, doi:10.1016/j.jcis.2017.09.077.
- 1122 35. Wang, Y.; Wang, F.; Chen, Y.; Zhang, D.; Li, B.; Kang, S.; Li, X.; Cui, L. Enhanced Photocatalytic  
1123 Performance of Ordered Mesoporous Fe-Doped CeO<sub>2</sub> Catalysts for the Reduction of CO<sub>2</sub> with H<sub>2</sub>O  
1124 under Simulated Solar Irradiation. *Appl Catal B* **2014**, *147*, 602–609,  
1125 doi:10.1016/j.apcatb.2013.09.036.
- 1126 36. Channei, D.; Inceesungvorn, B.; Wetchakun, N.; Phanichphant, S.; Nakaruk, A.; Koshy, P.; Sorrell, C.C.  
1127 Photocatalytic Activity under Visible Light of Fe-Doped CeO<sub>2</sub> Nanoparticles Synthesized by Flame  
1128 Spray Pyrolysis. *Ceram Int* **2013**, *39*, 3129–3134, doi:10.1016/j.ceramint.2012.09.093.
- 1129 37. Esposito, S. Introduction. In *Sol-Gel Synthesis Strategies for Tailored Catalytic Materials*; 2023; pp.  
1130 1–12, [https://doi.org/10.1007/978-3-031-20723-5\\_1](https://doi.org/10.1007/978-3-031-20723-5_1).
- 1131 38. Pileni, M.P. Reverse Micelles as Microreactors. *J Phys Chem* **1993**, *97*, 6961–6973,  
1132 doi:10.1021/j100129a008.
- 1133 39. Moragues, T.; Arguijo, D.; Beneyton, T.; Modavi, C.; Simutis, K.; Abate, A.R.; Baret, J.-C.; deMello,  
1134 A.J.; Densmore, D.; Griffiths, A.D. Droplet-Based Microfluidics. *Nature Reviews Methods Primers*  
1135 **2023**, *3*, 32, doi:10.1038/s43586-023-00212-3.
- 1136 40. Omidi, M.; Almeida, L.; Tayebi, L. Microfluidic-assisted Fabrication of Reverse Micelle/PLGA Hybrid  
1137 Microspheres for Sustained Vascular Endothelial Growth Factor Delivery. *Biotechnol Appl Biochem*  
1138 **2021**, *68*, 616–625, doi:10.1002/bab.1971.
- 1139 41. Quinlan, F.T.; Kuther, J.; Tremel, W.; Knoll, W.; Risbud, S.; Stroeve, P. Reverse Micelle Synthesis and  
1140 Characterization of ZnSe Nanoparticles. *Langmuir* **2000**, *16*, 4049–4051, doi:10.1021/la9909291.
- 1141 42. Morrison, S.A.; Cahill, C.L.; Carpenter, E.E.; Harris, V.G. Production Scaleup of Reverse Micelle  
1142 Synthesis. *Ind Eng Chem Res* **2006**, *45*, 1217–1220, doi:10.1021/ie050886l.

- 1143 43. Tammaro, O.; Costagliola di Polidoro, A.; Romano, E.; Netti, P.A.; Torino, E. A Microfluidic Platform  
1144 to Design Multimodal PEG - Crosslinked Hyaluronic Acid Nanoparticles (PEG-CHANPs) for Diagnostic  
1145 Applications. *Sci Rep* **2020**, *10*, doi:10.1038/s41598-020-63234-x.
- 1146 44. Lee, Y.; Lee, J.; Bae, C.J.; Park, J.-G.; Noh, H.-J.; Park, J.-H.; Hyeon, T. Large-Scale Synthesis of Uniform  
1147 and Crystalline Magnetite Nanoparticles Using Reverse Micelles as Nanoreactors under Reflux  
1148 Conditions. *Adv Funct Mater* **2005**, *15*, 503–509, doi:10.1002/adfm.200400187.
- 1149 45. Arsene, M.-L.; Răut, I.; Călin, M.; Jecu, M.-L.; Doni, M.; Gurban, A.-M. Versatility of Reverse Micelles:  
1150 From Biomimetic Models to Nano (Bio)Sensor Design. *Processes* **2021**, *9*, 345,  
1151 doi:10.3390/pr9020345.
- 1152 46. Laguna, O.H.; Centeno, M.A.; Boutonnet, M.; Odriozola, J.A. Fe-Doped Ceria Solids Synthesized by  
1153 the Microemulsion Method for CO Oxidation Reactions. *Appl Catal B* **2011**, *106*, 621–629,  
1154 doi:10.1016/j.apcatb.2011.06.025.
- 1155 47. Pournajaf, R.; Hassanzadeh-Tabrizi, S.A.; Jafari, M. Reverse Microemulsion Synthesis of CeO<sub>2</sub>  
1156 Nanopowder Using Polyoxyethylene(23)Lauryl Ether as a Surfactant. *Ceram Int* **2014**, *40*, 8687–  
1157 8692, doi:10.1016/j.ceramint.2014.01.086.
- 1158 48. Tescione, F.; Tammaro, O.; Bifulco, A.; Del Monaco, G.; Esposito, S.; Pansini, M.; Silvestri, B.;  
1159 Costantini, A. Silica Meets Tannic Acid: Designing Green Nanoplatfoms for Environment  
1160 Preservation. *Molecules* **2022**, *27*, 1944, doi:10.3390/molecules27061944.
- 1161 49. Addorisio, V.; Pirozzi, D.; Esposito, S.; Sannino, F. Decontamination of Waters Polluted with Simazine  
1162 by Sorption on Mesoporous Metal Oxides. *J Hazard Mater* **2011**, *196*, 242–247,  
1163 doi:10.1016/j.jhazmat.2011.09.022.
- 1164 50. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys Rev*  
1165 *Lett* **1996**, *77*, 3865–3868, doi:10.1103/PhysRevLett.77.3865.
- 1166 51. Vanderbilt, D. Soft Self-Consistent Pseudopotentials in a Generalized Eigenvalue Formalism. *Phys*  
1167 *Rev B* **1990**, *41*, 7892–7895, doi:10.1103/PhysRevB.41.7892.
- 1168 52. Giannozzi, P.; Andreussi, O.; Brumme, T.; Bunau, O.; Buongiorno Nardelli, M.; Calandra, M.; Car, R.;  
1169 Cavazzoni, C.; Ceresoli, D.; Cococcioni, M.; et al. Advanced Capabilities for Materials Modelling with  
1170 Quantum ESPRESSO. *Journal of Physics: Condensed Matter* **2017**, *29*, 465901, doi:10.1088/1361-  
1171 648X/aa8f79.
- 1172 53. Cococcioni, M.; de Gironcoli, S. Linear Response Approach to the Calculation of the Effective  
1173 Interaction Parameters in the  $\langle \text{LDA} \rangle \langle \text{U} \rangle$  Method. *Phys Rev B* **2005**, *71*, 035105,  
1174 doi:10.1103/PhysRevB.71.035105.
- 1176 54. Loschen, C.; Carrasco, J.; Neyman, K.M.; Illas, F. First-Principles  $\langle \text{LDA} \rangle \langle \text{U} \rangle$  and  $\langle \text{GGA} \rangle \langle \text{U} \rangle$   
1177  $\langle \text{LDA} \rangle \langle \text{U} \rangle$  and  $\langle \text{GGA} \rangle \langle \text{U} \rangle$  Study of Cerium Oxides: Dependence on the Effective U Parameter. *Phys Rev B*  
1178 **2007**, *75*, 035115, doi:10.1103/PhysRevB.75.035115.
- 1181 55. Fabris, S.; Vicario, G.; Balducci, G.; de Gironcoli, S.; Baroni, S. Electronic and Atomistic Structures of  
1182 Clean and Reduced Ceria Surfaces. *J Phys Chem B* **2005**, *109*, 22860–22867, doi:10.1021/jp0511698.

- 1183 56. Nolan, M.; Grigoleit, S.; Sayle, D.C.; Parker, S.C.; Watson, G.W. Density Functional Theory Studies of  
1184 the Structure and Electronic Structure of Pure and Defective Low Index Surfaces of Ceria. *Surf Sci*  
1185 **2005**, *576*, 217–229, doi:10.1016/j.susc.2004.12.016.
- 1186 57. Nolan, M.; Watson, G.W. The Surface Dependence of CO Adsorption on Ceria. *J Phys Chem B* **2006**,  
1187 *110*, 16600–16606, doi:10.1021/jp062499a.
- 1188 58. Da Silva, J.L.F.; Ganduglia-Pirovano, M.V.; Sauer, J.; Bayer, V.; Kresse, G. Hybrid Functionals Applied  
1189 to Rare-Earth Oxides: The Example of Ceria. *Phys Rev B* **2007**, *75*, 045121,  
1190 doi:10.1103/PhysRevB.75.045121.
- 1191 59. Zhang, C.; Michaelides, A.; King, D.A.; Jenkins, S.J. Structure of Gold Atoms on Stoichiometric and  
1192 Defective Ceria Surfaces. *J Chem Phys* **2008**, *129*, 194708, doi:10.1063/1.3009629.
- 1193 60. Yue, L.; Zhang, X.-M. Structural Characterization and Photocatalytic Behaviors of Doped CeO<sub>2</sub>  
1194 Nanoparticles. *J Alloys Compd* **2009**, *475*, 702–705, doi:10.1016/j.jallcom.2008.07.096.
- 1195 61. Ganduglia-Pirovano, M.V.; Da Silva, J.L.F.; Sauer, J. Density-Functional Calculations of the Structure  
1196 of Near-Surface Oxygen Vacancies and Electron Localization on  $\text{CeO}_2$   $\langle \text{Mn} \rangle_{111}$   
1197  $\langle \text{Mn} \rangle_{111}$  Surfaces. *Phys Rev Lett* **2009**, *102*, 026101,  
1198 doi:10.1103/PhysRevLett.102.026101,  
1199 doi:10.1103/PhysRevLett.102.026101.
- 1200 62. Szabová, L.; Camellone, M.F.; Huang, M.; Matolín, V.; Fabris, S. Thermodynamic, Electronic and  
1201 Structural Properties of Cu/CeO<sub>2</sub> Surfaces and Interfaces from First-Principles DFT+U Calculations. *J*  
1202 *Chem Phys* **2010**, *133*, 234705, doi:10.1063/1.3515424.
- 1203 63. Chen, A.; Yu, X.; Zhou, Y.; Miao, S.; Li, Y.; Kuld, S.; Sehested, J.; Liu, J.; Aoki, T.; Hong, S.; et al.  
1204 Structure of the Catalytically Active Copper–Ceria Interfacial Perimeter. *Nat Catal* **2019**, *2*, 334–341,  
1205 doi:10.1038/s41929-019-0226-6.
- 1206 64. Tran, N.-D.; Farnesi Camellone, M.; Fabris, S. Probing the Reactivity of Pt/Ceria Nanocatalysts toward  
1207 Methanol Oxidation: From Ionic Single-Atom Sites to Metallic Nanoparticles. *The Journal of Physical*  
1208 *Chemistry C* **2018**, *122*, 17917–17927, doi:10.1021/acs.jpcc.8b05735.
- 1209 65. Dvořák, F.; Szabová, L.; Johánek, V.; Farnesi Camellone, M.; Stetsovych, V.; Vorokhta, M.; Tovt, A.;  
1210 Skála, T.; Matolínová, I.; Tateyama, Y.; et al. Bulk Hydroxylation and Effective Water Splitting by  
1211 Highly Reduced Cerium Oxide: The Role of O Vacancy Coordination. *ACS Catal* **2018**, *8*, 4354–4363,  
1212 doi:10.1021/acscatal.7b04409.
- 1213 66. Oh, S.; Shin, W.S.; Kim, H.T. Effects of PH, Dissolved Organic Matter, and Salinity on Ibuprofen  
1214 Sorption on Sediment. *Environmental Science and Pollution Research* **2016**, *23*, 22882–22889,  
1215 doi:10.1007/s11356-016-7503-6.
- 1216 67. Ritacco, I.; Imparato, C.; Falivene, L.; Cavallo, L.; Magistrato, A.; Caporaso, L.; Farnesi Camellone, M.;  
1217 Aronne, A. Spontaneous Production of Ultrastable Reactive Oxygen Species on Titanium Oxide  
1218 Surfaces Modified with Organic Ligands. *Adv Mater Interfaces* **2021**, *8*, 2100629,  
1219 doi:10.1002/admi.202100629.
- 1220 68. Finkelstein-Shapiro, D.; Davidowski, S.K.; Lee, P.B.; Guo, C.; Holland, G.P.; Rajh, T.; Gray, K.A.; Yarger,  
1221 J.L.; Calatayud, M. Direct Evidence of Chelated Geometry of Catechol on TiO<sub>2</sub> by a Combined Solid-  
1222 State NMR and DFT Study. *The Journal of Physical Chemistry C* **2016**, *120*, 23625–23630,  
1223 doi:10.1021/acs.jpcc.6b08041.

- 1224 69. Liu, L.-M.; Li, S.-C.; Cheng, H.; Diebold, U.; Selloni, A. Growth and Organization of an Organic  
1225 Molecular Monolayer on  $\text{TiO}_2$ : Catechol on Anatase (101). *J Am Chem Soc* **2011**, *133*, 7816–7823,  
1226 doi:10.1021/ja200001r.
- 1227 70. Guo, L.; Huang, Y.; Ritacca, A.G.; Wang, K.; Ritacco, I.; Tan, Y.; Qiang, Y.; Al-Zaqri, N.; Shi, W.; Zheng,  
1228 X. Effect of Indole-2-Carboxylic Acid on the Self-Corrosion and Discharge Activity of Aluminum Alloy  
1229 Anode in Alkaline Al–Air Battery. *Molecules* **2023**, *28*, 4193, doi:10.3390/molecules28104193.
- 1230 71. Kaxiras, E.; Bar-Yam, Y.; Joannopoulos, J.D.; Pandey, K.C. *Ab Initio* Theory of Polar Semiconductor  
1231 Surfaces. I. Methodology and the ( 22 ) Reconstructions of GaAs(111). *Phys Rev B* **1987**, *35*, 9625–  
1232 9635, doi:10.1103/PhysRevB.35.9625.
- 1233 72. Qian, G.-X.; Martin, R.M.; Chadi, D.J. First-Principles Study of the Atomic Reconstructions and  
1234 Energies of Ga- and As-Stabilized GaAs(100) Surfaces. *Phys Rev B* **1988**, *38*, 7649–7663,  
1235 doi:10.1103/PhysRevB.38.7649.
- 1236 73. Reuter, K.; Scheffler, M. Composition, Structure, and Stability of  $\text{RuO}_2/\text{MnO}_2$  as a  
1237  $\text{RuO}_2/\text{MnO}_2$  as a  
1238  $\text{RuO}_2/\text{MnO}_2$  as a  
1239 Function of Oxygen Pressure. *Phys Rev B* **2001**, *65*, 035406, doi:10.1103/PhysRevB.65.035406.
- 1240 74. Meyer, B. First-Principles Study of the Polar O-Terminated ZnO Surface in Thermodynamic  
1241 Equilibrium with Oxygen and Hydrogen. *Phys Rev B* **2004**, *69*, 045416,  
1242 doi:10.1103/PhysRevB.69.045416.
- 1243 75. Henkelman, G.; Arnaldsson, A.; Jónsson, H. A Fast and Robust Algorithm for Bader Decomposition of  
1244 Charge Density. *Comput Mater Sci* **2006**, *36*, 354–360, doi:10.1016/j.commatsci.2005.04.010.
- 1245 76. Sanville, E.; Kenny, S.D.; Smith, R.; Henkelman, G. Improved Grid-Based Algorithm for Bader Charge  
1246 Allocation. *J Comput Chem* **2007**, *28*, 899–908, doi:10.1002/jcc.20575.
- 1247 77. Tang, W.; Sanville, E.; Henkelman, G. A Grid-Based Bader Analysis Algorithm without Lattice Bias.  
1248 *Journal of Physics: Condensed Matter* **2009**, *21*, 084204, doi:10.1088/0953-8984/21/8/084204.
- 1249 78. Friuli, V.; Bruni, G.; Musitelli, G.; Conte, U.; Maggi, L. Influence of Dissolution Media and Presence of  
1250 Alcohol on the In Vitro Performance of Pharmaceutical Products Containing an Insoluble Drug. *J*  
1251 *Pharm Sci* **2018**, *107*, 507–511, doi:10.1016/j.xphs.2017.06.001.
- 1252 79. Esposito, S.; Silvestri, B.; Russo, V.; Bonelli, B.; Manzoli, M.; Deorsola, F.A.; Vergara, A.; Aronne, A.; Di  
1253 Serio, M. Self-Activating Catalyst for Glucose Hydrogenation in the Aqueous Phase under Mild  
1254 Conditions. *ACS Catal* **2019**, *9*, 3426–3436, doi:10.1021/acscatal.8b04710.
- 1255 80. Esposito, S. Evolution of Sol–Gel Chemistry. In *Sol-Gel Synthesis Strategies for Tailored Catalytic*  
1256 *Materials*; Springer International Publishing: Cham, 2023; pp. 43–51 ISBN 978-3-031-20722-8,  
1257 [https://doi.org/10.1007/978-3-031-20723-5\\_5](https://doi.org/10.1007/978-3-031-20723-5_5).
- 1258 81. Bonelli, B.; Tamaro, O.; Martinovic, F.; Nasi, R.; Dell’Agli, G.; Rivolo, P.; Giorgis, F.; Ditaranto, N.;  
1259 Deorsola, F.A.; Esposito, S. Reverse Micelle Strategy for the Synthesis of  $\text{MnO}_x\text{-TiO}_2$  Active  
1260 Catalysts for  $\text{NH}_3$ -Selective Catalytic Reduction of  $\text{NO}_x$  at Both Low Temperature and Low Mn  
1261 Content. *ACS Omega* **2021**, *6*, 24562–24574, doi:10.1021/acsomega.1c03153.
- 1262 82. Nasi, R.; Esposito, S.; Freyria, F.; Armandi, M.; Gadhi, T.; Hernandez, S.; Rivolo, P.; Ditaranto, N.;  
1263 Bonelli, B. Application of Reverse Micelle Sol–Gel Synthesis for Bulk Doping and Heteroatoms

- 1264 Surface Enrichment in Mo-Doped TiO<sub>2</sub> Nanoparticles. *Materials* **2019**, *12*, 937,  
1265 doi:10.3390/ma12060937.
- 1266 83. Mancuso, A.; Blangetti, N.; Sacco, O.; Freyria, F.S.; Bonelli, B.; Esposito, S.; Sannino, D.; Vaiano, V.  
1267 Photocatalytic Degradation of Crystal Violet Dye under Visible Light by Fe-Doped TiO<sub>2</sub> Prepared by  
1268 Reverse-Micelle Sol–Gel Method. *Nanomaterials* **2023**, *13*, 270, doi:10.3390/nano13020270.
- 1269 84. Esposito, S. Synthetic Strategies for (Supported) Metal and Metal Oxide Catalysts: Case Studies. In  
1270 *Sol-Gel Synthesis Strategies for Tailored Catalytic Materials*; 2023; pp. 53–71,  
1271 [https://doi.org/10.1007/978-3-031-20723-5\\_6](https://doi.org/10.1007/978-3-031-20723-5_6).
- 1272 85. Malik, M.A.; Wani, M.Y.; Hashim, M.A. Microemulsion Method: A Novel Route to Synthesize Organic  
1273 and Inorganic Nanomaterials. *Arabian Journal of Chemistry* **2012**, *5*, 397–417,  
1274 doi:10.1016/j.arabjc.2010.09.027.
- 1275 86. Water in and around Micelles, Reverse Micelles, and Microemulsions. In *Water in Biological and*  
1276 *Chemical Processes*; Cambridge University Press, 2013; pp. 261–276.
- 1277 87. Choudhury, B.; Chetri, P.; Choudhury, A. Oxygen Defects and Formation of Ce<sup>3+</sup> Affecting the  
1278 Photocatalytic Performance of CeO<sub>2</sub> Nanoparticles. *RSC Adv.* **2014**, *4*, 4663–4671,  
1279 doi:10.1039/C3RA44603D.
- 1280 88. Shih, S.-J.; Wu, Y.-Y.; Chen, C.-Y.; Yu, C.-Y. Morphology and Formation Mechanism of Ceria  
1281 Nanoparticles by Spray Pyrolysis. *Journal of Nanoparticle Research* **2012**, *14*, 879,  
1282 doi:10.1007/s11051-012-0879-4.
- 1283 89. Anghel, E.M.; Petrescu, S.; Mocioiu, O.C.; Cusu, J.P.; Atkinson, I. Influence of Ceria Addition on  
1284 Crystallization Behavior and Properties of Mesoporous Bioactive Glasses in the SiO<sub>2</sub>–CaO–P<sub>2</sub>O<sub>5</sub>–  
1285 CeO<sub>2</sub> System. *Gels* **2022**, *8*, 344, doi:10.3390/gels8060344.
- 1286 90. Woan, K.; Tsai, Y.-Y.; Sigmund, W. Synthesis and Characterization of Luminescent Cerium Oxide  
1287 Nanoparticles. *Nanomedicine* **2010**, *5*, 233–242, doi:10.2217/nnm.09.106.
- 1288 91. Schmitt, R.; Nenning, A.; Kraynis, O.; Korobko, R.; Frenkel, A.I.; Lubomirsky, I.; Haile, S.M.; Rupp,  
1289 J.L.M. A Review of Defect Structure and Chemistry in Ceria and Its Solid Solutions. *Chem Soc Rev*  
1290 **2020**, *49*, 554–592, doi:10.1039/C9CS00588A.
- 1291 92. Luo, S.; Li, M.; Fung, V.; Sumpter, B.G.; Liu, J.; Wu, Z.; Page, K. New Insights into the Bulk and Surface  
1292 Defect Structures of Ceria Nanocrystals from Neutron Scattering Study. *Chemistry of Materials* **2021**,  
1293 *33*, 3959–3970, doi:10.1021/acs.chemmater.1c00156.
- 1294 93. Bao, H.; Qian, K.; Fang, J.; Huang, W. Fe-Doped CeO<sub>2</sub> Solid Solutions: Substituting-Site Doping versus  
1295 Interstitial-Site Doping, Bulk Doping versus Surface Doping. *Appl Surf Sci* **2017**, *414*, 131–139,  
1296 doi:10.1016/j.apsusc.2017.04.018.
- 1297 94. Li, G.; Smith, R.L.; Inomata, H. Synthesis of Nanoscale Ce<sub>1-x</sub>Fe<sub>x</sub>O<sub>2</sub> Solid Solutions via a Low-  
1298 Temperature Approach. *J Am Chem Soc* **2001**, doi:10.1021/ja016502.
- 1299 95. Zhao, B.; Shao, Q.; Hao, L.; Zhang, L.; Liu, Z.; Zhang, B.; Ge, S.; Guo, Z. Yeast-Template Synthesized  
1300 Fe-Doped Cerium Oxide Hollow Microspheres for Visible Photodegradation of Acid Orange 7. *J*  
1301 *Colloid Interface Sci* **2018**, *511*, 39–47, doi:10.1016/j.jcis.2017.09.077.
- 1302 96. Bao, H.; Chen, X.; Fang, J.; Jiang, Z.; Huang, W. Structure-Activity Relation of Fe<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> Composite  
1303 Catalysts in CO Oxidation. *Catal Letters* **2008**, *125*, 160–167, doi:10.1007/s10562-008-9540-3.

- 1304 97. Liu, H.; Wu, Y.; Liu, L.; Chu, B.; Qin, Z.; Jin, G.; Tong, Z.; Dong, L.; Li, B. Three-Dimensionally Ordered  
1305 Macroporous Fe-Doped Ceria Catalyst with Enhanced Activity at a Wide Operating Temperature  
1306 Window for Selective Catalytic Reduction of NO<sub>x</sub>. *Appl Surf Sci* **2019**, *498*, 143780,  
1307 doi:10.1016/j.apsusc.2019.143780.
- 1308 98. Aragón, F.F.H.; Aquino, J.C.R.; Ramos, J.E.; Coaquira, J.A.H.; Gonzalez, I.; Macedo, W.A.A.; da Silva,  
1309 S.W.; Morais, P.C. Fe-Doping Effects on the Structural, Vibrational, Magnetic, and Electronic  
1310 Properties of Ceria Nanoparticles. *J Appl Phys* **2017**, *122*, doi:10.1063/1.4999457.
- 1311 99. Martínez-Arias, A.; Fernández-García, M.; Salamanca, L.N.; Valenzuela, R.X.; Conesa, J.C.; Soria, J.  
1312 Structural and Redox Properties of Ceria in Alumina-Supported Ceria Catalyst Supports. *J Phys Chem*  
1313 *B* **2000**, *104*, 4038–4046, doi:10.1021/jp992796y.
- 1314 100. SCHWIDDER, M.; KUMAR, M.; KLEMENTIEV, K.; POHL, M.; BRUCKNER, A.; GRUNERT, W. Selective  
1315 Reduction of NO with Fe-ZSM-5 Catalysts of Low Fe Content. I. Relations between Active Site  
1316 Structure and Catalytic Performance. *J Catal* **2005**, *231*, 314–330, doi:10.1016/j.jcat.2005.01.031.
- 1317 101. Shafia, E.; Esposito, S.; Manzoli, M.; Chiesa, M.; Tiberto, P.; Barrera, G.; Menard, G.; Allia, P.; Freyria,  
1318 F.S.; Garrone, E.; et al. Al/Fe Isomorphic Substitution versus Fe<sub>2</sub>O<sub>3</sub> Clusters Formation in Fe-Doped  
1319 Aluminosilicate Nanotubes (Imogolite). *Journal of Nanoparticle Research* **2015**, *17*, 336,  
1320 doi:10.1007/s11051-015-3130-2.
- 1321 102. Katta, L.; Thrimurthulu, G.; Reddy, B.M.; Muhler, M.; Grünert, W. Structural Characteristics and  
1322 Catalytic Performance of Alumina-Supported Nanosized Ceria–Lanthana Solid Solutions. *Catal Sci*  
1323 *Technol* **2011**, *1*, 1645, doi:10.1039/c1cy00312g.
- 1324 103. Makuła, P.; Pacia, M.; Macyk, W. How To Correctly Determine the Band Gap Energy of Modified  
1325 Semiconductor Photocatalysts Based on UV–Vis Spectra. *J Phys Chem Lett* **2018**, *9*, 6814–6817,  
1326 doi:10.1021/acs.jpcclett.8b02892.
- 1327 104. George, S.; Pokhrel, S.; Ji, Z.; Henderson, B.L.; Xia, T.; Li, L.; Zink, J.I.; Nel, A.E.; Mädler, L. Role of Fe  
1328 Doping in Tuning the Band Gap of TiO<sub>2</sub> for the Photo-Oxidation-Induced Cytotoxicity Paradigm. *J Am*  
1329 *Chem Soc* **2011**, *133*, 11270–11278, doi:10.1021/ja202836s.
- 1330 105. El-Hagary, M.; Shaaban, E.R.; Moustafa, S.H.; Gad, G.M.A. The Particle Size-Dependent Optical Band  
1331 Gap and Magnetic Properties of Fe-Doped CeO<sub>2</sub> Nanoparticles. *Solid State Sci* **2019**, *91*, 15–22,  
1332 doi:10.1016/j.solidstatesciences.2019.03.005.
- 1333 106. Dhannia, T.; Jayalekshmi, S.; Santhosh Kumar, M.C.; Prasada Rao, T.; Chandra Bose, A. Effect of Iron  
1334 Doping and Annealing on Structural and Optical Properties of Cerium Oxide Nanocrystals. *Journal of*  
1335 *Physics and Chemistry of Solids* **2010**, *71*, 1020–1025, doi:10.1016/j.jpcs.2010.04.011.
- 1336 107. Yang, H.; Jia, L.; Zhang, Z.; Xu, B.; Zhang, Q.; Yuan, S.; Xiao, Y.; Nan, Z.; Zhang, M.; Zhang, Y.; et al.  
1337 Enhanced Photocatalytic VOCs Degradation Performance on Fe-Doped Ceria under Visible Light.  
1338 *Appl Mater Today* **2022**, *29*, 101651, doi:10.1016/j.apmt.2022.101651.
- 1339 108. Spanier, J.E.; Robinson, R.D.; Zhang, F.; Chan, S.-W.; Herman, I.P. Size-Dependent Properties  
1340 of CeO<sub>2</sub>- $\gamma$  Nanoparticles as Studied by Raman Scattering. *Phys Rev B* **2001**, *64*, 245407,  
1341 doi:10.1103/PhysRevB.64.245407.
- 1342 109. Wu, Z.; Li, M.; Howe, J.; Meyer, H.M.; Overbury, S.H. Probing Defect Sites on CeO<sub>2</sub> Nanocrystals with  
1343 Well-Defined Surface Planes by Raman Spectroscopy and O<sub>2</sub> Adsorption. *Langmuir* **2010**, *26*, 16595–  
1344 16606, doi:10.1021/la101723w.

- 1345 110. Dohčević-Mitrović, Z.D.; Šćepanović, M.J.; Grujić-Brojčin, M.U.; Popović, Z.V.; Bošković, S.B.;  
1346 Matović, B.M.; Zinkevich, M.V.; Aldinger, F. The Size and Strain Effects on the Raman Spectra of  
1347 Ce<sub>1-x</sub>Nd<sub>x</sub>O<sub>2-δ</sub> (0 ≤ x ≤ 0.25) Nanopowders. *Solid State Commun* **2006**, *137*, 387–390,  
1348 doi:10.1016/j.ssc.2005.12.006.
- 1349 111. Popović, Z. V.; Dohčević-Mitrović, Z.D.; Paunović, N.; Radović, M. Evidence of Charge Delocalization  
1350 in Ce<sub>1-x</sub>Fe<sub>x</sub>O<sub>2</sub> + (3+) O<sub>2-y</sub> Nanocrystals (x = 0, 0.06, 0.12). *Phys Rev B* **2012**, *85*, 014302,  
1351 doi:10.1103/PhysRevB.85.014302.
- 1352 112. Nakajima, A.; Yoshihara, A.; Ishigame, M. Defect-Induced Raman Spectra in Doped  $\text{CeO}_2$   
1353  $\text{CeO}_2$ . *Phys Rev B* **1994**, *50*, 13297–13307,  
1354 doi:10.1103/PhysRevB.50.13297.  
1355
- 1356 113. Gallucci, N.; Hmoudah, M.; Martinez, E.; El-Qanni, A.; Di Serio, M.; Paduano, L.; Vitiello, G.; Russo, V.  
1357 Photodegradation of Ibuprofen Using CeO<sub>2</sub> Nanostructured Materials: Reaction Kinetics, Modeling,  
1358 and Thermodynamics. *J Environ Chem Eng* **2022**, *10*, 107866, doi:10.1016/j.jece.2022.107866.
- 1359 114. Paparazzo, E. Use and Mis-Use of x-Ray Photoemission Spectroscopy Ce3d Spectra of Ce<sub>2</sub>O<sub>3</sub> and  
1360 CeO<sub>2</sub>. *Journal of Physics: Condensed Matter* **2018**, *30*, 343003, doi:10.1088/1361-648X/aad248.
- 1361 115. Romeo, M.; Bak, K.; El Fallah, J.; Le Normand, F.; Hilaire, L. XPS Study of the Reduction of Cerium  
1362 Dioxide. *Surface and Interface Analysis* **1993**, *20*, 508–512, doi:10.1002/sia.740200604.
- 1363 116. Idriss, H. On the Wrong Assignment of the XPS O1s Signal at 531–532 EV Attributed to Oxygen  
1364 Vacancies in Photo- and Electro-Catalysts for Water Splitting and Other Materials Applications. *Surf*  
1365 *Sci* **2021**, *712*, 121894, doi:10.1016/j.susc.2021.121894.
- 1366 117. Cardenas, L.; Molinet-Chinaglia, C.; Loridant, S. Unraveling Ce<sup>3+</sup> Detection at the Surface of Ceria  
1367 Nanopowders by UPS Analysis. *Physical Chemistry Chemical Physics* **2022**, *24*, 22815–22822,  
1368 doi:10.1039/D2CP02736D.
- 1369 118. Liu, T.; Guo, L.; Tao, Y.; Hu, T.D.; Xie, Y.N.; Zhang, J. Bondlength Alternation of Nanoparticles Fe<sub>2</sub>O<sub>3</sub>  
1370 Coated with Organic Surfactants Probed by EXAFS. *Nanostructured Materials* **1999**, *11*, 1329–1334,  
1371 doi:10.1016/S0965-9773(99)00425-0.
- 1372 119. Turco, R.; Bonelli, B.; Armandi, M.; Spiridigliozzi, L.; Dell’Agli, G.; Deorsola, F.A.; Esposito, S.; Di Serio,  
1373 M. Active and Stable Ceria-Zirconia Supported Molybdenum Oxide Catalysts for Cyclooctene  
1374 Epoxidation: Effect of the Preparation Procedure. *Catal Today* **2020**, *345*, 201–212,  
1375 doi:10.1016/j.cattod.2019.10.036.
- 1376 120. Wang, Y.; Wang, F.; Song, Q.; Xin, Q.; Xu, S.; Xu, J. Heterogeneous Ceria Catalyst with Water-Tolerant  
1377 Lewis Acidic Sites for One-Pot Synthesis of 1,3-Diols via Prins Condensation and Hydrolysis  
1378 Reactions. *J Am Chem Soc* **2013**, *135*, 1506–1515, doi:10.1021/ja310498c.
- 1379 121. Rebellato, J.; Natile, M.M.; Glisenti, A. Influence of the Synthesis Procedure on the Properties and  
1380 Reactivity of Nanostructured Ceria Powders. *Appl Catal A Gen* **2008**, *339*, 108–120,  
1381 doi:10.1016/j.apcata.2007.12.031.
- 1382 122. Badri, A.; Binet, C.; Lavalley, J.-C. An FTIR Study of Surface Ceria Hydroxy Groups during a Redox  
1383 Process with H<sub>2</sub>. *Journal of the Chemical Society, Faraday Transactions* **1996**, *92*, 4669,  
1384 doi:10.1039/ft9969204669.

- 1385 123. Natile, M.M.; Boccaletti, G.; Glisenti, A. Properties and Reactivity of Nanostructured CeO<sub>2</sub>  
1386 Powders: Comparison among Two Synthesis Procedures. *Chemistry of Materials* **2005**, *17*, 6272–  
1387 6286, doi:10.1021/cm051352d.
- 1388 124. Matussin, S.N.; Khan, F.; Harunsani, M.H.; Kim, Y.-M.; Khan, M.M. Visible-Light-Induced  
1389 Photocatalytic and Photoantibacterial Activities of Co-Doped CeO<sub>2</sub>. *ACS Omega* **2023**, *8*, 11868–  
1390 11879, doi:10.1021/acsomega.2c07058.
- 1391 125. Xu, B.; Yang, H.; Zhang, Q.; Yuan, S.; Xie, A.; Zhang, M.; Ohno, T. Design and Synthesis of Sm, Y, La  
1392 and Nd-doped CeO<sub>2</sub> with a Broom-like Hierarchical Structure: A Photocatalyst with Enhanced  
1393 Oxidation Performance. *ChemCatChem* **2020**, *12*, 2638–2646, doi:10.1002/cctc.201902309.
- 1394 126. Zdanowicz, T.; Rodziewicz, T.; Zabkowska-Waclawek, M. Theoretical Analysis of the Optimum Energy  
1395 Band Gap of Semiconductors for Fabrication of Solar Cells for Applications in Higher Latitudes  
1396 Locations. *Solar Energy Materials and Solar Cells* **2005**, *87*, 757–769,  
1397 doi:10.1016/j.solmat.2004.07.049.
- 1398 127. Rao, Y.; Xue, D.; Pan, H.; Feng, J.; Li, Y. Degradation of Ibuprofen by a Synergistic UV/Fe(III)/Oxone  
1399 Process. *Chemical Engineering Journal* **2016**, *283*, 65–75, doi:10.1016/j.cej.2015.07.057.

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## 1402 Highlights

- 1403 • Reverse micelle synthesis fosters Fe doping of nanocrystalline CeO<sub>2</sub>  
1404 • 2.5 mol % iron-doped ceria leads to high charge delocalization  
1405 • Efficient visible-light photodegradation of ibuprofen with 2.5 mol % Fe-CeO<sub>2</sub>  
1406 • Substitutional Fe favours the oxygen vacancies formation and ibuprofen adsorption.  
1407 • The by-product of the ibuprofen degradation is 1-ethenyl-4-(2-methylpropyl)benzene.

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