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1
2 **H₂ Production from Formic Acid over Highly Stable and Efficient Cu-Fe-O spinel**
3 **Based Photocatalysts under Flow, Visible-Light and at Room Temperature Conditions**
4

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21
22 **Abstract**

23 Catalytic dehydrogenation of liquid organic hydrogen carriers (LOHC), such as formic acid
24 (FAc), is considered as a promising approach to safely store and easily transport hydrogen at
25 ambient conditions. Generally, this process suffers from low activity, low reaction
26 selectivity, low stability of the catalysts and/or the use of noble-metal based catalysts. In this
27 study, a highly efficient CuFe₂O₄-based photocatalyst is reported for the photocatalytic
28 dehydrogenation of FAc under visible light at room temperature and under continuous gas
29 flow. The effects of various factors such as composition of the catalysts and thermal
30 pretreatment are investigated along a series of samples. The synthesis, dispersion, oxidation
31 states, photo-electrochemical properties and performances of these materials were
32 investigated in details. A synergetic effect, with relatively high dehydrogenation selectivity
33 (77% with 6.6 mmol.g⁻¹.h⁻¹ of H₂ production) is obtained on the copper-rich samples
34 without any significant deactivation for two cycles of 20h/cycle. This study opens up a new
35 route to design new Cu-based photocatalysts as cost-effective materials for visible-light
36 driven photocatalytic dehydrogenation of FAc at room temperature.

37

38 **Keywords:** Photocatalysis, Hydrogen, LOHC, Formic acid, Dehydrogenation.

39

40 **1. Introduction**

41 Hydrogen represents a clean and promising energy vector which can efficiently replace
42 the widely used fossil fuels. However, hydrogen generation from renewable sources under
43 mild conditions and its storage in a safe and reversible manner remains challenging [1]. In
44 this respect, formic acid (FAc), as a liquid organic hydrogen carrier (LOHC), is an excellent
45 candidate for hydrogen storage due to its non-toxic character, its stability and its high
46 hydrogen content (4.4 wt.%) [2]. Furthermore, FAc is readily available from sources such as
47 biomass reforming, CO₂ hydrogenation and as a by-product/product of the chemical
48 industry [3]. Its decomposition can proceed by two ways:



50 (1)

51 and



53 (2)

54 Traditionally, expensive noble-metal based materials (i.e. Pd, Au, Ag, Pt) are used to
55 achieve an acceptable conversion of FAc into H₂ [4,5,6,7,8,9]. Some of these systems
56 operate at relatively high temperatures (100-350°C) which lead to a negative energy balance
57 (the energy involved in the process is being higher than that elaborated from the produced
58 hydrogen) [10]. Thereby, the selective photocatalytic dehydrogenation of FAc at room
59 temperature (RT) using renewable source of energy (sun/visible light) has recently emerged
60 as an outstanding alternative to the traditional thermal catalysts. Aside from noble metal-
61 based photocatalysts, the utilization of low-cost systems such as heterojunctions
62 (CdS/Fe₂O₃, MoS₂/CdS, Ni-Co/CdS, Ni₂P/Zn₃In₂S₆, MoP/Zn₃In₂S₆, etc.) [11,12], layered

63 [13] or core-shell structures (CdS/TNT, CdS@ZIF-8, CdS–ZnS, etc.) [14,15,16] has shown
64 enhanced performances ascribed to the efficient electron–hole pair separation. Among these
65 systems, there have been only few studies reporting the use of visible-light responsive
66 copper-based photocatalysts for hydrogen production from FAc [17,18,19]. In addition,
67 most of these studies investigate the photo-reforming of FAc in the liquid phase, where the
68 photocatalyst’s instability at low pH is the main drawback (oxidation of sulfur-based
69 catalysts, metal leaching, etc.) [17,18,19]. Recently, Zhang *et al.* investigated binary
70 CuO/TiO₂ heterojunction nanofibers for FAc photo-reforming in liquid phase under
71 simulated sunlight irradiation at RT [18]. It was found that hydrogen production (2 mmol.g⁻¹
72 h⁻¹) begins after 2 h of irradiation, defined as the induction period, due to the photo-
73 assisted reconstruction of binary heterojunctions (CuO/TiO₂) into a quaternary
74 (Cu/Cu₂O/CuO/TiO₂) system. More recently, a very cheap and simple CuO/TiO₂ mixture
75 has been used to produce hydrogen by solar light irradiation from a FAc solution at pH = 2.5
76 [19]. The system was able to produce 2.4 mmol.g⁻¹.h⁻¹ of H₂ in the first cycle (1 day) but
77 reduced to 1.6 mmol.g⁻¹.h⁻¹ after five cycles (5 days) due to the Cu leaching.

78 Alternatively, we have investigated a metal organic framework (MOFs) based materials for
79 photocatalytic dehydrogenation of FAc [20]. The post-metalation of the MOFs structure
80 with Cu and the in-situ restructuring of this latter during the reaction accounted for its high
81 activity and the high selectivity of the reaction. However, the investigation of new copper-
82 based catalysts, for FAc dehydrogenation, that can be easily synthesized from earth-
83 abundant elements, such as Cu and Fe, is still of great interest due to the complexity and the
84 cost of both synthesis procedure and activation process of MOF-based structures.

85 Therefore, and to overcome the previous cited limitations, we aim in this work to
86 investigate the dehydrogenation of FAc in vapor phase under continuous flow over low-cost
87 and one-pot synthesized iron-copper oxide based photocatalysts. In this context, the
88 CuFe₂O₄ spinel is a material which attracts much attention in photocatalysis due to its

89 effectiveness under visible light irradiation, redox properties, non-toxicity, low cost, room-
90 temperature magnetic behavior and high charge transfer [21,22,23]. To date, CuFe_2O_4 was
91 mainly used for the photocatalytic degradation of organic effluent in the presence of H_2O_2 ,
92 (Fenton-like reaction) [21-27] and water splitting [28]. Herein, we investigate for the first
93 time the photocatalytic activity and stability of CuFe_2O_4 -based systems for a vapor-phase
94 dehydrogenation of FAc under visible-light irradiation at room temperature. The stability of
95 the photocatalysts, the effect of Cu:Fe ratio and the impact of the thermal treatment used to
96 prepare the materials were tested during this reaction. The nominal Cu:Fe ratios (1:11, 1:3,
97 1:2, and 2:1) are used in the following as a labeling of the samples for more clarity. The
98 preparation of the samples, the physicochemical and photo-electrochemical properties of the
99 catalysts were deeply inspected using *in-situ* X-ray powder diffraction (XRPD), scanning
100 electron microscopy coupled with energy dispersive X-ray (SEM-EDX), UV-Vis diffuse
101 reflectance (DR-UV-Vis), X-ray photoelectron spectroscopy (XPS) and potentiometry.
102 Then, the photocatalytic activity is explored using Fourier transform infrared (FTIR)
103 *operando spectroscopy*. Finally, a tentative mechanism of the reaction is proposed.

104 **2. Experimental part**

105 **2.1. Materials**

106 Iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; $\geq 98\%$), copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$; $\geq 99.99\%$), sodium
107 hydroxide pellets ($\geq 99.9\%$), maize starch ($(\text{C}_6\text{H}_{10}\text{O}_5)_n$), ascorbic acid ($\geq 99\%$), formic acid
108 ($\geq 99\%$) and acetic acid ($\geq 99.8\%$) were all purchased from Sigma Aldrich. Distilled water
109 and absolute ethanol were used as solvents. Commercial SiO_2 (Ultrasil 5500 GR) and Fe_2O_3
110 (99.5%) were used as received from Evonik-Degussa and Alfa Aesar, respectively.

111 **2.2. Catalyst synthesis**

112 It should be noted that all the syntheses reported in this study were reproduced at least twice
113 to attest of their reproducibility.

114 *Synthesis of CuFe_2O_4 -based catalysts with Cu:Fe ratios 1:11, 1:3, 1:2, and 2:1:*

115 These samples were synthesized by the starch-assisted sol-gel auto-combustion method
116 [29]. The desired amounts of iron nitrate and copper nitrate were dissolved in distilled water
117 to obtain a homogeneous solution. Then, an aqueous solution of starch ($C_6H_{10}O_5$)_n was
118 mixed with the metal-nitrate solution. The obtained mixture was heated at 100°C under
119 continuous stirring until the formation of a viscous brown gel. Then, the gel was heated at
120 180°C for 4 h to initiate a self-sustaining combustion reaction and produce the precursor.
121 The precursors were further ground to powder, and finally heated in air at various
122 temperatures as described in the following (*section 3*).

123 *Synthesis of CuO, Cu₂O, Cu₂O/Cu⁰ (used as reference material):*

124 CuO was synthesized using a chemical precipitation method described elsewhere [30].
125 Cu(NO₃)₂ solution (300 mL 0.02 M) was prepared and heated at 100°C under vigorous
126 stirring. Then, 0.5 g of solid NaOH was rapidly added resulting in the production of a
127 considerable amount of black precipitates. Next, the precipitates were heated at 100°C for
128 20 min under ambient atmosphere. The resulting products were then centrifuged, washed
129 with water and ethanol several times, and then dried in air at room temperature.

130 Cu₂O was synthesized using a hydrothermal method described elsewhere [31].
131 Cu(NO₃)₂·3H₂O (181.2 mg) was dissolved in 30 mL of anhydrous absolute ethanol in a
132 Teflon flask under vigorous stirring. After dropwise addition of acetic acid (1.5 mL), the
133 solution was ultrasonicated for 5 min and transferred to a Teflon-lined stainless-steel
134 autoclave (capacity 40 mL) to reach 80% filling. The reaction was performed at 180°C for 2
135 h. The brick red powder was then collected and washed several times with distilled water
136 and ethanol, and dried in air at 60°C for 12 h.

137 In a typical procedure for the synthesis of Cu₂O/Cu [32], 0.4 g of NaOH was added to 100
138 mL of 0.1 M Cu(NO₃)₂·3H₂O under magnetic stirring. After complete dissolution of NaOH,
139 2 g of ascorbic acid were added and stirred for 30 min at room temperature. During the

140 process, the color of the solutions changed from blue to brown colors. The precipitate was
141 washed several times with water and ethanol and finally dried overnight at 60°C.

142

143 **2.3. Characterization**

144 XRPD analysis of Cu:Fe oxides as well as the reference materials (CuO, Cu₂O, Cu₂O/Cu⁰
145 and Fe₂O₃, Fig. S 1) were carried out in PANalytical X'Pert Pro diffractometers with either
146 Co K α 1/ K α 2 ($\lambda = 1.7892 \text{ \AA}/1.7932 \text{ \AA}$ with ratio 0.5) or Cu K α 1 irradiation ($\lambda = 1.5406 \text{ \AA}$)
147 at room temperature. Additional XRPD patterns were collected during *in situ* high-
148 temperature synthesis in a Rigaku SmartLab diffractometer, equipped with a rotating anode
149 source (45 kV, 200 mA, $\lambda = \text{Cu K}\alpha 1/\text{K}\alpha 2$ with ratio 0.4970) and a HyPix-3000 detector in
150 1D mode. Measurements were performed in Bragg-Brentano geometry at constant
151 temperatures and also while heating from 500 to 900°C at a 1°C.min⁻¹ rate in an Anton Paar
152 XRK900 chamber, with an Inconel sample holder. For these *in-situ* experiments, the
153 precursors were previously heated *ex-situ* at 500°C overnight under air to avoid uncontrolled
154 combustions in the reaction chamber of the diffractometer.

155 Nitrogen adsorption/desorption measurements were performed with an ASAP 2020 MP
156 instrument. The specific surface area was calculated with the Brunauer-Emmett-Teller
157 (BET) equation, while the pore volumes were determined by the Barrett-Joyner-Halenda
158 (BJH) method (Table S1). Prior to the measurements, samples were degassed *in vacuum* at
159 300 °C for 3 h.

160 The content and distribution of Cu and Fe were determined by SEM-EDX on a JEOL JSM-
161 5500LV microscope or a MIRA TESCAN microscope (Table S1). The images were
162 collected with an acceleration voltage of 30 kV. Advanced transmission electron
163 microscopy (TEM) was carried out on an aberration probe, and image corrected JEM
164 ARM200F cold FEG microscope operated at 200 kV equipped with a CENTURIO EDX
165 detector and GIF Quantum spectrometer. The metal contents were also verified by a Varian

166 ICP-OES 720-ES inductively coupled plasma spectrometry (ICP). The Cu:Fe ratios
167 measured by ICP (Table S1) confirm the nominal ones.

168 XPS measurements were carried out on an AXIS Supra electron spectrometer (Kratos
169 Analytical Ltd.) with base vacuum in the analysis chamber in the order of 10^{-8} Pa. The
170 samples were irradiated with monochromatized Al K α radiation with photon energy of
171 1486.6 eV. The photoemitted electrons were separated according to their kinetic energy by a
172 180 o-hemispherical analyzer with a total instrumental resolution of 0.6 eV (as measured by
173 the FWHM of Ag 3d $_{5/2}$ line) at pass energy of 20 eV. Energy calibration was performed by
174 normalizing the C 1s line of adventitious adsorbed hydrocarbons on silver folio to 284.6 eV.
175 The analysis area was 700x300 μm^2 . DR-UV-Vis measurements relevant to Cu speciation
176 were carried using a Cary 4000 UV-Vis spectrophotometer and a HARRICK Praying
177 Mantis diffuse reflectance accessory. All spectra were recorded between 200-800 nm using
178 an average time of 0.2 s and a scan rate of 300 nm.min $^{-1}$.

179 Both electrochemical and photoelectrochemical experiments were performed by using a
180 potentiostat Autolab PGSTAT302N in two-compartment cell and in three-electrode
181 configuration. The cathodic compartment was physically separated from the anodic one by a
182 proton exchange membrane (Nafion 117; thickness 0.007 in). The fluorine-doped tin oxide
183 covered glass (FTO) was utilized as a conductive substrate for working electrode (geometric
184 area 0.71 cm 2), Pt wire was applied as counter electrode and mercury sulfate electrode
185 (Hg/Hg $_2$ SO $_4$ /sat. K $_2$ SO $_4$) as reference electrode. Potentials were converted to the reversible
186 hydrogen electrode (RHE) reference scale. The aqueous electrolyte solutions used were 0.1
187 mol.dm $^{-3}$ Na $_2$ SO $_4$ at pH = 6.4 after saturation in argon. For photoelectrochemical
188 experiments, the solar simulator (Quantum Design Model LSE341) used as a light source is
189 equipped with 300 W Xe lamp (light intensity = 100 mW.cm $^{-2}$) and AM 1.5 Global filter.
190 The photocurrent vs. time curves were measured with a potential sweep of 10 mVs $^{-1}$ at the
191 imposed potential of 0.0V vs. RHE under chopped light. The electrochemical experiments

192 were performed by scanning the potential from 1.02 V to 0.0 V vs. RHE (at 10 mV.s⁻¹).
193 Catalyst solutions were prepared by suspending 10 mg of photocatalyst in a mixture of 20
194 μ L Nafion solution (0.5 wt%) and 200 μ L of ethanol followed by sonification for 30 min.
195 Thereafter, 20 μ L of the sample solution was pipetted onto the FTO surface (geometric area
196 0.71 cm²) followed by drying at 80°C for 10 min.

197 **2.4. Photocatalytic test**

198 For the *operando* experiments, a ‘sandwich-like’ IR cell-reactor (scheme S1) was used to
199 study the performances of the different Cu-Fe based materials during the
200 photodecomposition of formic acid under visible light irradiation at room temperature (25
201 °C), as detailed in Ref. [33,34]. Due to magnetic aggregation in some of the samples, it was
202 difficult to prepare a self-supported pellet. Thus, the powders were mixed (50/50 wt.%) with
203 an inert/non-active SiO₂ support (Ultrasil 5500 GR, Evonik-Degussa) for preparing thin
204 pellets of \approx 20 mg. The catalyst was activated in argon gas at RT under visible irradiation
205 using a Xe lamp (LC8 Hamamatsu, 71 mW.cm⁻² of irradiance) with a pass-high filter >390
206 nm. Then, the reaction was studied in the presence of 2600 ppm of FAc (0.26 vol.%) with a
207 total flow rate of 25 cm³.min⁻¹ in argon. The relative concentrations of the effluent gases
208 were stabilized before being sent to the cell, then an adsorption step of FAc on the catalyst
209 surface was performed under dark conditions. Finally, the composition of the output gas
210 from the IR reactor cell was analyzed simultaneously by mass spectrometry (MS)
211 (Quadrupole Pfeiffer Omnistar GSD 301) and IR spectroscopy (ThermoNicolet NEXUS 670
212 FTIR) equipped with a mercury cadmium telluride (MCT) detector with a spectral
213 resolution of 4 cm⁻¹ and accumulating 64 scans. The evolution of FAc concentration in the
214 gas phase was monitored using the surface area of IR band at 1109–1101 cm⁻¹ and the FAc
215 MS signal ($m/z = 45$ and 46). The selectivity of CO₂ and CO were determined using the IR
216 band areas at 2395–2182 cm⁻¹ and 2140–2020 cm⁻¹, respectively. The amounts of hydrogen
217 were determined using the MS signal at $m/z = 2$ after correction from water contributions

218 and the results were confirmed by online gas chromatography (GC) analysis of the gas
 219 phase products at the steady-state using a Compact GC^{4.0} equipped with 3 analysis channels.
 220 The first thermal conductivity detector (GC-TCD, Interscience) is equipped with a
 221 Molseive5 A (25 m × 0.32 mm) and Rt-QBond (3 m × 0.32 mm) columns for respectively
 222 analyzing of O₂, N₂, CH₄, CO and CO₂ using helium as a carrier gas. The second TCD
 223 channel is equipped with Rt-QBond (3 m × 0.32 mm) and argon as a carrier gas for H₂
 224 analysis. The third channel with flame ionization detector (FID) and He as carrier gas
 225 equipped with Rt-QBond (25 m × 0.32 mm) column for hydrocarbons (HC) detection (C₁-
 226 C₆). The peak areas of CO₂, CO and H₂ were converted into concentrations by using their
 227 calibration curves (Fig. S 2) (operating conditions: split flow rate = 5 mL.min⁻¹ for both
 228 TCD and 10 mL.min⁻¹ for FID; inlet temperature 80°C; column temperature 60°C for O₂,
 229 N₂, CH₄, CO and CO₂, 50°C for H₂ and 45°C for HC).

230 The FAc conversion (expressed in % or mmol per g of photocatalyst per hour per irradiated
 231 surface) and the selectivity (%) were calculated from Equations 3-6, at the steady-state using
 232 the calibration curve for different products of the reaction (Fig. S 2). The apparent quantum
 233 yield was calculated using the actinometer method as detailed in the SI (Fig. S 3). It should
 234 be noted that the irradiated surface of the pellet is about 1.6 cm². The FAc conversion and
 235 conversion rates are calculated as follows:

$$236 \text{ FAc conversion (\%)} = \frac{[\text{FAc}]_0 \text{ (ppm)} - [\text{FAc}]_t \text{ (ppm)}}{[\text{FAc}]_0 \text{ (ppm)}} \times 100$$

237 (3)

$$238 \text{ Conversion rate (mmol.g}^{-1}.\text{ h}^{-1}\text{)} = \frac{\text{Total flow(L.h}^{-1}\text{)} \times [\text{FAc}]_0 \text{ (ppm)} \times 10^{-6} \times \frac{\text{conversion \%}}{100} \times 1000}{M_{\text{FAc}}(\text{g.mol}^{-1}) \times \frac{1}{d_{\text{FAc}}}(\text{L.g}^{-1}) \times m_{\text{catalyst}}(\text{g})} \quad (4)$$

$$239 \text{ Conversion in mmol.g}^{-1}.\text{ h}^{-1}.\text{ cm}^{-2} = \frac{\text{Conversion rate (mmol.g}^{-1}.\text{ h}^{-1}\text{)}}{S_{\text{irradiated}}(\text{cm}^2)} \quad (5)$$

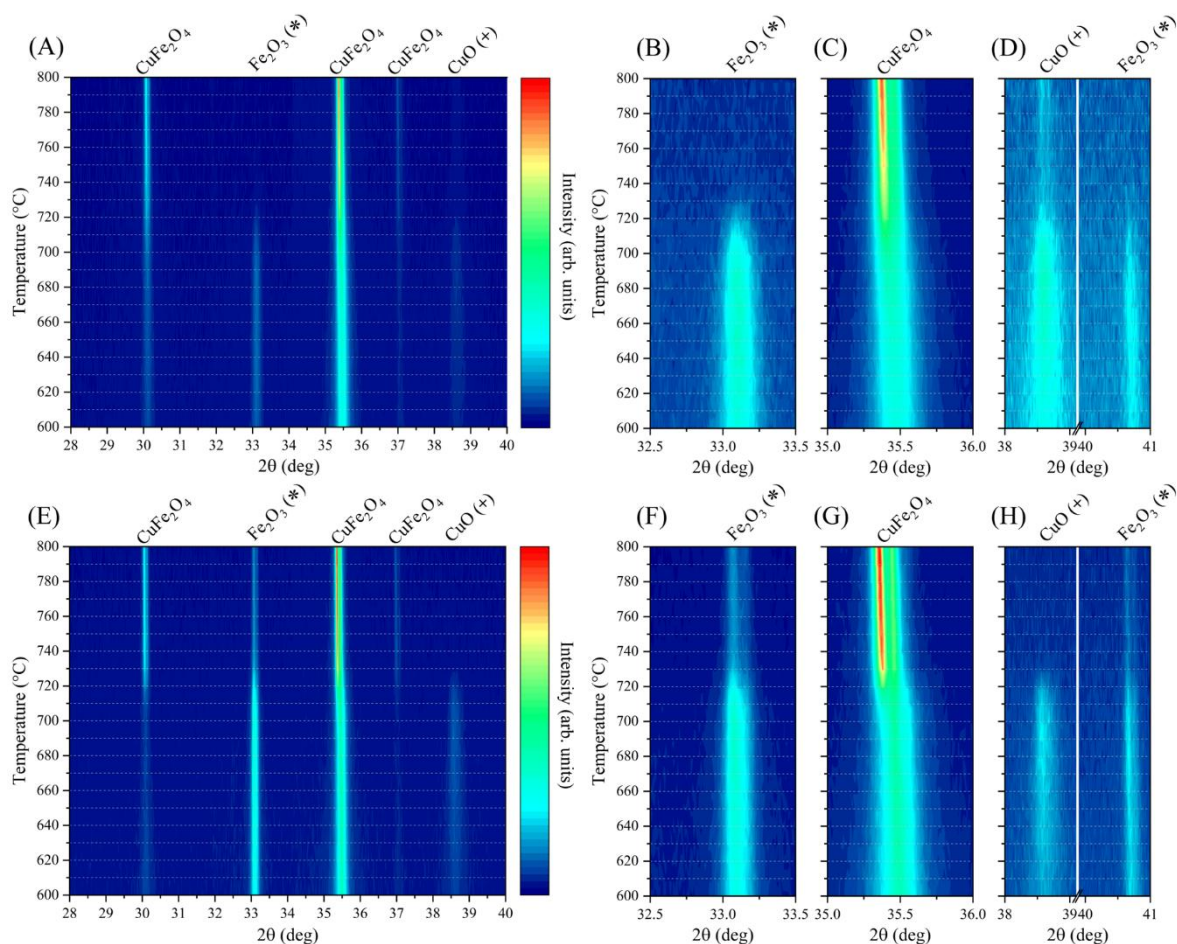
$$240 \text{ Selectivity (\%)} = \frac{\text{Concentration of target product (ppm)}}{\text{Concentration of FAc converted (ppm)}} \times 100, \text{ with target product} = \text{H}_2/\text{CO}_2 \text{ or CO} \quad (6)$$

242 **3. Results and discussion**

243 **3.1. Catalysts Characterizations**

244 To guide the preparation of samples starting from precursors prepared by sol-gel, *in-situ*
245 XRPD experiments were conducted on samples with Cu:Fe ratio 1:2 and 1:3. The full
246 results are shown in Fig. 1A and 1E up to 800°C, respectively. No further changes were
247 observed above this temperature beyond the expected thermal expansion of the materials.
248 These temperature-dependent plots show that the initial mixes (at 600°C) already contain
249 phases similar to the desired CuFe₂O₄ spinel together with the binary oxides Fe₂O₃ and
250 CuO. The CuFe₂O₄ spinel undergoes a reversible structural phase transition from tetragonal
251 (space group *I4₁/amd*) to cubic (space group *Fd-3m*) at approximately 390°C [35], meaning
252 that in Fig. 1 all spinel peaks are indexed in the high-temperature cubic phase. In the sample
253 with Cu:Fe ratio 1:2 (Fig. 1A), the peaks of the binary oxides markedly decrease with
254 heating until disappearing above 720°C (Fig. 1B and 1D), concurrently with an increase in
255 the intensities and decrease in the width of the Bragg peaks corresponding to CuFe₂O₄ (Fig.
256 1C), usually associated with an increase of the amount of phase and of its crystallinity,
257 respectively. In this sample prepared from a precursor with Cu:Fe ratio 1:2, only traces of
258 CuO can be detected after the high-temperature treatment, resulting in a product consisting
259 of an overwhelming majority of CuFe₂O₄. On the other hand, for the material obtained from
260 the Cu:Fe 1:3 precursor (Fig. 1E), peaks of Fe₂O₃ only decrease up to 800°C (Fig. 1F and
261 1H), without completely disappearing. This shows a similar formation of the CuFe₂O₄
262 spinel, with the excess of Fe from the precursor (compared to the CuFe₂O₄ formula)
263 remaining as additional Fe₂O₃ until very high temperatures (900°C) (Fig. 1F). In this sample
264 and contrary to the observations of the Cu:Fe 1:2 sample, no excess of CuO is detected after
265 the high-temperature treatment (Fig. 1H). These results demonstrate that changing the Cu:Fe

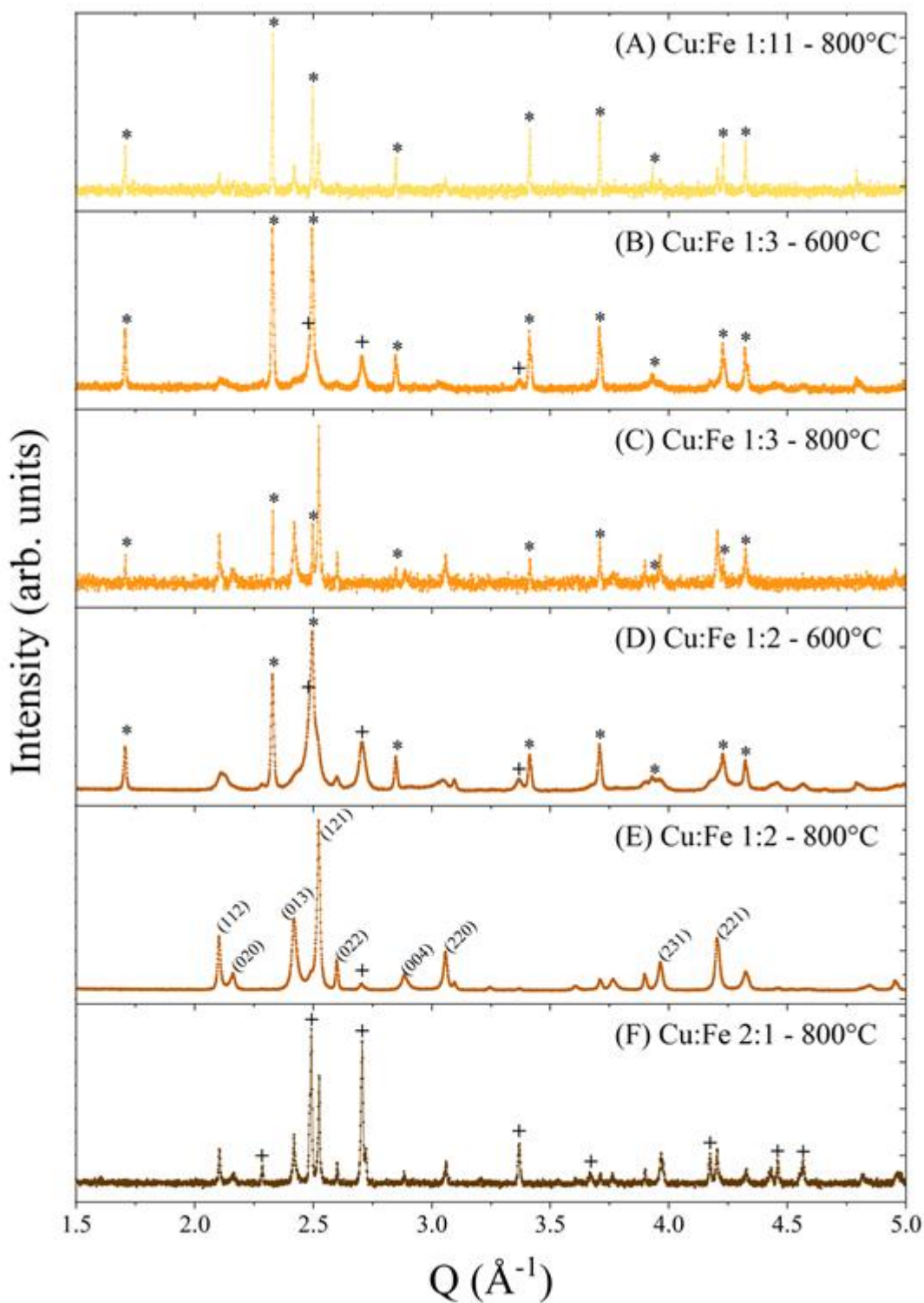
266 ratio from 1:2 to 1:3 drastically modifies the final constituents of the samples after thermal
 267 treatments. Heating mixtures of copper and iron oxides outside the 1:2 Cu:Fe ratio always
 268 results in CuFe_2O_4 plus an excess of the more abundant binary oxide. This is in accordance
 269 with early observations by Milligan and Holmes [36] who showed that non-stoichiometry
 270 does not occur in this spinel.



271
 272 **Figure 1.** (A) Temperature-dependent XRPD for *in-situ* synthesis of CuFe_2O_4 from a Cu:Fe
 273 1:2 precursor. (B-C-D) Details of peaks highlighting the evolution of Fe_2O_3 , CuFe_2O_4 and
 274 CuO, respectively. (E) Temperature-dependent XRPD for *in-situ* synthesis from a Cu:Fe 1:3
 275 precursor. (F-G-H) Details of peaks highlighting the evolution of Fe_2O_3 , CuFe_2O_4 and CuO,
 276 respectively. Marked peaks correspond to Fe_2O_3 (*) ($R\bar{3}c$ space group) or CuO (+) ($C2/c$
 277 space group). Arbitrary scales are independent between panels.

278
 279 Considering the *in-situ* experiments, samples with different Cu:Fe ratios and thermal
 280 treatment temperatures were prepared *ex-situ* to obtain catalysts with or without excess of
 281 the binary oxides. The sample with Cu:Fe 1:11 (Fig. 2A) was prepared with a clear excess

282 of Fe in the mixture with respect to the ideal copper iron spinel composition, and thus
283 results in a sample mainly composed of Fe_2O_3 , together with a small amount of CuFe_2O_4 . In
284 a similar manner, results for the Cu:Fe 1:3 mixture always show a strong presence of Fe_2O_3
285 (Fig. 2B and 2C) regardless of thermal treatment. However, in contrast with the previous
286 case, the spinel is the main phase in the high-temperature sample. In addition, CuO cannot
287 be detected, suggesting that all Cu resides within the CuFe_2O_4 spinel. Results for Cu:Fe 1:2
288 are shown in Fig. 2D (600°C) and 2E (800°C). In the low-temperature sample, CuFe_2O_4
289 peaks are identifiable, with additional Fe_2O_3 and CuO. When the temperature is increased to
290 800°C, the CuFe_2O_4 spinel clearly becomes the main phase together with a trace amount of
291 remaining CuO. Results for both *ex-situ* synthesis of Cu:Fe 1:2 and Cu:Fe 1:3 are in line
292 with those obtained during *in-situ* experiments. As shown in Fig. 1E-F, the samples obtained
293 from the Cu:Fe 1:3 precursor are always mixed with an excess of Fe_2O_3 . This marks a
294 strong difference between these two samples treated at high temperatures, as Cu:Fe 1:2
295 precursor produces samples with a negligible, trace amount of binary CuO, while the Cu:Fe
296 1:3 precursor generates a mixed sample with a marked presence of binary Fe_2O_3 . An
297 additional sample was prepared with Cu:Fe ratio 2:1, which is found to contain a large
298 amount of CuO together with CuFe_2O_4 as a secondary phase, producing a sample in which
299 most of the Cu now lies in the form of binary copper oxide.

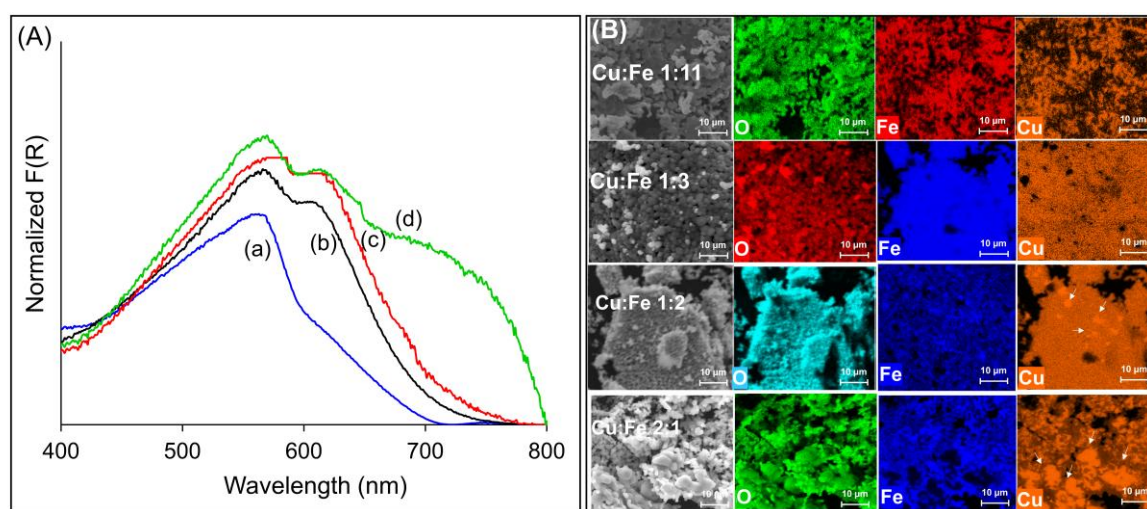


300

301 **Figure 2.** RT XRPD patterns for catalysts obtained from precursors with different Cu:Fe
 302 ratios and synthesis temperatures. Unmarked peaks correspond to CuFe_2O_4 (tetragonal,
 303 space group $I4_1/amd$), marked peaks correspond to Fe_2O_3 (*) ($R\bar{3}c$ space group) or CuO (+)
 304 ($C2/c$ space group). The indexation of the main Bragg peaks of the spinel is given in panel
 305 (E) as it corresponds to a near single-phase sample. As patterns were collected in different
 306 diffractometers with different X-ray sources, they are presented as a function of Q to
 307 facilitate the comparison.

308

309 The UV-Vis diffuse reflectance analysis of samples with various nominal Cu:Fe ratios and
 310 thus different constituents demonstrates that their optical behavior depends-on the involved
 311 phases (Fig. 3A and S 4). Starting from the Cu:Fe 1:11 sample, the increase of Cu content
 312 results in an increase of the band intensity at 567 nm, attributed to CuFe_2O_4 [37], with a
 313 redshift for the Cu:Fe 1:3 sample in respect to 1:11. An additional broad absorption band
 314 appears at around 690 nm for the 1:2 sample and becomes more intense for the 2:1 sample.
 315 It can be attributed to Cu^{2+} electron d-d transitions in distorted CuO_6 octahedra of CuO [38],
 316 as detected by XRPD. The presence of copper oxide in the Cu-rich samples is also
 317 confirmed by SEM (Fig. 3B). Contrary to the samples with Cu:Fe ratio lower than 1:2, the
 318 Cu:Fe 1:2 sample reveals the existence of copper oxide islands whose quantity increases in
 319 the 2:1 sample. The presence of excess of Cu in the Cu:Fe 1:2 was also confirmed by HR-
 320 TEM analysis (Fig. S5).



321
 322 **Figure 3.** (A) DR-UV-Vis spectra of (a) 1:11, (b) 1:3, (c) 1:2 and (d) 2:1 Cu:Fe samples.
 323 (B) SEM and elemental mapping analysis of Cu:Fe 1:11, 1:3, 1:2 and 2:1 samples.

324

325 **3.2. Photocatalytic activity**

326 First, the photocatalytic reforming of FAc was investigated upon Cu:Fe 1:2 sample treated
 327 at 600°C and 800°C. The catalytic tests were conducted under visible light irradiation at
 328 room temperature with an initial FAc concentration of 2600 ppm (~0.26%) in Ar
 329 atmosphere and with total flow of $25 \text{ cm}^3 \cdot \text{min}^{-1}$. Each experiment was repeated at least two

330 times with an estimated relative error of less than 7%. The FAc conversions as well as the
 331 produced amounts of H₂, CO₂ and CO, and their corresponding selectivity are summarized
 332 in Table 1.

333 CuFe₂O₄ treated at 600°C shows very low activity while it is around 9 times higher for the
 334 same catalyst treated at 800°C and tested under similar conditions (Table 1). The
 335 dehydrogenation (Eq. 1) selectivity is about 77 % (Table 1, Fig. S 6-7) vs. 23% of
 336 dehydration (Eq. 2). The molar conversion rates of FAc are almost equal to the sum of CO₂
 337 (or H₂) and CO, demonstrating the absence of other carbon beside products. This result
 338 reveals that the effect of the treatment temperature is very significant. As discussed
 339 previously, the composition of the two catalysts changes with the preparation temperature,
 340 as the 600°C sample still contains relatively high quantities of Fe₂O₃ and CuO, while only
 341 trace amounts of the latter remain in the 800°C sample; this explains their different
 342 photocatalytic behavior. Based on this, 800±25°C is chosen as the optimum calcination
 343 temperature of Cu-Fe spinel samples with different Cu:Fe ratio.

344 **Table 1.** Results of the activity and reaction selectivity of the FAc reforming at the steady
 345 state over the catalysts with different Cu:Fe ratios and treatment temperatures.^a

Cu:Fe ratio (treatment temperature in °C)	Conv.% ^b	Conversion rate (mmol.g ⁻¹ .h ⁻¹ .cm ⁻²) ^c	H ₂ (mmol.g ⁻¹ .h ⁻¹ .cm ⁻²)	CO ₂ (mmol.g ⁻¹ .h ⁻¹ .cm ⁻²)	CO (mmol.g ⁻¹ .h ⁻¹ .cm ⁻²)	dehydroge nation selectivity (%)	apparent quantum yield %
1:11 (800)	1.5	0.17	n.d ^d	n.d	n.d	n.d	n.d
1:3 (800)	1.9	0.20	n.d	n.d	n.d	n.d	n.d
1:2 (600)	5.6	0.60	0.47	0.60	n.d	n.d	n.d
1:2 (800)	47.4	5.22	4.14	4.23	1.41	77	9.0
2:1 (800)	51.5	5.56	4.10	4.30	1.54	76	9.9

346 ^aReaction conditions: [FAc]=2600 ppm (0.26%) in Ar; total flow 25 cm³.min⁻¹; T=25 °C; Xe-lamp 150 W with
 347 visible light pass filter (λ>390 nm); irradiance=71 mW.cm⁻²; mcat=10 mg+10mg of inert silica (self-supported
 348 pellet with irradiated surface of 1.6 cm²); reaction time =17 h.

349 ^b relative conversion error is ± 7%

350 ^c unit expressed in mmol per g of catalyst (m_{cat}=10 mg) per hour per cm² of irradiated surface (1.6 cm²).

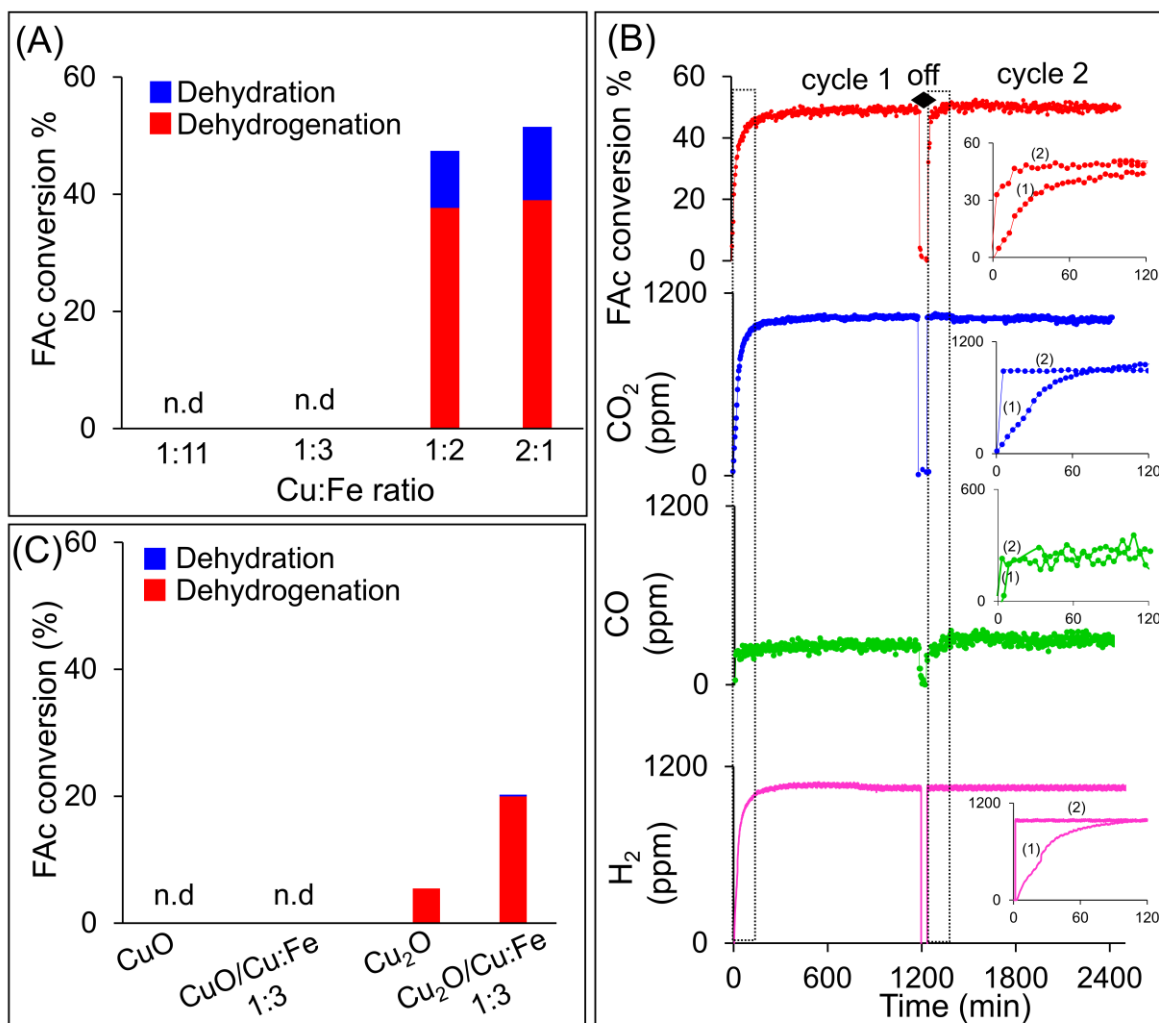
351 Values should be multiplied by 1.6 cm² for a rate in mmol.g⁻¹.h⁻¹.

352 ^dn.d. non determined (under the detection limit of the apparatus).

353
 354

355 For better understanding the CuFe_2O_4 catalyst behaviors, additional photocatalytic tests
356 have been performed over samples with Cu:Fe ratios 1:11, 1:3 and 2:1 after their calcination
357 at 800 °C using similar reaction conditions to those for Cu:Fe (1:2). The results, assembled
358 in Figure 4A and Table 1, demonstrate that samples with Cu:Fe 1:11, and 1:3 do not exhibit
359 any significant activity towards H_2 production from formic acid (< 2%), revealing that
360 samples with additional Fe_2O_3 have their photocatalytic activities noticeably hindered. This
361 is confirmed by characterizing additional samples synthesized from a Cu:Fe ratio ranging
362 between 1:11 and 1:3 (e.g. Cu:Fe = 1:5) that did not show any activity (the results are not
363 shown here for the sake of brevity). From these preliminary results, it can be inferred that
364 the presence of extra- spinel-structure Cu species beyond CuFe_2O_4 spinel is crucial for the
365 photocatalytic activity of the samples (Cu:Fe (1:2) and (2:1)). However, it seems that the
366 presence of extra-structure iron species (e.g. Fe_2O_3) didn't make the CuFe_2O_4 spinel
367 photocatalytically active for the conversion of FAc (Cu:Fe (1:11), (1:5) and (1:3)). On the
368 other hand, the similar results obtained over Cu:Fe (2:1) in respect to Cu:Fe (1:2) indicate
369 that the excess of CuO (Cu:Fe 2:1) is not enhancing the photocatalytic activity. In what
370 follows, we will focus on two main samples for highlighting the origin of the photocatalytic
371 activity: the non-active Cu:Fe (1:3) and the highly active Cu:Fe (1:2).

372 The time-dependent FAc conversion over Cu:Fe 1:2 has been then investigated for two
373 successive cycles with 20 h of visible light irradiation per cycle separated by 1 h of dark
374 (Fig. 4B). The first cycle manifests an induction period before reaching a steady state after
375 1 h with similar profiles of FAc conversion and CO_2/H_2 production.



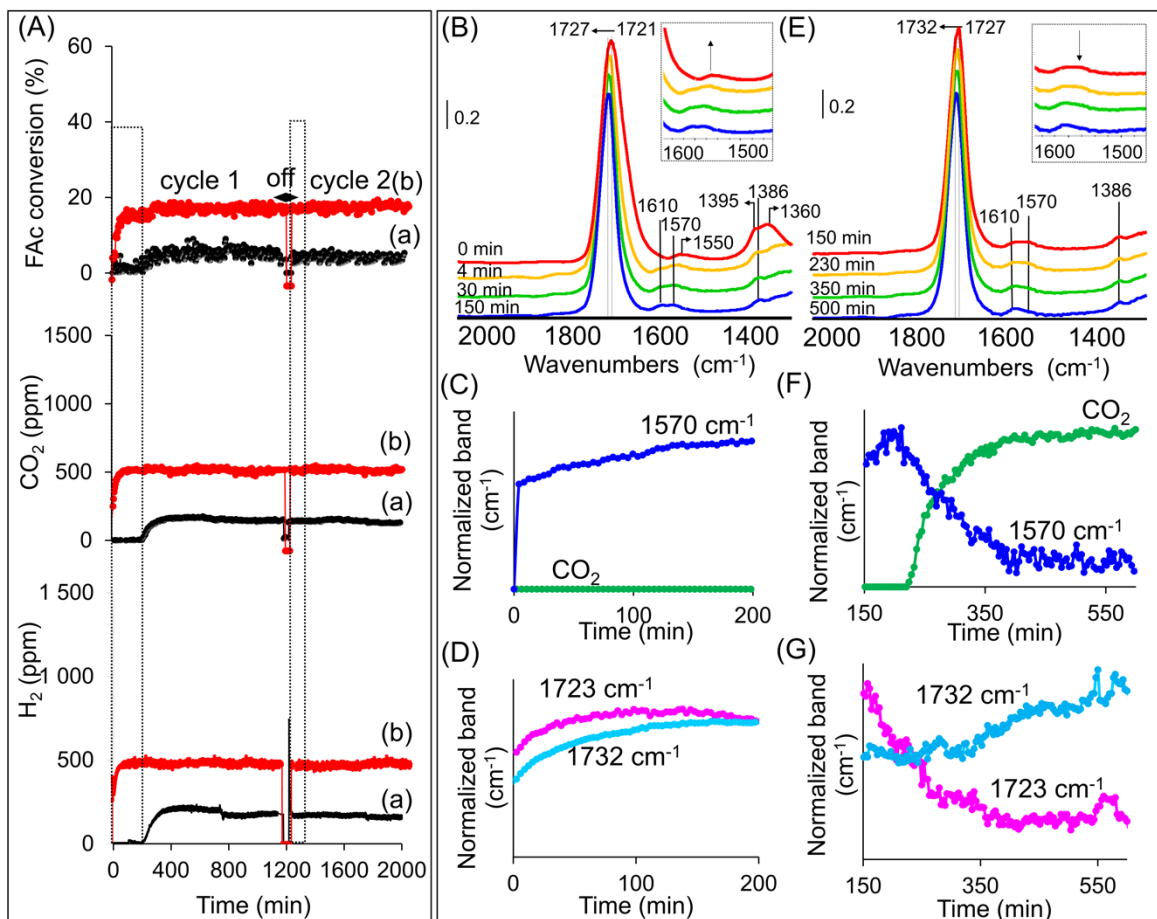
376
 377 **Figure 4.** (A) FAc conversion (%) and the corresponding selectivity (%) at $t = 17$ h of
 378 reaction over samples with different Cu:Fe ratios treated at 800°C . (n.d. = non detected) (B)
 379 Evolution of the FAc conversion (%) and the corresponding gas phase products (CO_2 , CO
 380 and H_2) during the FAc photo-reforming over Cu:Fe 1:2 under visible irradiation at RT.
 381 Insert: zooming on the early period of the reaction during first (1) and second (2)
 382 cycle (dotted zones). (C) FAc conversion (%) and the corresponding selectivity (%) at $t = 17$ h of
 383 reaction over CuO, Cu_2O and their 1:1 mixture with Cu:Fe 1:3.

384 A comparable behavior with an equivalent induction period is observed for the Cu:Fe 2:1
 385 sample (Fig. S 8). The presence of an induction time indicates an *in-situ* structuring of the
 386 catalyst. Taking into account our recent work, Cu^{2+} reduction to Cu^{+0} clusters is very
 387 probable [20]. This induction period totally disappears in the 2nd cycle and the FAc
 388 conversion spontaneously reaches the steady state after irradiation (see Inserts Fig. 4B).
 389 Importantly, the results reveal the absence of any significant deactivation of the catalyst
 390 tested constantly for two days. To the best of our knowledge, this activity (around 6.6
 391 $\text{mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ of H_2 production) is the highest for a dehydrogenation of FAc under visible

392 light irradiation at room temperature when comparing to other Cu-based materials reported
393 in literature (Table S 4). Nevertheless, it is important to mention that the comparison
394 between different works is approximate and could not be absolute due to differences in
395 various factors (liquid phase and batch vs. vapor phase and under flow condition (our work),
396 reactor geometry, intensity, wavelength and surface of irradiation, reaction conditions, and
397 the absence of information on the photocatalyst stability in some studies).

398 To gain further insight on the active sites of Cu:Fe 1:2 catalyst treated at 800°C, other Cu-
399 containing oxides were considered and tested towards H₂ production from FAc under
400 similar experimental conditions. Particularly, CuO and Cu₂O were tested separately and also
401 in 1:1 mixtures with the Cu:Fe 1:3 catalyst. The Cu:Fe 1:3 sample was chosen due to the
402 absence of extra-framework copper oxide. The results are presented in Fig 4C and
403 summarized in Table S2. Even though CuO is characterized by narrow band gap and high
404 absorption in visible range of solar spectrum [18,39], this oxide alone or in a mixture with
405 Cu:Fe 1:3 does not show any H₂ generation. This is probably because of its unsuitable
406 conduction band (CB) position (~ +0.35 V vs. NHE at pH = 3) situated below the reduction
407 potential of H⁺/H₂ (-0.18 V vs. NHE at pH = 3) (scheme S 2) [18]. Meanwhile, Cu₂O
408 displays a low photocatalytic activity with 5.6 % of FAc conversion and almost 100% of
409 dehydrogenation selectivity at the steady state (Fig. 4C). The low efficiency of Cu₂O is
410 attributed to the fast recombination of electron-holes charge carriers (scheme S 2) [40].
411 However, the evolution of the conversion versus the irradiation time reveals a significant
412 induction period without any photocatalytic activity for more than 3.5 h (vs. <1 h for Cu:Fe
413 1:2), followed with a progressive increase in the activity until reaching the steady state at ~5
414 h (Fig. 5A). Interestingly, a fourfold enhanced photocatalytic activity with respect to Cu₂O
415 (5.6 % of FAc conversion) is obtained by mixing Cu₂O with Cu:Fe 1:3 (about 20 % of FAc
416 conversion at steady state) with a shorter induction period (~0.5 h) and a similar behavior in
417 the second cycle (Fig. 5A). Moreover, a minor amount of CO was detected for this mixture

418 (Fig. S 9), suggesting that CO production mainly occurred on copper iron spinel rather than
419 on Cu₂O, being characterized by a high selectivity towards dehydrogenation. We should
420 underline that these results could not be compared directly with the spinel-based samples as
421 we used a high amount of Cu₂O (25 wt.%) in the mixture in order to provide a good
422 dispersion and accessible Cu₂O/ferrite interface. Based on these results, we can assume that
423 the spinel plays an important role and significantly enhances the photocatalytic activity of
424 the system. Furthermore, spinel can stabilize the active copper sites, i.e. the activity of
425 Cu:Fe 1:2 was not significantly changed after several months of aging time, contrary to
426 Cu₂O. On the other hand, this result supports a possible restructuring of the Cu species
427 under the reaction, e.g. formation of Cu⁺⁰. This hypothesis is supported by the inactivity of
428 the spinel with a 1:3 Cu:Fe ratio, the inactivity of CuO and the induction time observed on
429 Cu₂O and its decrease when the inactive 1:3 Cu:Fe spinel is used as support. This agrees
430 with our recent study on the *in-situ* restructuring of Cu²⁺ in UiO-66-(COOH)₂-Cu (18 wt.%)
431 into Cu₂O/Cu⁰ during FAc reforming under visible light [20]. In this study, the formation of
432 highly active Cu₂O/Cu⁰ species trapped in the UiO-66 cages has been evidenced using high-
433 resolution HAADF-STEM images and XPS. However, the detection of such Cu active
434 species in Cu:Fe 1:2 photocatalyst was not possible due to its highly dispersion and/or low
435 amount in respect to the Cu of the spinel-framework.



436
 437 **Figure 5.** (A) Evolution of the FAc conversion (%) and the corresponding gas phase
 438 products (CO_2 and H_2) during the FA photo-reforming over (a) Cu_2O and (b)
 439 with Cu:Fe 1:3 under visible irradiation at RT. Evolution of the IR surface spectra of Cu_2O ,
 440 the surface monodentate formate (1570 cm^{-1}) species vs. CO_2 production in gas phase and
 441 the band at 1721 vs. 1735 cm^{-1} during the induction period (B,C,D) and the photocatalytic
 442 cycle (E,F,G), respectively. Insert in B and E: zoom on the FTIR region of $1500\text{--}1600\text{ cm}^{-1}$.
 443

444 *Operando*-FTIR spectroscopy shed more light on the induction time as the evolution of the
 445 surface species is simultaneously monitored with the gas phase analysis during the reaction.
 446 Unfortunately, we were not able to monitor the surface of the Cu:Fe 1:2 photocatalyst due to
 447 depression of IR transmittance through the pellet once the lamp is turned on (Fig. S 10). It is
 448 probably due to the resonance saturation of IR absorption in semiconductors caused by the
 449 multiphoton inter-band absorption, spectral hole burning and carrier heating [41,42]. This
 450 phenomenon is less significant in case of less active Cu:Fe 1:3 in presence or absence of
 451 Cu_2O , but the spectra collected during the reaction are still not exploitable (Fig. S 11-12).
 452 For this reason, Cu_2O was chosen as a model to shed some light on the evolution of catalyst
 453 surface during the reaction. This allows to identify the reaction intermediates, to understand

454 the induction period and to propose a reaction mechanism over Cu:Fe 1:2 photocatalyst by
455 analogy with Cu₂O. The IR spectra of Cu₂O at different irradiation time were subtracted
456 from the one before FAc adsorption for clarity. The adsorption of FAc on Cu₂O
457 photocatalyst leads to the formation of new bands at 1550, 1360, 1395 and 2945 cm⁻¹ (red
458 spectrum on Fig. 5B). Similar bands are observed on pure SiO₂ (Fig. S 13) and are attributed
459 to weakly adsorbed FAc [43]. The formation of an intense band at 1721 cm⁻¹ parallel to the
460 decrease of Si-OH and/or Cu(OH) band at 3735 cm⁻¹ is associated with the C=O stretching
461 mode of molecularly adsorbed FAc (Fig. S 13-14A). When the lamp is turned on, bands of
462 weakly adsorbed FAc (1360-1395 and 1550 cm⁻¹) disappear, while new features appear at
463 1386 and 1610-1570 cm⁻¹ which can be assigned to the $\delta(\text{CH})$ vibration of adsorbed
464 monodentate formate on copper [44]. These bands gradually increase during the induction
465 period without any production of CO₂ (Fig. 5C), indicating the rearrangement of adsorbed
466 formate on the photocatalyst surface. This is also confirmed by the increase in the carbonyl
467 band intensity at 1721 and 1732 cm⁻¹ during the induction period (Fig. 5D). The absorption
468 at around 1732 cm⁻¹ indicates either formation of weaker hydrogen bond with the FAc or
469 that FAc is in a less polar environment (surrounded by less -OH groups) [45,46] probably
470 caused by *in-situ* restructuring of Cu²⁺ into Cu⁺⁰ with less OH groups. A further decrease in
471 the band intensity of monodentate formate is also observed after 3 h of irradiation
472 accompanied by the production of CO₂ (Fig. 5E-F), which confirms the decomposition of
473 monodentate formate into CO₂ and H₂. During this photocatalytic cycle, a growth in the
474 band at 1732 cm⁻¹ simultaneously to a decrease of the band located at 1721 cm⁻¹ is also
475 observed (Fig. 5G), indicating the conversion of C=O groups from hydrogen-bonded to non
476 or less-hydrogen-bonded carbonyl groups during the reaction. These results allow, by
477 analogy with Cu₂O, to propose a plausible reaction mechanism over Cu:Fe 1:2 governing
478 the restructuring and the dissociation of FAc on the copper active sites, as detailed in the
479 next section.

480

481 ***In-situ* restructuring of the Cu active sites in Cu:Fe 1:2**

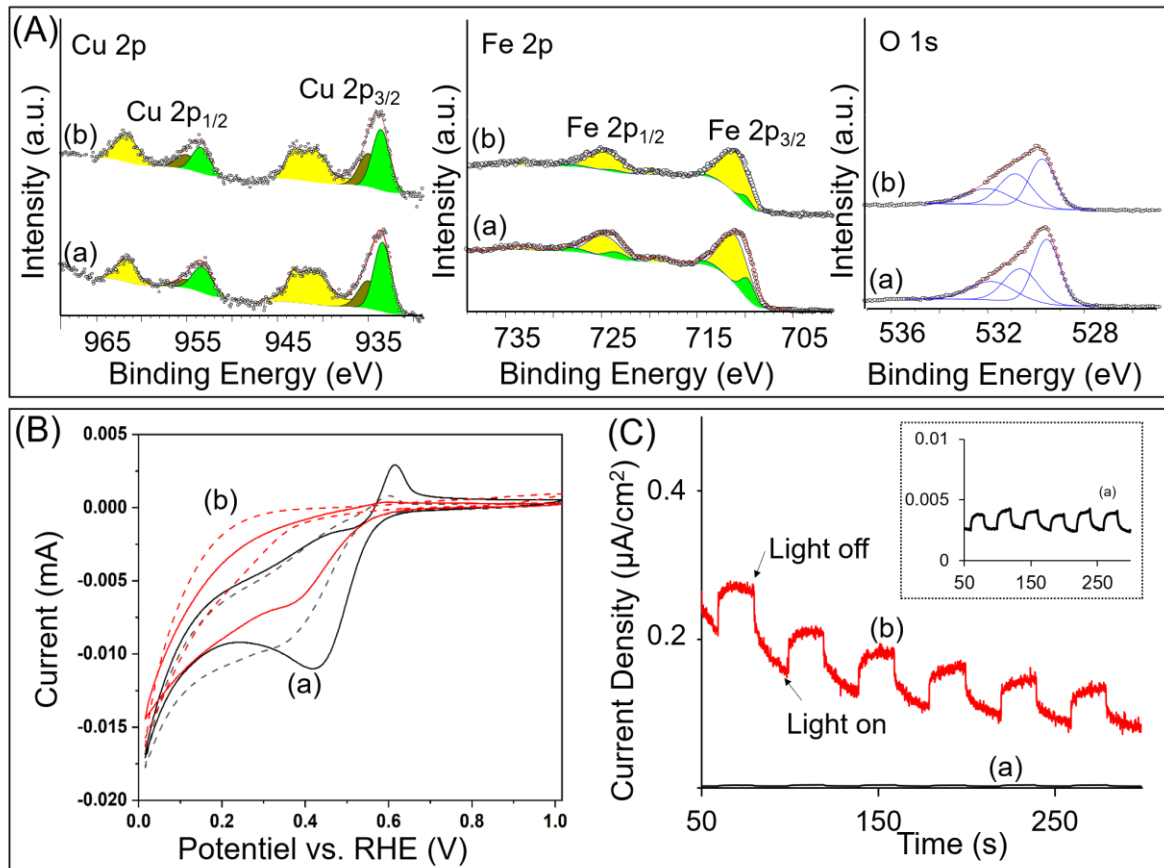
482 The crystallinity and optical properties of Cu₂O after photodecomposition of formic acid
483 have been investigated by XRPD and DR-UV-Vis techniques (Fig. S 15). The results
484 confirm a change of the catalyst in respect to the as-prepared sample and reveals the
485 appearance of Cu characterized by diffraction peaks at 43.7, 50.7, and 74.3° and a Surface
486 Plasmonic Resonance (SPR) absorption band at 566 nm [47,48,49]. The above results
487 confirm that a part of the photoinduced electrons is not involved in the reaction during the
488 induction period, i.e. rearrangement of formate species without H₂/CO₂ production in the
489 first 3h, but is accumulated on the CB of photocatalyst to trigger the *in-situ* reduction and
490 the restructuring process of Cu₂O into binary Cu₂O/Cu composite. Once the binary system is
491 formed, the charge-carriers transport channel improves due to the enhanced charge
492 separation and so the decomposition of formate species into CO₂ and H₂ occurs. This
493 hypothesis is confirmed by testing under similar reaction condition an additional Cu₂O/Cu
494 sample, which preparation is detailed in the experimental part. Higher activity (48% vs. 6%)
495 and much shorter induction period were observed for Cu₂O/Cu in respect to Cu₂O (Table S2
496 and Fig. S 16). This confirms that the induction period is related to the restructuring of Cu₂O
497 into Cu₂O/Cu and that the binary system exhibits higher photocatalytic activity. However,
498 no direct evidence of the Cu formation was found in the case of Cu:Fe 1:2 after reaction
499 (Fig. S 17), which is probably due to the high dispersion with low particle size and the
500 relatively low amount of Cu active sites on this sample with respect to its total Cu content.

501 Additional XPS as well as the Cu L₃M₄₅M₄₅ Auger analyses of Cu:Fe 1:3 and 1:2 were
502 performed in order to gain insight the environment of Cu and Fe in these photocatalytically
503 inactive and active samples, respectively. The results reveal the absence of Cu⁺ in both
504 samples (Figures 6A and S 18). However, two types of coordination environments of Cu²⁺

505 are detected: Cu^{2+} in octahedral (oct) sites (with Cu $2p_{3/2}$ and Cu $2p_{1/2}$ binding-energies at
506 933.5 and 953.5 eV, respectively) and a minor one for Cu^{2+} in tetrahedral (tet) coordination
507 with binding-energies of the Cu 2p doublet at 934.9 eV and 954.9 eV [50]. The
508 photoelectron peak contributions of both Cu^{2+} are colored in green and dark yellow while
509 their common satellites are colored in yellow in Fig. 6A. $\text{Cu}^{2+}_{\text{tet}}$ is ascribed to copper
510 coordinated with four oxygens, linked to two neighboring FeO_6 octahedra via corners to
511 form $[(\text{Fe-O})_{2+x}\text{-Cu}(\text{OH})_{2-x}]$ (with $0 \leq x \leq 2$). These species are more abundant in CuFe_2O_4
512 ($\text{Cu}_{\text{tet}}/\text{Cu}_{\text{oct}} = 0.64$) compared with Cu:Fe 1:3 ($\text{Cu}_{\text{tet}}/\text{Cu}_{\text{oct}} = 0.47$, Table S3). Also, Fe^{3+} and
513 Fe^{2+} oxidation states are detected by analyzing their Fe 2p spectra (Fig. 6A). The peak
514 contributions colored in yellow and green correspond to Fe 2p doublet and the satellites of
515 Fe^{3+} and Fe^{2+} , respectively [51]. The O 1s-spectrum can be fitted with three peak
516 contributions as the two low-energy peaks at 529.6 eV and 530.7 eV can be assigned to
517 bridging (Cu-O-Cu and Fe-O-Fe) and mixed bridging Cu-O-Fe bonds, respectively [52,53].
518 The third peak-contribution at 532.0 eV is usually attributed to oxygen in -O-H bonds, thus
519 confirming the interpretation given above for the presence of Cu-O-H bonding. The
520 $\text{Cu}^{2+}(\text{OH})_2$, usually supported on different materials (TiO_2 , ZnO/ZnS, $\text{Fe}(\text{OH})_3$ and etc.), is
521 well known as an efficient co-catalyst for hydrogen production and easily reducible into
522 $\text{Cu}^{+/0}$ during the reaction [54,55,56].

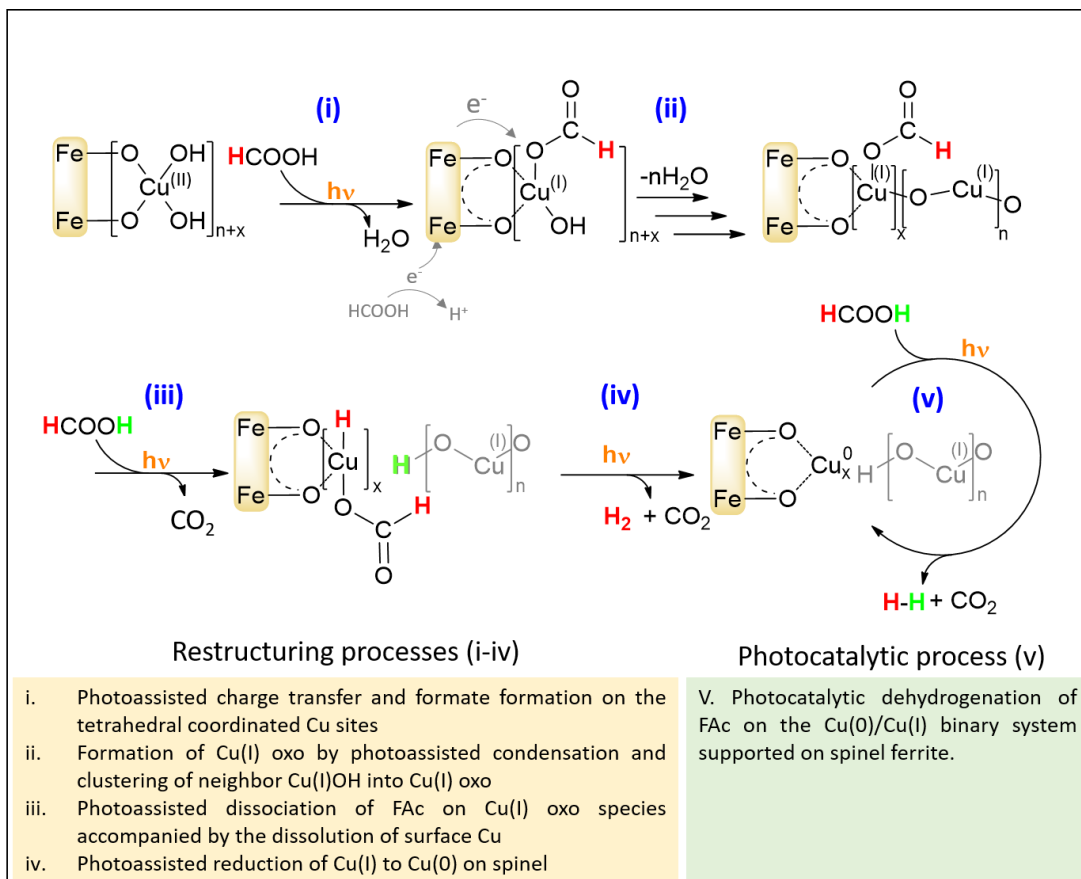
523 Therefore, the photoelectrochemical properties of the Cu:Fe 1:2 were studied and compared
524 to the non-active Cu:Fe 1:3 sample (Fig. 6(B-C)). For Cu:Fe 1:3, the cyclic voltammetry
525 response, investigated in 0.1 M sodium sulfate solution at the potential window of 1.02 V-
526 0.0 V vs. RHE, demonstrates that the reduction/oxidation transitions of spinel are still well
527 distinguished either before or after 100 min of simulated solar irradiation. Moreover, an
528 obvious change in electrochemical behavior of Cu:Fe 1:2 after simulated solar irradiation is
529 observed. The intensity of the redox peaks associated with copper oxide decrease in
530 intensity compared to the as-prepared Cu:Fe 1:2 sample. On the other hand, the

531 electrochemical response of Cu:Fe 1:2 after irradiation shows higher anodic currents in the
532 range between 0.68 V and 1.02 V vs. RHE than both Cu:Fe 1:2 and Cu:Fe 1:3 before
533 irradiation and even than Cu:Fe 1:3 analyzed after induction period. This observation is
534 probably attributed to gradual oxidation of Cu(I) oxide to Cu(II) hydroxide [57,58]. This
535 confirms that, in contrast to Cu:Fe 1:3, the Cu^+ species are formed in Cu:Fe 1:2 under
536 visible light irradiation by an electron transfer (oxidation of formate species and/or from the
537 photoexcited spinel support). The transient photocurrent response tests under several on-off
538 cycles of solar irradiation reveal as well a higher photoresponse efficiency of Cu:Fe 1:2 with
539 regard to Cu:Fe 1:3 (Fig. 6C). It can be explained by the presence of higher amount of
540 tetrahedral $-\text{Cu}^{2+}(\text{OH})_{2-x}$ species in Cu:Fe 1:2 responsible for an efficient charge separation,
541 therefore elucidating the superior photocatalytic activity of this photocatalyst. It is worth
542 noting that no significant thermo-activity was observed in dark at 100°C over Cu:Fe 1:2
543 (Fig. S 19). This confirms that the reaction is mainly photocatalytic without excluding a
544 plasmonic behavior due to the possible formation of Cu^0 .



545
 546 **Figure 6.** (A) High resolution XPS spectra of Cu 2p, Fe 2p and O1s for (a) Cu:Fe 1:3 and
 547 (b) Cu:Fe 1:2. (B) Cyclic voltammety response of (a) Cu:Fe 1:3 and (b) Cu:Fe 1:2
 548 electrode before (solid line) and after 100 min under simulated solar light irradiation (dash
 549 curve) in 0.1 mol.dm⁻³ Na₂SO₄ aqueous solution. (C) Plots of photocurrent vs. time recorded
 550 for (a) Cu:Fe 1:3 and (b) Cu:Fe 1:2. Insert: zoom on the photoresponse of Cu:Fe 1:3.
 551

552 Based on the obtained results and by analogy with the various photocatalysts tested in this
 553 work, a plausible *in-situ* restructuring mechanism of the Cu:Fe 1:2 and the formation of
 554 ultra-dispersed photocatalytic active clusters during the induction period can be described as
 555 follows (Scheme 1): i) charge transfer and formation of surface formate species on the
 556 tetrahedral Cu²⁺(OH)_{2-x} active sites, ii) formation of Cu⁺ oxo species, promoted by a charge
 557 transfer from the spinel and followed by condensation and clustering of Cu with neighbor
 558 Cu⁺-OH to form Cu₂O like clusters, iii) formation of Cu⁺ hydrides by dissociation of FAC
 559 accompanied by partial dissolution of surface copper, iv) subsequent CO₂ and H₂ production
 560 on Cu⁺ oxo and v) reductive hydride elimination on Cu⁺ oxalate leading to the formation of
 561 Cu⁺/Cu⁰.



562
563
564

Scheme 1. Proposed mechanism of restructuring process of tetrahedral $\text{Cu}^{2+}(\text{OH})_2$ active sites on Cu:Fe 1:2 during the photoreforming of formic acid under visible light irradiation.

565 Z-scheme heterojunction and charge transfer mechanism

566 In order to explain the charge separation mechanism, the positions of the conduction band
567 (CB) and valence band (VB) of spinel in both Cu:Fe 1:3 and 1:2 photocatalysts were
568 computed using the atom's Mulliken electronegativity equations with respect to the (NHE)
569 scale [59,60]:

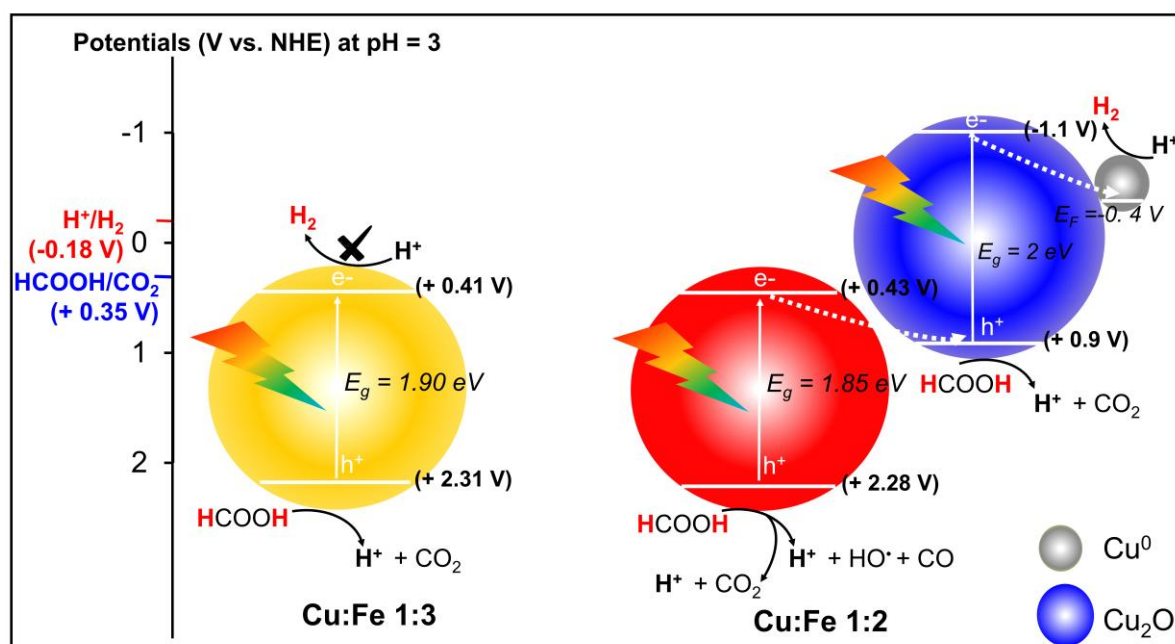
$$570 E_{VB} = X - E_e + \frac{1}{2} E_g \quad (7)$$

$$571 E_{CB} = E_{VB} - E_g \quad (8)$$

572 Where E_{VB} is the VB potential, E_{CB} is the CB potential, E_e is the energy of free electrons on
573 the hydrogen scale (ca. 4.5 eV), E_g is the band gap energy of spinel (1.90 for Cu:Fe 1:3 and
574 1.85 eV for Cu:Fe 1:2, Fig. S 4) and X is the absolute electronegativity of the copper iron
575 spinel (5.86 eV [61,62]). On the basis of the above equations, the E_{VB} and E_{CB} of Cu:Fe 1:3
576 were calculated with respect to NHE as + 2.31 V and + 0.41 V, whereas the potentials for
577 1:2 sample were estimated to + 2.28 V and + 0.43 V, respectively. Consequently, the

578 hydrogen reduction cannot take place on Cu:Fe 1:3 due to its unsuitable CB position (+ 0.41
579 V) compared to H^+/H_2 potential (-0.18 V vs. NHE at pH = 3; 0.0 V vs. RHE). Considering
580 that Cu:Fe 1:2 contains $-Cu^{2+}(OH)_2$ active species that are restructured into Cu^+ and Cu^0 , an
581 efficient charge separation mechanism can be proposed by assuming that Cu^+ of the Cu:Fe
582 1:2 is similar to Cu_2O (scheme 2): Under visible light ($\lambda > 390$ nm), the excited electrons are
583 transferred from the VB of the spinel to its CB thereby oxidizing FAc mainly into CO_2 (with
584 a small amount of CO) and H^+ by combination with the photogenerated holes of spinel.
585 Simultaneously, the electrons accumulated on $Cu^{2+}(OH)_{2-x}$ are involved in the reduction and
586 *in situ* restructuring of Cu^{2+} (scheme 1) into ternary Cu^+/Cu^0 /spinel Z-scheme heterojunction
587 (scheme 2), promoting then the proton reduction into H_2 .

588



589 **Scheme 2.** Schematic diagram showing the photoinduced charge-carriers transfer and the H_2
590 production through the photodecomposition of formic acid under visible light over Cu:Fe
591 1:3 and Cu:Fe 1:2.

592

593 4. Conclusion

594 The H_2 production via photoreforming of FAc is studied in vapor phase under continuous
595 flow over low-cost $CuFe_2O_4$ -based photocatalyst under visible light ($\lambda > 390$ nm) and at
596 room temperature. The influence of Cu:Fe ratio on the photocatalytic activity was
597

598 investigated. We demonstrated that nor spinel with equal or lower Cu:Fe ratio than 1:3,
599 neither those treated below 700°C are photocatalytically active under visible light
600 irradiation. By contrast, a synergetic activity is observed for CuFe₂O₄ (Cu:Fe 1:2) once
601 annealed at 800 °C. This photocatalyst exhibits the highest hydrogen production rate (~ 6.6
602 mmol.g⁻¹.h⁻¹), with an apparent quantum yield equal to 7.3%, together with a relatively good
603 dehydrogenation-selectivity (77 %) and ultra-high stability (> 20 h) compared to other
604 copper-based systems investigated in the literature. As confirmed by XPS, this excellent
605 photocatalytic behavior is attributed to the existence of highly dispersed tetrahedral-
606 Cu²⁺(OH)_{2-x} sites on the spinel surface. Based on the presence of an induction period in the
607 first cycle of reaction and by analogy with other Cu₂O based photocatalyst and Cu based
608 oxides, an *in-situ* restructuring of tetrahedral Cu²⁺ into a ternary (Cu⁺/Cu⁰/spinel) with Z-
609 scheme heterojunction is proposed, promoting the electron/holes charge separation and thus
610 the proton reduction into H₂. Although the selectivity of the reaction is lower than the one
611 reported in our previous work using Cu/MOFs based catalyst, the high activity observed for
612 the CuFe₂O₄ photocatalyst, its low cost and its simple synthesis procedure motivate
613 investigating new Cu-Fe based materials for various applications in photocatalysis under
614 visible light.

615

616 **Author Contributions**

617 †These authors contributed equally. The manuscript was prepared written through the
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