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Enhanced photocatalytic hydrogen production from glucose aqueous matrices on Ru-doped LaFeO₃

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1 Abstract

2 In the present work, the renewable hydrogen production by the photocatalytic degradation of 3 glucose over Ru-doped LaFeO₃ photocatalyst under UV or visible irradiation has been assessed 4 for the first time. The perovskite doped with ruthenium was successfully synthesized by solution 5 combustion synthesis. The effects on the hydrogen production and glucose degradation of 6 reaction parameters, such as amount of ruthenium, initial concentration of glucose, reactor 7 configuration and light source were systematically investigated. The results show that the 8 photocatalytic H₂ production from the glucose solution can be significantly enhanced (2179 9 µmol/g_{cat} after 4 hour of UV irradiation) using a specific amount of ruthenium (0.47 mol % of Ru) 10 in LaFeO₃. Moreover, photocatalytic performances were strongly affected by reactor 11 configuration; the comparison between two cylindrical reactors with different diameters showed 12 improved performances in the reactor with the smaller diameter due to the enhanced photons 13 flow that intercept the photocatalysts particles dispersed into the glucose solution. In particular, under UV light, the hydrogen production increased from 2179 to 3474 µmol/g_{cat} and the glucose 14 15 degradation was complete after 3 hours of irradiation.

Finally, the optimized photocatalyst was also tested under visible light on a real wastewater taken from a brewing process; the results showed an interesting hydrogen production as high as 2128 μ mol/g_{cat} (after 4 hours of visible irradiation). In conclusion, this work further support the interesting perspectives in the applicability of the photocatalytic process for the valorization of wastewater with the aim to obtain hydrogen from the degradation of target organic compounds.

Keywords: Photocatalytic wastewater valorization, hydrogen production, glucose degradation,
 Ru-doped LaFeO₃, LEDs, photoreactor configuration.

23 24

1. Introduction

25 In recent years, the limited availability of fossil fuels and the increasing environmental pollution 26 derived from their use as main source of energy has led to the development of new technologies 27 for the production of zero environmental impact energy vectors such as hydrogen [1]. Hydrogen 28 is a storable, clean and environmentally friendly fuel whose combustion results in the solely 29 generation of water, with no emissions of atmospheric pollutants, greenhouse gases or 30 particulates. However, about 95% of hydrogen currently derives from fossil fuels, mainly by 31 steam reforming of natural gas and petroleum, while the remaining 5% comes from the 32 electrolysis of water [2]. Because these processes involve the use of nonrenewable resources or 33 high energy consumption, the corresponding routes of hydrogen production are not sustainable 34 or economically feasible. Over the last few years, biomass, mainly glycerol, has been used to 35 produce hydrogen by different methods, such as steam reforming [3], gasification [4], 36 autothermal reforming [5] and electrochemical reforming [6]. Alternatively, hydrogen can be 37 also produced from biomass in mild conditions (room temperature and atmospheric pressure) 38 through heterogeneous photocatalysis [2].

39 Photocatalysis has been extensively studied for environmental remediation (i.e., pollutant 40 degradation) and solar energy conversion (i.e., hydrogen production and CO₂ reduction) [7-15]. 41 Up today, the photocatalytic production of hydrogen can be obtained mainly by two processes, 42 i.e. either by the direct splitting of water into H₂ and O₂, or by the photo-reforming of organic compounds [16-22]. In many studies regarding the photocatalytic production of H₂, different 43 44 substances (e.g., organic acids, alcohols, sulfide/sulfite) acting as electron donors, have been 45 generally used [23-26]. However, this approach requires the use of sacrificial agents in order to 46 get a good hydrogen production, which makes the process expensive. On the contrary, if the 47 organic pollutants present in wastewater are seen as electron donors for H_2 production, the 48 overall process may be potentially cost-effective. Glucose is the most diffused and cheapest 49 carbohydrate as it can be directly obtained from cellulose, the most abundant and renewable 50 biomass on Earth. It is used for ethanol or butanol production, a wide variety of useful bio-based 51 chemicals as industrial feedstocks for bioplastics and also to obtain hydrogen [27]. But glucose is 52 also present at high concentration in wastewaters from some agro-food industries. Accordingly, 53 the heterogeneous photocatalysis applied to wastewater treatment offers the opportunity to 54 simultaneously recovery valuable products (such as hydrogen and methane) to be converted into 55 energy [28-30]. Moreover, photocatalytic technology can be also operated under natural sunlight 56 [31] so drastically cutting energy costs down. The most widely used semiconductor in 57 photocatalysis is TiO₂ because of its physical and chemical properties, excellent stability, high availability and low cost [32]. With regard to the photocatalytic hydrogen production, the use of 58 59 semiconductor (such as TiO₂ or ZnO) doped with nobles metals (Au, Pt, Pd) has been 60 extensively reported [28, 33-38]. Alternatively, LaFeO₃, one of the most common perovskite 61 type oxide, has a general formula ABO₃, where position A is occupied by the rare earth ion (La³⁺), and position B by the transition metal ion (Fe³⁺). LaFeO₃ (conduction band 62 63 potential=0.025 eV [39]) has shown excellent photocatalytic activity because of its interesting 64 properties such as high stability, non-toxicity and small band gap energy (2.07 eV), that qualify 65 this perovskite as visible light active photocatalyst [40, 41].

Generally, the functional properties of perovskite materials can be controlled either by modulating the crystalline structure or by the incorporation of different metal ions into the perovskite lattice [42]. LaFeO₃ powders doped with Sr and Cu have been recently tested in a photoelectrochemical process [42]. However, studies about the photocatalytic hydrogen production from aqueous solution on doped LaFeO₃ systems are still lacking in the literature. Among the several possible dopants for perovskites, ruthenium is the most suitable since a large amount of Ru^{3+} ions can be introduced within the perovskite network (in particular by replacing the transition metal cation of the perovskite) keeping it single-phase[43].

Therefore, in this work Ru-doped LaFeO₃ samples were synthesized and characterized and their effectiveness in the photocatalytic hydrogen production from glucose aqueous matrices has been assessed for the first time. The influences of Ru loading and photoreactor configuration have been analyzed. Finally, the optimized photocatalyst was also tested under visible light on a real wastewater taken from a brewing process.

80

81 **2.** Experimental

82 2.1 Synthesis of photocatalysts

83 Ru-LaFeO₃ samples were prepared by solution combustion synthesis, using citric acid as organic 84 fuel and metal nitrate as metal precursor (oxidizer) [44]. In detail, 1.66 g of $Fe(NO_3)_3 \cdot 9H_2O$ 85 (Riedel-deHaen, 97 wt%), 1.78g of La(NO₃)₃·6H₂O (Fluka, 99%), 0.86g of citric acid (Fluka, 99 86 wt%) and a specific amount of RuCl₃ (Sigma Aldrich, 99%) used as dopant, were completely 87 dissolved in 100 ml of bidistilled water. The solution was kept stirred continuously at 60 °C for 5 88 minutes. Then, ammonium hydroxide (Carlo Erba, 37 wt %) was slowly added to regulate the pH 89 of the solution up to 7.0. The solution was dried at 130° C and then calcined at 300° C for 3 90 hours in static air using a muffle furnace to ignite the solution combustion reaction [41]. 91 Different amounts of RuCl₃ were used for the doping of LaFeO₃ to obtain photocatalysts with 92 different amounts of Ru (Table 1). The Ru nominal loading is expressed as molar percentage and93 it was evaluated through Eq. 1:

94

95
$$\% molRu = \frac{nRu}{nLa + nFe} \cdot 100$$
 Eq. 1

96 Where:

97 nRu is the number of moles of RuCl₃ used in the synthesis;

98 nLa is the number of moles of $La(NO_3)_3 \cdot 6H_2O$ used in the synthesis;

and nFe is the number of moles of $Fe(NO_3)_3 \cdot 9H_2O$ used in the synthesis.

100

101 **Table 1**

102

103 2.2 Photocatalysts characterization

104 Different techniques were used to characterize the photocatalysts. In particular the crystallite size 105 and crystalline phase of Ru-LaFeO₃ photocatalysts were studied with an X-ray diffractometer 106 (Assing), using Cu-Ka radiation. Total Ru content of the samples were determined by X-ray 107 fluorescence spectrometry (XRF) in a thermoFischer ARL QUANT'X EDXRF spectrometer 108 equipped with a rhodium standard tube as the source of radiation and with Si-Li drifted crystal 109 detector. The specific surface area analysis was performed by BET method using N₂ adsorption 110 with a Costech Sorptometer 1042 after a pretreatment at 150°C for 30 minutes in He flow 111 (99.9990 %). The Raman spectra of the samples were recorded with a Dispersive MicroRaman system (Invia, Renishaw), equipped with 785 nm diode-laser, in the range 100-1000 cm⁻¹ Raman 112 113 shift. UV-vis reflectance spectra (UV-vis DRS) of powder catalysts were recorded by a Perkin Elmer spectrometer Lambda 35 using a RSA-PE-20 reflectance spectroscopy accessory (Labsphere Inc., North Sutton, NH). All spectra were obtained using an 8° sample positioning holder, giving total reflectance relative to a calibrated standard SRS-010-99 (Labsphere Inc., North Sut-ton, NH). Band-gap energy determinations of the photocatalysts were obtained from Kubelka–Munk function $F(R_{\infty})$ by plotting $[F(R_{\infty}) \times hv]^2 vs$. hv [45–47]. Scanning electron microscopy (SEM) (Assing, mod. LEO 420) was used to characterize the morphology of the samples at an accelerating voltage of 20 kV.

121 2.3 Photocatalytic tests.

The photocatalytic experiments for hydrogen production from glucose aqueous matrices were carried out in a photocatalytic pyrex cylindrical reactor [10, 48, 49] (ID = 2.5 cm) (R1) equipped with a N₂ distributor device (Q=0.122 NL/min) to assure the absence of O₂ during the tests. The experimental setup is represented in Figure 1.

126

127 **Figure 1**

128

129 In a typical photocatalytic test, 0.12 grams of the catalyst were suspended in 80 ml of an aqueous solution containing 1000 mg/L of glucose (D ⁺ Glucose VWR, Sigma-Aldrich). The pH of the 130 131 solutions has not been changed and it was equal to about 6 for all the photocatalytic tests, 132 corresponding to the spontaneous pH of glucose aqueous solutions. To ensure complete mixing 133 of the solution in the reactor, a peristaltic pump was used. The photoreactor was irradiated with a strip of UV-LEDs (nominal power: 10W; light intensity: 57 mW/cm²) with wavelength emission 134 135 in the range 375–380 nm, or with a strip of visible LEDs with the main wavelength emission at about 460 nm (nominal power: 10W; light intensity: 32 mW/cm²). The LEDs strip was 136

137 positioned around the external surface of the reactor so that the light source uniformly irradiated 138 the reaction volume. The suspension was left in dark conditions for 2 hours to reach the 139 adsorption-desorption equilibrium of glucose on the photocatalyst surface, and then the reaction 140 was started under UV (or visible) light up to 4 hours. About 2 mL of sample were taken from the 141 photoreactor at different times and filtered (filter pore size: 0.45 µm) in order to remove 142 photocatalyst particles before the analyses. To evaluate the effect of reactor design, another 143 photoreactor (R2) with a nominal volume equal to the first one (R1) but with an internal diameter 144 equal to half (1.25cm) was also investigated. Finally, to evaluate the effect on real wastewater 145 containing glucose, the optimized photocatalyst was tested under visible light on a wastewater 146 sample taken from a brewing process (pH: 6; total suspended solids: 450 mg/L, TOC: 1000 147 mg/L).

148 2.4 Chemical Analysis

149 The characterization of the gaseous phase coming from the photoreactor was performed by 150 continuous CO, CO₂, O₂, H₂ and CH₄ analyzers (ABB Advance Optima). The concentration of 151 glucose was measured by a spectrophotometric method [50] at 490 nm using UV-vis 152 spectrophotometer (Lambda 35, Perkin Elmer). According to the method, 2 mL of a 153 carbohydrate solution was mixed with 1 mL of 5 wt% aqueous solution of phenol (Sigma-154 Aldrich) in a test tube. Subsequently, 5 mL of concentrated sulfuric acid (Sigma-Aldrich) was 155 added rapidly to the mixture. The gluconic acid formed during the irradiation time was 156 quantified by analyzing the UV absorption of liquid samples at 264 nm [26] using the same 157 equipment. Leaching tests were carried out to check the release of La and Ru from the samples 158 during the photocatalytic tests, analysing the solution by inductive coupled plasma-mass 159 spectrometry (7500c ICP-MS, Agilent).

160 **3. Results and Discussion**

161 3.1 Photocatalysts characterization

162 **3.1.1 X-ray diffraction (XRD)**

Figure 2 shows the XRD patterns of the LaFeO₃ photocatalyst doped with different amounts of ruthenium. XRD showed well indexed diffraction peaks, clearly indicating the formation of orthorhombic perovskite type structure, as reported in literature [41, 51]. Additional peaks due to ruthenium oxide were not observed up to a Ru loading of 1.16 mol %. In fact, for 1.16%Ru and 2.33%Ru catalysts, XRD patterns showed an additional diffraction peak at 20 value of about 35 degree due to the presence of RuO₂ on the surface, indicating only a partial doping of perovskite structure [52].

170

171 **Figure 2**

172

173 XRD data in the range 29-35 ° (Figure 3) also show that the peak of the X-ray diffraction at 32.2 174 degree of undoped LaFeO₃ shifted towards lower 2 θ values for all the Ru-LaFeO₃ samples. The 175 reason for this phenomenon is that the radius of Ru³⁺ (0.0820 nm) cation is larger than Fe³⁺ 176 (0.0645 nm), which leads to the decrease of unit cell lattice parameter, according to literature for 177 perovskite samples doped with ruthenium [53]. This last result indicates that Ru³⁺ cation partially 178 substitutes Fe³⁺ cation in the perovskite structure.

179

180 **Figure 3**

181

182 The crystallite size of the samples was calculated by Scherrer formula for a diffraction line 183 positioned at 2θ value of about 32 degree [51] (Table 1).

Comparing doped and undoped LaFeO₃, it can be observed that the doping process induced a slight decrease of photocatalysts crystallite size, though no clear relationship could be established between Ru contents. A similar result was previously observed for $SrTiO_3$ perovskite doped with Ru [53].

188

189 3.1.2 BET surface area and XRF results

BET surface area values (S_{BET}) of the catalysts are shown in Table 1. In agreement with XRD results, S_{BET} values did not change when Ru amount used in the catalyst preparation was increased. In particular, S_{BET} increased from 4 to 5 m²/g for undoped LaFeO₃ and Ru-doped LaFeO₃, respectively. The total amount of Ru in the samples was determined by XRF (Table 1). In every case, the real Ru content well fits the nominal metal content indicating a good yield of the synthesis process.

196 3.1.3 UV-Vis Diffuse Reflectance spectra

197 The reflectance spectra (Figure 4) showed the typical absorption band edge of the LaFeO₃ 198 semiconductor at around 814 and 600 nm for all the samples and it can be attributed to electron 199 transitions from valence to conduction band ($O_{2p} \rightarrow Fe_{3d}$) [54]. It is worthwhile to note that these 200 bands disappeared for the catalysts with the higher Ru content (1.16%Ru and 2.33%Ru). This 201 result could be due to the presence of RuO₂ on the LaFeO₃ surface, observed in XRD 202 measurements (Figure 2). The absorption edge of Ru-doped LaFeO₃ catalysts has a red shift and also a stronger absorption than the pure LaFeO₃ in the visible region. Similar results were observed for Li-doped LaFeO₃ samples [55].

206

207 Figure 4

208

209 The data obtained from UV–Vis reflectance spectra were used for evaluating the band-gap 210 energy of the photocatalysts (Figure 5). The obtained results are reported in Table 1. The 211 increase of Ru amount resulted in a decrease of band-gap energy from 2.12 (band-gap of 212 undoped LaFeO₃) to 1.72 eV for 2.33%Ru. The decrease of band-gap energy was due to the 213 electronic transition from donor levels formed with dopants to the conduction band of the host photocatalysts [56]. In our case, the dopant exist as a trivalent ion (Ru^{3+}) on the Fe³⁺ site, which 214 215 forms a donor level at a lower potential than the top of the valence band composed of O 2p 216 orbitals, and the apparent band-gap energy consequently became narrowed [56].

217

218 **Figure 5**

219

220 **3.1.4** SEM analysis

The morphology of the LaFeO₃ and Ru-doped LaFeO₃ photocatalysts was investigated by SEM microscopy and the obtained results are presented in Figure 6. For sake of brevity, together with undoped LaFeO₃, only the analysis on 0.47%Ru photocatalyst are reported, being similar the results obtained for all the others Ru-doped LaFeO₃ samples. The SEM images show that the size of photocatalysts particles is not uniform due to agglomeration phenomena induced by particle-particle interactions. However, porous structure can be clearly seen in the SEM images, revealing the low density product, loose and porous material [57] due to the role of citric acid in the combustion of gel formed after the drying process at 130°C. In particular, at the combustion point, the citric acid generates gases that tried to come out from the gel by breaking the gel and generating the porous structure of LaFeO₃ (Figure 6a) and Ru-doped LaFeO₃ (Figure 6b) photocatalysts [57].

232

233 Figure 6

- 234
- 235 3.2 Photocatalytic activity results

236 **3.2.1** Effect of Ru content on H_2 production and glucose degradation.

During the dark phase, no product was detected in gaseous phase. Figure 7 reports the behavior of glucose degradation and hydrogen production as a function of Ru loading obtained after 4 hours of irradiation under UV-LEDs light at the spontaneous pH of the solution (pH=6).

240 The hydrogen production was reported as the ratio between the µmoles produced and the catalyst

 $241 \quad \text{amount } (g_{cat}) \text{ used in the tests.}$

242

243	Figure 7

All the Ru-doped LaFeO₃ photocatalysts demonstrated a better activity compared to undoped LaFeO₃. The higher glucose degradation (about 70 %) was achieved for 0.47%Ru catalyst. Glucose degradation efficiency increased as Ru% was increased from 0.12 to 0.47 mol%, and decreased when Ru% was increased from 0.47 to 2.33 mol %, reaching a value lower also than pure LaFeO₃. In parallel, the same trend was observed for H_2 production with the higher value (2179 μ mol/g_{cat}) achieved for 0.47%Ru after the same irradiation time. The observed H_2 production was higher than that one reported in the literature concerning the generation of hydrogen from the photocatalytic degradation of glucose on perovskites [41].

252 Ru^{3+} ions in the crystalline structure of the LaFeO₃ could act as electron scavengers preventing 253 the holes-electrons (h^+/e^-) recombination, and consequently causing the enhancement of the 254 photocatalytic activity [58]. This effect could be predominant for a Ru loading up to 0.47 mol%. 255 The decreased efficiency observed when Ru% was increased from 0.47 to 2.33 mol% is probably 256 due to the presence of RuO₂ on the catalyst surface (XRD analysis, Figure 2). The presence of 257 RuO_2 crystallites may reduce the light penetration, retarding the activation of the photocatalyst 258 and the generation of photoinduced charge carriers or can act as recombination centers 259 diminishing the H_2 production and the glucose degradation [24, 59].

The possible release of La and Ru was investigated by inductive coupled plasma-mass spectrometry analyzing the solution recovered after the photocatalytic test on 0.47%Ru sample showing that no release of La nor Ru was detected.

According to these results 0.47 mol% of Ru loading was considered to be the optimal value for the studied reaction.

265 3.2.2 Influence of the reactor configuration on the photocatalytic activity

The optimized photocatalyst (0.47%Ru) was used to investigate the influence of the reactor configuration. In particular a new set of experiments was carried out with the new reactor (R2) with a nominal volume equal to the first one (R1) but with an internal diameter equal to half (1.25cm). The aim was to enhance the photonic transport by increasing the photons flow that intercept the photocatalysts particles dispersed into the glucose solution. Figure 8 shows the

271 comparison in terms of photocatalytic activity between the two reactors. R2 resulted in a 272 significantly higher glucose degradation compared to R1: in particular, an almost complete sugar 273 degradation after 3 hours of UV irradiation was observed for R2 compared to 70% removal in 4 274 hours of UV irradiation observed for R1 (Figure 8a). Noteworthy, glucose degradation had 275 already reached about 70% after 2 hours of irradiation in the experiments performed with the 276 reactor R2. Moreover, in parallel, the hydrogen production (Figure 8b) was higher with the 277 photoreactor R2 (3474 µmol/L) compared to that one obtained with the photoreactor R1 (2179 278 μ mol/g_{cat}).

279

280 **Figure 8**

281

These results are in agreement with a previous work where a similar photoreactor configuration was investigated in the removal of chemical oxygen demand (COD) of a highly polluted wastewater [48]. It is underlined that the percentage of irradiated catalyst volume is different. For an ID of 1.25 cm (photoreactor R2), it is larger than that obtained for an ID of 2.5 cm (photoreactor R1) indicating that the attenuation of the available light energy is a key parameter that affects the photocatalytic performances of the reactor [60, 61].

288 3.2.3 Optimization of catalyst dosage for photocatalytic tests

The optimization of the catalyst dosage was carried out under UV irradiation with the photoreactor R2 by testing different dosages of 0.47%Ru photocatalyst, in the range 0.75-3 g/L. Photocatalytic efficiency increased as catalyst loading was increased up to 1.5 g/L (Figure 9). 292

Figure 9

294

Further increase in catalyst loading resulted in a decreased degradation of glucose and lower H_2 production. Possibly, the increase in the catalyst dosage over the optimum value resulted in a decreased light penetration through the solution because of the increased opacity of the aqueous suspension [62].

299

300 3.2.4 Influence of initial glucose concentration

Figure 10 shows the effect of the initial glucose concentration on both its degradation (Figure 10a) and hydrogen production (Figure 10b), under UV light. In particular, glucose degradation decreased as the initial concentration was increased. It is worthwhile to note that an increase of the hydrogen production was observed up to 1000 mg/L of initial concentration of glucose, in agreement with the results available in scientific literature [63].

306

307 Figure 10

308

309 The H₂ production from glucose degradation could be obtained according to the sugar 310 photoreforming reaction:

$$311 \quad C_6 H_{12} O_6 + 6 H_2 O = 12 H_2 + 6 C O_2$$
 Eq. 2

312	In this reaction the H_2/CO_2 ratio is equal to 2. However, in our case, the ratio H_2/CO_2 is in the
313	range $28 - 46$, as initial glucose concentration was varied, and never equal to 2 (Figure 11a).
314	On the other hand, the analysis of the liquid phase showed that gluconic acid is formed during
315	photocatalytic process and the ratio between the moles of gluconic acid produced and the moles
316	of glucose converted is approximately equal to 1 for all the tested concentrations (Figure 11b),
317	according to a previous work on LaFeO ₃ based photocatalysts [41].

318

319 Figure 11

320

Part of the additional CO_2 produced could come from the decarboxylation reaction of gluconic acid [64, 65]. But, taking into account the results reported in Figure 10a, this last reaction is expected to take place at a limited extend. On the basis of these observations and considering the behavior shown in Figure 10b, H₂ and gluconic acid could be mainly produced from the photocatalytic degradation of glucose, according to the following reaction:

326

$$327 C_6H_{12}O_6 + H_2O = H_2 + C_6H_{12}O_7 Eq. 3$$

328 3.2.5 Water splitting reaction on 0.47%Ru photocatalyst

The ability of 0.47%Ru photocatalyst in the hydrogen production through water splitting reaction
(without glucose) under UV irradiation was also evaluated. The results are reported in Figure 12
Figure 12

332

The production of hydrogen and oxygen progressively increased as irradiation time increased. Moreover, the H_2/O_2 ratio was about 2. This result confirms that hydrogen is produced from water splitting according the following reaction:

336

$$H_2O = H_2 + \frac{1}{2}O_2$$
 Eq. 4

338

It is worthwhile to note that the amount of hydrogen reached a value of 1230 µmol/g_{cat} (after 4 339 340 hours of irradiation), significantly lower than that obtained in presence of glucose. In fact, to 341 promote photocatalytic water splitting, various oxidizing sacrificial agents have been added to 342 water; the role of sacrificial agent is to scavenge the coproduced O_2 due to water splitting, and, 343 thus, to prevent the reverse reaction of O_2 with H_2 to H_2O [23, 66]. Typically, the sacrificial 344 compounds are hydrocarbons such as saccharides, alcohol and acetic acid [67]. However it must 345 be taken into account that, in our case, the water splitting reaction plays an important role in the 346 photocatalytic hydrogen production.

347

348 3.3 Photocatalytic activity of 0.47%Ru under visible light irradiation

The effect of different light sources (UV or visible LEDs) was evaluated on the 0.47%Ru catalyst (Figure 13), which showed the best performances. According to UV-Vis DRS results (Table 1), this catalyst was expected to be active also in the presence of visible light (band-gap equal to 1.98 eV). In particular, the photocatalytic experiment was carried out with a solution containing 1000mg/L of glucose, a catalyst dosage equal to 1.5g/L and the optimized R2 configuration. The observed glucose degradation was equal to 40% after 4 hour of visible light irradiation (Figure 13a) and the hydrogen production was equal to 1098 μ mol/g_{cat} (Figure 13b) after the same irradiation time. These results, also if lower than that obtained in presence of UV light, confirm the activity of the optimized photocatalyst also in presence of visible light irradiation.

359

360 Figure 13

361

362 3.4 Photocatalytic hydrogen production from real wastewater with 0.47%Ru catalyst under
 363 visible light

364 Since the investigated photocatalytic process was really effective in the hydrogen production 365 from glucose-containing solutions, the effect of the phtocatalyst 0.47% Ru was also investigated 366 in the treatment and valorization of real wastewater from brewing process (supplied by an Italian company producing beer) (Figure 14). the wastewater sample was filtered before the 367 368 photocatalytic process to remove the suspended solids. Typically the main component of this 369 type of wastewater is maltose $(C_{12}H_{22}O_{11})$, a sugar of the family of glucides disaccharides, 370 consisting of two glucose molecules bonded by an oxygen atom [66]. The degradation of maltose 371 during photocatalytic process (visible light) was evaluated by measuring absorbance changes at 372 the wavelength of 268 nm (Figure 14a).

373

Figure 14 374 Figure 14

375

After 4 hours of visible light irradiation, a degradation of maltose equal to 50% was observed. In parallel photocatalytic hydrogen production reached the value of about 2128 μ mol/g_{cat} within four hours of irradiation (Figure 14b). These results confirm the applicability of the photocatalytic process also to a real wastewater and the possibility to valorize the wastewater obtaining hydrogen from the degradation of maltose under visible light.

381

4. Conclusions

Non-doped and Ru-doped LaFeO₃ nanoparticles were successfully synthesized by the solution combustion synthesis method. Characterization results showed the formation of orthorhombic perovskite type structure and that Ru^{3+} cation partially substitutes Fe³⁺ cation in the perovskite structure. Moreover the absorption edge of Ru-doped LaFeO₃ catalysts has a red shift and also a stronger absorption than the pure LaFeO₃ in the visible region due to the electronic transition from donor levels formed with Ru³⁺ to the conduction band of the host perovskite structure.

389 The highest photocatalytic glucose degradation and hydrogen production was observed for 0.4 mol% Ru-doped LaFeO₃ sample (0.47%Ru). Ru³⁺ in the crystalline structure of the LaFeO₃ 390 391 could act as electron scavengers preventing the holes-electrons recombination, and consequently 392 causing the enhancement of the photocatalytic activity. For Ru content higher than 0.47 mol%, the photocatalytic activity decreased because of the presence of RuO₂ on the catalyst surface. 393 394 Therefore 0.47 mol% of Ru loading is considered to be an optimal value for the studied reaction. 395 In particular, after 4 hours of UV irradiation with 0.47%Ru, glucose degradation and hydrogen 396 production were equal to 70% and 2179 µmol/g_{cat}, respectively.

397 Moreover the effect of the reactor configuration on the hydrogen production and degradation of 398 glucose was assessed. The results showed that with the same volume but reducing the diameter 399 of the photocatalytic reactor from 2.5 to 1.25 cm, the photonic transport was enhanced and 400 consequently the activity of the 0.47%Ru increased. In particular, under UV light, the hydrogen 401 production passed from 2179 to 3474 μ mol/g_{cat} and the glucose degradation was complete after 3 402 hours of irradiation.

403 The optimized 0.47%Ru has shown high efficiency also under visible light obtaining about 40% 404 of glucose degradation after 4 hours of irradiation and a hydrogen production equal to 1919 405 µmol/L. Finally the efficiency of 0.47%Ru photocatalyst under visible light was also tested on a 406 real wastewater from the brewing process; the results showed a hydrogen production equal to 407 2128 µmol/g_{cat} in 4 hours of irradiation denoting a good performance of the optimized 408 photocatalytic system also for the treatment of real wastewater with the aim to obtain the 409 simultaneously degradation and valorization (through hydrogen production) of organic 410 pollutants.

411

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531

Catalyst	Ru nominal amount [mol %]	Ru measured amount (XRF) [mol %]	Crystallite size (XRD) [nm]	Specific surface area [m²/g]	Band gap (UV-Vis DRS) [eV]
LaFeO ₃	0	0	37	4	2.12
0.12% Ru	0.12	0.11	29	5	2.08
0.23% Ru	0.23	0.19	30	5	2.04
0.38% Ru	0.37	0.35	30	5	2.01
0.47% Ru	0.47	0.49	29	5	1.98
0.70% Ru	0.70	0.72	31	5	1.85
1.16% Ru	1.16	1.22	28	5	1.90
2.33% Ru	2.33	2.43	30	5	1.72

Table 1. Summary of the characterization results



Figure 1. Experimental set up for photocatalytic tests



Figure 2. XRD spectra for undoped and Ru-doped LaFeO₃ in the range 20-70°



Figure 3. XRD spectra for undoped and Ru-doped LaFeO₃ in the range 29-35°



Figure 4. UV Vis DRS spectra for undoped and Ru-doped LaFeO₃





Figure 6. SEM image of $LaFeO_3$ (a) and 0.47% Ru (b) photocatalysts.



Figure 7. Behavior of glucose degradation and hydrogen production after 4 hours of irradiation for all the photocatalysts; light source: UV-LEDs; glucose initial concentration: 1000 mg/L; catalyst dosage: 1.5 g/L; solution volume: 80 mL.



Figure 8. Influence of reactor configuration on glucose degradation (a) and hydrogen production (b) with 0.47% Ru photocatalyst; light source: UV-LEDs; glucose initial concentration: 1000 mg/L; catalyst dosage: 1.5 g/L; solution volume: 80 mL.



Figure 9. Influence of catalyst dosage on glucose degradation and hydrogen production after 2 hours of irradiation; photocatalyst: 0.47%Ru; light source: UV-LEDs; glucose initial concentration: 1000 mg/L; photoreactor R2; solution volume: 80 mL.



Figure 10. Glucose degradation (a) and hydrogen production (b) as a function of irradiation time for different glucose initial concentrations; photocatalyst: 0.47% Ru light source: UV-LEDs; catalyst dosage: 1.5 g/L; photoreactor R2; solution volume: 80 mL.



Figure 11. Influence of initial glucose concentration on CO_2/H_2 molar ratio (a) and gluconic acid formed/glucose converted molar ratio (b) for different initial glucose concentrations; irradiation time: 4 h; photocatalyst: 0.47%Ru; light source: UV-LEDs; catalyst dosage: 1.5 g/L; photoreactor R2; solution volume: 80 mL.



Figure 12. Behavior of hydrogen and oxygen during the photocatalytic water splitting reaction. Photocatalyst: 0.47%Ru; light source: UV-LEDs; catalyst dosage: 1.5 g/L; photoreactor R2; solution volume: 80 mL.



Figure 13. Glucose degradation (a) and hydrogen production (b) during UV and visible light irradiation. Photocatalyst: 0.47% Ru; initial glucose concentration: 1000 mg/L; catalyst dosage: 1.5 g/L; photoreactor R2; solution volume: 80 mL.



Figure 14. Maltose degradation (a) and hydrogen production (b) from real wastewater. Photocatalyst: 0.47% Ru; light source: visible LEDs; catalyst dosage: 1.5 g/L; photoreactor R2; solution volume: 80 mL.



- 1. Enhanced H₂ production from glucose on Ru-doped LaFeO₃ under UV or visible light
- 2. The optimal Ru loading was found to be 0.47 mol %.
- 3. The photoreactor configuration strongly affects the photocatalytic performances
- 4. Good photocatalytic performanc also for the treatment of a real wastewater