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Photocatalytic reforming of formic acid for hydrogen production in aqueous
 solutions containing cupric ions and TiO₂ suspended nanoparticles under UV simulated solar radiation
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- 12 Graphical abstract



13

- 14 Highlights:
- 15
- Assessment on the efficient photocatalytic system Cu²⁺/HCOOH/Cl⁻/nano-TiO₂/UV_{SSR} for H₂
 evolution
- Evaluation of the system behavior at varying selected experimental variables
- Setting of the best operating conditions to maximize the H₂ generation rate

20

Depiction of a consistent reaction mechanism for the photocatalytic system proposed

21

22 Abstract

23 Hydrogen is the ideal candidate to fulfill the growing energy demand in a sustainable manner because of its high energy content and no emission of greenhouse gases from its combustion. Currently most 24 25 of hydrogen generation techniques involve the employment of fossil fuels, with consequent production 26 of toxic greenhouse gases. The possibility to produce hydrogen by means of photocatalytic processes 27 using the solar radiation as energy source fits in perfectly with the switch to a more sustainable energy production. The solar photocatalytic hydrogen generation can be achieved by reforming 28 29 organic substances contained in civil or industrial wastewaters. This could allow to combine water decontamination with production of an energy carrier starting from a renewable source, the solar 30 31 radiation.

32 Within this perspective, a novel nano-TiO₂ photocatalytic system based on the solar reforming of 33 formic acid in presence of cupric ions and chlorides has been investigated. The effect on hydrogen 34 generation rate of the initial concentrations of formic acid, chloride and cupric ion, and pH values 35 has been evaluated. For both formic acid and chloride ions, at least up to a starting concentration of 10^3 mM, the higher the initial concentration, the higher the rate of hydrogen generation. Hydrogen 36 37 production has turned out to be noticeably dependent on cupric ion concentration. An almost opposite 38 behavior has been found varying the starting cupric ion concentration in the range 2.5–20 mM, with 39 the highest value of hydrogen production rate recorded for Cu(II) initial concentration equal to 5.0 40 mM. The pH value has been identified to be a crucial parameter of the system. A decrease in hydrogen 41 production has been also observed rising pH of the solution from 1.0 to 4.0. A characterization of the solid samples recovered at the end of the runs has been performed by X-ray Diffractometry. These 42 43 experimental outcomes have been rationalized within a consistent reaction mechanism able to predict the system behavior under different operating conditions. This work opens the way to the development 44

of new competitive processes able to use waste organic streams for hydrogen generation through
photacatalytic system based on solar energy.

47

Keywords: nano-sized TiO₂ photocatalyst; hydrogen production; photocatalytic reforming; solar
photocatalytic processes; copper "in-situ" photoreduction.

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52

53 Introduction

The possibility to produce hydrogen through photocatalytic processes from aqueous solutions containing organics (photoreforming) or from water (photosplitting) has emerged in recent years as a new field of investigation and has renewed the interests of researchers in photocatalysis [1–3].

However, the simple idea that it is sufficient to remove gaseous oxygen from the photocatalytic systems [4,5] to favor protons reduction by photogenerated electrons – after radiation absorption by TiO₂ particles – appears only partially true. In fact, most of bare metal oxides used in photocatalysis (TiO₂, ZnO and WO₃) exhibit low efficiencies in hydrogen generation mainly due to the relevant occurrence of recombination reaction between photogenerated holes and electrons [6]. Two different approaches are generally adopted to reduce the incidence of this recombination reaction:

The use of metals, such as Pt, Pd, Au and Cu, as co-catalysts: once incorporated on the photosemiconductor surface, they help promote electrons transfer to protons, which are reduced to
hydrogen [7–9].

66 2) The addition to the reacting solution of a sacrificial organic agent which irreversibly reacts 67 (oxidizes) with positive holes [10,11]. It is particularly interesting to remember that the hole 68 scavenger may be also represented by an organic aqueous pollutant: in this case, hydrogen generation 69 may combine with water decontamination [12,13, 34].

Literature shows that many organic species, such as alcohols [14, 35-37] and sugars [15], have been
so far proposed as hole scavengers.

Moreover, a great enhancement of hydrogen generation has been observed with copper-doped TiO₂ catalysts both under UV and near-UV range of radiation [16,17], or under irradiation with both visible and solar light [18,19]. The results of these investigations have indicated that copper-incorporated TiO₂ photocatalysts show a hydrogen production significantly higher than that obtained with bare TiO₂ [20,21].

77 Moreover, copper-doped TiO₂ photocatalysts other have been used for photocatalytic applications too. For example, according to literature indications [33] these materials 78 79 are capable of enhancing the sunlight-mediated degradation of organic compounds and indicator 80 microorganisms in water.

Some of the Authors recently reviewed the intense research activity recorded during last years in the
field of copper-incorporated TiO₂ photocatalysts for hydrogen production [22].

83 In a previous paper [11], a new photocatalytic system for hydrogen generation was proposed by some 84 of the Authors. The system is based on the photoreforming of an organic species (formic acid) in an 85 aqueous TiO₂ suspension containing copper (in different oxidation states) and in the presence of 86 chloride ions, under artificial UV-Vis radiation. The adoption of such a system was stimulated by 87 literature indications [23] on the tendency of zero-valent copper to undergo a photocorrosive process, 88 at very low pH (0.0–2.0), in presence of chloride ions and under UV-solar simulated radiation. As 89 reported by Eisel et al. [23], the photo-oxidation of zero-valent copper in presence of chloride ions (r_1-r_2) results into hydrogen generation through proton reduction (r_3) : 90

$$CI_{ads}^{\bullet} + Cu^{0} \rightarrow CuCI_{aq,ads} \qquad r_{2}$$

91 In addition, in this system hydrogen can be produced also by photolysis of cuprous complexes formed 92 in the solution (r_4-r_8) [24]:

$$Cu^{1+} + 2CI^{-} CuCI_{2}^{-} \qquad r_{4}$$

$$Cu^{1+} + 3CI^{-} \rightleftharpoons CuCI_{3}^{2-} \qquad r_{5}$$

$$CuCI_{2}^{-} + H^{+} \xrightarrow{hv} Cu^{2+} + 2CI^{-} + e^{-}_{s} \qquad r_{6}$$

$$CuCI_{3}^{2-} + H^{+} \xrightarrow{hv} Cu^{2+} + 3CI^{-} + e^{-}_{s} \qquad r_{7}$$

$$H^{+} + e^{-}_{s} \rightarrow \frac{1}{2}H_{2(g)} \qquad r_{8}$$

A continuous production of hydrogen could be thus imagined coupling the last system (Figure 1, Subsystem 2) with another one (Figure 1, Subsystem 1). The resulting complete system allows the photocatalytic reduction of cupric ions to zero-valent copper in presence of solid TiO_2 – and the oxidation of an organic species, such as formic acid, used as sacrificial agent – followed by a copper reoxidation with a simultaneous hydrogen generation.

The complete system makes possible, at least in principle, the generation of hydrogen through thephotoreforming of an organic species which could also be contained in wastewaters.

100 Although in the previous work [11] the possibility to generate hydrogen through the complete system 101 was presented as proof of concept, the data collected so far indicate that hydrogen production cannot 102 only be attributed to a simple combination of Subsystems 1 and 2. In fact, hydrogen generation was 103 observed for prolonged reaction times only for particular initial values of some experimental 104 variables, such as the following: formic acid concentration, chloride ion concentration, total dissolved 105 copper concentration, starting oxidation state of copper (zero-valent or cupric ions) and TiO₂ load. 106 For all the experimental conditions tested in which initially zero-valent copper was used starting from 107 the complete system, no hydrogen production was recorded during the run, although its formation 108 only due to Subsystem 2 was surely observed (for this uncertainty a dotted line is adopted to indicate 109 this pathway in Figure 1). On the other hand, the formation of hydrogen was observed in some runs 110 starting from copper initially present as cupric ions and TiO_2 load not higher than 100 mg/L. However, 111 in the previous work [11] no detailed investigations were carried out to clearly identify for these 112 variables the concentration range which can guarantee the best performances of the complete system. 113 In particular, no indications were reported on the system reactivity over a wide concentration range

neither of formic acid, chloride or total cupric ions (separately or simultaneously added to the reacting
system), nor of pH of the solution.

The present work aims at fulfilling this lack of information in order to provide the best conditions which maximize the hydrogen generation rate, which is proportional to the maximum efficiency of hydrogen production.

119

120 **Experimental**

121 *Procedures and analytical methods*

Photocatalytic runs have been carried out in an annular glass batch reactor (V=300 mL) covered with
a layer of aluminum foil. On the top of the reactor, an inlet has allowed to feed reactants and nitrogen

124 gas, and an outlet has been used to collect liquid and gaseous samples at different reaction times.

The reactor has been endowed with a high–pressure mercury vapor lamp by Helios Italquartz (power input: 125 W), principally emitting at 305, 313 and 366 nm (manufacturer's data), located inside a glass cooling jacket in the center of the reactor and surrounded by the reacting solution. The effective radiative powers of the lamp (P_{λ}) at 305, 313 and 366 nm are 4.69•10⁻⁵, 8.11•10⁻⁵ and 2.59•10⁻⁴ E/min, respectively. The reactor has been cooled at 25 °C during each run by means of a thermostatic bath

130 (Falc GTR 90).

For each photocatalytic run, a proper amount of commercial nano- TiO_2 anatase has been added directly to an unbuffered aqueous solution (V=300 mL), magnetically stirred, containing formic acid as sacrificial agent.

The pH of the solution has been successively regulated by means of perchloric acid and sodium
hydroxide additions and monitored by means of an Orion 420Ab pH–meter (Thermo). The resulting
suspension has been fed into the batch reactor under magnetic stirring.

In order to avoid the undesired reaction of dissolved oxygen with photogenerated electrons, before
starting the photocatalytic runs, a nitrogen stream has been bubbled into the solution for 30 minutes

139 for removing atmospheric oxygen.

6

140 After this period, cupric sulfate pentahydrate and sodium chloride have been quickly added to the mixture. Throughout the experiments, nitrogen has been continuously fed at a flow rate (Q_{N_2}) of 0.3 141 L/min to prevent any entrance of air into the reactor. Indeed, as previously reported [37], some Cu-142 143 TiO₂-based materials suffer from a dramatic copper leaching under oxidizing and acidic conditions. 144 The liquid samples, collected at different reaction times, have been quickly filtered on regenerated 145 cellulose filters (pore diameter 0.20 µm, Scharlau) and the filtrate has been used to measure dissolved 146 copper and formic acid concentrations. The gaseous samples have been recovered from the reactor 147 outlet in Tedlar gas sampling bags and then used to evaluate hydrogen concentration.

148 Dissolved copper concentration has been measured by means of a colorimetric method using an 149 analytical kit (Macherey–Nagel) based on oxalic acid bis–cyclohexylidene hydrazide (cuprizone) [4]. 150 A UV/Vis spectrometer (Cary 100 UV–Vis, Agilent) has been employed for the measurements at a 151 wavelength of 585 nm. The concentration of formic acid has been measured by means of HPLC 152 analysis. For this purpose, the HPLC apparatus (Agilent 1100) has been equipped with a UV–Vis 153 detector (λ =210 nm) and a Alltech OA–1000 column, using a mobile phase of sulphuric acid 2.5•10⁻ 154 ³ mol/L, flowing at 0.8 mL/min.

Hydrogen concentration has been measured by a gas-chromatograph (Agilent 7820A) equipped with
a HP–PLOT Molesieve 5A column (Agilent) and a TCD detector using argon as carrier gas. Each
photocatalytic run has been carried out in duplicate.

158

159 *Materials*

160 Cupric and chloride ions have been introduced in the system as cupric sulphate pentahydrate, 161 (CuSO₄•5H₂O) and sodium chloride, respectively. Formic acid, copper sulphate, perchloric acid, 162 sodium perchlorate and potassium sulfate have been purchased from Sigma Aldrich and used as 163 received.

TiO₂ catalyst has been purchased from Sigma Aldrich (pure anatase phase, average size 25-70 nm).

166 *Catalyst recovery, cleaning and characterization*

167 At the end of the run, the suspension has been allowed to settle overnight under inert atmosphere 168 producing two distinct layers: aqueous solution on the top and solid particles deposited on the bottom. 169 After removal of most part of the aqueous solution by decanting it, the remaining part has firstly been 170 washed with degassed water and then evaporated by means of a gentle inert flow.

171 The X-ray diffraction (XRD) patterns of the solid samples have been recorded by a Bruker D2 172 Phaser Diffractometer employing a CuK α source (40 kV, 30 mA) and operating at diffraction angles 173 ranging between 20 and 80° 2 Θ with a scan rate of 0.02° 2 Θ s⁻¹.

174

175 **Results and discussion**

In Figure 2 is shown an example of the results collected during a typical photocatalytic run starting 176 from a suspension containing cupric ions (5.0 mM), chloride ions (10^3 mM), formic acid (10^3 mM) 177 and TiO₂ (10^2 mg/L). The hydrogen production rate increases until a value of about 8 μ mol/min is 178 reached and slightly reduces after the first hour of reaction time, whereas the total dissolved copper 179 180 concentration keeps approximately constant throughout the experiment. The idea that the trend observed is due to a decrease of formic acid concentration cannot be demonstrated, since no 181 appreciable decreasing of formic acid concentration has been detected by HPLC analysis (data not 182 shown). 183

184

185 *Effect of formic acid concentration*

As reported in Figures 3a–b, the effect of changing the initial formic acid concentration towards the hydrogen production rate and Cu(II) consumption has been investigated between 10 mM and $5.0 \cdot 10^3$ mM. It is evident that, keeping constant initial cupric ion and chloride concentrations, TiO₂ load and pH, the higher the formic acid concentration, the higher the maximum hydrogen production rate observed. The values of hydrogen production rate vary from 0.7 to 8.3 µmol/min, at least until formic acid concentration is equal to 10^3 mM. Since hydrogen production proceeds through an initial

reduction of cupric ions (r_9) , made possible by a contemporary oxidation of formic acid (r_{10}) , a monotonic increase of hydrogen generation rate is clearly expected for higher concentrations of formic acid according to the results previously reported [11]:

HCOOH
$$\xrightarrow{h_{VB}^+}$$
 CO₂ $\xrightarrow{-}$ + 2H⁺ r_{10}

As previously reported, the concentration of the organic species influences the rate of cupric ion reduction during the sacrificial photocatalytic process [25]. It can be thus supposed that reduced copper species, i.e. cuprous ones formed through reaction r_9 , in presence of chlorides and under UV irradiation immediately reoxidize ($r_6 - r_7$), therefore ejecting electrons (e^-s) in the solution and allowing a prompt reduction of protons (r_8).

200 Only a moderate reduction, if any, of total dissolved copper and low hydrogen generation rates have been recorded during the runs with the lowest initial formic acid concentration (Figure 3, full 201 diamonds and triangles). For a starting formic acid concentration of 10^3 mM, a reduction in dissolved 202 203 copper of about 20% has been recorded within a reaction time of 300 minutes (Figure 3, full circles). 204 It is worth considering that the formation of hydrogen proceeds through two consecutive steps: a first 205 one (r_9) in which a preventive reduction of cupric ions to cuprous ones occurs with a contemporary 206 formic acid oxidation (r_{10}) , and a second one consisting in the photolysis of some chloride complexes of cuprous ions $(r_6 - r_7)$. It can be thus hypothesized that any increase in initial concentration of 207 formic acid may result into a faster reduction of cupric ions. The results collected indicate that, for 208 formic acid concentrations up to 10^3 mM, the rate determining step is represented by cupric ion 209 reduction. It is therefore enough to accelerate the determining step to have a faster hydrogen 210 generation for formic acid concentrations between 10 mM and 10^3 mM. 211

At the highest formic acid concentration tested, equal to $5.0 \cdot 10^3$ mM (Figure 3, cross symbols), dissolved copper has been completely reduced after 180 minutes of reaction, casting doubt on the catalytic role of copper. In other words, it seems that the complete system (Figure 1) is characterized by a certain tendency of zero-valent copper to precipitate and be not capable of undergoing further

reoxidations; therefore, zero-valent copper can be deemed completely unreactive for increasing 216 reaction times. It could be reasonably considered that, under the adopted conditions (formic acid 217 concentration equal to $5.0 \cdot 10^3$ mM), the photocatalytic reduction rate of cuprous ions is by far higher 218 than the reoxidation rate of zero-valent copper $(r_1 - r_2)$, provided that this reoxidation occurs. 219 Alternatively, it should be taken into account the possibility that the complete system (Figure 1) 220 inhibits zero-valent copper oxidation together with hydrogen formation. An attempt to throw light on 221 222 this specific point has been made by investigating hydrogen generation in the system zero-valent copper/formic acid/chlorides/nano-TiO2/UV irradiation at pH=1.0. The data indicate values of 223 224 hydrogen generation as lower as those recorded in the system formic acid/chlorides/nano-TiO₂/solar 225 UV radiation at pH=1.0, without any significant accumulation of dissolved copper as Cu(I) or Cu(II) 226 ions. This result clearly indicates that a photoxidation of zero-valent copper in presence of chloride ions, formic acid and nano-TiO₂ does not occur at all. 227

228

229 Effect of chloride ion concentration

230 The effect of changing the initial chloride ion concentration has been investigated in the range 231 $10^2-2.0\cdot10^3$ mM (Figures 4a-b).

For fixed formic acid concentration, any increase in addition of chloride ions to the reacting solution results into a higher hydrogen generation rate (the maximum value recorded is 8.3 μ mol/min for a chloride ion concentration of 10³ mM). However, it is interesting to stress that, contrary to what observed in the runs with variable formic acid concentration, for the lowest value of chloride ion tested (10² mM) a significant reduction of total dissolved copper has been recorded, along with the precipitation of a reddish–brown solid on TiO₂.

These results may be explained by supposing that, if chloride ion concentration is reduced, Cu(I) reoxidation through chloride complexes photolysis $(r_6 - r_7)$ is slowed down and becomes the rate determining step. As a consequence of this behavior, the rate of hydrogen generation decreases too.

On the other hand, a reduction in hydrogen production rate has been observed for further increases in 241 chloride ion concentration from 10^3 mM up to $2.0 \cdot 10^3$ mM (Figure 4, full triangles). It is known that 242 243 at rising chloride ion content both Cu(I) and Cu(II) may form different complexed species, such as $CuCl_2^-$ and $CuCl_3^{2-}$ (for cuprous ions) [26] or $CuCl^+$, $CuCl_2$ and $CuCl_3^-$ (for cupric ions) [27]. The 244 245 formation of Cu(II)-chloride complexes results into the occurrence of a shielding effect which reduces the radiation absorption by Cu(I)-chloride complexes. Indeed, both cuprous and cupric 246 complexes are capable of absorbing in the same radiation range of the lamp used (305–366 nm) with 247 248 comparable extinction coefficients, although those belonging to Cu(I) complexes type are slightly 249 higher (Figure 5).

For higher chloride ion concentrations, an increase in concentration of all chloride complexes occurs, causing two opposite effects: (i) a rise in concentration of cuprous-chloride complexes ($CuCl_2^-$ and $CuCl_3^{2-}$), which absorb and photolyze at wavelengths higher than 290 nm [26]; (ii) an increase in concentration of cupric–chloride complexes ($CuCl^+$, $CuCl_2$ and $CuCl_3^-$) and, consequently, of their shielding effect. It can be considered that the shielding effect prevails for chloride concentrations higher than 10^3 mM, with a consequent reduction in hydrogen generation rate. However, only the availability of a suitable kinetic model could help to completely throw light on this issue.

So as to determine the nature of the precipitate, a sample recovered at the end of a run at pH=1 washed accordingly with the procedure reported in the experimental has been submitted to a XRD measurement (Fig 6). Two peaks at 2Θ equal to $43^{\circ}3'$ and $50^{\circ}5'$ which can be ascribed to zero-valent copper have been observed. Therefore, it can be concluded that the solid recovered is represented by zero-valent copper.

262

263 *Effect of cupric ion concentration*

The influence of initial cupric ion concentration on hydrogen production rate and dissolved copper concentration is reported in Figure 7. Distinct behaviors have been recorded when initial cupric ion concentration changes from 2.5 mM to 5.0, 10.0 and 20.0 mM (Figures 7a–b).

A delayed hydrogen production and a lower decrease in dissolved copper have been observed at rising initial cupric ion concentration from 5.0 to 20 mM. A complete reduction of cupric ions and a reddish solid precipitation within 300 minutes of reaction have been recorded only for the run starting from a cupric ion concentration of 2.5 mM. XRD measurements have demonstrated that the solid is represented by zero-valent copper (data not shown).

To explain these observations it has to be considered that at increasing cupric ion concentration between 5.0 and 20 mM, the shielding effect due to the formation of Cu(II)–chloride complexes becomes more significant and lowers the rate of hydrogen production. When cupric ion concentration is hugely reduced through the reaction between cupric ions and photoelectrons (r_9) (with a significant increase in concentration of Cu(I) in the form of Cu(I)–chloride complexes), the rate of hydrogen production reaches a maximum value (Figure 7).

For initial cupric ion concentration equal to 2.5 mM, the less important shielding effect promotes a faster hydrogen production, but also a rapid photocatalytic reduction of Cu(I) to zero-valent copper (r_9) which does not reoxidize. Indeed, in this case the maximum value of hydrogen production rate is lower with respect to that recorded starting from a cupric ion concentration of 5.0 mM.

A more careful examination of these data indicates that different quantities of hydrogen are produced 282 per moles of precipitated copper ($P_{H_2}/P_{Cu(0)}$, Table 1) for reaction times of 300 and 600 minutes 283 respectively, depending on the initial concentration of cupric ion adopted. The best results, consisting 284 in highest values of $P_{H_2}/P_{Cu(0)}$, have been recorded in the run with a starting cupric ion concentration 285 of 5.0 mM for both reaction times. The results collected indicate that a complete precipitation of 286 dissolved copper happens at about 600 minutes of reaction. This demonstrates a certain tendency of 287 the catalytic system to deactivate, as already observed in the run starting from a cupric ion 288 concentration of 2.5 mM. In other words, it is clear that, even for different reaction times depending 289 290 on the initial cupric ion concentration and still in presence of significant quantities of formic acid, the

system becomes no more capable of producing hydrogen. This deactivation of the system can be

272 considered as a consequence of the complete precipitation of zero-valent cop	on of zero-valent coppe	precipitation	of the complete	red as a consequence	292 considered	292
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[Cu(II)] ₀	$P_{H_2}/P_{Cu(0)}$	$P_{H_2}/P_{Cu(0)}$
mM	300 min	600 min
2.5	1.8	1.8
5.0	3.8	3.5
10	2.7	1.8
20	1.7	-

293

Table 1 – Effect of cupric ion concentration: correlation between micromoles of H₂ generated (P_{H_2}) and micromoles of Cu(0) precipitated ($P_{Cu(0)}$) after 300 and 600 minutes of reaction at pH=1.0, T=25 °C, [HCOOH]₀=10³ mM, [NaCl]₀=10³ mM, TiO₂ load=10² mg/L.

297

298 Effect of pH of the solution

Since a dependence of hydrogen generation rate on protons concentration (and pH) may be assumed, the best results could be expected under low pH condition. Indeed, proton reduction is a fundamental reaction through which the process develops. However, in most of the researches appeared in literature on copper–based TiO₂ photocatalysts for hydrogen generation, the best performances are reported for basic or strong basic condition [28–30]. The prevailing explanation seems to rely on the detrimental effect that acidic conditions exert on the catalyst stability, with a continuous copper leaching into the solution [31,32].

306 To assess the effect on the system reactivity of pH in the solution, two additional photocatalytic runs

307 have been performed at pH 2.5 and 4.0 respectively, for both chloride ion and formic acid initial

308 concentrations equal to 10^3 mM, cupric ion concentration at 5.0 mM and TiO₂ load equal to 10^2 mg/L.

309 The results collected during these runs are shown in Figure 8a-b.

310 It is interesting to observe that both at pH 2.5 and 4.0 hydrogen production appears to be depressed 311 and reaches zero after about 120 minutes of reaction. For the same reaction time total dissolved copper 312 reduces to zero and a black solid is formed on TiO₂ nano-particles.

Also in this case, an attempt to characterize the nature of copper deposited on TiO_2 nanoparticles has been made. The solid sample has been firstly washed as reported in the experimental and then submitted to X-ray diffraction analysis. XRD spectrum (Figure 9) shows two peaks at 2 Θ equal to 43°3' and 50°5', indicating the presence of zero-valent copper in agreement with what reported by Li et al. [38].

As discussed above, in the system studied hydrogen production proceeds through a complex pathway made up of several reaction steps, the last and faster being proton reduction by solvated electrons. When pH is increased in the range 1.0-4.0, the resulting reduction in proton concentration slows down the rate of solvated electrons capture by protons. Therefore, in such cases solvated electron capture by protons becomes the rate-controlling step, thus lowering the hydrogen generation rate.

In these conditions, a higher availability of solvated electrons may be expected in solution with a consequent enhancement in Cu(I) and Cu(II) reduction. In other words, copper is continuously separated from the solution through a reduction of dissolved copper species until the system becomes completely unreactive.

327 The behavior of the system investigated may be depicted by means of the scheme illustrated in Figure328 10.

Hydrogen formation in a system containing copper in the initial form of cupric ions is strictly connected to the reduction of cupric ions to cuprous ones (Step A, Figure 10) and the photolysis of Cu(I)-chloride complexes (Step B, Figure 10). In fact, during the photolytic process electrons $(e^{-}s)$ are ejected into the solution and protons promptly react with them but not with the photogenerated ones (e^{-}_{CB}) . Chloride complexes provide an important reservoir of Cu(I) in solution; therefore, in the presence of low Cl⁻ concentrations, Cu(I) more easily reduces to Cu(0) which precipitates (Step C, Figure 10). When pH is increased, the low proton concentration makes available a higher

- concentration of solvated electrons which reduce both Cu(II) and Cu(I) and lead to the deposition of
 a black solid, formed by zero-valent copper (Step C, Figure 10).
- 338

339 Conclusions

The present investigation proposes a new competitive process for hydrogen generation through the system cupric ions/formic acid/chloride ions/nano-TiO₂/UV-solar radiation. The efficiency of the process in terms of hydrogen production has been studied at varying the initial concentrations of formic acid, chloride and cupric ion and pH.

Hydrogen generation has revealed similar dependences on formic acid and chloride ion concentrations. The rate of hydrogen production increases up to a formic acid concentration of 10^3 mM. On the other hand, a huge decrease in the maximum value of hydrogen production rate has been observed for a formic acid concentration equal to $5.0 \cdot 10^3$ mM, with a contemporary precipitation of zero-valent copper. With regard to chloride ions in solution, an increase in hydrogen generation rate has been observed up to a chloride concentration of 10^3 mM, with a clear decrease for higher concentrations.

Hydrogen production is also strongly dependent on cupric ion concentration. Initial increases in cupric ion concentration have resulted in a reduction of hydrogen generation rate. An early loss of reactivity of the system has been recorded during the run at the lowest value of cupric ion tested (2.5 mM), with a complete precipitation of cupric ions as zero-valent copper within a reaction time of 300 minutes. A similar behavior has been observed for higher starting concentration of cupric ion, but at longer reaction times. No re-oxidation of zero-valent copper has been observed in the complete system during the present investigation.

The increase in pH of the solution from 1.0 to 2.5 to 4.0 has shown a decrease in hydrogen generation rate and the precipitation of zero-valent copper.

- 360 A consistent reaction mechanism able to predict the system behavior under different operating
- 361 conditions has been proposed. This study lays the groundwork for the future development of a suitable
- 362 kinetic model that will completely throw light on this issue.
- 363

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 417 418 419 420 421 422 423 424 425 426 427 428 	Captions Figure 1 – Schematic illustration of the complete system for hydrogen generation through nano-TiO2 photocatalytic reforming of formic acid in presence of copper species and chloride ions. Figure 2 – Hydrogen production rate (•) and dissolved copper normalized concentration (•) at pH=1.0 (with HClO4), [HCOOH]_0=10 ³ mM, [Cu(II)]_0=5.0 mM, [NaCl]_0=10 ³ mM, TiO2 load=10 ² mg/L. Figure 3 – Effect of formic acid concentration: hydrogen production rate (a) and dissolved copper normalized concentration (b) at pH=1.0 (with HClO4), [Cu(II)]_0=5.0 mM, [NaCl]_0=10 ³ mM, TiO2
 417 418 419 420 421 422 423 424 425 426 427 428 429 	 Captions Figure 1 – Schematic illustration of the complete system for hydrogen generation through nano-TiO₂ photocatalytic reforming of formic acid in presence of copper species and chloride ions. Figure 2 – Hydrogen production rate (●) and dissolved copper normalized concentration (●) at pH=1.0 (with HClO₄), [HCOOH]₀=10³ mM, [Cu(II)]₀=5.0 mM, [NaCl]₀=10³ mM, TiO₂ load=10² mg/L. Figure 3 – Effect of formic acid concentration: hydrogen production rate (a) and dissolved copper normalized concentration (b) at pH=1.0 (with HClO₄), [Cu(II)]₀=5.0 mM, [NaCl]₀=10³ mM, TiO₂ load=10² mg/L, [HCOOH]₀ (mM): (+) 5.0•10³, (●) 10³, (■) 5.0•10², (◆) 10², (▲) 10.
 417 418 419 420 421 422 423 424 425 426 427 428 429 430 	 Captions Figure 1 – Schematic illustration of the complete system for hydrogen generation through nano-TiO₂ photocatalytic reforming of formic acid in presence of copper species and chloride ions. Figure 2 – Hydrogen production rate (●) and dissolved copper normalized concentration (●) at pH=1.0 (with HClO₄), [HCOOH]₀=10³ mM, [Cu(II)]₀=5.0 mM, [NaCl]₀=10³ mM, TiO₂ load=10² mg/L. Figure 3 – Effect of formic acid concentration: hydrogen production rate (a) and dissolved copper normalized concentration (b) at pH=1.0 (with HClO₄), [Cu(II)]₀=5.0 mM, [NaCl]₀=10³ mM, TiO₂ load=10³ mM, TiO₂ load=10² mg/L.

431	Figure 4 - Effect of chloride ion concentration. Hydrogen production rate (a) and dissolved copper
432	normalized concentration (b) at pH=1.0 (with HClO ₄), $[Cu(II)]_0=5.0$ mM, $[HCOOH]_0=10^3$ mM, TiO ₂
433	load=10 ² mg/L, [NaCl] ₀ (mM): (\blacktriangle) 2.0·10 ³ mM, (\bullet) 10 ³ mM, (\blacksquare) 5.0·10 ² mM, (\blacklozenge) 10 ² mM.
434	
435	Figure 5 – UV spectra of Cu(I) and Cu(II) chloride complexes (data source: Davis et al., 1978 [25]).
436	
437	Figure 6 – XRD patterns registered for a solid sample recovered at the end of a photocatalytic run at
438	pH=1, bare TiO ₂ (anatase) and Cu(0) powders.
439	
440	Figure 7 – Effect of cupric ion concentration. Hydrogen production rate (a) and dissolved copper
441	normalized concentration (b) at pH=1.0 (with HClO ₄), [HCOOH] ₀ = 10^3 mM, [NaCl] ₀ = 10^3 mM, TiO ₂
442	load=10 ² mg/L, [Cu(II)] ₀ (mM): (\blacktriangle) 2.5, (\blacklozenge) 5.0, (\blacksquare) 10, (\blacklozenge) 20.
443	
444	Figure 8 – Effect of pH. Hydrogen production rate (\mathbf{a}) and dissolved copper normalized concentration
445	(b), [Cu(II)] ₀ =5.0 mM, [HCOOH] ₀ =10 ³ mM, [NaCl] ₀ =10 ³ mM, TiO ₂ load=10 ² mg/L, pH: ● 1.0, ■
446	2.5,
447	
448	Figure 9 – XRD patterns registered for a solid sample recovered at the end of a photocatalytic run at
449	pH=4, bare TiO ₂ (anatase) and Cu(0) powders.
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451	Figure 10 – Schematic illustration of the reaction mechanism for the investigated system.
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Figure 4















Figure 10

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