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1 Ternary systems based on ZnO/CeO₂/Cu₂O for the degradation of phenol and 2 carbamazepine

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6

7 **Key words:** ZnO mixed system, CeO₂, Cu₂O, hydrothermal synthesis, organic pollutants degradation

8

9 **Abstract**

10 In this paper we prepared via different synthetic processes, two ternary systems based on ZnO, CeO₂
11 and Cu₂O for the abatement of organic pollutants. The system ZnO/CeO₂ was already known to be
12 efficient in the degradation of emergent contaminants, the addition of cuprous oxides allows also
13 to enhance reductive properties to the material thanks to its specific potential. The mixed oxides
14 were characterized via power X Ray Diffraction, UV visible Diffuse Reflectance and Electron
15 Paramagnetic Resonance. The materials obtained through hydrothermal synthesis shown better
16 performances in the abatement of phenol and carbamazepine.

17

18 **1. Introduction**

19 The search for new materials that work as photocatalysts is constantly evolving. In recent years,
20 much attention has been paid to various methods for modifying the classic first generation
21 semiconductors such as TiO₂. Among the different types of material engineering, the most used are
22 the intrinsic and extrinsic doping, the formation of solid solutions and the creation of
23 heterojunctions at the interface between two materials that have no tendency to form solid
24 solutions. The development of semiconductor-semiconductor composite heterojunctions for
25 efficient photocatalytic pollutant degradation is of great interest. ZnO is one of the most abundant,
26 cheap and non-toxic semiconductor, already employed for degradation of different pollutants¹⁻³.
27 The photocatalytic degradation process depends on various factors: the light-absorption ability of
28 the semiconductor, which in turn depends on its surface area and morphology, optical band gap
29 and in particular the charge separation capability⁴. The photocatalytic performances of ZnO can be
30 improved either through doping with metals or nonmetals or via the preparation of ZnO
31 heterostructures with other semiconductor elements⁵. Composite nanostructures of transition
32 metal oxides are of great interest because of their tunable optical as well as catalytic properties.

33 Recently, our and other ⁶⁻⁸ research groups started to investigate the role of cerium as dopant of
34 oxides. In our approach, cerium ions are not soluble in the ZnO matrix. This composite system has
35 shown an amazing, unexpected activity in the mineralization of acesulfame K, a so-called emerging
36 pollutant, performed under visible light ⁹. This result led us to an in-depth study of this new material.
37 We observed that the CeO₂/ZnO system is biphasic and the role of the solid–solid interface plays a
38 crucial role in the photo-activity of the material.

39 Coupled semiconductors formed by ZnO and other metal oxides or sulfides (e.g., CuO, Cu₂O, CdO,
40 CuS, CdS, and ZnS) have been employed as photocatalysts, enhancing the charge carrier separation
41 ability (electrons and holes) between adjacent semiconductors ¹⁰. In particular, cupric and cuprous
42 oxides (CuO and Cu₂O) are nontoxic p-type metal oxide semiconductor having an optical band gap
43 in the range from 1.2 to 2.2 eV ¹¹. Moreover, Cu₂O is considered very interesting thanks to its relative
44 band position with respect to the normal hydrogen electrode (NHE) (- 1.2 eV for the conduction
45 band and +1.3 eV for the valence band). It has been demonstrated that it instigates reduction and
46 oxidation of different pollutants via the formation of hydroxyl and superoxide radicals (with
47 formation energies of approximately +1.23 and - 0.28 eV, respectively), which are the main reactive
48 species in photocatalytic reactions ¹². Accordingly, addition of Cu₂O to ZnO in a ZnO–Cu₂O–CuO
49 nanocomposite configuration could result in photocatalytic activity superior to that of the intrinsic
50 ZnO semiconductor system. As it will be shown below, it is indeed the role of these interfaces (or
51 heterojunctions) that allows a better understanding of this novel promising photocatalytic system.
52 In the present work we prepared nanocomposite systems coupling CeO₂/ZnO materials with Cu₂O
53 particle with two different synthetic methods. The preparation process influences the surface area
54 and the crystallinity of the photocatalysts affecting also their photocatalytic properties. We tested
55 these materials in the degradation of a classic probe molecule like phenol and of an emergent
56 pollutant such as carbamazepine.

57

58 **2. Experimental section**

59 All reactants employed were purchased by Sigma-Aldrich and used without any further
60 purification treatment. Distilled water was used in the synthesis procedures. Synthesis procedure
61 will be described for each system in the following corresponding section.

62 The investigated samples were mainly prepared via hydrothermal and precipitation synthetic
63 routes, described hereafter.

64 *2.1 Hydrothermal synthesis.*

65 Pristine ZnO and ZnO containing 1% molar of cerium were prepared by means the hydrothermal
66 method and they were labelled ZnO-H, CZ1-H, respectively. The bare sample were synthesized
67 preparing a solution 1M of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in 20 ml of H_2O . Subsequently, NaOH 4M was added
68 to the solution until to reach a pH value of 11. The obtained solution was transferred into a PTFE-
69 lined stainless steel 100 mL autoclave and heat at 448 K for 12 hours. The product was centrifuged,
70 washed three times with distilled water and dried at 343 K overnight. The mixed sample CZ1-H was
71 synthesized adding to the starting solution the corresponding stoichiometric amount of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$.

72

73 *2.2 Precipitation synthesis.*

74 Even with this synthetic approach a bare sample of ZnO and a sample containing 1% of Ce were
75 prepared, labelled as ZnO-P and CZ1-P, respectively. The synthesis of the pristine material provides
76 the dissolution of 2.2 g of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in 160 mL of H_2O and 80 mL of EtOH; the formed
77 solution is left in stirring for 1 h and subsequently 120 mL of NaOH 1M were added. The precipitated,
78 after 48 h, was separated via filtration, washed with H_2O and dried at 343 K for 12 h. the final product
79 was obtained after calcination at 573 K in air for 30 h. The mixed sample CZ1-P, containing 1% molar
80 of Ce, was synthesized adding the corresponding stoichiometric amount of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ to the
81 starting mixture.

82 *2.3 Cupper modified oxide systems.*

83 Cu_2O -ZnO-P, Cu_2O -CZ1-P and Cu_2O -ZnO-H Cu_2O -CZ1-H were prepared by chemical reduction
84 followed by deposition method. At 10 mL of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ $7.9 \cdot 10^{-3}$ M (0.5% wt on the basis of the
85 oxide) water solution were added 0.0568 g of glucose and 15 mL of NaOH $2.36 \cdot 10^{-3}$ M. The solution
86 was stirred for 50 min at 343 K. At the end of the reaction an orange suspension was formed
87 (indicated as suspension A). In this reaction, known as Benedict reaction¹³, glucose reduces Cu^{2+} to
88 Cu^+ allowing the formation of Cu_2O oxide. 1 g of oxide was added in 20 mL of deionized water and
89 the suspension was sonicated at 333 K for 10 min (indicated as suspension B). The suspension B was
90 added to the suspension A and stirred for 10 min at 343 K. After this time the obtained orange
91 powder was filtered and washed three times with water and ethanol, in order to remove the
92 reaction residues and finally dried at 343 K.

93 *2.4 X-Ray Powder Diffraction*

94 Powder X-ray diffraction (XRD) patterns were recorded with a PANalytical PW3040/60 X'Pert PRO
95 MPD diffractometer using a copper K_α radiation source (0.154056 nm). The intensities were

96 obtained in the 2θ range between 20° and 80° . X'Pert High-Source software was used for data
97 handling.

98 *2.5 UV Visible Diffuse Reflectance Spectroscopy (DRS)*

99 UV-Visible absorption spectra were recorded using a Varian Cary 5 spectrometer, coupled with
100 an integration sphere for diffuse reflectance acquisition, using a Carywin-UV/scan software. A
101 sample of PTFE with 100% reflectance was employed as the reference. Spectra were registered in
102 the 200-800 nm range at a scan rate of 240 nm/min with a step size of 1 nm. The measured
103 intensities were converted with the Kubelka-Munk function.

104 The optical band gap energies were calculated considering that the energy dependence of the
105 absorption coefficient (α) for semiconductors in the region near the absorption edge is given by:

$$106 \quad \alpha \propto \frac{(h\nu - E_{bg})^\eta}{h\nu}$$

107 Where $h\nu$ is the energy of the incident photon and E_{bg} is the optical absorption energy. η depends
108 on the type of optical transition and since ZnO shows a direct-allowed optical transition its value is
109 of 1/2. Finally, since the scattering coefficient weakly depends on energy and $F(R_\infty)$, it can be
110 assumed as proportional to the absorption coefficient within the narrow range of energy containing
111 the absorption edge feature.

$$112 \quad F(R_\infty) = \frac{(h\nu - E_{bg})^\eta}{h\nu}$$

113 Then, the plot $(F(R_\infty) \cdot h\nu)^{1/\eta}$ vs $h\nu$ can be used to determine the absorption edge energy (Tauc
114 plot) method¹⁴.

115 The UV-Visible DRS studies after irradiation of the copper oxide impregnated samples were
116 performed irradiating 0.4 g of samples suspended in 2 ml of water/ethanol solution (10% v/v) in a
117 quartz cell for DRS measurements. After irradiation, prior to spectra acquisition the sample were let
118 to sediment on the bottom of the DRS cell. The UV-Visible DRS spectra were recorded in the 200-
119 800 nm range at a scan rate of 240 nm/min with a step size of 1 nm. Since during the irradiation was
120 not possible to stir the samples, after every irradiation the samples were sonicated in order to
121 homogenize the powders.

122 *2.6 BET surface area*

123 The specific surface area measurements were carried out on a Micrometrics ASAP 2020 using the
124 Brunauer-Emmett-Teller (BET) model on the N₂ adsorption measurement. Prior to the adsorption
125 run, all the samples were outgassed at 573K for 2h.

126 2.7 EPR

127 Electron Paramagnetic Resonance (EPR) spectra were recorded at room temperature and at
128 liquid nitrogen temperature (77 K). They were run on a X-band CW-EPR Bruker EMX spectrometer
129 equipped with a cylindrical cavity operating at 100 kHz field modulation.

130 2.8 Photocatalytic tests

131 The irradiation experiments were carried out in closed Pyrex cells (40 mm id x 25mm) on 5 mL of
132 suspension in Milli-Q water containing 1 g/L of catalyst and 20 mg/L of compound kept under
133 continuous stirring. The samples were irradiated using a Philips TLK 05 Blacklight lamp (40 W) with
134 a maximum emission of 365 nm. The suspensions were then filtered with Millipore 0.45 µM Millex
135 LCR hydrophilic PTFE filters and analysed via HPLC-UV.

136 The analyses for carbamazepine and phenol were carried out with a Merck-Hitachi HPLC system
137 equipped with a L-6200A Intelligent Pump, a L-4200 UV-VIS Detector and a six-way Rheodyne valve
138 injection system. Isocratic elution was performed with a mixture of phosphoric acid solution at pH
139 2.8 and acetonitrile at a flow rate of 1 ml/min. Condition are as follows: 60/40 and 70/30 v/v with
140 retention times of 3.77 and 4.83 min for carbamazepine and phenol, respectively. Detection
141 wavelength were 285 for carbamazepine and 220 nm phenol.

142

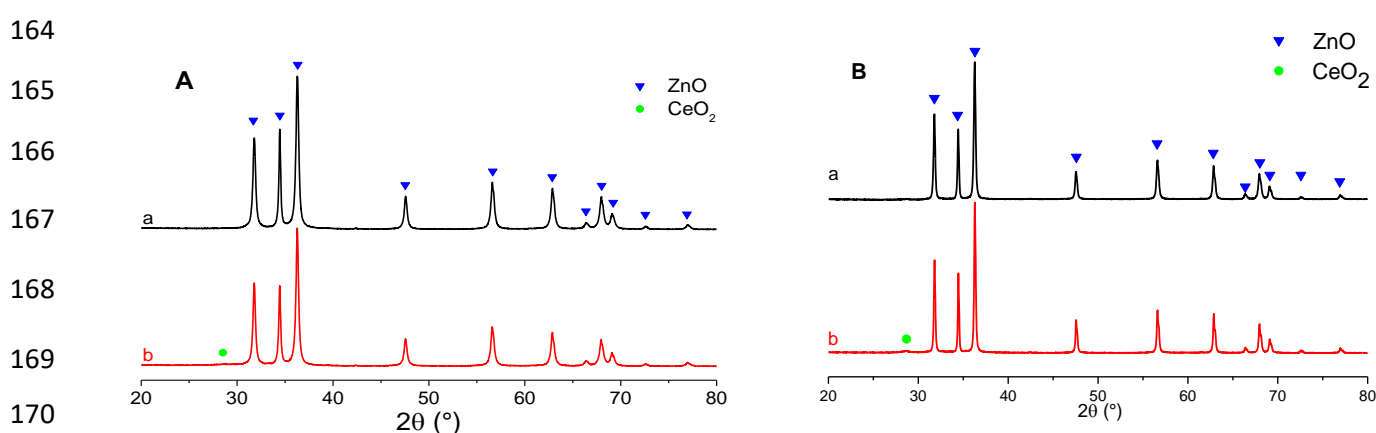
143 **3. Results and discussion**

144 3.1 Structural and optical characterization

145 The ZnO nanoparticles synthesized via precipitation and hydrothermal methods were analysed
146 from a structural point of view by means of X-ray powder diffraction. The structural analysis of these
147 materials has been already well described elsewhere^{2, 15}, the diffractograms have been reported in
148 the supporting information section (see figure S1), showing the typical pattern of ZnO wurtzitic
149 hexagonal phase (00-036-1451 ICDD pattern)¹⁶.

150 The optical properties of the synthesized samples were investigated by UV-Vis diffuse reflectance
151 spectroscopy; in Fig. S2 the reflectance measurements and the derived absorbance, obtained by the
152 application of the Kubelka-Munk equation, are reported. The reflectance and absorbance spectra
153 of CZ1 are dominated by the valence band (VB) – conduction band (CB) transition of ZnO, as already
154 explained in previous paper^{2, 15}.

155 Figure 1 panel A reports the XRD patterns of the bare ZnO-P and of the mixed system CZ1-P
156 following the impregnation of 0.5 % of Cu₂O, occurring through the reaction described in the
157 experimental section, named ZnO-Cu₂O-P and CZ1-Cu₂O-P, respectively. Figure 1 panel B reports
158 the XRD diffraction patterns of the sample prepared via hydrothermal way. As in the cases reported
159 in the SI section, the impregnated bare oxide shows the pattern typical of the wurtzitic hexagonal
160 phase and no additional reflections due to impurities or to the cubic Cu₂O lattice were detected.
161 The same diffraction pattern has been also registered for CZ1-Cu₂O-P, with the unique difference
162 that in this case a slightly and very weak reflection is present around 2θ = 28.6°, due to the presence
163 of CeO₂ phase.



171 **Figure. 1.** XRD patterns of the synthesized materials. Panel A: a) ZnO-Cu₂O-P and b) CZ1-Cu₂O-P. Panel B: a) ZnO-Cu₂O-H and b) CZ1-
172 Cu₂O-H The green dot evidences a weak diffraction peak due to CeO₂.

173 Then, XRD analysis was not able to detect the fingerprints of the Cu₂O crystal structure, probably
174 because of the too lower concentration of copper compounds (0.5 %) and characterized by very
175 small size. In addition, the most intense reflections should be at 2θ angles around 30° and 40°, where
176 the intense reflections of the ZnO phase are already present.

177 Nevertheless, XRD analysis didn't evidence the presence of copper(II) oxide, the occurred
178 impregnation was guaranteed by a net visible pink/orange color hired by the previously white
179 samples (ZnO-P, ZnO-H and CZ1-P, CZ1-H).

180 We already described elsewhere ¹⁵ that the presence of cerium oxide has been demonstrated
181 both via XRD measurements and also via TEM images where it is clear that the crystals of CeO₂ are
182 much smaller than the ZnO ones. Also the measure of the surface area of the non-impregnated
183 materials have been already reported. In the case of impregnated materials, we observed that the
184 presence of copper oxide does not affect the surface area that remains identical to the samples
185 without impregnation. The surface area for the pure ZnO samples (impregnated and non-

186 impregnated with copper) obtained via precipitation process or hydrothermal synthesis are 20 m²/g
187 and less than 10 m²/g respectively, while the mixed samples CZ1 (impregnated and non-
188 impregnated with copper) obtained via precipitation process or hydrothermal synthesis are 31 m²/g
189 and less than 10 m²/g, respectively. Again precipitation synthesis process leads to the formation of
190 samples with higher surface area.

191 In this sense, DR UV-vis spectroscopy gave a clear outcome, as reported in Figure 2, where the
192 presence of Cu₂O can be deduced.

193

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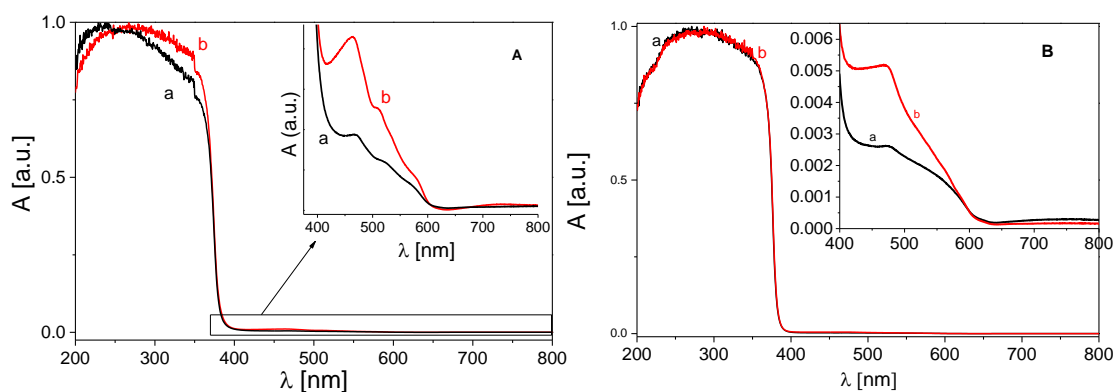
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200



201 **Figure 2.** Normalized Absorbance Kubelka-Munk transformed diffuse reflectance spectra. Panel A: a) ZnO-Cu₂O-P and b) CZ1-Cu₂O-
202 P; panel B: a) ZnO-Cu₂O-H and b) CZ1-Cu₂O-H

203 Indeed, the spectra for the modified samples show, beside the band gap transition in the UV region,
204 due to the excitation of electrons from the valence band to the conduction band ¹⁷, further
205 absorptions in the visible λ region. The zoom evidences the presence of absorption bands in the range
206 of wavelength between 400-600 nm, typical of Cu₂O particles ¹⁸⁻²¹. More in details, the shoulder
207 around 460 nm is suggested to derive by the interface charge transfer from the VB of ZnO to the
208 Cu²⁺ that may also cause a partial reduction of the copper species. The second well recognizable
209 band around 520 nm is due to the electronic transition from the valence band to the conduction
210 typical of Cu₂O, showing a band gap width of 2.39 eV ¹⁹. Less visible is the broad absorption between
211 600-800 nm, witnessing the presence of Cu(II) species, and in particular related to d-d transitions:
212 this seems suggest that, beside Cu₂O nanoparticles, also a small fraction of Cu(II) is present in the
213 impregnated samples.

214 Definitely, the presence of the impregnating Cu₂O phase greatly modify the optical behavior of the
215 two different samples (P and H), particularly inducing absorption in the visible range, not previously
216 detected for the not impregnated samples.

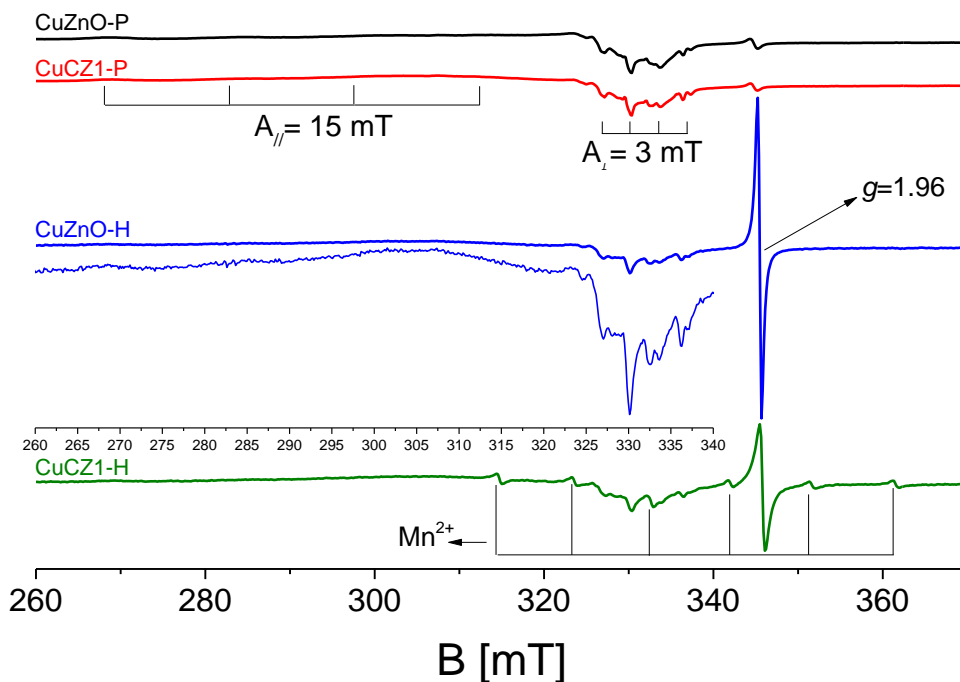
217 Finally, none appreciable red-shift in the energy gap of ZnO has been observed, suggesting that
218 the Cu incorporation inside the matrix has been not occurred, but the Cu₂O particles are adsorbed
219 at the surface of ZnO.

220

221 3.2 EPR characterization of the Cu₂O impregnated materials

222 The presence of the Cu²⁺ species has been also confirmed performing EPR spectra of the
223 impregnated ZnO-Cu₂O and CZ1-Cu₂O samples. Indeed, Cu²⁺ ions (3d⁹) show one unpaired electrons,
224 differently from the diamagnetic Cu⁺ and Cu⁰, characterized by distinguishable fingerprint. The
225 signal exhibits an axial *g* tensor splitted in four hyperfine lines since the Cu nucleus has a nuclear
226 spin $I = 3/2$ and the derived line multiplicity is $n = 2I+1 = 4$, so four lines are expected.

227 Both EPR spectra of the two materials, represented in Figure 3, are dominated by the typical axial
228 signal of Cu²⁺; in addition, the signal always visible in ZnO around $g = 1.96$ and attributed to electrons
229 trapped in shallow donors [4], is also recorded. The signal at $g = 1.96$ is more likely associated to
230 electrons in the conduction band or in a band built up by donor levels just below the bottom of the
231 conduction band^{2, 22-24}. This indicates that some (paramagnetic) defects, related to the matrix are
232 always present but their concentration is strictly dependent on the synthesis procedure. In the case
233 of precipitation process the intensity of this signal is much lower respect to that obtained for the
234 sample prepared via hydrothermal synthesis; most probably this difference in intrinsic defectivity
235 will affect the photocatalytic properties of the materials, as it will be demonstrated later.



236

237 **Figure. 3.** EPR spectra at 77K of ZnO-Cu₂O-P (black line), CZ1-Cu₂O-P (red line) ZnO-Cu₂O-H (blue line) and CZ1-CU₂O-H (green line).

238

239 In Figure 3 it is possible to observe that the hyperfine structure results slightly visible in the
240 parallel component while it is better resolved in the perpendicular one. The signal features are A_{\parallel}
241 = 15 mT and A_{\perp} = 3.1 mT where A is the hyperfine tensor: the fact that both the parallel and the
242 perpendicular hyperfine structure are observable has been ascribed as isolated Cu(II) ions, that in
243 our case come as synthetic “waste”, caused by unavoidably oxidation during the synthesis
244 procedure. Another confirmation that the Cu^{2+} ions are not embedded inside ZnO or CeO_2 lattices
245 is represented by the fact that for this situation the A values reported would be smaller than in our
246 case²⁵⁻²⁸.

247 Thus, combining DR-UV-vis and EPR spectroscopy the samples impregnated with copper(I) oxide
248 exhibit, in addition to small Cu_2O particles (not visible with XRD but certified by DR UV-vis) anchored
249 to oxide surfaces, a certain amount of Cu(II), dispersed on the surface of the two materials.

250

251 *3.3 Photocatalytic efficiency of the developed materials*

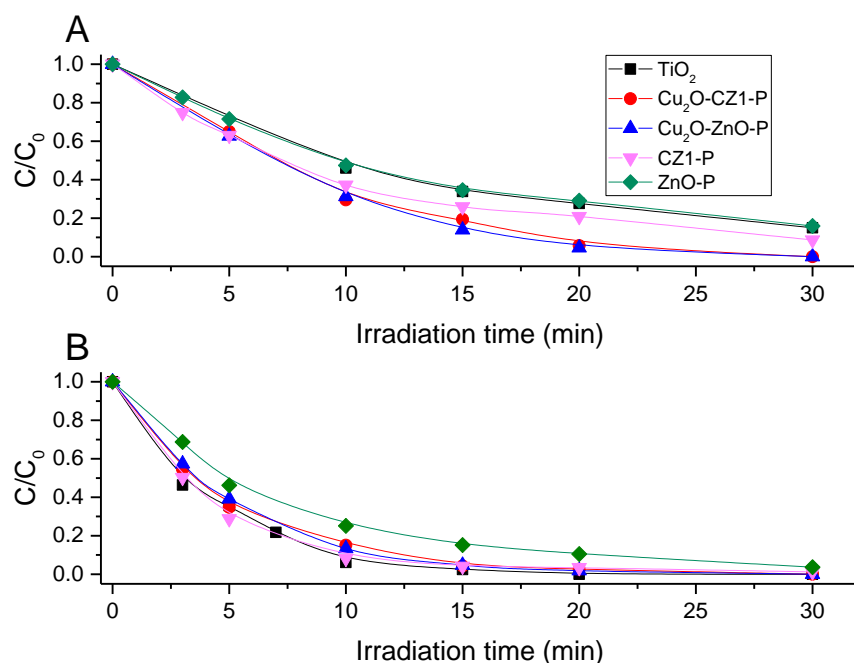
252 The efficiency of the developed materials was tested toward the abatement of two molecules:
253 carbamazepine (CBZ) and phenol (PHE). Preliminarily, adsorption in the dark was performed with all
254 materials toward the two analytes and was negligible. A contribution of direct photolysis in the
255 considered time window (2h) can be excluded as well.

256 *3.3.1 Photocatalysts synthesized via precipitation*

257 The degradation profiles obtained for the two investigated molecules in the presence of the
258 developed photocatalysts are plotted in Figure 4; the degradation achieved in the presence of the
259 benchmark TiO_2 P25 is reported as well for comparison purpose. In all cases, the degradation
260 process approximates a pseudo first order kinetic and the calculated constants are collected on
261 Table 1.

262 Considering the case of samples P shown in Figure 4 A, P25 and pristine ZnO exhibit the lowest
263 photoactivity and the changes introduced to the ZnO matrix by the presence of Cu_2O clearly increase
264 the performance of the materials. In fact, even if the single heterojunction with cerium (CZ1) leads
265 to a slight increase in the photocatalytic performance, copper single (Cu_2O -ZnO) and double (Cu_2O -
266 CZ1) heterojunction prompted a faster degradation. This suggests that impregnation with Cu(I) may
267 increase the charge separation produced within the material and the mobility of the charge carriers
268 in the system with heterojunction.

269 In the case of CBZ, we observed the same trend for ZnO-based materials, and modifications with
 270 Cu(I) and Ce(IV) oxides favor the photocatalytic activity of the materials. However, the performance
 271 for all the precipitates are worse than P25 as perceived in Figure 4 B.



272
 273 **Figure 4.** Degradation of phenol (A), carbamazepine (B) in the presence of photocatalysts prepared with precipitation method
 274

275 3.3.2 Photocatalysts synthesized via hydrothermal method

276 We noticed that all ZnO-based materials exhibit a higher efficiency than P25 toward all the tested
 277 molecules as reported in Table 1.

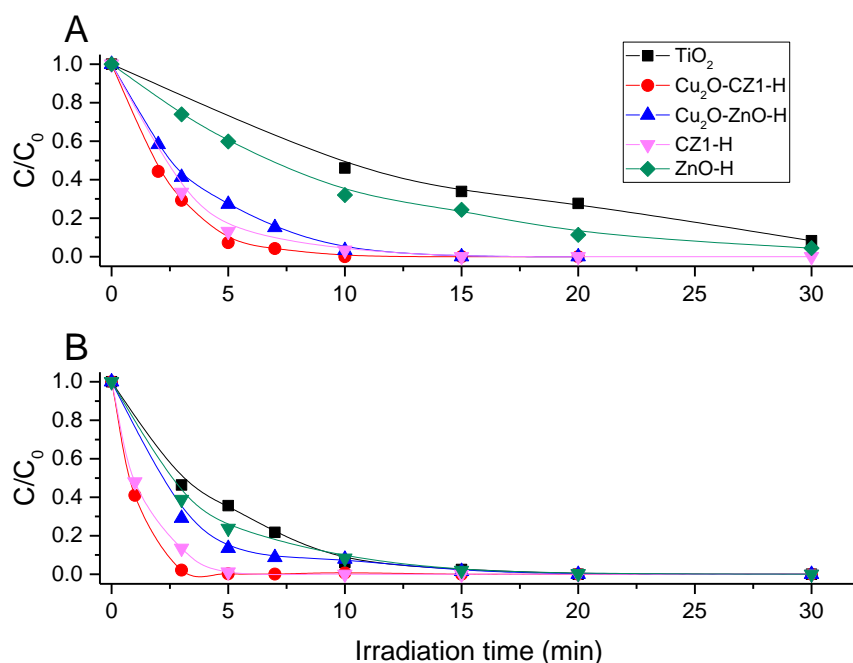
278 **Table 1.** Kinetic constants for synthesized materials

K, min ⁻¹	TiO ₂	ZnO-P	CZ1-P	Cu ₂ O- CZ1-P	Cu ₂ O- ZnO-P	ZnO-H	CZ1-H	Cu ₂ O- CZ1-H	Cu ₂ O- ZnO-H
Phenol	0.061	0.060	0.080	0.139	0.153	0.104	0.340	0.478	0.327
Carbamazepine	0.257	0.108	0.145	0.189	0.203	0.252	0.873	1.249	0.256

279
 280 Hydrothermal synthesis appears to be the optimal strategy for increasing the efficiency of the
 281 heterojunctions that form in the modified ZnO matrix. In fact, as it can be seen from the degradation
 282 curves in Figure 5, the system with single heterojunction between ceria and ZnO (CZ1) shows an
 283 improved performance compared to the same material produced by precipitation, while the double
 284 heterojunction composite (Cu_2O-CZ1) is the most active towards phenol. The positive role played by
 285 copper is confirmed with these experiments but, in this case, the synthesis strategy adopted seems

286 to optimize the synergistic effect of the two heterojunctions in promoting the mobility of the charge
287 carriers, with a positive effect on the degradation of the target molecule.

288



289

290 **Figure 5.** Degradation of phenol (A), carbamazepine (B) in the presence of photocatalysts prepared with hydrothermal method.

291

292 Analyzing more in detail samples P and H and comparing with the kinetic constants obtained for the
293 different materials with the two different synthesis strategies, the choice of hydrothermal method
294 seems decisive for the performance of the catalysts. The $Cu_2O-CZ1-H$ system proves to be the most
295 effective for the removal of this molecule from the aqueous medium, as depicted in Figure 5. In fact,
296 the constants obtained with the hydrothermal materials are significantly higher than those
297 calculated for the precipitated materials (0.34 min^{-1} for $CZ1-H$ vs 0.08 min^{-1} for $CZ1-P$, 0.11 min^{-1} for
298 $ZnO-H$ vs 0.06 min^{-1} for $ZnO-P$, 0.48 min^{-1} for $Cu_2O-CZ1-H$ vs 0.14 min^{-1} for the precipitate and 0.38
299 min^{-1} for $Cu_2O-ZnO-H$ vs 0.15 min^{-1} for the precipitate). These results may be linked to the
300 crystallinity of the samples obtained with the two synthesis methods; with hydrothermal method,
301 a higher crystallinity is observed allowing a better and selective contact surface between the catalyst
302 and the adsorbate, so favouring the oxidation-reduction reactions occurring among the charge
303 carriers, the hydroxyl radicals and the pollutants.

304 Also for CBZ the hydrothermal synthesis has led to a higher degradation efficiency, as clearly shown
305 in Figure 5 B. The activity shown by the CeO_2/ZnO system towards CBZ further supports that the
306 addition of ceria and the formation of the heterojunction could allow charge separation and

307 electron stabilization in the f orbitals of Ce⁴⁺. Moreover, thanks to the results obtained with the
308 double heterojunction composite system (Cu₂O-CZ1), the synergistic effect of the double
309 heterojunction seems to be confirmed; for it the calculated kinetic constant is 1.25 min⁻¹, the highest
310 observed, and is five times higher than pristine ZnO-H (0.25 min⁻¹).

311 The type of synthesis method plays an important role in determining the efficiency for the
312 abatement of the target molecules. In particular, hydrothermal materials are able to reduce 70 to
313 90% of the initial concentration of carbamazepine and phenol within five minutes of irradiation. The
314 effectiveness of materials obtained by precipitation is always less than that of materials obtained
315 by hydrothermal means. In fact, by comparing the kinetic constants, it comes up that the materials
316 produced by precipitation have a lower performance than the materials synthesized by
317 hydrothermal method. The employment of a double heterojunction Cu₂O/ZnO/CeO₂ seems the
318 most promising in degrading phenol and carbamazepine. The role of the synthesis way seems to be
319 crucial. It comes out also from the spectroscopic characterization that the two materials are
320 different.

321

322 **4. Conclusions**

323 The formation of heterojunction between ZnO and CeO₂ has been observed experimentally in the
324 past, the addition of Cu₂O nanoparticles on the surface of the mixed systems leads to the formation
325 of a very active material in the abatement of phenol and carbamazepine molecules. Residual traces
326 of Copper (II) not reduced have been evidenced by UV Vis analysis and EPR measurements. These
327 species seem to be well dispersed over the surface of the semiconductors. The role of these species
328 in the photo degradation process has still to be clarified. Moreover, also the photoactivity under
329 visible light is an interesting point that should be taken into consideration in the next future. From these
330 preliminary results we underlined the crucial role of the synthesis method in obtaining a suitable
331 material for pollutants degradation.

332

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- 340 1. Paganini, M. C.; Dalmasso, D.; Gionco, C.; Polliotto, V.; Mantilleri, L.; Calza, P., Beyond TiO₂: Cerium-
341 Doped Zinc Oxide as a New Photocatalyst for the Photodegradation of Persistent Pollutants. *ChemistrySelect*
342 **2016**, *1* (12), 3377-3383.
- 343 2. Cerrato, E.; Gionco, C.; Paganini, M. C.; Giamello, E.; Albanese, E.; Pacchioni, G., Origin of Visible Light
344 Photoactivity of the CeO₂/ZnO Heterojunction. *ACS Applied Energy Materials* **2018**, *1* (8), 4247-4260.
- 345 3. Kodera, M.; Wang, J.; Nail, B. A.; Liu, J.; Urabe, H.; Hisatomi, T.; Katayama, M.; Minegishi, T.; Osterloh,
346 F. E.; Domen, K., Investigation of charge separation in particulate oxysulfide and oxynitride photoelectrodes
347 by surface photovoltage spectroscopy. *Chemical Physics Letters* **2017**, *683*, 140-144.
- 348 4. Yang, S.; Wang, L. J.; Yan, Y. S.; Yang, L. L.; Li, X.; Lu, Z. Y.; Zhai, H. J.; Han, D. L.; Huo, P. W., Two Hybrid
349 Au-ZnO Heterostructures with Different Hierarchical Structures: Towards Highly Efficient Photocatalysts.
350 *Scientific Reports* **2019**, *9*.
- 351 5. Saravanan, R.; Shankar, H.; Prakash, T.; Narayanan, V.; Stephen, A., ZnO/CdO composite nanorods
352 for photocatalytic degradation of methylene blue under visible light. *Materials Chemistry and Physics* **2011**,
353 *125* (1-2), 277-280.
- 354 6. Gionco, C.; Paganini, M. C.; Giamello, E.; Burgess, R.; Di Valentin, C.; Pacchioni, G., Cerium-Doped
355 Zirconium Dioxide, a Visible-Light-Sensitive Photoactive Material of Third Generation. *Journal of Physical*
356 *Chemistry Letters* **2014**, *5* (3), 447-451.
- 357 7. Bechambi, O.; Jlaiel, L.; Najjar, W.; Sayadi, S., Photocatalytic degradation of bisphenol A in the
358 presence of Ce-ZnO: Evolution of kinetics, toxicity and photodegradation mechanism. *Materials Chemistry*
359 *and Physics* **2016**, *173*, 95-105.
- 360 8. Bechambi, O.; Touati, A.; Sayadi, S.; Najjar, W., Effect of cerium doping on the textural, structural and
361 optical properties of zinc oxide: Role of cerium and hydrogen peroxide to enhance the photocatalytic
362 degradation of endocrine disrupting compounds. *Materials Science in Semiconductor Processing* **2015**, *39*,
363 807-816.
- 364 9. Calza, P.; Gionco, C.; Giletta, M.; Kalaboka, M.; Sakkas, V. A.; Albanis, T.; Paganini, M. C., Assessment
365 of the abatement of acelsulfame K using cerium doped ZnO as photocatalyst. *J Hazard Mater* **2017**, *323* (Pt
366 A), 471-477.
- 367 10. Madhusudan, P.; Wang, Y.; Chandrashekar, B. N.; Wang, W. J.; Wang, J. W.; Miao, J.; Shi, R.; Liang, Y.
368 X.; Mi, G. J.; Cheng, C., Nature inspired ZnO/ZnS nanobranch-like composites, decorated with Cu(OH)₂(
369 clusters for enhanced visible-light photocatalytic hydrogen evolution. *Applied Catalysis B-Environmental*
370 **2019**, *253*, 379-390.
- 371 11. Harish, S.; Archana, J.; Sabarinathan, M.; Navaneethan, M.; Nisha, K. D.; Ponnusamy, S.;
372 Muthamizhchelvan, C.; Ikeda, H.; Aswal, D. K.; Hayakawa, Y., Controlled structural and compositional
373 characteristic of visible light active ZnO/CuO photocatalyst for the degradation of organic pollutant. *Applied*
374 *Surface Science* **2017**, *418*, 103-112.
- 375 12. Basnet, P.; Zhao, Y. P., Tuning the Cu_xO nanorod composition for efficient visible light induced
376 photocatalysis. *Catalysis Science & Technology* **2016**, *6* (7), 2228-2238.
- 377 13. Markina, N. E.; Pozharov, M. V.; Markin, A. V., Synthesis of Copper(I) Oxide Particles with Variable
378 Color: Demonstrating Size-Dependent Optical Properties for High School Students. *Journal of Chemical*
379 *Education* **2016**, *93* (4), 704-707.
- 380 14. Martra, G.; Gianotti, E.; Coluccia, S., The Application of UV - Visible - NIR Spectroscopy to Oxides. In
381 *Metal Oxide Catalysis*, Jackson, S. D.; Hargreaves, J. S. J., Eds. WILEY-VCH Verlag GmbH & Co. KGaA,
382 Weinheim: 2009; pp 51-94.
- 383 15. Cerrato, E.; Gionco, C.; Paganini, M. C.; Giamello, E., Photoactivity properties of ZnO doped with
384 cerium ions: an EPR study. *J Phys Condens Matter* **2017**, *29* (44), 444001.
- 385 16. Özgür, Ü.; Alivov, Y. I.; Liu, C.; Teke, A.; Reshchikov, M. A.; Doğan, S.; Avrutin, V.; Cho, S. J.; Morkoç,
386 H., A comprehensive review of ZnO materials and devices. *Journal of Applied Physics* **2005**, *98* (4), 041301.
- 387 17. Janotti, A.; Van de Walle, C. G., Absolute deformation potentials and band alignment of wurtzite ZnO,
388 MgO, and CdO. *Physical Review B* **2007**, *75* (12).
- 389 18. Banerjee, S., Optical Absorption by Nanoparticles of Cu₂O. *Europhys. Lett.* **D. Chakravorty**, *52*, 468-
390 473.

- 391 19. Bi, F.; Ehsan, M. F.; Liu, W.; He, T., Visible-Light Photocatalytic Conversion of Carbon Dioxide into
392 Methane Using Cu₂O/TiO₂ Hollow Nanospheres. *Chin. J. Chem.* **2015**, *33* (1), 112-118.
- 393 20. Tamiolakis, I.; Papadas, I. T.; Spyridopoulos, K. C.; Armatas, G. S., Mesoporous Assembled Structures
394 of Cu₂O and TiO₂ Nanoparticles for Highly Efficient Photocatalytic Hydrogen Generation from Water. *RSC*
395 *Advances* **2016**, *6* (60), 54848-54855.
- 396 21. Polliotto, V.; Livraghi, S.; Krukowska, A.; Dozzi, M. V.; Zaleska-Medynska, A.; Selli, E.; Giamello, E.,
397 Copper-Modified TiO₂ and ZrTiO₄: Cu Oxidation State Evolution during Photocatalytic Hydrogen Production.
398 *ACS Appl Mater Interfaces* **2018**, *10* (33), 27745-27756.
- 399 22. Cerrato, E.; Gionco, C.; Berruti, I.; Sordello, F.; Calza, P.; Paganini, M. C., Rare earth ions doped ZnO:
400 Synthesis, characterization and preliminary photoactivity assessment. *Journal of Solid State Chemistry* **2018**,
401 *264*, 42-47.
- 402 23. Cerrato, E.; Zickler, G. A.; Paganini, M. C., The role of Yb doped ZnO in the charge transfer process
403 and stabilization. *Journal of Alloys and Compounds* **2020**, *816*, 152555.
- 404 24. Evans, S. M.; Giles, N. C.; Halliburton, L. E.; Kappers, L. A., Further characterization of oxygen
405 vacancies and zinc vacancies in electron-irradiated ZnO. *Journal of Applied Physics* **2008**, *103* (4), 043710.
- 406 25. R. Buchheit; F. Acosta-Humanez; Almanza, O., Structural, EPR and Optical Studies on Cu-doped ZnO
407 Nanoparticles Synthesized by the Sol-Gel Method at Different Calcination Temperatures *Rev. Cub. Fis.* **2016**,
408 *33*, 4-12.
- 409 26. Elilarassi, R.; Chandrasekaran, G., Structural, optical and electron paramagnetic resonance studies on
410 Cu-doped ZnO nanoparticles synthesized using a novel auto-combustion method. *Frontiers of Materials*
411 *Science* **2013**, *7* (2), 196-201.
- 412 27. Sreethawong, T.; Yoshikawa, S., Enhanced photocatalytic hydrogen evolution over Pt supported on
413 mesoporous TiO₂/TiO₂ prepared by single-step sol-gel process with surfactant template. *International*
414 *Journal of Hydrogen Energy* **2006**, *31* (6), 786-796.
- 415 28. Parveen, F.; Sannakki, B.; Mandke, M. V.; Pathan, H. M., Copper nanoparticles: Synthesis methods
416 and its light harvesting performance. *Solar Energy Materials and Solar Cells* **2016**, *144*, 371-382.
- 417