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Reverse micelle strategy for effective substitutional Fe-doping in small-1 assessment CeO₂ nanocrystals: of adsorption sized and 2 photodegradation efficiency of ibuprofen under visible light 3

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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 CeO₂ catalysts with

- an iron content (0.50-10 mol %) compliant with the nominal value were prepared and tested for the
- first time for the removal of ibuprofen both in the dark and under UV or visible light irradiation.

The effective inclusion and distribution of iron in the ceria lattice were ascertained through in-depth 32 physicochemical characterization. In particular, X-ray diffraction suggested the formation of an F-33 type crystal structure, ruling out the formation of separate iron-containing crystalline phases. On the 34 other hand, substitutional doping of CeO₂ with Fe atoms favoured the formation of Ce³⁺ defects and 35 vacancy sites (VOs) with a maximum for the sample with 2.5 mol % iron (Fe2.5), as evidenced by 36 X-ray photoelectron spectroscopy (XPS) measurements and Raman spectroscopy. UV-Vis 37 spectroscopy showed that the optical properties were successfully modified by the presence of iron, 38 39 which causes a gradual decrease in band gap as iron content increases. The experimental evidence was further verified and supported by density functional theory calculations. DFT calculations also 40 revealed that the surface iron and oxygen vacancies are the preferential sites for ibuprofen adsorption. 41 Nevertheless, it was found under dark conditions that adsorption capacity does not monotonically 42 increase with iron content, revealing contrasting roles of surface characteristics. Indeed, catalytic 43 experiments have identified a trade-off between adsorption and photodegradation, identifying Fe2.5 44 as the best-performing catalyst for ibuprofen removal under visible light irradiation. These results 45 were discussed by considering the key properties of the catalysts as well as their different surface 46 charge determined by ζ potential measurements. The best catalyst was tested through reuse 47 experiments that proved its stability over 4 cycles. Finally, an attempt was made to identify the 48 photodegradation by-products, allowing the detection of 1-ethenyl-4-(2-methylpropyl)benzene as the 49 main by-product. 50

- 51
- 52 **Keywords:** Substitutional Fe doped CeO₂, Reverse micelle, Ibuprofen, Photodegradation, DFT.
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- 54
- 55

56 **1. Introduction**

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

67

Compound	IUPAC name	Molecular formula	Molecular weight	Solubility in water	Structure
IBU	2-[4-(2-methyl propyl) phenyl]propanoic acid	C ₁₃ H ₁₈ O ₂	206.28 g/mol	21 mg/L (at 25 °C)	CH3 CH3 OH

68 Table 1 - Structure and properties of ibuprofen

69

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

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

Cerium oxide was selected for its many trade-offs between reactivity, photochemical stability, costeffectiveness, and the environmentally friendly nature of CeO_2 nanoparticles (CeO_2 -NPs) [18–21].

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

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

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

In this scenario, it should be noted that many methods reported in the literature suffer from poor 100 reproducibility and control of process parameters, often failing to achieve real doping or, on the other 101 hand, requiring harsh operating conditions [31–36]. The hydrothermal method was exploited by Cai 102 103 et al. [32] for preparing Fe-doped ceria materials with different doping amounts. They obtained a catalyst with a crystallite size of approximately 100 Å and observed that the low Fe³⁺ doping could 104 effectively improve the concentration of Ce^{3+} , enhancing the degradation ability of the model dye 105 Acid Orange 7 (AO7). However, despite the versatility of the hydrothermal approach, it still 106 represents a "black box" method as is impossible to have strict control over the process. Channei et 107 al. [36] used flame pyrolysis to produce photocatalysts based on Fe-doped CeO₂ nanoparticles for the 108 conversion of both formic acid and oxalic acid. This method, such as the aforementioned 109 hydrothermal method, does not easily allow the control and variation of synthesis parameters 110 invalidating the simplicity of the experimental setup [37]. 111

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

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

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

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

To assess the physicochemical properties and to understand the structure/composition-activity relationship of Fe-doped CeO₂ in the photodegradation of ibuprofen, an in-depth characterisation was conducted. In detail, the prepared catalysts were characterised using various analytical techniques such as inductively coupled plasma mass spectrometry (ICP-MS), Thermogravimetric analysis (TGA), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), Field

- emission scanning electron microscopy (FESEM), Diffuse reflectance spectroscopy (DR/UV-Vis),
- 137 Raman spectroscopy, N₂ adsorption/desorption at -196 °C, X-ray photoelectron spectroscopy (XPS) 138 and ζ -potential measurements.

Density Functional Theory (DFT) calculations were performed in order to investigate the stability and the effects on the electronic and structural properties of the CeO₂(111) in the presence of substitutional and interstitial Fe atoms. The calculations suggest that, in a wide range of temperatures and pressure, the thermodynamically most stable structures are the ones where Fe atoms substitute Ce sites in the presence or absence of oxygen vacancies in agreement with the experimental observations. Additional calculations were performed to investigate the interaction between undoped and Fe-doped ceria surfaces with ibuprofen in order to identify preferential sites for adsorption.

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

152

153 **2. Materials and methods**

154 Cyclohexane (ACS reagent \geq 99.5%), cerium nitrate hexahydrate, iron chloride (reagent grade 97%), 155 ammonia (ACS reagent 28-30%), 1-butanol (ACS reagent \geq 99.4%), polyoxyethylene (10) cetyl ether 156 (Brij C10) and ethanol (puriss \geq 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- α -methylphenylacetic acid, 99% (manufactured by Alfa Aesar).

159

160 2.1 Precipitation by reverse micelles

In a typical synthesis, adapted from the literature [46,47], the oil/surfactant phase is prepared by 161 dissolving 8.2 g of surfactant (Brij C10) in 100 mL of cyclohexane under stirring at room temperature. 162 An aqueous solution is prepared by dissolving the proper amount of cerium and iron precursors in 163 distillate water to achieve a final concentration of 0.5M. The volume of the aqueous precursor solution 164 has been selected to obtain a w_0 value of 25 (w_0 is defined as the water-surfactant molar ratio). The 165 aqueous solution is slowly added dropwise to the oil phase to obtain appropriate water-in-oil (w/o) 166 micelles. To preserve the optical transparency of the emulsion, avoiding the formation of flocculates, 167 4 mL of co-surfactant (1-butanol) are also added. The optimised protocol involves alternating the 168 additions of water and the co-surfactant. Finally, 5.4 mL of precipitating agent, ammonia solution, 169 are slowly dripped. The mixture is stirred for 1.5h at room temperature. The solid phase is then 170 collected by centrifugation, washed twice with ethanol and dried under a hood for 2 days. The dried 171 172 powder has been manually ground before being calcinated at 120 °C for 6 h. The amounts of cerium and iron were calculated to obtain a nominal composition expressed as a molar % of iron equal to 0 173 mol % (CeO₂), 0.5 mol % (Fe0.5), 2.5 mol % (Fe2.5), 5 mol% (Fe5) and 10 mol % (Fe10). Samples 174 Fe2.5 after its use as a catalyst for the ibuprofen degradation under visible light was labelled 175 Fe2.5_post reaction. 176

- 178 2.2 Structural, morphological and surface characterization
- Thermogravimetric analysis was performed on Mettler-Toledo TGA/SDTA 851e instrument. The 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 α radiation (2 θ range = 5° - 90°; step = 0.02° 2 θ ; 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, λ is the X-ray wavelength equal to 190 0.154 nm, β is the full width at half maximum, and θ 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 $(F(R)h\nu)^{1/2} = f(h\nu)$.

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

Transmission Electron Microscopy characterization was carried out with a Thalos F200X instrument 200 (ThermoFisher) and Energy Dispersive X-ray spectroscopy (EDX) spectra were acquired with four 201 Silicon drift detectors (SDD). The catalysts as dry powders were dispersed in isopropyl alcohol and 202 subsequently drop-casted onto Cu holey carbon grids. Before insertion in the TEM column, the 203 samples were plasma-cleaned in Ar atmosphere. Thermo Scientific Velox software was used for the 204 analysis of TEM and EDX data. The crystallographic model for cubic CeO₂ (Fm-3m space group) is 205 provided in the Crystallography Open Database (COD ID: 4343161). To complete the morphological 206 characterization a field emission scanning electron microscopy (FE-SEM) was used (ZEISS 207 MERLIN instrument (Oberkochen, Germany)). 208

Textural properties have been evaluated through N_2 physisorption and desorption at 77K (Quantachrome Autosorb1 Instruments.). Before the measurement, the sample was outgassed under a high vacuum at 120°C for 3 hours to remove pollutants previously adsorbed. From the isotherm obtained by nitrogen adsorption, the specific surface area (SSA) of the samples was calculated according to the BET (Brunauer–Emmet–Teller), total pore volume, Vp, was determined from the amount of adsorbed N₂ at p/p°=0.98. BJH pore size distribution was determined by the desorption 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 α 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 α at 529 eV, while

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

223 ζ -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 1mg/50mL, and subsequently, 0.1 M NaOH or 0.1 M HCl were added 226 to varying the pH. The ζ -potential measurements were carried out in an Omega cuvette (Anton Paar) 227 accessory. The measurements were performed in triplicate.

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

235

236 2.3 Computational Details

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

All the calculations were performed on the (111) termination of CeO₂ (Fig. SI.1), being the most stable one and the most present in the experiment (see Fig. 1a). We are aware that this represent a simplification of the system prepared from experiments but from a computational point of view is not possible to capture the complexity of the real system. The Ibuprofen (IBU) molecule is anionic in experimental pH-neutral conditions [66], therefore it was simulated in its deprotonated form when adsorbed on the CeO₂(111) surface. The proton released by the molecule is transferred to O3c (tricoordinated O) atoms of the surface similarly to previous theoretical studies [67–70].

256 The CeO₂ (111) surface was modelled using a (5x4) slab supercell with three O-Ce-O trilayers (180) atoms) and separated by more than 20 Å of vacuum in the direction perpendicular to the surface. 257 During the optimizations, the bottom tri-layer of the slab was fixed to simulate the equilibrium bulk-258 259 like position, while the upper two tri-layers and the organic ligand were fully relaxed. The O-defective systems were modeled by removing O3c and O4c atoms from the surface and subsurface layers of 260 the CeO₂ (111) slab (VO_x). The formation energies of the oxygen vacancies were computed as 261 $E_{FORM(VO_x)} = E_{VO_x} - E_{CeO_2} + \frac{1}{2}E_{O_2}$, where E_{CeO_2} is the energy of the stoichiometric surface, while 262 E_{VO_r} and E_{O_2} are the energies of the surface with oxygen vacancies and of the gas phase O_2 molecule, 263 respectively. 264

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

The substitutional and interstitial Fe-doping effects were evaluated by replacing and adding Ce atomsin all considered systems.

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

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

where A is the surface area, E_{tot} and E_{CeO2} are the total energies of the considered ceria system and 277 stoichiometric ceria surface, respectively. The quantities N_0 and N_{Ce} represent the number of O and Ce vacancies present in the structure under consideration, whereas $E_{CeO_2}^{bulk}$ is the energy of a formula 278 279 unit of the CeO₂ bulk phase. Finally, μ_{Fe} and μ_{o} are the oxygen and iron chemical potentials. The 280 chemical potential of Fe, μ_{Fe} , is set to be the total energy per atom of the bulk Fe crystal, whereas the 281 upper bound of the chemical potential of O₂, $\mu_0(T, p)$, is given by the total energy of molecular 282 oxygen, $\frac{1}{2}E_{O2}$. This upper bound is taken as the zero of our energy scale by using $\Delta \mu_O(T, p) = \mu_0 - \frac{1}{2}$ 283 E_{02} . In addition, assuming that volume and entropy contributions are negligible in $\Delta G_{ads}(T, p)$ [73], 284 285 the Gibbs energies are approximated by the total energies of our DFT calculations.

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

290

291 2.4 Catalytic and kinetic tests

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

of the lamp in the experimental apparatus was estimated to be 510 W/m². One neck of the lid was left free for collecting samples during the reaction, while the last neck is used for measuring the solution temperature through a dedicated thermocouple. The reaction temperature was controlled using an ultra-thermostat while the dispersion agitation was ensured by magnetic stirring. The airflow rate was set through an electronic gas flowmeter regulator (supplied by Bronkhorst). Air dispersion was enhanced by connecting the outlet of the gas flowmeter regulator to a sintered filter of 50 mesh,

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

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

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

Before any subsequent operation, a first sample was collected to check the initial ibuprofen concentration ($C_{IBU,0}$); subsequently, samples were collected every 30 minutes for the first 2 hours of reaction, and every hour for the remaining three hours (0, 30, 60, 90, 120, 180, 240 and 300 minutes).

Each sample was then centrifuged at 3300 rpm for 30 minutes, and the resulting liquid sample was

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).

333 2.4.1 Regeneration experiments

The stability of the most active catalyst was tested via reuse experiments, adopting the following reaction conditions: T=30°C, $C_{IBU,0}=12.4$ mg/L, $\rho_B=0.07$ g/L, visible light, Fe2.5 catalyst. In particular, the catalyst was recovered after each photodegradation test, by filtering it on a Buchner funnel. Before reusing it, the catalyst was washed several times on the funnel itself using water, and then was recovered by filtration and oven-dried for 12 h at 60 °C. The procedure was repeated for four cycles [79].

340

341 2.4.2 Photodegradation products identification

A dedicated kinetic experiment was performed to identify the reaction products. The experiment was performed using the Fe2.5 catalyst under visible irradiation, adopting an initial concentration of ibuprofen of 12.4 mg/L, a catalyst loading of 0.07 g/L, a stirring rate of 750 rpm, and a temperature of 30 °C.

LC-MS analysis was performed by an Agilent HPLC system (1260 Series) coupled to an Agilent 346 6230 TOF mass spectrometer apparatus. The HPLC separation was carried out on a reverse-phase 347 C18 column (Poroshell 120 EC-C18 3x50 mm 2.7 um from Agilent Life Sciences) by using water 348 and acetonitrile as mobile phases A and B, respectively, both acidified with 0.1% formic acid. A 349 linear gradient was employed by increasing mobile phase B from 50% to 95% over 9 min at a flow 350 rate of 0.3 mL min⁻¹. The injection volume of each sample was 20 µL and the MS source was an 351 electrosprav ionization (ESI) interface in the positive ion mode with a capillary voltage of 3000 V, 352 gas temperature at 325 °C, dry gas (N₂) flow at 5 L min⁻¹ and the nebulizer pressure at 35 psi, the 353 fragment at 50 V. The MS spectra were acquired in a mass range of 50-1000 m/z with a rate of 354 1 spectrum/s, abundance threshold 200 (0.015 relative thresholds). 355

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

- 364
- 365

366 3. Results and discussion

367

368 3.1 *About the adopted reverse micelle approach*

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

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

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

The synthesis parameters, in particular the type and nature of the surfactant and the water/surfactant 379 ratio, were optimized after careful variation. The value w, defined as the water-surfactant molar ratio 380 ([H₂O/BrijC10]), is considered a key parameter for tuning the size of the spherical droplet, affecting 381 the dynamics of water and defining the spatial confinement of the reaction [85,86]. The occurrence 382 of chemical reactions was clearly visible through the colour change of the macrosystem, which moved 383 from a colourless/pale yellow to purple-dense, turning yellow after the fixed reaction time (estimated 384 at one and a half hours). The formation of the purple slurry was attributed to the generation of 385 insoluble Ce^{3+} species that after the complete oxidation turned to yellow Ce^{4+} species [46,87]. The 386 obtained material was recovered by centrifugation, washed to purify from the oil/surfactant, and left 387 catalysts to dry under the hood. Then, the dried powders were heat treated at 120 °C for 6h. The 388 absence of significant quantities of organic residues, confirming the effectiveness of the protocol 389 without the need to use high calcination temperatures, was revealed by the thermogravimetric analysis 390 (Fig. SI.3). The thermal behaviour of the material was explained by identifying three regions in the 391 thermogravimetric curve: (i) from room temperature to 120 °C where the weight loss is due to 392 physisorbed water, (ii) 200-350 °C related to the removal of chemisorbed water occurs, (iii) 400-800 393 394 °C characteristic of combustion of organic compounds [88–90]. The synthesis procedure was designed to ensure the highest reproducibility. The effective presence of iron species into the ceria 395 phase was highlighted by the different colour of the powders, changing from light yellow for pure 396 ceria to a reddish-yellow with increasing in the Fe contents (Fig. SI.4). 397

The results of the quantitative analysis performed by ICP-MS are shown in Table 2. The Fe/Ce ratio is in excellent agreement with the nominal value, showing that the adopted synthesis protocol 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 OCe4 units 405 [91]. Defect chemistry and the numerous studies conducted on doped and undoped nanometric CeO₂ 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].

XRD diffraction patterns of ceria and Fe-containing ceria samples are reported in Fig. 1a. The 409 pristine ceria shows an XRD profile corresponding to a cubic fluorite structure (JCPDS files 34-410 0394), where the peak at 28.5° , 33.3° , 47.1° and 56.1° can be associated with the planes 111, 200, 411 220, and 311, respectively [46]. Although the diffraction patterns of Fe-containing samples reveal 412 that the F-type crystalline structure is retained, the diffraction lines show a progressive shift towards 413 higher 2-teta values, Fig. 1b [46]. As reported by many authors, an isomorphic substitution of Ce⁴⁺ 414 ions (ionic radius 0.97 Å, coordination number CN=8) by smaller Fe³⁺ ions (ionic radius 0.78Å, 415 CN=8) can account for the lattice shrinkage, appearing as a displacement of the diffraction patterns 416 towards higher angles [25,93]. The observed lattice constraint follows Vegard's law [94] as suggested 417 by the lattice parameters reported in Table 2 and further evidenced by Fig. SI.5. Substitutional doping 418 with the formation of oxygen vacancies, one oxygen vacancy paired with two M³⁺ for charge 419

420 neutrality, is a dominant mechanism for ceria doped with aliovalent cations [93,95]. Nevertheless, 421 the small size of Fe^{3+} also allows for a dopant interstitial compensation mechanism where three 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 CeO₂ 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]

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430

431

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

434

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

	Nominal ratio	Actual ratio	D			
	T /0	Fe/Ce	Lattice Parameter	Cell Volume	Crystallite size, L	
Sample	Fe/Ce	ICP-MS	(Å) ^a	(Å ³)	(Å) ^b	
	(morar 70)	(molar %)				
CeO ₂	-	-	5.4269±3*10 ⁻⁴	159.83±2*10	² 42	

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Fe0.5	0.5	0.66	$5.4259 \pm 3 * 10^{-4}$ $159.74 \pm 2 * 10^{-2}$	44			
Fe2.5	2.58	2.87	$5.4234\pm3*10^{-4}$ 159.52± 2*10 ⁻²	40			
Fe5	5.31	4.3	$5.4162 \pm 3 * 10^{-4}$ $158.89 \pm 2 * 10^{-2}$	40			
Fe10	11.2	11.1	$5.4030 \pm 3 * 10^{-4}$ $157.72 \pm 2 * 10^{-2}$	34			

437 ^a for fluorite phase; ^b Calculated using Scherrer equation due to (1 1 1) plane

438

Further insight into the morphology and structure of the iron-doped ceria catalysts is provided by 439 Transmission and Scanning Electron Microscopy (Fig. 2 and Fig.SI.6, respectively). Based on TEM 440 images (Fig. 2a), the catalyst powders are constituted of aggregates of approximately spherical 441 nanoparticles. Inspection of high-resolution images reveals that the nanoparticles are single 442 443 crystalline, with a crystalline structure corresponding to cubic CeO₂ (Fm-3m space group). It is worth pointing out that the characteristic size of the nanoparticles is in the order of 5 nm or lower, in 444 accordance with the crystallite size estimation based on the application of the Scherrer formula on 445 446 XRD data.



448 Fig. 2: a) TEM high-resolution images of the different Fe-doped CeO₂ 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).

451

Moreover, from high-resolution images, there is no evidence of secondary iron-containing crystalline 452 phases. This is confirmed by rotationally-averaged selected area electron diffraction (SAED) patterns, 453 such as the ones provided in Fig. 2b. For each Fe-containing catalyst sample, the diffraction patterns 454 only show peaks corresponding to the (111), (200), (220), and (311) family of crystallographic planes 455 of cubic CeO₂, in agreement with the previously discussed XRD results. Finally, EDX spectra of the 456 catalysts (Fig. 2c) indicate the presence of Fe in all the samples besides pristine CeO₂. It is interesting 457 to notice that the contribution from the Fe K α line (~ 6.4 keV) in EDX spectra correlates with the 458 nominal increase of Fe in the catalysts, confirming that the crystalline nanoparticles host an increasing 459 460 amount of Fe ions, without significant changes in the F-type crystalline structure of CeO₂. The SEM micrographs (Fig.SI.6) show a quasi-spherical shape of nanoparticles with a uniform distribution, in 461 agreement with the morphologies obtained from TEM data. To further confirm the presence of Fe in 462 all samples a compositional analysis has been done also by EDS. The atomic ratio Fe/Ce obtained 463 464 (average in 5 spots) is in good accordance with the theoretical molar ratio and experimental ICP data (see Table SI.1 for details). The optical properties of the prepared materials were evaluated by UV-465 Vis diffuse reflectance spectroscopy. The D(R) spectra are shown in Fig. 3a. The UV-Vis spectrum 466 of pure CeO₂, black line, consisted of a strong absorption band located in the 200-400 nm range where 467 different transitions can be observed. The absorption at low wavelength, one centered at 215 nm and 468 the other at around 275 nm (blue rectangle and green rectangle in Fig. 3a, respectively), are generally 469 470 attributed to charge-transfer transitions between O 2p and Ce 4f orbital. In particular, the absorption due to $Ce^{3+} \leftarrow O^{2-}$ charge transfer is observed at 215 nm while the peak at a higher wavelength is 471 ascribed to $Ce^{4+} \leftarrow O^{2-}$ transition [97,99]. The shoulder at 340 nm is assigned to interband transitions 472 [46]. The reported behaviour is also observed in the spectra of iron-containing samples; however, a 473 474 careful examination reveals some modifications.

The shift to the lower wave number of the main peak recorded for the Fe0.5 sample could be caused 475 by the isolated Fe³⁺ species [100,101]. Indeed, Fe Oh and Td species show the typical transitions in 476 the UV range, allowing a not easy assignment due to overlapping absorption range with ceria. The 477 absorption at 215 nm appears more prominent when increasing the iron doping percentage up to 478 Fe2.5, thus suggesting a more pronounced presence of defective sites [102]. The spectrum recorded 479 for the Fe10 sample (purple curve) shows a feature at about 380 nm that is generally assigned to the 480 presence of oligomeric hematite-like clusters, as reported by Schwidder et al [42]. However, the 481 typical d-d transitions of α -Fe₂O₃, located at 533 nm, are not observed. The lack of stoichiometric iron 482 phase is in accordance with the XRD results, whereas the oligomeric clusters are in accordance with 483 the Raman results, which evidence a contribution at (~ 670 cm⁻¹) only into the sample at higher iron 484 loading (vide infra). The spectra of all the iron-doped catalysts show a red shift in the absorption 485 486 edge, indicative of the Ce-Fe interaction.

The effect of iron doping on the optical band gap was assessed by Tauc plot relation. In Fig. 3b (F(R)(hv)^1/2) is plotted versus the photon energy, hv, and the indirect band gap energy (Eg) was obtained by applying the double tan approximation [103]. The band gap value of pristine CeO₂ was found to be 3.0 eV. The effective inclusion of the Fe species in the ceria lattice results in a decrease in Eg, ascribable to the introduction of vacant 3d orbitals between the valence and conduction bands of CeO₂ [104].

Table 3 shows that Eg values decrease monotonically with iron content [36,60]. This trend is also observed in the theoretical Eg values calculated for the undoped and Fe-doped CeO₂ discussed in the following DFT study section. The band gap values obtained in the iron-doped samples reported here are somewhat lower than those reported in the literature for the same compositions [36,60,105–107]. Once again, all the previous features can be attributed to the adopted reverse micelle strategies.



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499

Fig. 3: a) DR UV-Vis spectra of synthetized samples plotted as Kubelka- Munk function F(R). b)
 The indirect band gap calculation of pristine and Fe-doped porous CeO₂ based on the Kubelka Munk function by Tauc plot relation using the double tan approximation. CeO₂ (black curve); Fe0.5 (red curve), Fe2.5 (orange curve), Fe5 (green curve) and Fe10 (purple curve).

504

Significant information on the fate of iron in ceria nanocrystals can be obtained from Raman. The 505 spectra corresponding to the iron-doped samples are shown in Fig. 4a along with that of pure CeO₂ 506 nanocrystals. Three main contributions are observed. The prominent peak corresponds to the F_{2g} peak 507 and it results from the vibration of the O sublattice. It stands at 458.5 cm⁻¹ for the pure CeO₂ 508 nanocrystals, some 6.5 cm⁻¹ lower than the position of pristine bulk CeO₂. This shift is consistent with 509 the reported decrease of peak position with particle size reduction [91] and a Gruneisen parameter 510 value of 1.57. For instance, Spanier et al. [108] reported a 4 cm⁻¹ redshift for 6 nm nanocrystals. The 511 peak shows an asymmetry towards low wavenumbers. Such an asymmetry is often seen in nanocrystal 512 samples and related to size dispersion [91,109,110]. 513

As iron is incorporated into the nanocrystals, the F_{2g} peak mode is further softened and broadened. 514 Such behaviour was previously observed by Popovic et al. [111] for Fe-doped CeO₂ nanocrystals. 515 The trend is not strictly monotonous with the nominal Fe concentration. Fig. 4b shows the correlation 516 between the F_{2g} peak shift ($\Delta \omega$) and the corresponding variation of the peak FWHM (full-width-at-517 half-maximum). The variation is linear as previously observed by Popovic et al. However, the slope 518 of our curve is -6.9, slightly higher than that reported in [111], with a value of -5.3. This behaviour 519 originates from two causes: grain size and strain effect (causing homogeneous line broadening) and 520 charges delocalization in oxygen-deficient ceria. Since all the samples have about the same 521 522 nanocrystal mean size, neither the mode softening nor the line broadening can be attributed to any size effect. The observed linear variation thus results from changes in strain within the nanocrystals 523 and charge delocalization. The two phenomena are hard to disentangle without further modelling. 524

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

Two supplementary peaks are noticed at 270 cm⁻¹ and 606 cm⁻¹ respectively. They are assigned to 532 the F_{1TO} and F_{1LO} phonon modes. These vibrations are forbidden in pristine CeO₂ but are often seen 533 in nanocrystal samples as a result of the long-range symmetry breaking of the crystals. The magnitude 534 of the F_{1LO} peak increases with Fe content as evidenced in Fig. SI.7 where the change in the ratio 535 between the F1LO contribution and the F2g contribution is plotted versus the sample composition. 536 The F_{1LO} feature can be assigned to defects involving dopant cation complexes close to VO [112]. It 537 can be clearly observed that moving from sample Fe0.5 to sample Fe2.5 the ratio is almost doubled. 538 indicating the increased presence of the aforementioned VO-related complexes. 539

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

544



546

Fig. 4: a) Raman spectra of pristine and Fe-doped CeO₂ nanocrystals for different doping 547 concentrations. All spectra are normalized to the maximum intensity of the F_{2g} peak. b) Variation of 548 the F_{2g} peak FWHM concerning its position variation as a function of the Fe concentration in CeO₂ 549 nanocrystals. $\Delta \omega$ is referred to the value of pristine CeO₂. 550

551

The textural properties were evaluated by N₂ adsorption at low temperatures (-196 °C). The 552 adsorption/desorption isotherms, Fig. SI.8a, resemble type IV, typical of mesoporous material with a 553 hysteresis loop indicating block-neck pores shape (hysteresis type H2). All the studied samples have 554

a BET-specific surface area higher than or equal to 180 m² g⁻¹ Table 3, with the exception of the 555 sample Fe10 that shows a surface area of 274 m² g⁻¹. Considering that the surface area is interparticle, 556 the discordant value of Fe10 can be explained by the smaller particle size, Table 2. The limited 557 particle growth observed at high iron contents may be correlated with the presence of iron-containing 558 species on the surface [46,93]. The pore size distribution (PSD) evaluated by the BJH method on 559 560 desorption branches, Fig.SI.8b, suggests that the synthetic route is effective for the preparation of mesoporous (doped) ceria. 561

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

565

567			Eg	BET SSA	Vp		
568		Sample	(eV)	$(m^2 g^{-1})$	(cm ³ g ⁻¹)		
569					X		
570		CeO ₂	3.00	182	0.196		
571		Fe0.5	2.91	180	0.184		
572		Fe2.5	2.79	191	0.188		
573							
574		Fe5	2.77	189	0.192		
575 576 577	In order to have a better surface a XPS analysis was spectrum although highly	Fe10	2.68	274	0.280	comprehension of materi conducted. Ce3d X	als PS be
511	speedan, annough many					complex, cull	00

Table 3: Energy of band gap (Eg) and textural properties of pristine and Fe-doped CeO₂ sample 566

deconvolved with some precautions [114,115]. Here Ce3d XPS spectra, shown in Fig. 5a, were 578 579 solved with five 3d_{5/2} components denoted as v₀ (880.6 eV), v (882.6 eV), v'(885.45 eV), v''(888.85 eV) and v'''(898.4 eV) with ± -0.3 eV resolution and their $3d_{3/2}$ counterparts (called u_x) separated by 580 18.45 eV (+/-0.15 eV) with a ratio u_x/v_x of 1.5(+/-0.1). The amount of surface Ce³⁺ ion was 581 determined using the area of v0, u0, v' and u' peaks, while v, u, v'', u'', v''' and u''' were assigned 582 to surface Ce⁴⁺ ion. 583

The two ions appear for different environments of Ce atoms, resulting in different charge transfers. 584 Ce^{3+} is indeed present in Ce_2O_3 , while CeO_2 is made of Ce^{4+} ions. Since the O1s core level is sensitive 585 to changes in the coordination of the oxygen atoms, its deconvolution should also allow the evaluation 586 of the charge transfer between oxygen and cerium atoms. Three components are usually considered 587 to resolve XPS spectra of the O1s core level in CeO₂. The first one, labeled Oa at 529 eV, is usually 588 associated with lattice oxygen, i.e. Ce^{4+} in CeO₂. Following [116], Oβ feature at 531 eV and Oγ 589 feature at 532 eV are attributed to surface hydroxyl groups, resulting from the dissociation of 590 adsorbed water and irreversibly adsorbed molecular water, respectively. These energies (+/-0.1 eV) 591 592 were fixed to fit our XPS data, as shown in Fig. 5b. Finally, relative atomic concentration was

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





Fig. 5: Experimental and fitted XPS spectra. Ce3d (a) and O1s (b) core level spectra as a function of the Fe concentration in CeO2 nanocrystals. Experimental data are in black, shirley background in green. The sum of 5 components of doublets (2 of Ce3⁺, blue area, 3 of Ce4+, orange area) are used to fit the Ce3d signal (a) or of 3 components ($O\alpha$, $O\beta$ and $O\gamma$, areas in orange, blue and cyan, respectively) to fit O1s signal in red.



Fig. 6: Relative atomic composition of the synthetized pristine and doped CeO₂ nanocrystals as a function of Fe content.

610

As shown in Fig. 6, the Ce⁴⁺ relative atomic concentration follows nicely that of O α . Both signals decrease as the Fe content increases from CeO₂ to Fe2.5 and next decrease and reach an almost constant value. This is consistent since both signals come from the CeO₂ units in the nanocrystal bulk. Remarkably, the variation of the Ce³⁺ relative atomic concentration is opposite to that of Ce⁴⁺. This reveals that the increase in Fe content from CeO₂ to Fe2.5 promotes the enrichment of Ce³⁺ within the Ce. Adding more Fe does not lead to more Ce³⁺ ions. On the contrary, it appears that the further addition of Fe atoms, beyond Fe2.5, is less effective in generating Ce³⁺ ions.

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

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

- 631
- 632 *3.3 DFT study*

634 *3.3.1. Fe-doped CeO*² 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_2 (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_{Int}).

The optimized geometry of the system with surface substitutional Fe doping (Fe@Ce₁), reported in 639 Fig. 7a, results in more stable than the subsurface one (Fe@Ce₂) by 1.1 eV. The presence of such a 640 Fe substitutional point defect induces a rearrangement of the neighboring O atoms. As a result, on the 641 642 doped CeO₂ (111) surface, two non-equivalent O atoms (O₁ and O₄) and two equivalent (O₂=O₃) O sites are present, whereas in the subsurface layer all the O atoms (O₅, O₆ and O₇) results to be 643 equivalent (see Fig. 7b). In this configuration, the Fe atom relaxes inward and binds to an O atom of 644 645 the surface O₁, to three O atoms of the second layer O₅, O₆ and O₇, and to an O atom of the third layer O₈ (yellow O in Fig. 7b). The Fe-O bond lengths are found to be in the range of 1.84-2.14 Å, and 646 therefore, corresponding to the distances in α - and γ -Fe₂O₃(1.89-2.10 Å) [118]. In addition, the Bader 647 charge of the substitutional Fe dopant is 14.28 e⁻ similar to those computed for the metal in α - and γ -648 Fe₂O₃ (14.34 and 14.49 e⁻). The Fe-O bond lengths of the five-coordinate moiety and the Bader charge 649 calculations suggest that in our system the iron atom has an oxidation state of +3. In the doped surface, 650 the Bader charges of the Ce atoms $(9.6 e^{-})$ are consistent with the presence of Ce⁴⁺, indicating that no 651 Ce^{4+} is reduced to Ce^{3+} in presence of the Fe dopant (see PDOS Fig. SI.10a). In the presence of a 652 substitutional Fe atom in the CeO₂ system the computed value of the bandgap is 1.7 eV, thus 0.2 eV 653 lower with respect to the undoped case, that is 1.9 eV (compare Fig. SI.10a and SI.10b). 654



Fig. 7. Panel a) optimized structure of Fe@Ce₁ (111). Panel b) First and second coordination spheres of the Fe dopant. Ce, O, $O_{1,5-8}$, O_{2-4} and Fe surface atoms are represented in balls and sticks and depicted in blue, red, yellow, purple and green, respectively. Panel c) optimized structure of Fe_{Int}.

Panel d) coordination sphere of the interstitial Fe dopant. Ce, O, $O_{3,5,6}$, O_9 and Fe surface atoms are represented in balls and sticks and depicted in blue, red, yellow, orange, and green, respectively.

Fig. 7.c shows the optimized structure of the Fe_{Int} system. Also in this case, the presence of the 662 interstitial Fe dopant induces structural distortions on the surface. In fact, the Fe atom relaxes outward 663 binding to the surface O_3 atoms and to the three O atoms of the second layer O_5 , O_6 and O_9 , (yellow 664 and orange O in Fig. 7d). The formation of these new Fe-O bonds and the breaking of the pre-existing 665 Ce-O bonds generates three reduced Ce^{3+} . The Bader charges of these Ce atoms (9.9 e⁻) are consistent 666 with the presence of Ce^{3+} , also confirmed by the formation of two bandgap states below the Fermi 667 level (black peaks in Fig. SI.11a of the SI) and by the spin density analysis, where the electron excess 668 on the Ce^{3+} are indicated with black densities analogously to the colors of the respective bandgap 669 peaks (Fig. SI.11c). In Fe_{Int} system the computed value of the bandgap is 1.7 eV similar to the 670 671 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 experimentally calculated one and reported in Table 3. 673

Next, we have considered the formation of O vacancies on the most stable Fe@Ce1 system. The 674 presence of a Fe substitutional point defect generates four non-equivalent O atoms, namely O₁, 675 $O_2=O_3$, O_4 in the outermost layer and $O_5=O_6=O_7$ in the subsurface layer, as discussed above (Fig. 7b). 676 It is, therefore, possible to create four non-equivalent oxygen vacancies: VO₁, VO₂₌₃ and VO₄ in the 677 external layer and VO₅₌₆₌₇ in the subsurface layer. The computed values of the formation energies 678 (E_F) of VO₁, VO₂₌₃, VO₄ and VO₅₌₆₌₇ are found to be 0.7, 0.8, 2.13 and 1.1 eV, respectively. Our 679 results show low formation energies for those oxygen vacancies arising from oxygen atoms directly 680 coordinating or close enough to the Fe dopant (see VO₁, VO₂₌₃ and VO₅₌₆₌₇) and high E_F for those 681 682 far from the iron atom. This occurs because the oxygen atoms very close to Fe are more affected by the structural distortions generated by the Fe dopant. The formation of a second oxygen vacancy VO₂ 683 on the most stable reduced surface VO₁ (Fe@Ce₁:VO₁₋₂) is also favored, with an E_F of 0.9 eV, 684 685 suggesting that the Fe dopant is likely the center of the oxygen vacancy cluster. A close inspection of the Bader charges, PDOS and spin density plots of the most stable Fe@Ce₁:VO₁(111) system shows 686 that the formation of an O vacancy leads to the reduction of two Ce⁴⁺ atoms that are formally Ce³⁺ 687 (see Fig. SI.12). 688

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.

Fig. 8 shows a plot of the Gibbs energies $\Delta G_{ads}(T, p)$ of the system discussed above as a function of 692 the O chemical potential including a conversion to oxygen partial pressures at several relevant 693 temperatures. It is possible to identify three thermodynamically stable phases. The first phase, which 694 holds for values of $\mu_0 > -0.7$ eV, corresponds to the system where a Fe atom substitutes a surface Ce 695 ion, Fe@Ce1 (red line). Under O-rich conditions this structure becomes the thermodynamically most 696 stable one. The second most stable structure is the one obtained by removing a surface O atom from 697 the Fe@Ce₁ system (green line). This structure becomes thermodynamically stable in the range -1.05 698 $<\mu_o < -0.7$ eV (purple line). Finally, for $\mu_o < -1.05$ the Fe@Ce₁ system in the presence of two surface 699 O vacancies becomes thermodynamically stable. These findings are in line with the experimental data 700 suggesting that in the presence of Fe atoms substituting Ce ions the formation of O vacancies is 701 favored. In addition, we predict that subsurface substitutional and interstitial Fe doping are never 702 thermodynamically stable (blue and black lines, respectively). 703



705

Fig. 8. Gibbs energies ΔG_{ads} (*T*, *p*) for substitutional, interstitial Fe atom in CeO₂ (111) and for reduced Fe@Ce₁:VO₁ and Fe@Ce₁:VO₁₋₂ (111) as a function of the oxygen chemical potential $\Delta \mu_0$ in eV.

3.3.2. Ibuprofen absorption on the surfaces

The interaction of IBU with stoichiometric (reduced) undoped CeO_2 (111) and the most stable Fe@Ce₁ surfaces was investigated, simulating IBU in its deprotonated form according to the experimental conditions.

Fig. 9 shows the optimized geometries of the most stable configurations of the IBU adsorbed on CeO₂(111), Fe@Ce₁ (111), CeO₂:VO₁(111), and Fe@Ce₁:VO₁(111) (panel a-d, respectively).

IBU interacts with $CeO_2(111)$ through an ionic-like bond between an oxygen atom of its carboxylate 715 group (O^{1}_{IBU}) and a surface Ce atom of 2.38 Å and an E_{ads} of -0.58 eV (Fig. 9a). In Fe@Ce₁ (111), 716 the ligand binds the surface by a covalent-like bond between O^{1}_{IBU} and the Fe dopant of 2.12 Å and 717 an E_{ads} of -0.98 (Fig. 9b). In the stoichiometric system, the Fe dopant presence improves the 718 719 adsorption energy of IBU by 0.4 eV due to i) the greater orbital availability of Fe³⁺ with respect to Ce⁴⁺ to host electrons and, thus, form new bonds and to ii) the structural distortions generated by the 720 substitutional dopant. In fact, in the presence of Fe, the surface oxygen atom O₁ goes down towards 721 the subsurface oxygen layer allowing a better interaction of the ligand with the $Fe@Ce_1(111)$ surface. 722

These energy stabilizations are also reflected in the reduced undoped and Fe-doped systems (Fig. 9c 723 and 9d, respectively). The experiments are performed in aqueous solution and, therefore, water 724 molecules will fill surface O vacancies of the ceria surface leading to a hydroxylated surface. 725 726 However, if we assume that O vacancies are present on the catalysts, IBU molecules will adsorb on CeO₂@VO₁ (111) and Fe@Ce₁:VO₁ (111) through an ionic and covalent bond of 2.56 and 2.10 Å, 727 respectively, and with E_{ads} of -2.28 and -2.43 eV for the undoped (panel c in Fig.9) and Fe-doped 728 (panel d in Fig.9) reduced systems. Therefore, the hypothetical presence of the surface oxygen 729 vacancy VO₁ improves the ligand E_{ads} of about 1.5 eV with respect to the stoichiometric surfaces as 730 O^{2}_{IBU} tends to occupy the vacant site stabilizing the IBU adsorption. 731



732

Fig. 9. Optimized structure of a) CeO_2 (111), b) $Fe@Ce_1$ (111), c) $CeO_2@VO_1$ (111) and d) Fe@Ce₁:VO₁ (111) with the corresponding E_{ads} (eV). Ce, O and O^{1-2}_{IBU} , O₁, C, H and Fe surface atoms are represented in balls and sticks and depicted in blue, red, yellow, cyan, white and green, respectively.

737

739 3.4 *Ibuprofen adsorption and photodegradation activity*

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



Fig. 10 – a) Potential (ζ) of the pristine and Fe-doped CeO₂ vs the adsorption capacity. b) Trend of the adsorption equilibrium constant. The present experimental conditions were adopted for each experiment: *T*=30 °C, *C*_{IBU,0}=12.4 mg L⁻¹, ρ_{B} = 0.07 g L⁻¹, reaction time of 300 min.

754

750

From the results shown in Fig. 10a, it is interesting to observe that Fe0.5 and Fe5 samples are 755 positively charged at pH=4.6, namely the pH of the ibuprofen solution, while Fe2.5 is negatively 756 charged. It is worth mentioning that the surface of both ceria and doped ceria is not "naked" but 757 hydroxylated. Thus, being ibuprofen a weak acid (pKa 4.41), in water it is partially dissociated in its 758 anionic form. Therefore, the strongest interactions are expected to be with positively charged 759 materials. Accordingly, the adsorption efficiency passes through a minimum for the Fe2.5 catalyst 760 where the surface is negatively charged, inhibiting the ibuprofen adsorption. The different surface 761 charge may be related to the type of hydroxyls exposed by Fe-CeO₂ surfaces, their distribution and 762 their location with respect to oxygen vacancies [119,120]. 763

The CeO₂ sample shows an opposite trend showing a very low adsorption efficiency even if the 764 surface is positively charged, a finding not explainable by the above-mentioned hypothesis. But it is 765 important to remind that from DFT computations (see Fig. 9), the adsorption energy of ibuprofen 766 767 improves when it interacts with Fe rather than Ce, clearly leading to a lower adsorption efficiency compared with the samples containing Fe. As previously stated, the Fe10 sample is not included in 768 the trend of doped samples discussion, because of its different properties such as very high surface 769 770 area and the presence of surface oligomers (vide supra) that may promote higher adsorption efficiency. Furthermore, the type of adsorption was further evaluated by FT-IR spectroscopy. The 771

spectra obtained from the Fe2.5 sample and from the same sample after contact with a saturated 772 ibuprofen solution are shown in Fig. SI.14. The spectra show a broad band between 3750 and 3000 773 cm⁻¹ due to O-H stretching vibration of surface hydroxyl groups and undissociated water 774 characterized by its bending mode at 1630 cm⁻¹ [121,122]. Bands at around 1364 and 1529 cm⁻¹ can 775 be attributed to carbonate species, whose presence results from interactions of CeO₂ with atmospheric 776 777 carbon dioxide [123]. Metal-oxygen vibration are generally observed at low wavenumbers, below 800 cm⁻¹. The absence of new chemical bonds in the post-saturation sample, inferred from the 778 absence of new peaks in the saturated Fe2.5 catalyst, suggests a physisorption mechanism. 779

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

786
$$IBU + * \leftrightarrow IBU^*$$

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

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

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

791
$$\frac{dc_{IBU}}{dt} = -r_{ADS} \cdot \rho_B \tag{4}$$

The ordinary differential equation was solved in MATLAB R2023a environment, using *ode*45 function, and the related adsorption kinetic and equilibrium constants were obtained by parameter estimation activity on the adsorption kinetic experiments. In detail, the objective function, defined as the square root of the squares of the residuals, was minimized using *lsqnonlin* algorithm. The results of the parameter estimation activities are reported in Figs 10b and Table 4.

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

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

805

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

(2)

Journal	Pre_	nro	ofe
Journar	110-	\mathbf{p}_{10}	UI

810	The		k _{ADS}	KeqADS	k deg
811	experiments were	Sample	$(\mathbf{I} \mathbf{a}^{-1} \mathbf{min}^{-1})$	()	$(\mathbf{I} \ a^{-1} \ min^{-1})$
812	the presence of UV		(Lg IIIII)	(-)	(Lg IIIII)
813	irradiation. The				
814	reported in Fig. 11,	C ₀ O.	0.00 ± 0.02	0.23 ± 0.01	0.03 ± 0.01
815	that UV irradiation		0.09 ±0.02	0.23 ± 0.01	0.03 ±0.01
816	efficient than				
817	for all the catalysts.	Fe0.5	0.25 ± 0.01	1.19 +0.02	0.03 ± 0.01
818	of pure ceria settles	10000	0.20 = 0.01	1.17 _0.02	0100 20101
819	(see Table 3), which				
820	to mainly exploit	Fe2.5	0.16 ± 0.02	0.49 ± 0.02	0.11 ± 0.01
821	UV light. The				
822	the ceria lattice				
823	onset of absorption	Fe5	0.23 ± 0.02	0.69 ± 0.02	0.04 ± 0.01
824	samples. For this				
825	samples can be	F-10	0.27 .0.02	1 52 0 02	0.0010 - 0.0002
826	visible irradiation.	reiu	0.37 ± 0.02	1.52 ± 0.03	0.0010 ± 0.0003
827	performance				

photodegradation conducted either in visible or results main are where it is evident is slightly more visible irradiation The band gap value at the value of 3 eV allows the material the absorption of presence of iron in induces a shift in the in the studied reason, the doped more active under However, between UV and

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



832

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

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

$$841 \qquad r_{DEG} = k_{DEG} \cdot c_{\mathrm{IBU}^*}$$

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

Thus, the mass balance equation needs to be further modified, supposing that IBU* undergoesphotodegradation, Eq. 6.

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

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

of the parameter estimation activities for all catalysts are reported in Table 4 and Fig. 12b.







Fig. 12. a) Example of data fit on the kinetic data measured using the Fe2.5 catalyst for both dark and 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 constant as a function of Fe loading.

859

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

(5)

Raman and XPS findings revealed (*vide supra*) that Fe2.5 has the highest content of Ce^{3+} and defectsrelated oxygen vacancies. Raman results also suggested the highest charge delocalization for Fe2.5 (Fig. 4).

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

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

For the mentioned reasons, it is interesting to further investigate the performance of Fe2.5 in terms of stability. Thus, reuse experiments were conducted under visible light irradiation. As reported in Fig. 13, the activity of Fe2.5 did not change after four cycles of photodegradation tests, demonstrating

- good stability, thus a potential use in continuous apparatus, allowing the scale-up of the process from
- 875 batch to continuous operation.

876



877

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

881

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

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

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

Finally, XPS analysis performed on the sample post-catalysis shows first no contamination. Ce3d spectra obtained before and after photocatalysis are quite similar (Fig. SI.16a). A minor change of the v component (at 882.6 eV) can be seen, meaning that the Ce⁴⁺ contribution may have increased slightly. However, that variation is so small that it hardly affects its 3d3/2 counterpart. Consequently, in accordance with the other analyses, the XPS study confirms that the photocatalytic tests did not 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.

The samples collected during the kinetic experiments were analysed via UV-Vis spectrophotometry and allowed the identification of an absorbance peak characteristic of an unknown chemical compound, at the wavelength λ =260 nm. Fig. 14 shows an example of the absorbance spectrum obtained at two different times, collected during a kinetic run conducted imposing the following reaction conditions: catalyst Fe2.5, *T*=30°C, *C*_{IBU,0}=12.4mg/L, $\rho_{\rm B}$ =0.07 g/L. In particular, the T0 sample was collected at time=0, while T1 at time = 30 min of reaction time.





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

Fig. 15: Results obtained from spectrophotometer analyses. Experimental conditions: catalyst Fe2.5, $T = 30^{\circ}$ C, $C_{IBU,0} = 12.4 \text{ mg L}^{-1}$, $\rho_B = 0.07 \text{ g L}^{-1}$.

930

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

The identification of neo-formed by-products obtained from the ibuprofen photodegradation was also performed by LC-MS analysis. The MS analysis was preliminarily performed on the standard solution (T0) of ibuprofen to set up the chromatographic conditions and MS parameters. The ion current of the chromatographic peak (3.4 min, Fig. 16 panel A) detected in the mixture at T0 was assigned to the molecular ion (M+H⁺) of ibuprofen (IBU) at 207.1 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
- 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.



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

945

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



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

959

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

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

The presence of the mentioned by-product was already reported in the literature as possible intermediate in a more complex mechanism involving several degradation species In particular, Rao et al., [127], reported that 1-ethenyl-4-(2-methylpropyl)benzene is produced by the dehydration and decomposition of two intermediates as described in Scheme 2. In the present work, the mentioned two intermediates were not detected, probably because the related reactions of formation and disappearance are relatively fast in the presence of Fe2.5 catalyst.



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

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.

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

The effect of the different iron content in the various samples revealed the role of iron heteroatoms 992 in the delicate balance between adsorption and relative photodegradation of ibuprofen. Light was 993 shed on the relationship between composition-structure and activity through numerous catalytic 994 experiments, conducted both in the dark and under UV or visible irradiation. The results were 995 supported by a combination of advanced characterisation techniques and DFT calculations, showing 996 997 that the doping of the $CeO_2(111)$ surface with a substitutional Fe atom i) causes a decrease in the band gap of the system, improving the catalytic performance of the catalyst, ii) favours the formation 998 of vacant sites (VOx) when the oxygen atoms are directly coordinated with the dopant or very close 999 to it, iii) favours the IBU adsorption both in the stoichiometric and reduced model. Despite the 1000 presence of iron and vacancies being beneficial for ibuprofen adsorption, experimentally we find a 1001 non-linear trend of the adsorption capacity with the iron content. The latter was explained by 1002 measuring the z-potential of each sample, finding that adsorption is more efficient when the catalyst 1003 1004 surface is positively charged. The combination of this effect and the non-linear trend of ibuprofen adsorption with Fe content leads to the identification of an optimal composition of the photocatalyst, 1005 namely 2.5 mol% Fe doped CeO₂. The mentioned material showed good stability along 4 cycles of 1006 1007 re-use experiments, demonstrating to be a promising material for a future application in flow.

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

1011

		Jour	mal Pre	e-proofs
1013	List of a	bbreviations		
	IBU	Ibuprofen	1014	
	(*)	Free site	1015	List of symbols
	(IBU)	Ibuprofen		
	(IBU*)	Ibuprofen adsorbed into the solid	đ	
	AOPs	Advanced oxidation processes		
	NSAIDS	Non-steroidal anti-inflammatory	drugs	
	CIBU,0	ibuprofen initial concentration	(mg	$g(L^{-1})$
	CIBU	concentration of ibuprofen at t tim	e (mg	$g(L^{-1})$
	C _{IBU*}	concentration of adsorbed ibuprof	en (mg	$g L^{-1}$)
	<i>k_{ADS}</i>	adsorption kinetic constant	(L	$(g min)^{-1})$
	k _{DEG}	desorption kinetic constant	(L	$(g min)^{-1})$
	K _{eqADS}	adsorption constant	(-)	
	qt	adsorbed amount	(mg	$(g g^{-1})$
	r _{ADS}	adsorption rate	(mg	$g g^{-1} min^{-1}$)
	r DEG	desorption rate	(<i>m</i> g	$g g^{-1} min^{-1}$)
	t	time	(mi	n)
	Т	temperature	(°C	')

1017 Greek symbol

 ρ_B sorbent bulk density $(g L^{-1})$

1018

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- 1400
- 1401
- 1402 Highlights
- Reverse micelle synthesis fosters Fe doping of nanocrystalline CeO₂
- 2.5 mol % iron-doped ceria leads to high charge delocalization
- Efficient visible-light photodegradation of ibuprofen with 2.5 mol % Fe-CeO₂
- Substitutional Fe favours the oxygen vacancies formation and ibuprofen adsorption.
- The by-product of the ibuprofen degradation is 1-ethenyl-4-(2-methylpropyl)benzene.
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