

Near UV-Irradiation of CuOx-Impregnated TiO2 Providing Active Species for H2 Production Through Methanol Photoreforming

*Original*

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## Accepted Article

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1 **Accepted Article**

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5 **Near UV-irradiation of CuO<sub>x</sub>-impregnated TiO<sub>2</sub> providing active**  
6 **species for H<sub>2</sub> production through methanol photoreforming**

7

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### 34 **Abstract**

35 Copper doped-TiO<sub>2</sub> (P25) nanomaterials have been intensively studied as promising catalysts for H<sub>2</sub>  
36 production by photo-reforming of selected organic compounds. However, the role of copper oxidation  
37 states on the improvement of photocatalytic activity is still debated. In this work, CuO<sub>x</sub>-impregnated  
38 P25-TiO<sub>2</sub> catalysts were used for photocatalytic production of hydrogen from methanol. Copper  
39 species/oxidation states both in the as-prepared catalysts and after the photocatalytic process were  
40 investigated. To this purpose, H<sub>2</sub> production rates were correlated to physico-chemical properties of  
41 the samples, both before and after photocatalytic process, by means of Raman, X-Ray Diffraction,  
42 Electron Paramagnetic Resonance spectroscopy, X-Ray Photoelectron Spectroscopy, Temperature-  
43 Programmed Reduction and High Resolution Transmission Electron Microscope techniques. Results  
44 revealed the presence of both Cu<sub>2</sub>O and CuO deposits on the samples surface after calcination.  
45 Notably, under near-UV irradiation, the fraction of highly dispersed CuO particles undergo a partial  
46 dissolution process, followed by reduction to metallic copper Cu<sub>(s)</sub> by photogenerated electrons,  
47 boosting H<sub>2</sub> production rate. Our findings indicate that both Cu<sub>2</sub>O and Cu<sub>(s)</sub> act as co-catalysts for H<sub>2</sub>  
48 generation, yet by different mechanisms. Overall this study, lies the basis to enhance catalytic  
49 performance of red-ox active systems through UV-irradiation approach.

50

51 *Keywords:* copper-based TiO<sub>2</sub>, hydrogen production, photoreforming, photocatalysis, methanol.

52

## 53 **Introduction**

54 Limited availability of fossil fuels as well as their environmental impact has prompted scientific  
55 research towards cleaner and renewable energy sources. In this scenario, sunlight-driven H<sub>2</sub>  
56 production by either photo-reforming or water photo-splitting holds a great promise.<sup>[1,2]</sup> However,  
57 photoreforming-based technologies have been far from practical application and suffer from poor  
58 efficiencies.<sup>[1]</sup> Thus, improvement and optimization of photocatalytic systems are crucial tasks to  
59 make this technology feasible.<sup>[3]</sup> Indeed, photocatalysts with appropriate band-gap and adequate  
60 stability for either organic photo-reforming or water-splitting under visible light irradiation with  
61 suitable energy efficiencies are still unavailable, and their development is considered a significant  
62 challenge in photocatalysis research.<sup>[4,5]</sup>

63 Even though titanium dioxide in P25 form (80:20 w/w anatase:rutile) is considered one of the most  
64 promising commercial material for photocatalytic processes, it shows significant limitations, such as  
65 fast electron/hole recombination and absorption/activity restricted to the UV region due to its wide  
66 bandgap.<sup>[6,7]</sup> Among the various methods employed for improving TiO<sub>2</sub> properties, doping with noble  
67 metals (Au, Pt, Pd) acting as co-catalysts has proven to be effective to enhance the photo-efficiency  
68 of titanium dioxide.<sup>[3,8-10]</sup>

69 Alternatively, doping with transition metal ions such as Cu, Fe, Co, Ni is a cheaper promising  
70 option.<sup>[6,9,11-13]</sup> The advantages of adopting these species lie in their behavior as electron scavengers,  
71 thus limiting charge recombination.<sup>[9, 10, 14-16]</sup> In particular, copper loaded-P25 nanomaterials,  
72 prepared by impregnation method, have been proposed as promising catalysts for photo-reforming.<sup>[17-</sup>  
73 <sup>19]</sup> Although several studies have investigated the effect of copper loading on P25 nanoparticles for  
74 the photocatalytic hydrogen generation through reforming of organics (Table 1), the effect of copper  
75 oxidation state on the improvement in photocatalytic activity, is not yet entirely clarified. Different  
76 conflicting opinions have been provided on synergistic effects of active copper species in photo-  
77 catalytic reactions.

78

79 **Table 1** - Selected research papers devoted to testing Cu/P25 photocatalysts, prepared by  
 80 impregnation method, in various photocatalytic processes.

Precursor	Calcination temperature (°C)	Cu oxidation state	Diagnostic technique	Application	Ref.
$\text{Cu}(\text{NO}_3)_2 \times 3\text{H}_2\text{O}$	300 – 500 for 0.5 h	CuO	TPR, XRD	Hydrogen production	[20]
$\text{Cu}(\text{NO}_3)_2 \times 2.5\text{H}_2\text{O}$	300 for 5 h (in air)	CuO	TPR	CO oxidation	[21]
$\text{Cu}(\text{NO}_3)_2 \times 2.5\text{H}_2\text{O}$	300 for 5 h (in air)	CuO/Cu <sub>2</sub> O	TPR, XRD, XPS, Raman	CO oxidation	[22]
$\text{Cu}(\text{NO}_3)_2$	400 for 16 h (in air)	CuO	TPR, XRD, FTIR	Hydrogenation of 1,3-cyclooctadiene	[23]
$\text{Cu}(\text{CH}_3\text{COO})_2 \times \text{H}_2\text{O}$	250 for 4 h (in air)	Cu <sup>2+</sup> /Cu <sup>+</sup>	TPR, XPS, FTIR	Hydrogenation of crotonaldehyde	[24]
$\text{Cu}(\text{NO}_3)_2$	400 for 1h (in Helium)	CuO/Cu <sub>2</sub> O	TPR, XPS, FTIR,	CO oxidation	[25]
$\text{Cu}(\text{NO}_3)_2$	300 – 500 for 5 h	CuO/Cu <sub>2</sub> O	DRS, XPS, FTIR	Hydrogen production	[26]
$\text{Cu}(\text{NO}_3)_2 \times 3\text{H}_2\text{O}$	300 for 0.5 h (in air)	CuO/Cu <sub>2</sub> O	XPS, XRD	Hydrogen production	[27]
$\text{Cu}(\text{CH}_3\text{COO})_2 \times \text{H}_2\text{O}$ or $\text{Cu}(\text{NO}_3)_2$	500 – 600 for 1 h (in Argon)	CuO/Cu <sub>2</sub> O	XRF, XRD	Acetic acid decomposition, hydrogen production	[28]
$\text{Cu}(\text{NO}_3)_2 \times 3\text{H}_2\text{O}$	400 for 2 h	CuO	XANES, EXAFS	Methylene blue degradation	[29]
$\text{Cu}(\text{NO}_3)_2$	350 for 4 h (in air)	CuO	XRD	Hydrogen production	[30]
$\text{Cu}(\text{NO}_3)_2 \times 3\text{H}_2\text{O}$	350 for 2 h (in air)	Cu <sub>2</sub> O	XPS, XRD	Hydrogen production	[31]

$\text{Cu}(\text{NO}_3)_2$	100 – 600 n.r.	CuO	XPS, XRD	Hydrogen production	[32]
$\text{Cu}(\text{NO}_3)_2$	350 for 4 h (in air)	CuO	XRD	Hydrogen production	[33]
$\text{Cu}(\text{NO}_3)_2 \times 3\text{H}_2\text{O}$	450 for 4 h (in air)	CuO	XPS, XRD	Hydrogen production	[34]
$\text{Cu}(\text{NO}_3)_2 \times 3\text{H}_2\text{O}$	450 for 4 h (in air)	$\text{CuO}$ , $\text{Cu}_x\text{Ti}_{1-x}\text{O}_2$	XRD, XANES, EXAFS	Hydrogen production	[35]
$\text{CuCO}_2\text{CH}_3$	400 for 1h (in air)	$\text{Cu}_2\text{O}$ , CuO	XPS, XRD, DRUV	Gallic Acid degradation	[36]

81

82 Several studies report that  $\text{Cu}_2\text{O}$  species are responsible for enhanced photocatalytic  $\text{H}_2$  production  
83 from water.<sup>[8,9,25,37]</sup> On the other hand, the presence of CuO was argued by different authors to be  
84 responsible for the enhanced separation of photoinduced electrons and holes.<sup>[3,30,32,33]</sup> Similarly,  
85 Valero et al. proposed that easily reduced  $\text{Cu}^{2+}$  species could be responsible for higher Cu/P25  
86 photoactivity.<sup>[38]</sup> Other scientific studies also ascribe the improved photocatalytic activity of Cu/P25  
87 systems to the presence of finely dispersed and easily reducible  $\text{CuO}_x$  ( $\text{Cu}^+/\text{Cu}$ ) species on the  $\text{TiO}_2$   
88 surface.<sup>[39]</sup> Such widespread variability in scientific conclusions is due to an intrinsic complexity of  
89 materials during photocatalytic experiments, along with different impregnation procedures for copper  
90 doping of P25 resulting in mixed oxidation states of copper on the catalyst surface. Typically, copper  
91 exists in different oxidation states ( $\text{Cu}_{(s)}$ ,  $\text{Cu}^+$ ,  $\text{Cu}^{2+}$ ), that can change under UV-irradiation.<sup>[40-42]</sup>  
92 In this scenario, the present paper aims at elucidating the nature of copper species in Cu/ $\text{TiO}_2$   
93 photocatalysts prepared via impregnation-calcination method. Moreover, evolution of copper species  
94 under UV-irradiation during phot-reforming process was investigated, in order to clearly identify the  
95 active species involved in  $\text{H}_2$  production. Hydrogen production rates were compared and integrated  
96 with a detailed physico-chemical characterization of the catalyst before and after the photo-catalytic

5

97 process, through a combined approach of complementary techniques, including X-Ray diffraction  
98 (XRD), X-Ray Photoelectron Spectroscopy (XPS), Raman and Electron Paramagnetic Resonance  
99 (EPR) Spectroscopies, Scanning Electron Microscopy (SEM), High Resolution Transmission  
100 Electron Microscopy (HR-TEM), and Temperature Programmed Reduction (TPR) analysis. This  
101 study is expected to deliver significant insights on the molecular factors responsible for the improved  
102 photocatalytic activity of Cu-based TiO<sub>2</sub> materials, thus providing critical guidelines for the design  
103 of new copper doped photocatalysts for UV-solar photoreforming.

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## 105 **Results and Discussion**

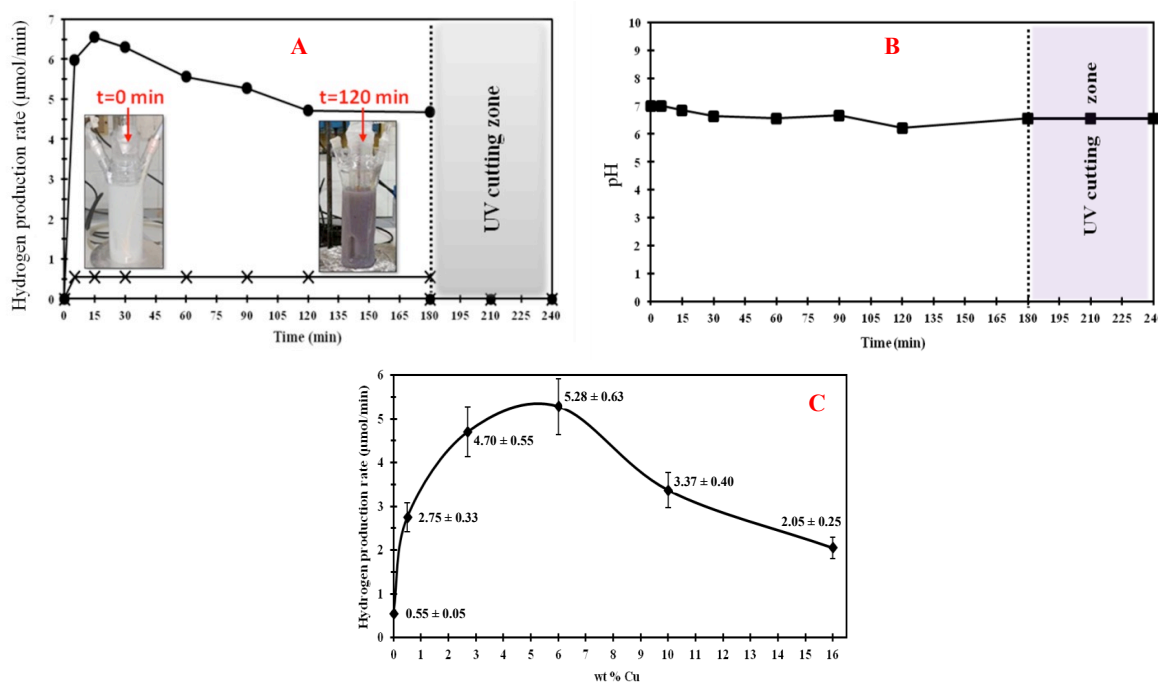
### 106 **Photocatalytic tests**

#### 107 *Effect of photocatalyst copper content on H<sub>2</sub> generation*

108 P25-based samples with different copper weight percentages, in the range 0.5-16 wt%, were tested  
109 for hydrogen generation through photoreforming of methanol. Figure 1A shows H<sub>2</sub> production rate  
110 of Cu(3%)/P25 after calcination at 350 °C; this trend, approaching a plateau within about 120 minutes,  
111 is representative of all compositions. During the photocatalytic run, the suspension turned from light  
112 teal to deep indigo, thus suggesting that a change in copper oxidation state occurred under UVA  
113 irradiation.<sup>[27]</sup> After 180 minutes of reaction, UVA radiation was cut off by inserting a NaNO<sub>2</sub> solution  
114 (1 M) into the cooling system, as previously proposed and described in the Experimental section.<sup>[43]</sup>  
115 Such procedure allowed to test the photocatalytic activity under only visible light irradiation. No  
116 hydrogen generation was recorded for any catalysts tested under only visible light irradiation, thus  
117 indicating that such system are activated by UV irradiation. Furthermore, hydrogen production rates  
118 were remarkably higher than values obtained over bare P25-TiO<sub>2</sub> calcined under inert atmosphere at  
119 350 °C for 5 hours (0.55 μmol/min) and comparable to the values measured by Jung et al. by using  
120 H<sub>2</sub>-treated Cu/P25 samples.<sup>[27]</sup> Figure 1B depicts the change in solution pH during the photoreforming  
121 run. There was no changes in pH, which kept constant at about 6.5 throughout the experiment.  
122 Furthermore, no trace of dissolved copper was detected throughout the experiment, thus suggesting



123 a high stability of the photocatalyst. Figure 1C shows hydrogen production rate as a function of copper  
 124 content. A non-monotonic trend was observed, with catalysts containing 3% and 6% weight  
 125 percentages of copper displaying comparable similar values of hydrogen production rate, which were  
 126 also the highest recorded. All Cu/P25 systems showed higher light absorption capability than bare  
 127 P25-TiO<sub>2</sub> both in the UV and visible range (Figure S1A-B), although this did not result in a catalytic  
 128 activity of the Cu-doped catalyst under visible light irradiation.



129 **Figure 1. Panel A:** Hydrogen production rate over (●) Cu(3%)/P25 and (×) bare P25-TiO<sub>2</sub>, both  
 130 calcined under inert atmosphere at 350 °C for 5 hours. After 180 minutes of reaction, UVA radiation  
 131 has been cut off by inserting 1 M NaNO<sub>2</sub> solution into the cooling system. Catalysts load =150 mg/L.  
 132 [CH<sub>3</sub>OH]<sub>0</sub> = 2.47 M. T=25 °C. P=1atm. The insets represent the colour suspension with Cu(3%)/P25  
 133 before and after 120 min of reaction. **Panel B:** Solution pH throughout the photoreforming run over  
 134 Cu(3%)/P25 catalyst calcined under inert atmosphere at 350 °C for 5 hours. After 180 minutes of  
 135 reaction, UVA radiation was cut off by inserting 1M NaNO<sub>2</sub> solution into the cooling system.  
 136 Cu(3%)/P25 catalyst load=150 mg/L. [CH<sub>3</sub>OH]<sub>0</sub> = 2.47 M. T=25 °C. P=1 atm). For each value, 12%  
 137 error was considered, based on the results of a reproducibility photoreforming run performed over  
 138 Cu(3%)/P25 calcined at 350 °C. **Panel C:** Plateau values of hydrogen production rate recorded over  
 139 P25-TiO<sub>2</sub> catalysts calcined under inert atmosphere at 350 °C for 5 hours with different copper  
 140 content. Weight percentages of copper: 0.5%, 3%, 6%, 10%, 16%.Cu/P25-TiO<sub>2</sub> catalysts load=150  
 141 mg/L. [CH<sub>3</sub>OH]<sub>0</sub> = 2.47 M. T=25 °C. P=1 atm.

142  
 143  
 144  
 145 *Effect of photocatalyst calcination temperature on H<sub>2</sub> generation*

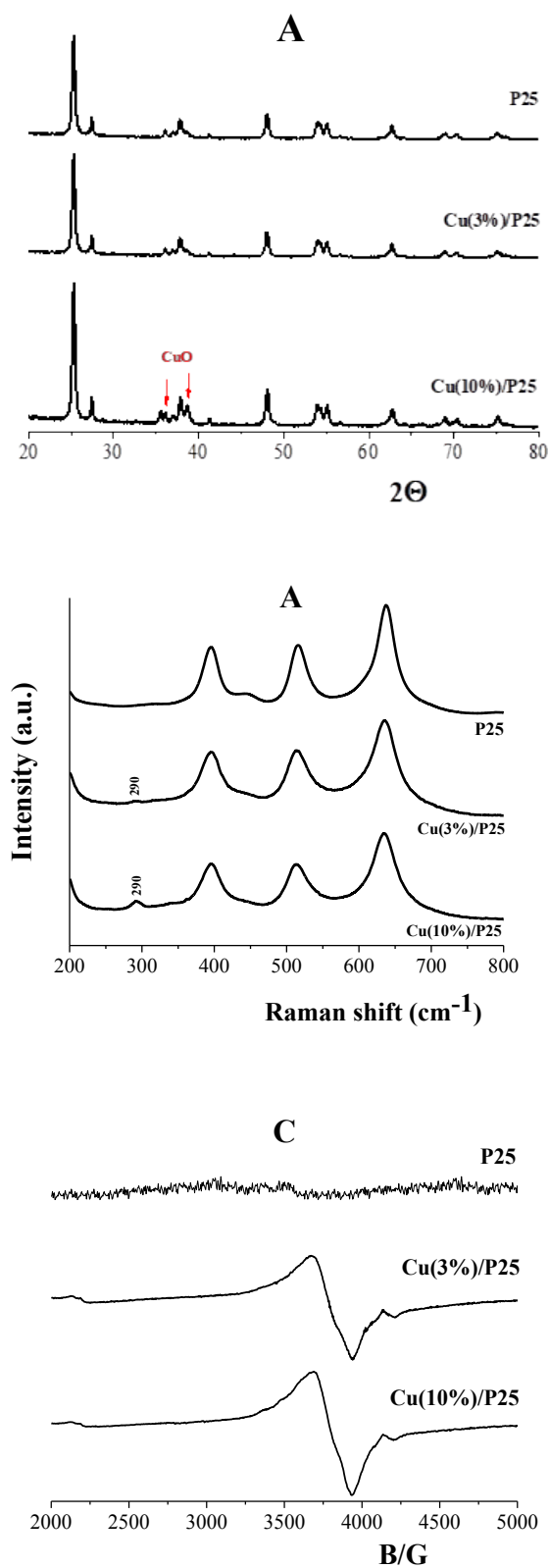
146 Cu/P25 samples calcined under inert N<sub>2</sub> atmosphere for 5 hours at different temperatures were tested  
 147 for hydrogen generation through photo-reforming of methanol. Calcination temperatures were

148 investigated in the range of 150-550 °C (Figure S2, Supplementary Information). Similar values of  
149 hydrogen generation rates were achieved by using catalysts calcined at 150-350 °C, though, further  
150 increase in calcination temperature showed detrimental results in terms of photoefficiency for  
151 hydrogen generation. Once again, no hydrogen evolution was recorded by excluding UV irradiation  
152 for all catalysts tested.

### 153 **Characterization of the fresh photocatalysts**

154 Detailed physico-chemical characterizations of Cu/P25 samples were carried, before and after  
155 photocatalytic experiments, in order to investigate changes in catalysts' properties upon use for H<sub>2</sub>  
156 production under near-UV irradiation. In particular, copper oxidation states in Cu deposited species  
157 on P25 surface were assessed both before and after photocatalytic experiment with the aim of  
158 revealing their role in the enhancement of photocatalytic H<sub>2</sub> production. The measured values of BET  
159 surface specific area ( $S_{\text{BET}}$ ) for Cu/P25 catalysts calcined at different temperatures or with different  
160 Cu loads are summarised in Table S1 (Supplementary Information). No particular changes were  
161 observed before and after use (data not shown), but a significant decrease in the surface area was  
162 recorded for the catalyst calcined at 550 °C, likely due to some aggregation phenomenon.  
163 Specifically, the highest surface area of 41 m<sup>2</sup>/g was recorded for Cu(3%)/P25 calcined at 350 °C.  
164 XRD spectra were collected in order to assess crystalline properties in the catalysts. Figure 2A shows  
165 XRD spectra of bare P25, fresh Cu(3%)/P25 and Cu(10%)/P25 calcined at 350 °C for 5h. Peaks of  
166 anatase and rutile structures appeared in all samples. Furthermore, XRD profiles of the fresh  
167 Cu(3%)/P25 samples did not show any diffraction peaks of CuO<sub>x</sub> species, in agreement with the low  
168 amount of Cu. On the contrary, XRD spectrum of Cu(10%)/P25 sample highlighted two diffraction  
169 peaks at about 36.5° and 38.5°, displaying the presence of CuO.<sup>[27]</sup> Comparison of the peak intensities  
170 of rutile and anatase revealed the typical composition of P25 samples that was not altered neither by  
171 Cu impregnation (Figure 2A). Furthermore, no relevant changes in peak position and intensity were

172 appreciated the XRD patterns of samples treated up to 450 °C (Figure S3), revealing that thermal  
173 treatment did not significantly alter the samples crystalline structure.

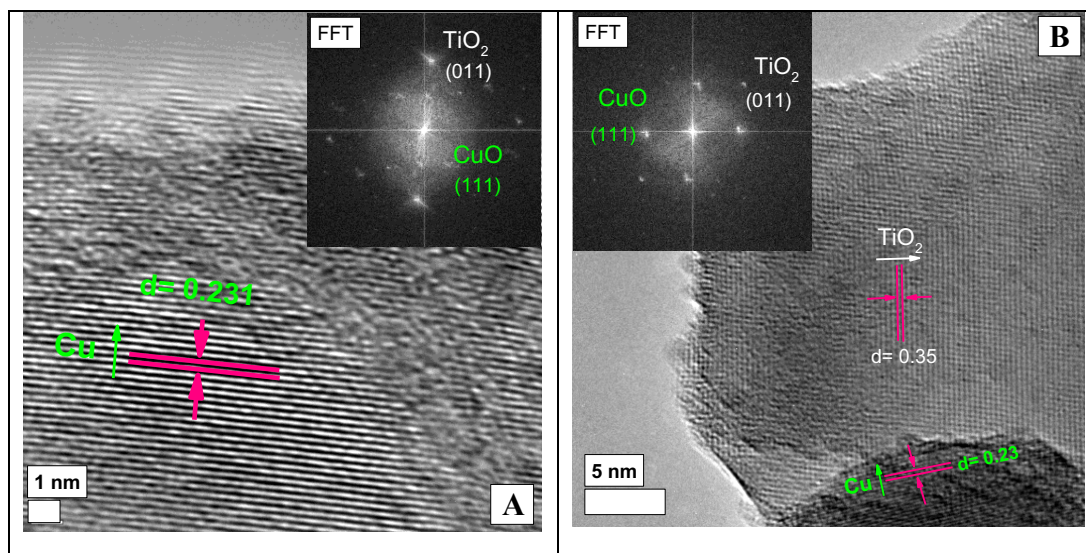


174

175 **Figure 2.** XRD patterns (**panel A**), Raman spectra (**panel B**) and normalized EPR spectra (**panel C**)  
176 of bare P25, fresh Cu(3%)/P25 and Cu(10%)/P25 calcined at 350 °C for 5h.

177 Raman and EPR spectra were also recorded in order to define the oxidation state of copper  
178 impregnated on the P25 surface for materials before their use (Figure 2B-C). Concerning the fresh  
179 Cu/P25 catalyst, Raman spectra were recorded on Cu(3%)/P25 and Cu(10%)/P25 samples (Figure  
180 2B) also compared to P25 as reference material. Both catalysts showed a peak at  $290\text{ cm}^{-1}$ , which is  
181 ascribable to the Raman band of CuO. Although it is usually detected around  $279\text{ cm}^{-1}$ , and is  
182 associated to an  $A_g$  mode,<sup>[45]</sup> the upshift in wavenumbers observed in our experiments compared to  
183 pure CuO can occur either due different structuring or to interactions with the hosting matrix (herein  
184  $\text{TiO}_2$ ). On the other hand, the typical most intense Raman band of  $\text{Cu}_2\text{O}$  and corresponding to the  
185 second order overtone  $2\Gamma_{12^-}$  ( $216\text{ cm}^{-1}$ )<sup>[44]</sup> was never visible in any analysed catalyst (Figure 2B). The  
186 presence of cupric species in pre-used (fresh) Cu(3%)/P25 and Cu(10%)/P25 catalysts was also  
187 confirmed by EPR spectra (Figure 2C) showing an asymmetric signal for both samples at a g-factor  
188 of  $\sim 2.0800$ , which is larger than the g-value of free electron  $g_e = 2.0023$  and is related to the presence  
189 of  $\text{Cu}^{2+}$  in the distorted octahedral coordination of  $\text{TiO}_2$ .<sup>[46]</sup> The broadness of the EPR spectra indicates  
190 the presence of dipolar interaction among neighboring  $\text{Cu}^{2+}$  ions that leads to the increase in the width  
191 of the EPR signal.

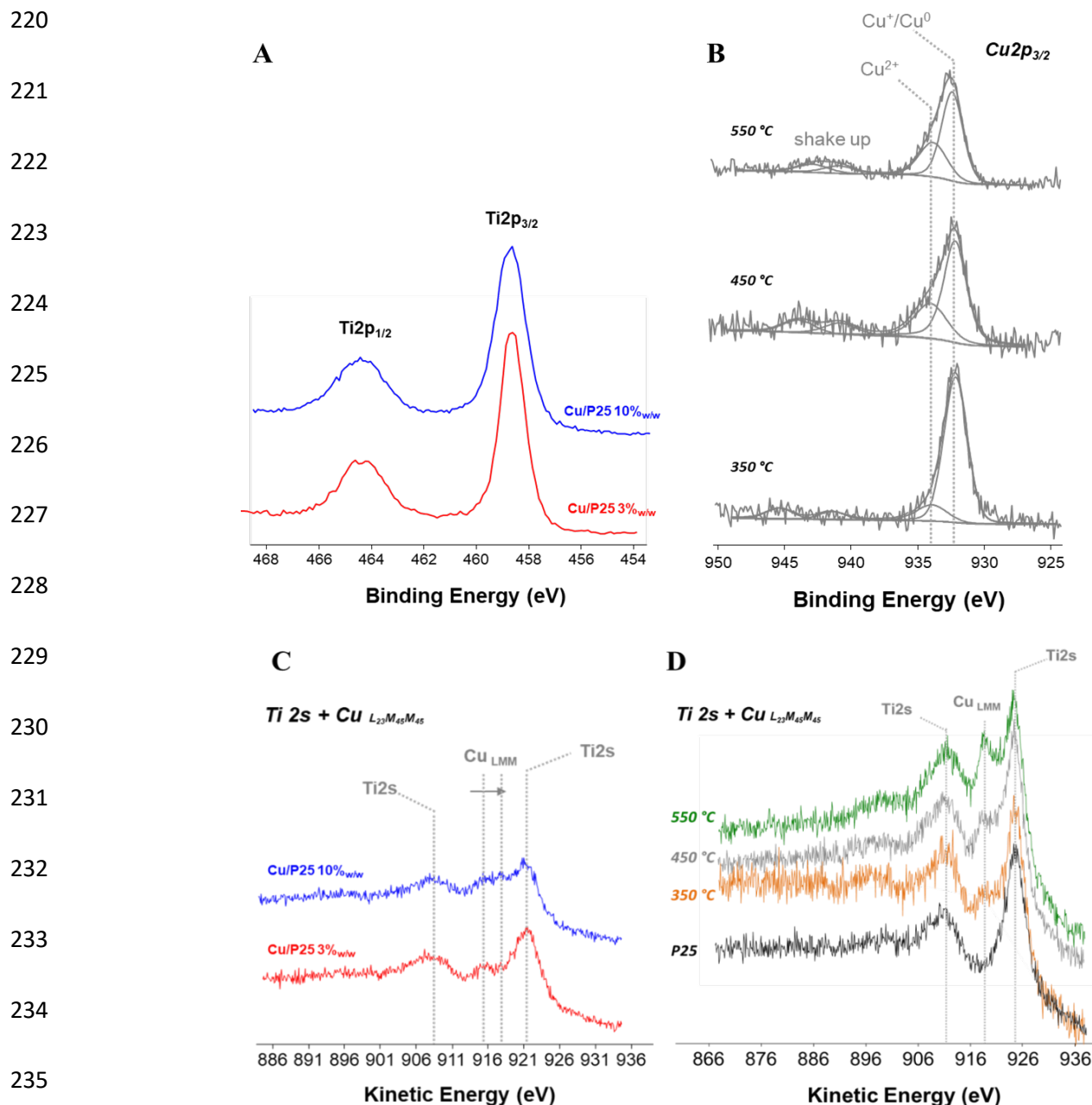
192 Therefore, XRD, EPR and Raman analyses confirm the presence of CuO in Cu/P25 samples.  
193 Morphology, crystal structure and copper oxidation states were also assessed through TEM analyses.  
194 Figure 3A shows HR-TEM and Fast Fourier Transform (FFT) analyses for fresh Cu(3%)/P25 sample  
195 calcined at  $350\text{ }^\circ\text{C}$ . An interplane distance of  $d_{\text{Cu}} = 0.231\text{ nm}$  calculated from the HR-TEM micrograph  
196 (Figure 3A), corresponding to the (111) plane of CuO, further confirmed its presence on  $\text{TiO}_2$  ( $d_{\text{TiO}_2}$   
197  $= 0.33\text{ nm}$ ), in accordance with XRD, Raman and EPR results. Moreover, FFT image (*inset* of Figure  
198 3C) clearly justified the existence of  $\text{TiO}_2$  material in amorphous structure with some clear spots  
199 related to the co-existed CuO particles.



200

201 **Figure 3.** HR-TEM for fresh Cu(3%)/P25 sample calcined at 350 °C (**A**, inset: FFT analysis) and for  
 202 fresh Cu(10%)/P25 catalyst calcined at 350 °C (**B**, inset: FFT analysis).  
 203

204 Changing Cu composition in Cu/P25 catalyst to 10% while maintaining the calcination temperature  
 205 at 350 °C did not lead to a significant alteration in the catalyst structure (Figure 3B), however larger  
 206 surface deposits were appreciated (Figure 3B). To further clarify the oxidation state of surface Cu-  
 207 species, samples were analyzed by means of XPS analysis. Higher temperatures led to an increase of  
 208 copper surface availability, as evident from Cu/Ti atomic ratio in Cu(3%)/P25 samples (Table S2).  
 209 At 550 °C aggregation phenomena of copper particles can occur, resulting in higher Cu detected  
 210 amount in the same analyzed spot. A similar trend is shown when the catalysts were prepared with  
 211 increasing bulk copper loading, even at the lowest calcination temperature (Table S3). Actually, both  
 212 the total copper increase and the eventual surface aggregation phenomena could contribute to the  
 213 increase of copper amount detected on the surface. Indeed, the observed increase in Cu surface  
 214 availability was not proportional to the overall Cu content; actual difference between them got wider  
 215 with increasing copper loading, suggesting a different size distribution of copper species on TiO<sub>2</sub>  
 216 surface. Apart from total surface copper availability, XPS measurements were aimed at elucidating  
 217 Cu and Ti oxidation state of Ti on TiO<sub>2</sub> surface. Figure 4A shows Ti2p XP spectral region of fresh  
 218 Cu(3%)/P25 and Cu(10%)/P25 catalysts. XPS spectra of all catalysts with different copper loadings  
 219 are reported in Figure S5.



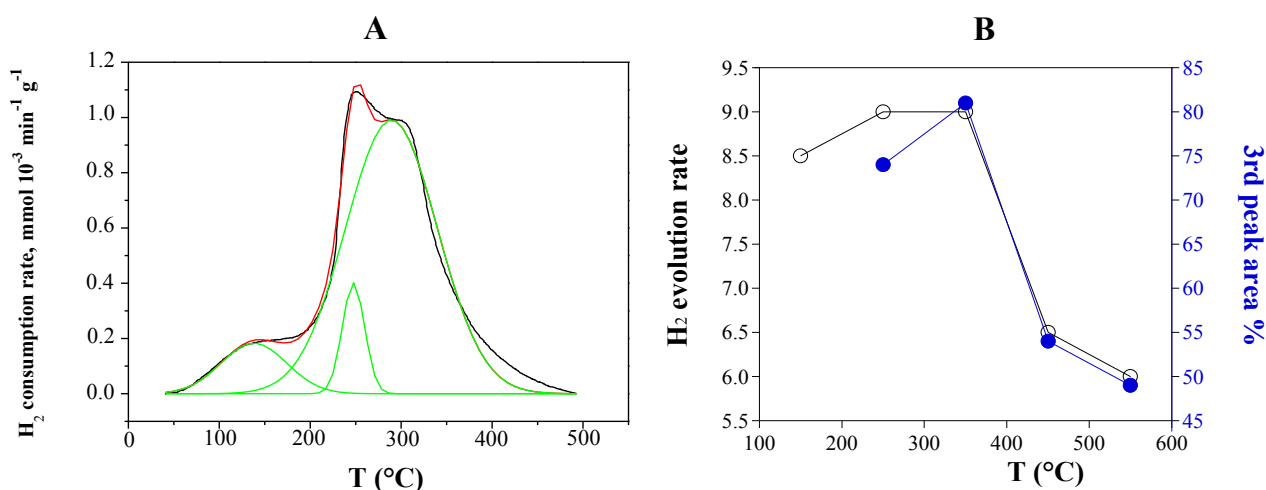
236 **Figure 4.** Ti2p XP spectra of the fresh Cu(3%)/P25 and Cu(10%)/P25 catalysts calcined at 350 °C  
 237 (A). Cu2p<sub>3/2</sub> XP spectra of the fresh Cu(3%)/P25 sample at different calcination temperatures (B).  
 238 Ti2s XP+Cu<sub>LMM</sub> XAE spectra of Cu(3%)/P25 and Cu(10%)/P25 calcined at 350 °C (C) and of  
 239 Cu(3%)/P25 at different calcination temperatures (D).

240

241 In all the spectra, the characteristic peaks of Ti2p<sub>3/2</sub> and Ti2p<sub>1/2</sub> were observed at BE values of  
 242 458.7±0.1 eV and 464.4±0.1 eV, respectively, and were assigned to Ti<sup>4+</sup> in TiO<sub>2</sub>.<sup>[1]</sup> A possible  
 243 interaction between Cu species and P25 would result not only in the BE shift but also in the change  
 244 of the spin-orbit splitting value in the Ti2p signal.<sup>[1]</sup> Nevertheless, no significant variation was

245 observed neither changing the copper loading nor increasing the calcination temperature (Figure 4A,  
246 Figure S5 in Supplementary Information); the value was measured to be constant and equal to 5.7  
247 eV, therefore no Cu incorporation into the TiO<sub>2</sub> lattice could be hypothesized.<sup>[2]</sup> Figure 4B reports  
248 Cu2p<sub>3/2</sub> XP spectra of the Cu(3%)/P25 catalyst calcined at different calcination temperatures. After  
249 curve-fitting procedures, the main peak was identified at BE=932.4±0.1 eV in all the cases and was  
250 ascribed to Cu<sup>+</sup>/Cu<sup>0</sup> species.<sup>[1,3]</sup> Furthermore, shake up satellites were visible (940-945 eV) along with  
251 a peak at 934.0±0.1 eV, that was assigned to Cu<sup>2+</sup> species.<sup>[1,3]</sup> The copper spectral regions of the  
252 catalysts prepared at higher bulk copper loadings (Figure 4A, Figure S5) as well as at different  
253 calcination temperatures (Figure 4B) showed similar results. Particularly, for Cu(3%)/P25 sample at  
254 different temperatures, a main peak due to Cu<sup>+</sup>/Cu<sup>0</sup> species along with variable amounts of Cu<sup>2+</sup>,  
255 depending on the Cu loading, was detected (Figure 4B). Since the binding energies of Cu<sup>+</sup> and Cu<sup>0</sup>  
256 are not distinguishable based on Cu2p<sub>3/2</sub> XP peak, the spectral region relative to X-ray excited Auger  
257 copper spectra (XAES Cu<sub>LMM</sub>) were investigated to fully elucidate the oxidation state of the reduced  
258 copper species. Figure 4 reports Cu<sub>LMM</sub> spectra for fresh Cu(3%)/P25 and Cu(10%)/P25 samples  
259 treated at 350 °C (C) and 3%Cu bulk loading at different calcination temperatures (D) .  
260 A further challenge in the Cu<sup>+</sup>/Cu<sup>0</sup> discrimination was represented from the partial overlapping of  
261 Cu<sub>LMM</sub> and the predominant Ti2s spectral regions (black line in Figure 4D). Nevertheless, the main  
262 peak for copper was still detectable in all the samples and was found at KE=916.3±0.3 eV. Moreover,  
263 the Auger parameter – the sum of the binding energy from XPS and the kinetic energy from XAES –  
264 was calculated to be 1848.7±0.1 eV. Both the values demonstrated that the Cu<sup>+</sup>/Cu<sup>0</sup> peak is ascribable  
265 to Cu<sup>+</sup> species.<sup>[3]</sup> However, the absence of Cu<sup>0</sup> traces could not be completely ruled out under these  
266 experimental conditions, since the peak would fall at KE=918.6 ±0.2 eV, overlapped with Ti2s  
267 peak.<sup>[46]</sup> Similar results were obtained for XPS spectra of the samples at different calcination  
268 temperatures (Figure 4D). When the relative abundance of Cu<sup>2+</sup> is increased, the peak is shifted to  
269 slightly higher KE values, according to KE values for oxidized copper species (Figure 4C).<sup>[3]</sup>

270 To get a greater insight into the Cu-TiO<sub>2</sub> interaction as function of the annealing temperature, the  
 271 reducibility of the samples was studied by means of the TPR technique. The TPR profile of  
 272 Cu(3%)/P25 sample after calcination at 350 °C is shown in Figure 5A, while the TPR profiles of  
 273 Cu(3%)/P25 sample after calcination at 250, 450 and 550 °C are reported in Figure S6  
 274 (Supplementary Information). All of them are reported in the temperature range characteristic of  
 275 copper oxide reduction,<sup>[22,38,52]</sup> where instead TiO<sub>2</sub> reduction was hardly observed.



276 **Figure 5. Panel A:** TPR profile of Cu(3%)/P25 sample calcined at 350 °C. **Panel B:** H<sub>2</sub> evolution  
 277 rate (○) and percentage of TPR 3<sup>rd</sup> peak area (●) as a function of calcination temperature for  
 278 Cu(3%)/P25 sample.  
 279

280

281 As indicated by the curve fit analysis, the samples showed a distribution of copper species;  
 282 conversely, the unsupported CuO showed a single peak at 400 °C.<sup>[45,46]</sup> The hydrogen consumption  
 283 relative to each fitting peak for Cu(3%)/P25 is listed in Table 2 and Table S4 along with T<sub>max</sub> values.  
 284

284

285 **Table 2 - Results of TPR measurements for fresh Cu(3%)/P25 sample calcined at 350 °C**

Sample	T <sub>max</sub> (°C)	Hydrogen consumption (μmol/g)
Cu(3%)/P25	138, 246, 290	101, 76, 759

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287 The assignment of the reduction peak at lower temperature is quite controversial: it is generally  
 288 ascribed to the reduction of highly reducible Cu<sup>2+</sup> species, though the presence of Cu<sup>+</sup> species cannot



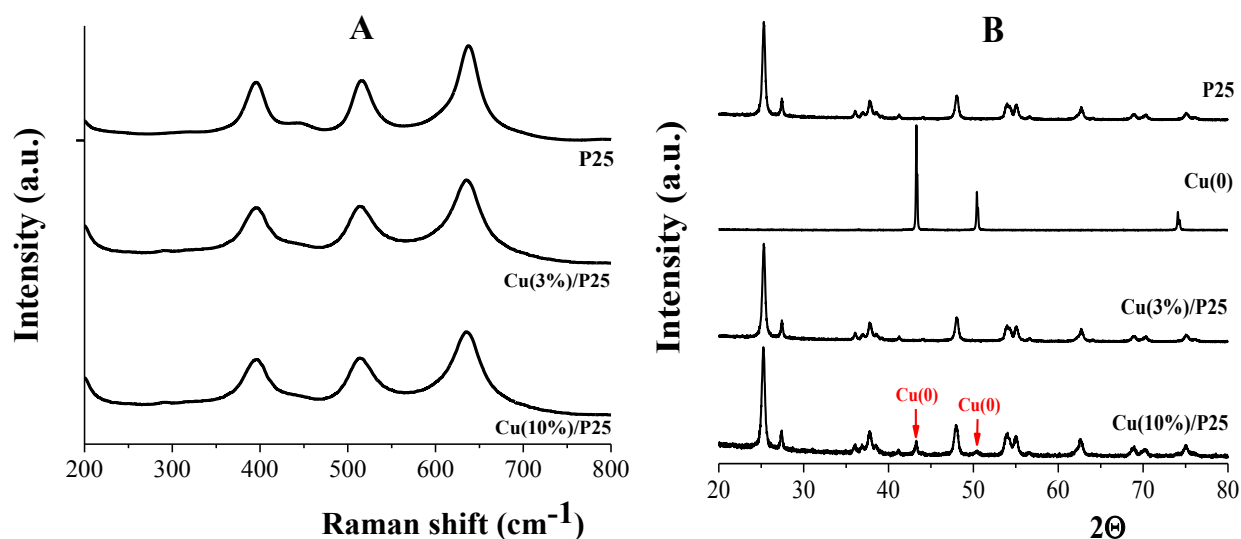
289 be ruled out.<sup>[38]</sup> Indeed, Chen et al. <sup>[22]</sup> assigned the TPR peak in this range to the reduction of Cu<sup>+</sup>  
290 species in Cu(3%)/P25 sample. The formation of Cu<sup>+</sup> species was ascribed to the presence of oxygen-  
291 defect vacancies in the TiO<sub>2</sub> structure. The presence of isolated Cu<sup>+</sup> species and small Cu<sub>2</sub>O cluster  
292 with reduction peak at 157 °C and 208 °C, respectively was also proposed by Minsu Jung et al.<sup>[52,53]</sup>  
293 Samples treated at 250 °C and 350 °C, *i.e.* Cu(3%)/P25\_250 and Cu(3%)/P25\_350, showed the  
294 highest hydrogen consumption in correspondence of the peak at about 280-290 °C associable to small  
295 and/or highly dispersed CuO particles. TPR profile gradually changed by increasing the calcination  
296 temperature, leading to a decrease of the peak at 280-290 °C and to the occurrence of another  
297 reduction peak at higher temperature. Peaks located in the 320-400 °C temperature range are  
298 indicative of the formation of bulky CuO species.<sup>[45,46]</sup> Thus, it can be inferred that a lower calcination  
299 temperature resulted in a better dispersion of copper species on the support. As far as the overall H<sub>2</sub>  
300 consumption is concerned, it was much higher with respect to the stoichiometric amount as calculated  
301 under the hypothesis of the occurrence of all Cu as Cu<sup>2+</sup> species. This likely indicated some spillover  
302 phenomena of H<sub>2</sub> occurring over the support with the likely partial reduction of the latter, as generally  
303 observed for copper doped anatase.<sup>[54]</sup>

304 The influence of calcination temperature on hydrogen production rate is reported in Figure 5B,  
305 together with the percentage of amount of the third peak area in TPR analysis. Actually, evolved H<sub>2</sub>  
306 amount appeared closely related to the fraction of highly dispersed CuO particles strongly interacting  
307 with the support, probably accounting for the third peak area in TPR analysis (Table 2 and Table S4).

### 308 **Characterization of the used Cu/P25 photocatalysts**

309 The Cu/P25 catalysts were also analyzed after their use to assess any evolution of Cu oxidative state  
310 during photocatalytic runs, so as to identify the nature of Cu-active species towards H<sub>2</sub> evolution as  
311 well as their role in photocatalytic. Particularly, this investigation was carried out on both  
312 Cu(3%)/P25 and Cu(10%)/P25 samples, calcined at 350 °C. Specifically, Raman spectra of both  
313 samples after photocatalytic run, reported in Figure 6A, indicated that no peak ascribable to the

314 presence of cupric species was observed. This result was also confirmed by the EPR evidence  
315 indicating that these considered samples did not show any paramagnetic signal. Since no significant  
316 release of cupric ions was observed during photoreforming tests, obtained results suggest the  
317 reduction of the copper during the photoreforming process. Actually, the indigo color of the final  
318 suspension supported a change of the oxidation state of copper deposited on titania, further confirmed  
319 by XRD diffraction analysis too. Notably, XRD patterns of used Cu(10%)/P25 collected after the  
320 photocatalytic run, no longer showed diffraction peaks of CuO phase and clearly indicated the  
321 presence of Cu(0) diffraction peaks (Figure 6B). Unfortunately, due to the low Cu content, this peak  
322 was not detectable in the XRD spectrum of the used Cu(3%)/P25 sample.

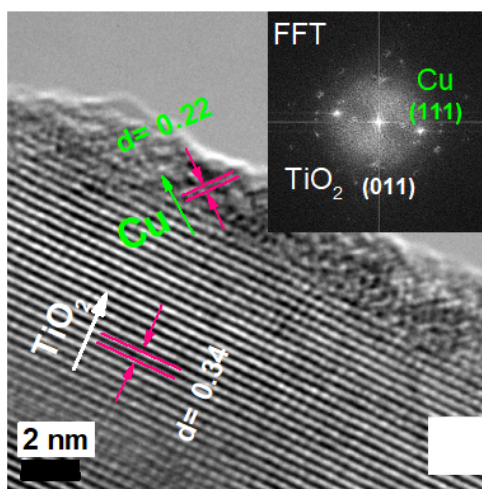


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324 **Figure 6. Panel A:** Raman spectra of bare P25, used Cu(3%)/P25 and Cu(10%)/P25 samples calcined  
325 at 350 °C for 5h. **Panel B:** XRD patterns of bare P25, Cu(0), used Cu(3%)/P25 and Cu(10%)/P25  
326 calcined at 350 °C for 5h.

327

328 HR-TEM and FFT analyses were performed on used Cu(3%)/P25 catalyst calcined at 350 °C, showing  
329 co-existence of Cu<sub>2</sub>O and Cu<sup>0</sup> on the TiO<sub>2</sub> particles, thus indicating CuO reduction (Figures 7) during  
330 the photocatalytic experiment. It is noteworthy mentioning the co-existence of Cu<sub>2</sub>O and Cu<sup>0</sup> in the  
331 used Cu/P25 catalysts was deduced from the indicated phase (111) that corresponds to both Cu<sub>2</sub>O and  
332 Cu<sup>0</sup>,<sup>[55]</sup> the latter also confirmed by XRD analysis. Again, Cu<sub>2</sub>O (111) and Cu<sup>0</sup> (111) were the  
333 dominant copper species in the 10%Cu-containing catalyst (Figure S7).



**Figure 7.** HR-TEM for used Cu(3%)/P25 sample calcined at 350 °C.

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337 The comparison of XPS copper spectra of Cu(3%)/P25 before and after use are reported in Figure 8

338 while Cu/Ti ratio for the same samples are reported in Table S5 (Supplementary Information).

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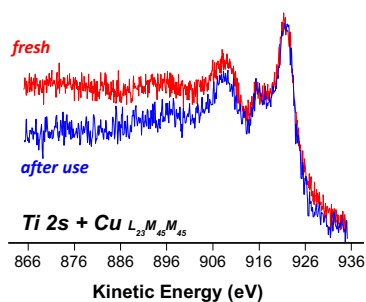
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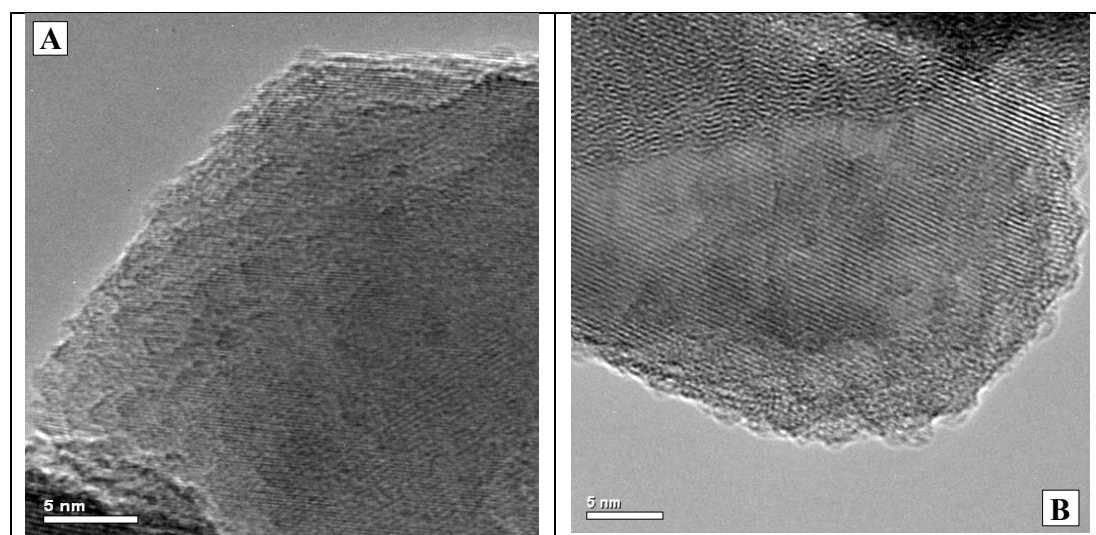
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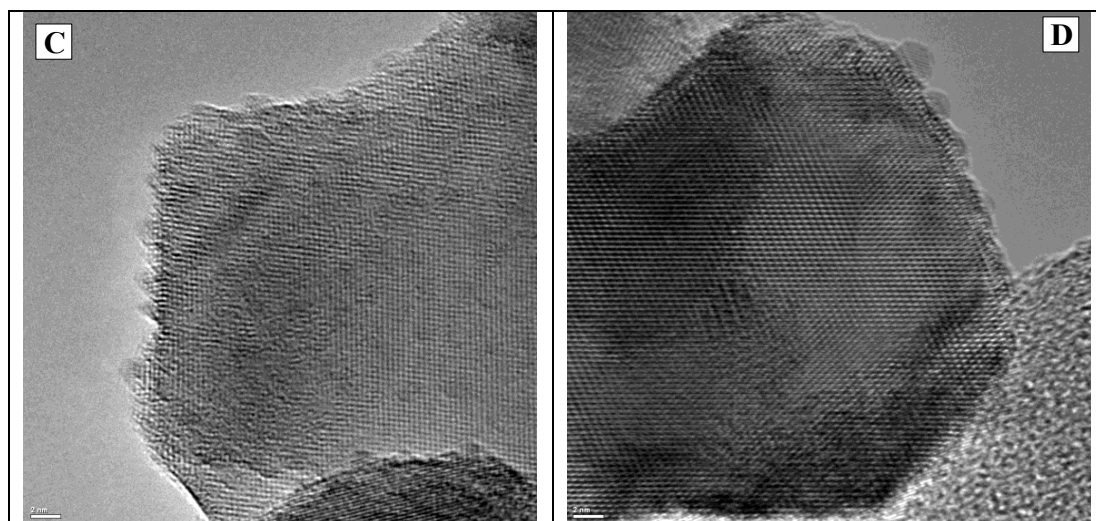
370 **Figure 8.** Cu2p<sub>3/2</sub> XP spectra for Cu(3%)/P25\_350°C fresh and after use. Corresponding Cu<sub>LMM</sub> XAE  
371 spectra in the inset.

372 From XPS and XAES results no specific differences could be derived on the surface of the catalyst  
373 before and after use. Both spectra presented a small amount of Cu<sup>2+</sup> (peak at BE=, 934.0±0.1 eV,  
374 along with shake up features) and the predominant Cu<sup>+</sup>/Cu<sup>0</sup> oxidation state on the catalyst's surface  
375 (main peak at BE=932.4±0.1 eV). Moreover, XAES peaks are completely overlapped. Furthermore,  
376 Cu<sup>0</sup> peak, if any, is overlapped with Ti2s peak in XAE spectrum: this makes any possible change in  
377 Cu<sup>0</sup> amount hardly appreciable in the studied systems.<sup>[49]</sup> Finally, Cu/Ti ratio slightly increased after  
378 use (Table S5), probably due a different distribution of surface copper species.

379 Despite Cu-doped TiO<sub>2</sub> catalysts have been intensively studied for H<sub>2</sub> production through photo-  
380 reforming, published results are still controversial on the activity of different Cu oxidation states.<sup>[20,26-</sup>

381 <sup>34]</sup> Our results clearly showed that calcination of  $\text{Cu}(\text{NO}_3)_2 \times 3\text{H}_2\text{O}$ -impregnated P25 samples under  
382 nitrogen atmosphere leads to a mixture of CuO and  $\text{Cu}_2\text{O}$  nanostructures on P25 surface. The former  
383 was clearly evidenced by bulk characterization techniques, in particular EPR and Raman  
384 spectroscopy. Furthermore, XPS analysis proved the presence of surface  $\text{Cu}_2\text{O}$  as the predominant  
385  $\text{CuO}_x$  species. The poor CuO amount measured through this methodology, can be explained  
386 considering this technique revealing composition of the more exposed layer on the surface. These  
387 results supported earlier reports, where both oxidation states are observed for copper.<sup>[22,24-28,36]</sup>  
388 Furthermore, as a major point, from TPR analysis different populations of  $\text{CuO}_x$  species could be  
389 distinguished on the catalysts. A highly dispersed fraction of small and dispersed CuO particles  
390 strongly interacting with the support was appreciated on the catalysts with the highest  $\text{H}_2$  evolution  
391 rate. During photocatalytic process,  $\text{CuO}_x$  based deposits were reduced to  $\text{Cu}_2\text{O}/\text{Cu}^0$  and concurrently  
392 a morphological evolution was also appreciated (Figure 9). Notably, deposits with less defined  
393 morphology were observed in Cu(3%)/P25 sample after use, while larger  $\text{CuO}_x$  surface deposits were  
394 observed in Cu(10%)/P25 sample. Previous reports provided evidence of  $\text{Cu}^{2+}$  reduction to  $\text{Cu}^+$  <sup>[22, 36]</sup>  
395 and to  $\text{Cu}^0$  <sup>[41]</sup> under UVA irradiation.



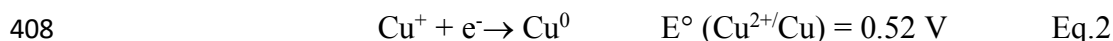
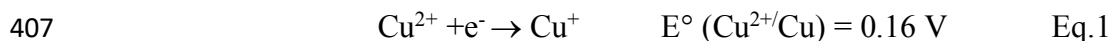


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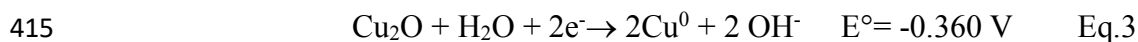
397 **Figure 9.** HR-TEM for Cu(3%)/P25 sample fresh (A) and after used (B) and for Cu(10%)/P25  
 398 sample, before (C) and after used (D).

399

400 Experimental findings and in particular morphological evolution from HR-TEM analysis as well as  
 401 Cu changes in copper surface availability after use (Table S5, Supplementary Information) suggested  
 402 that CuO<sub>x</sub> species undergo in situ dynamic nanostructuring during photocatalytic run. The process is  
 403 driven by the dissolution-redeposition of CuO<sub>x</sub> deposits on the TiO<sub>2</sub> surface under UV irradiation.<sup>[56-  
 404 57]</sup> In more detail, CuO<sub>x</sub> species must be involved in a dissolution process, leading to Cu<sup>2+</sup> ions, that  
 405 upon illumination are reduced to Cu<sub>2</sub>O and then to Cu, by photo-generated electrons, according to  
 406 Equations 1 and 2, both involving dissolved Cu ions:



409 In fact, electrochemical potentials of both half-reactions are higher than H<sup>+</sup> species, supporting the  
 410 hypothesis of Cu<sup>2+</sup> and Cu<sup>+</sup> preferential reduction by TiO<sub>2</sub> photogenerated electrons. The excess of  
 411 electrons in the Cu deposits, accompanied by the consumption of photogenerated holes by methanol,  
 412 allowed for the deposits to keep a metallic state throughout the reaction, as experimentally confirmed.  
 413 Actually, negative electrochemical potential of solid state reduction further supports the hypothesis  
 414 of reduction from solution (Equation 3).

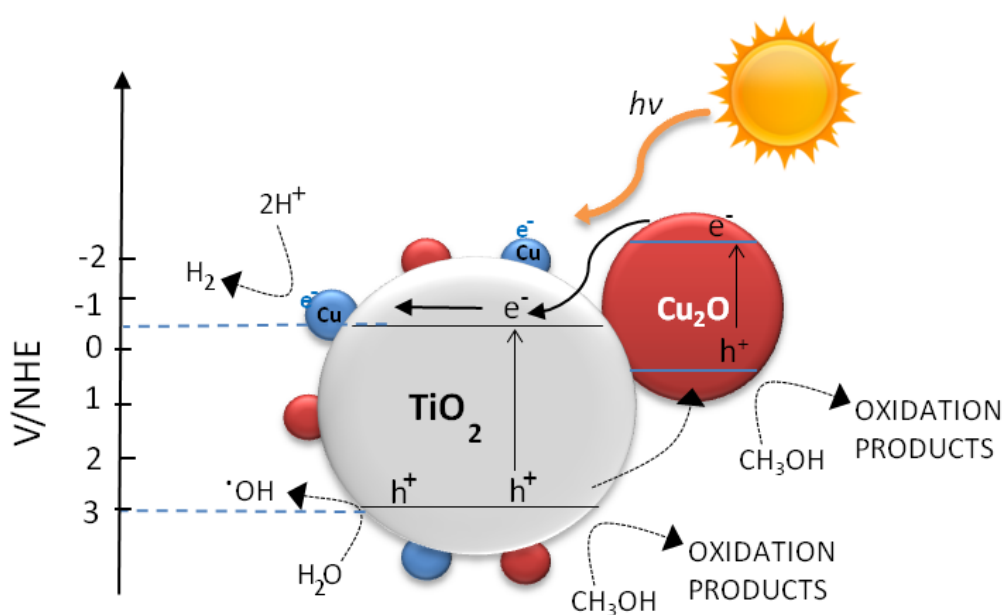


416 Indeed,  $\text{Cu}_2\text{O}$  reduction to metallic Cu was not revealed by previous studies on Cu impregnated  
 417  $\text{TiO}_2$ ,<sup>[22]</sup> however these differences should depend on the size of  $\text{CuO}_x$  deposits and their interaction  
 418 with  $\text{TiO}_2$  surface, strongly influencing their reducibility.

419 Actually, change in size and distribution of Cu species on the surface, as evidenced by HR-TEM,  
 420 supports this mechanism.

421 Actually, island-like morphology of copper species on  $\text{TiO}_2$  surface suggests deposition-reduction  
 422 process occurred according to the Volmer-Weber mechanism<sup>[58]</sup>. Notably, the lattice parameters of  
 423 the substrate, significantly affect the sizes and oxidation level of Copper deposits. On this basis, as  
 424 evidenced by experimental results, Cu and  $\text{Cu}_2\text{O}$  species must be preferentially deposited on  $\text{TiO}_2$   
 425 surface, due to their very good crystal lattice matching with P25 substrate ( $a_{\text{Cu}} = 0,3615 \text{ nm}$ ,  $a_{\text{TiO}_2}$   
 426  $\text{anatase} = 0,378 \text{ nm}$ ;  $a_{\text{Cu}_2\text{O}} = 0,427$ ,  $a_{\text{TiO}_2 \text{ rutile}} = 0,459 \text{ nm}$ ). As a further support, electrochemical deposition  
 427 on a semiconducting surface leads to coexistence of Cu and  $\text{Cu}_2\text{O}$  species on the surface .

428 Metallic Cu nanoparticles, should act as a co-catalyst for  $\text{H}_2$  production, attracting photogenerated  
 429 electrons from  $\text{TiO}_2$  and promoting their transfer to the protons,<sup>[27]</sup> according to the scheme in Figure  
 430 10.



431

432 **Figure 10.** Proposed hydrogen photogeneration mechanism for Cu/ $\text{Cu}_2\text{O}$ / $\text{TiO}_2$  system.

433

434 At the same time, upon illumination,  $\text{Cu}_2\text{O}$  should inject photoelectrons into  $\text{TiO}_2$  conduction band  
435 and hosting holes from  $\text{TiO}_2$  valence band (Figure 10). Electrons injected into  $\text{TiO}_2$  bands should be  
436 involved in  $\text{H}^+$  reduction, thus accounting for  $\text{H}_2$  production since the beginning of the photocatalytic  
437 run. The increased presence of holes in  $\text{Cu}_2\text{O}$  may limit further reduction of the  $\text{Cu}^+$  to  $\text{Cu}^0$  as well as  
438 methanol oxidation, thus accounting for constant pH values during photo-reforming. Both processes  
439 restrict electron/hole recombination phenomena and account for improved photocatalytic activity of  
440 Cu doped P25.<sup>[27]</sup>

441

## 442 Conclusions

443 Altogether, our photocatalytic tests and the in-depth investigation on impregnated Cu/P25 systems  
444 elucidated the nature of copper species active in hydrogen production on Cu/P25 systems. Our  
445 findings showed that:

- 446 1) Both  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  nanostructures were obtained onto Cu/P25 by impregnation and further heat  
447 treatment in nitrogen.
- 448 2) The sample allowing the highest  $\text{H}_2$  production rates showed the highest fraction of finely  
449 dispersed  $\text{CuO}$  nanostructures, that during the photocatalytic process,  $\text{CuO}$  species undergo an  
450 in situ dynamic nanostructuring, leading to a significant change in both oxidation state and size  
451 distribution. This evolution is probably based on a dissolution-redeposition process. In particular,  
452  $\text{CuO}$  species were involved in a dissolution process, followed by reduction of  $\text{Cu}^{2+}$  ions to  $\text{Cu}^+$   
453 and  $\text{Cu}^0$  by photo-generated electrons.
- 454 3) Both  $\text{Cu}_2\text{O}$  and  $\text{Cu}^0$  acted as co-catalysts for  $\text{H}_2$  generation. Upon illumination, the former injected  
455 photoelectrons into  $\text{TiO}_2$  conduction band. The latter acted as a co-catalyst, hosting  
456 photogenerated electrons from  $\text{TiO}_2$  and mediating their transfer to the protons. Both processes



457 restricted electron/hole recombination phenomena and accounted for improved photocatalytic  
458 activity of Cu doped P25.

459 The obtained findings clearly outline Cu/P25 catalysts as complex and dynamic systems. Their  
460 evolution during photocatalytic process must be influenced by solution properties as well as by  
461 preparation conditions of the catalyst itself, that markedly affect both size distribution and dispersion  
462 of Cu species, and ultimately lead to different ratios between copper oxidation states on the catalyst  
463 surface, thus affecting H<sub>2</sub> production rate.

464 The present work highlights that in situ catalysts transformation could improve their performance,  
465 lying the basis to explore this strategy to optimize activity of other catalytic systems.

466

467

## 468 **Experimental Section**

### 469 *Materials*

470 Methanol (99.8% v/v), P25-TiO<sub>2</sub> (80:20 anatase:rutile), sodium nitrite (NaNO<sub>2</sub>, purity ≥97.0%) used  
471 as filter and cupric nitrite hydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, purity 99.9%) were purchased from Sigma  
472 Aldrich. Bi-distilled water was used for the preparation of the reacting mixtures.

### 473 *Cu/P25 material preparation*

474 Copper (0.5, 3, 6, 10 and 16 wt %) was loaded on P25-TiO<sub>2</sub> by impregnation method.<sup>[23]</sup> For each Cu-  
475 modified P25-TiO<sub>2</sub> sample (Cu/P25), a required amount of P25-TiO<sub>2</sub> was dispersed in Cu(NO<sub>3</sub>)<sub>2</sub>  
476 aqueous solution. Excess water was evaporated to dryness with slow heating rate and constant  
477 stirring. The samples were dried at 110 °C and then calcined under nitrogen atmosphere for 5h at  
478 different temperatures ranging between 150 °C and 550 °C.

### 479 *Photocatalytic runs*

480 Photocatalytic runs were carried out in triplicate in an annular glass batch reactor (V=300 mL)  
481 covered with a layer of aluminum foil. The reactants and nitrogen gas were fed to the reactor through

482 its top inlet hole, while collection of outflow liquid and gaseous samples was performed at the bottom  
483 hole of the reactor at different reaction times. The reactor has been endowed with a high-pressure  
484 mercury vapor lamp (input power: 125 W) manufactured by Helios Italquartz emitting in both  
485 ultraviolet and visible range.

486 The lamp had ultraviolet emission peaks at 305, 313, and 366 nm corresponding to irradiances of  
487  $2.23 \times 10^{-6}$ ,  $2.76 \times 10^{-6}$  and  $3.37 \times 10^{-6}$  (E/s). The visible emission peaks at 405, 408, 436, and 546,  
488 corresponded to irradiances of  $6.18 \times 10^{-7}$ ,  $1.41 \times 10^{-7}$ ,  $1.03 \times 10^{-6}$ , and  $1.16 \times 10^{-6}$  E/s, respectively. The  
489 reactor was cooled at 25 °C during each run by means of a thermostatic bath (Falc GTR 90).

490 In order to evaluate the response of the photocatalytic system under visible light irradiation, during  
491 the experimental runs water in the cooling jacket was replaced by 1M NaNO<sub>2</sub> solution absorbing  
492 ultraviolet radiation, as reported elsewhere.<sup>[40]</sup> The pH of the solution was monitored by means of an  
493 Orion 420A<sub>p</sub> pH-meter (Thermo).

494 In order to avoid the undesired reaction of dissolved oxygen with photogenerated electrons, before  
495 starting the photocatalytic runs, a nitrogen stream was bubbled into the solution for 30 minutes for  
496 removing atmospheric oxygen. Moreover, throughout the experiments, nitrogen was continuously fed  
497 at a flow rate ( $Q_{N_2}$ ) of 0.3 L/min to prevent any entrance of air into the reactor. For each run, fixed  
498 amounts of photocatalysts and methanol (10% v/v) were added to 300 mL of aqueous solution; the  
499 resulting suspension was sonicated and fed into the batch reactor under magnetic stirring. The liquid  
500 samples, collected at different reaction times, were quickly filtered on regenerated cellulose filters  
501 (pore diameter 0.20 μm, Scharlau) and the filtrate was used to measure dissolved copper and formic  
502 acid concentrations. The gaseous samples were recovered from the reactor outlet in Tedlar gas  
503 sampling bags and then used to evaluate hydrogen concentration.

504 Dissolved copper concentration was measured by means of a colorimetric method using an analytical  
505 kit (Macherey–Nagel) based on oxalic acid bis-cyclohexylidene hydrazide (cuprizone). A UV/Vis  
506 spectrometer (Cary 100 UV–Vis, Agilent) was employed for the measurements at a wavelength of  
507 585 nm.

508 Hydrogen concentration was measured by a gas-chromatograph (Agilent 7820A) equipped with a  
509 HP-PLOT Molesieve 5A column (Agilent) and a TCD detector using argon as carrier gas. During  
510 the experiments, the radiation transmitted by the reactor was measured by means of a radiometer (not  
511 shown in the figure) in the range 315-400 nm and 401-1100 nm.

#### 512 *Physico-chemical characterization of the Cu/P25 nanomaterials*

513 A physico-chemical investigation on Cu/P25 nanomaterials was performed by using a combined  
514 approach of different analytical techniques, such as High Resolution Transmission Electron  
515 Microscope (HR-TEM, X-Ray Diffraction (XRD), Temperature-Programmed Reduction (TPR),  
516 Raman, Electron Paramagnetic Resonance (EPR), and X-Ray Photoelectron Spectroscopy (XPS)  
517 spectroscopies. Also, the specific surface area ( $S_{\text{BET}}$ ) of catalysts was also determined through BET  
518 porosimetry. Finally, H<sub>2</sub> Temperature Programmed Reduction (H<sub>2</sub>-TPR) analysis was also  
519 performed. The characterization was specifically focused on Cu(3%)/P25 and Cu(10%)/P25 catalysts  
520 before and after their use in the photo-reforming process.

521 BET analysis allowed determining the specific surface area ( $S_{\text{BET}}$ ), that was evaluated by generating  
522 seven-point isotherms at 77 K for N<sub>2</sub> adsorption (Autosorb-1, Quantachrome) using the charred  
523 sample capable of providing a specific surface area equal to 5 m<sup>2</sup> in the sample cell.

524 Raman spectra of the prepared catalysts were performed by using a confocal Raman Microscope  
525 (Jasco, NRS-3100). Both the 514 nm line of an air-cooled Ar<sup>+</sup> laser (Melles Griot, 35 LAP 431-220)  
526 and the 647 nm line of a water-cooled Kr<sup>+</sup> laser (Coherent Innova 302C) were used. The laser line  
527 was injected into an integrated Olympus microscope and focused to a spot size of approximately 2  
528 mm by using a 100× or 20× objective. A holographic notch filter was used to reject the excitation  
529 laser line. Raman scattering was collected by using a Peltier-cooled 1024×128 pixel CCD photon  
530 detector (Andor DU401BVI). For most systems, it took 60s to collect a complete data set. XRD  
531 measurements were performed using a PANalytical diffractometer with a nickel filter and Cu K<sub>α</sub>  
532 radiation.

533 EPR experiments were carried out by means of X-band (9 GHz) Bruker Elexys E-500 spectrometer  
534 (Bruker, Rheinstetten, Germany), equipped with a super-high sensitivity probe head. Solid samples  
535 were transferred to flame-sealed glass capillaries which, in turn, were coaxially inserted in a standard  
536 4 mm quartz sample tube. Measurements were performed at room temperature. The instrumental  
537 settings were as follows: sweep width, 1500 G; resolution, 1024 points; modulation frequency, 100  
538 kHz; modulation amplitude, 1.0 G. 16 scans were accumulated to improve the signal-to-noise ratio.  
539 TPR measurements were carried out in a laboratory flow apparatus, using a 5% H<sub>2</sub>/Ar ( $Q=20\text{ cm}^3/$   
540 min), with a heating rate of 10 °C/min up to 800 °C. The sample (60 mg) was loaded in a quartz  
541 down-flow cell with a K thermocouple in close contact with the sample.  
542 The nanoparticles morphology and crystallinity were investigated using a JEOL (JEM-2010F) high  
543 resolution-transmittance electron microscope (HR-TEM) with the filed transmission of 200 kV. To  
544 prepare the samples for HR-TEM, the catalysts were suspended in ethyl alcohol and sonicated for 45  
545 min, then fixed on a Lacy Carbon grid (LC300, EMS) by the drop-casting method.  
546 X-ray Photoelectron Spectroscopy (XPS) analysis was performed with a Versa Probe II Scanning  
547 XPS Microprobe spectrometer (Physical Electronics GmbH). The measurements were done with a  
548 monochromatized AlK $\alpha$  source (X-ray spot 100  $\mu\text{m}$ ), at a power of 24.4 W. Wide scans and detailed  
549 spectra were acquired in Fixed Analyzer Transmission (FAT) mode with a pass energy of 117.40 eV  
550 and 29.35 eV, respectively. An electron gun was used for charge compensation (1.0V 20.0  $\mu\text{A}$ ). All  
551 binding energies were referenced to C1s at 284.8 $\pm$ 0.1 eV for adventitious hydrocarbon. Data  
552 processing were performed using MultiPak software v. 9.5.0.8.

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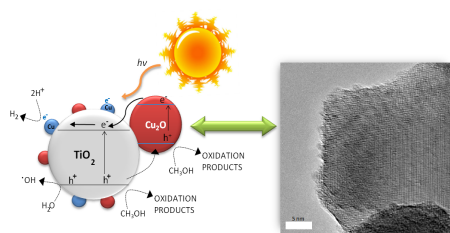
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648 **Table of Contents**

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650 CuO active species undergo in situ dynamic nanostructuring, through dissolution and photodeposition,  
651 changing both oxidation state and size distribution

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