



**HAL**  
open science

## **Photocatalytic activity of TiO<sub>2</sub>-P25@n-TiO<sub>2</sub>@HAP composite films for air depollution**

Guy Didier Fanou, Mamadou Traore, Benjamin Kouassi Yao, Andrei Kanaev, Khay Chhor

### ► To cite this version:

Guy Didier Fanou, Mamadou Traore, Benjamin Kouassi Yao, Andrei Kanaev, Khay Chhor. Photocatalytic activity of TiO<sub>2</sub>-P25@n-TiO<sub>2</sub>@HAP composite films for air depollution. *Environmental Science and Pollution Research*, 2021, 28 (17), pp.21326-21333. <10.1007/s11356-020-11924-4>. <hal-03412180>

**HAL Id: hal-03412180**

**<https://hal.science/hal-03412180v1>**

Submitted on 5 Nov 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

# 1 Photocatalytic activity of $\text{TiO}_2\text{-P}_{25}\text{@ n-TiO}_2\text{@HAP}$ Composite Films for Air 2 depollution

3 Guy Didier FANOU<sup>1,2</sup>, Mamadou TRAORE<sup>1</sup>, Benjamin Kouassi YAO<sup>2</sup>, Andrei KANAIEV<sup>1</sup>,  
4 Khay CHHOR<sup>1</sup>

5 <sup>1</sup> *Laboratoire des Sciences des Procédés et des Matériaux, CNRS, Université Paris 13,*  
6 *Sorbonne Paris Cité, 93430 Villetaneuse, France*

7 <sup>2</sup> *Laboratoire des Procédés de Synthèse, de l'environnement et des Energies Nouvelles-*  
8 *LAPISEN, INPHB ; Côte d'ivoire*

9 *Corresponding author :traore@lspm.cnrs.fr/ 0149404052 / 0149403414*

## 10 Abstract

11 We report on an elaboration of new composite photocatalysts ( $\text{TiO}_2\text{-P}_{25}\text{@ n-TiO}_2\text{@HAP}$ )  
12 based of grafted size-selected 5nm titanium-oxo-alkoxo nanoparticles on P25- $\text{TiO}_2$   
13 nanoparticles and HAP obtained by co-precipitation of salts. The 5-nm oxo- $\text{TiO}_2$  particles  
14 were prepared in a sol-gel reactor with rapid reagents micromixing. The photocatalytic test of  
15 ethylene degradation, in a continuous-flow fixed bed reactor, showed an increase of the  
16 photocatalytic yield for the composite photocatalysts with an addition of HAP. This result was  
17 interpreted by a synergy between adsorption and photooxidation.

18  
19 **Keywords:**  $\text{TiO}_2$ , hydroxyapatite, composite nanoparticles, photocatalysis.

## 20 21 1.Introduction

22 The industrial, domestic and military activities are increasingly rejecting toxic materials,  
23 especially in recent decades (Jacobson 2002; Atkinson 2000; Jia 2013; Bryne et al. 1998; Guo  
24 et al. 2003). The water and air quality is decreasing which represents a serious threat for all  
25 living species. Among the possible techniques for the destruction of pollution traces are the

26 Advanced Oxidation Technologies (TOA), the most important of which are ozonation, the use  
27 of ultraviolet (UV), plasma degradation and photocatalysis. From 2000 to 2018, the number  
28 of publications on TOA increases by more than fourfold and reaches 7000 publications (Giwa  
29 et al, 2021). Honda and Fujishima (1972) suggested the use of TiO<sub>2</sub> excited by ultraviolet  
30 radiation to decompose organic pollutants.. The principle of photocatalysis involves  
31 photogeneration of electron-hole pairs. Under light excitation, the electrons (e<sup>-</sup>) of the valence  
32 band (BV) of the TiO<sub>2</sub> pass to the conduction band (BC), leaving a positive charge or hole  
33 (noted h<sup>+</sup>) in the BV. These electron-hole pairs can recombine by releasing heat, or react  
34 separately with pollutant molecules of the environment. The recombination of the  
35 photoinduced charges served to be the main shortcoming of the photocatalytic process, which  
36 can be reduced by doping of the active component and/or its integration in a composite  
37 medium. In this connection, the combination of nano-TiO<sub>2</sub> and HAP may be an interesting  
38 solution.

39 Because of a large band gap energy ~7.7 eV ( $\lambda = 160$  nm), measured e.g. by Feldbach et al.  
40 (2015) and calculated by Tsukada et al. (2011), appreciable photocatalytic activity of this  
41 material cannot be expected. However, HAP was capable forming oxygen defects under UV  
42 illumination serving as active centers (Nishikawa et al. 2002) and some photocatalytic activity  
43 of HAP has been observed on the reduction of methyl mercaptan and dimethyl sulfide  
44 (Tanaka et al. 2012). The use of hydroxyapatite (HAP) as an adsorbent material is of  
45 increasing interest because of its remarkable property of ion exchange, bonding with organic  
46 molecules, low solubility in water (Iliev et al. 2007; Krestou et al. 2004; Ma et al. 1994; Qian  
47 et al 2014; Bahdod et al. 2009). Hydroxyapatite also has catalytic properties that have been  
48 studied in several fields (Monma 1982; Matsumura et al. 1984; Joris et al. 1971; Kibby et al.  
49 1972; Bett et al., 1968; Matsumura et al. 1994; Matsumura et al. 1997; Chlala 2016):  
50 dehydrogenation, dehydration, combustion, oxidation, reforming, etc. Several studies have

51 focused on the use of the adsorption-photocatalytic coupling of the TiO<sub>2</sub> / HAP composite for  
52 the removal of gaseous pollutants (Azouani et al. 2010a; Azouani et al. 2010b; Azouani et al.  
53 2007; Benmami et al. 2006). Thus, NO adsorption was observed by Nonami et al. (2004),  
54 Mitsionis et al. (2011) as well as Nasr-Esfahani et al. (2012) in photocatalytic studies.  
55 However, the improvement of the gas phase photocatalytic activity due to the presence of  
56 hydroxyapatite on the surface of TiO<sub>2</sub> is controversial; a negative or no effect can be observed  
57 with regard to the process procedure and the UV wavelengths used.  
58 The coupling between TiO<sub>2</sub> and HAP and the overall process efficiency are expected to  
59 depend on the process procedure. In this work, we applied a new approach to the  
60 photocatalyst synthesis by using titanium oxo-alkoxy (TOA) nanoparticles as a link between  
61 TiO<sub>2</sub> P25 and HAP components. The photocatalytic activity of the prepared TiO<sub>2</sub>-P<sub>25</sub>@ n-  
62 TiO<sub>2</sub>@HAP materials has been evaluated.

63

## 64 **2. Material and Methods**

65

### 66 **2.1 Elaboration of TiO<sub>2</sub>-P<sub>25</sub>@ n-TiO<sub>2</sub>**

67 The general approach to synthesize the TiO<sub>2</sub>-P<sub>25</sub>@n-TiO<sub>2</sub> has been proposed by Fanou et al.  
68 (2016). The sol nanoparticles are prepared in the sol-gel reactor using titanium  
69 tetraisopropoxide (TTIP) as a precursor. Two stock solutions: 50 cm<sup>3</sup> of a TTIP/propan-2-ol  
70 solution and 50 cm<sup>3</sup> of a H<sub>2</sub>O/propan-2-ol solution, was synchronously injected under  
71 nitrogen into the turbulent mixing zone (Re = 4500) of sol-gel reactor (Azouani et al. 2010b)  
72 where the oxo-TiO<sub>2</sub> nanoparticles were generated from hydrolysis condensation reactions.  
73 The particle size can be tuned by adjusting the hydrolysis ratio  $H = C_{H_2O}/C_{TTIP}$ , where  $C_{H_2O}$   
74 and  $C_{TTIP}$  are respectively water and titanium precursor concentrations. We have prepared  
75 colloids using hydrolysis ratio  $H = 2$ , which corresponds to one of stability domains of the  
76 sol-gel process and enables particles size of 5.2 nm (Azouani et al. 2007). The suspended

77 oxoparticles solution was subsequently transferred to a glove box LABstar MBraun where  
78 they were combined slowly with TiO<sub>2</sub>-P25 powder under stirring. The ratio 66 % of TiO<sub>2</sub>-  
79 P25/ n-TiO<sub>2</sub> was the same for all prepared samples. A stable nanocoating, with a specific area  
80 of 72 m<sup>2</sup>/g, was prepared by immobilization of nanoparticles on glass bed by dip-coating.

81

## 82 **2.2 Elaboration of TiO<sub>2</sub>-P<sub>25</sub>@ n-TiO<sub>2</sub>@HAP**

83 Two types of composites were prepared by i) crystallization on the surface of the TiO<sub>2</sub>-P25 @  
84 n-TiO<sub>2</sub> of hydroxyapatite in a physiological solution SBF (CPS / HAP-SBF) ii) incorporation  
85 of hydroxyapatite in the matrix TiO<sub>2</sub>-P25 @ n-TiO<sub>2</sub> (CPS / HAP).

86

### 87 2.2.1 Co-precipitation method

88 The chemicals (Sigma Aldrich) involved in this experiment are calcium nitrate  
89 Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (purity 99%), ammonium dihydrogen phosphate NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (purity ≥ 98%)  
90 and Ammonia (purity 99,5%). 125 ml of calcium nitrate (0.5 mol.L<sup>-1</sup>) and 75 ml of  
91 ammonium phosphate (0.5 mol.L<sup>-1</sup>) are mixed with vigorous stirring. Then, concentrated  
92 ammonia is added dropwise to pH≈10-10.5 to give a white precursor precipitate of HAP.  
93 After stirring for 1 hour, the suspension is filtered and stored in a hermetically sealed beaker  
94 in order to avoid carbonation due to atmospheric carbon dioxide. HAP is then mixed with the  
95 colloid suspension TiO<sub>2</sub>-P<sub>25</sub>@n-TiO<sub>2</sub> so as to obtain different mass percentage. The mixture  
96 of the hydroxyapatite and composite particles are immobilized by dip-coating on the 1 mm  
97 diameter glass beads for photocatalytic tests. Prepared materials are noted as CPS / HAP.

98

### 99 2.2.2 Simulated Body Fluid (SBF) method

100 This preparation method is advocated by Li et al. (1993). The chemicals were purchased from  
101 Sigma Aldrich in quantities indicated in Table 1.

102 In general, 250 ml of distilled water were poured into a beaker and placed in a water bath at  
103 36.5 °C with magnetic stirring. Each reagent was then subsequently added to the reaction  
104 medium during the synthesis. The pH was adjusted to 7.25 using 1N HCl. At the end, the  
105 volume of the solution was completed to 500 mL with distilled water and stored in a  
106 refrigerator at 5-10 °C. The crystallization of hydroxyapatite on TiO<sub>2</sub>-P25 @ n-TiO<sub>2</sub>  
107 composite was carried out by placing the composite samples and the SBF solution in contact  
108 under slight agitation. The crystallization time varies from 30 min to 5h. Longer calcination  
109 times were also used in the preparation and specified if applicable. Prepared materials are  
110 noted as CPS / HAP-SBF.

111

### 112 **2.3. Photocatalyst Characterization**

113 The prepared samples were structurally characterised by X-ray diffraction XRD (INEL XRG  
114 3000) using CuK $\alpha$  radiation with Nickel filter. The surface morphology of photocatalyst was  
115 examined by SEM JEOL JSM 64400F with acceleration voltage of 10 kV. Raman spectra  
116 were measured at 516 nm using micro-Raman high-resolution HR800 installation (HORIBA  
117 JobinYvon) with the spectral and spatial resolution respectively 0.25 cm<sup>-1</sup> and 5  $\mu$ m. The  
118 scattered light is collected by Peltier cooled CCD camera in a backscattering configuration.  
119 The photocatalytic activity of the prepared samples was tested in a continuous-flow fixed-bed  
120 reactor on ethylene decomposition. A gas flow of pollutant (120 ppm) mixture with dry air  
121 and flow rate of 7.5 mL/min passes through a reactor tube of 6-mm diameter and 35 cm  
122 length made of glass transparent in the UV-A spectral range (Benmami et al. 2005; Tieng et  
123 al. 2011). The glass beads coated photocatalyst samples were filled the reactor tube of 15 cm  
124 length around the middle. Inside the tube, just after the glass bead, a chromel / alumel  
125 thermocouple monitors the temperature. The tube is surrounded at a radial distance of 3 cm by  
126 six 8-W lamps of 29 cm length emitting at 362 nm ( $\Delta\lambda_{\text{hwfm}} = 22$  nm). During the experiments,

127 the reactor is cooled by compressed air stream. Ethylene concentrations before ( $C_{in}$ ) and after  
128 ( $C_{out}$ ) the photocatalytic reactor were monitored by online gas chromatography (Varian 191  
129 CP 3800) equipped with a capillary column (HP-PLOT/Q) and a flame ionization detector  
130 FID. Before turn on the UV lamps, one hour period is applied for the stabilization of Ethylene  
131 concentrations and the gas inlet stream temperature at 25 °C. Two injection loops of 250  $\mu$ L  
132 and heated at 80 °C allow measurements of pollutant concentration in continuous mode. The  
133 reactor yield (or ethylene conversion) is calculated according to the formula:  $\eta(\%) = (C_{in} -$   
134  $C_{out})/C_{in} \times 100$ . The column temperature and flow rate of the carrier gas ( $N_2$ ) were respectively  
135 50 °C and 5 mL/min.

136

### 137 **3. Characterization**

#### 138 **3-1. X-ray diffraction**

139 The X-ray plots of pure hydroxyapatite (figure 1) show well-defined peaks indicating that the  
140 solids are well crystallized.

141

142 In the range of  $2\theta$  between 25 and 35 °, they reveal clear diffractions of the (002) planes at  
143 25.7 ° and those of the (211), (300), and (202) planes at 31.6, 32, 7 ° and 33.9 ° respectively.

144 All these planes can be indexed in the hexagonal space group system  $P6_3/m$  (Nathanael et al.  
145 2010). The average size of the crystallites was estimated using the Sherrer formula (Smith  
146 1989) and the Bragg reflection of the (002) planes. These parallel planes with the  $c^{\rightarrow}$  axis  
147 represent the preferential direction of growth of the hydroxyapatite.

$$d = \frac{k\lambda}{b(2\theta) \cos \theta}$$

148  $d$  is the diameter of the crystallites ( $\text{\AA}$ ),  $k$  is a constant (0.9),  $\lambda$  is the incident wavelength ( $\text{\AA}$ ),  
149  $\theta$  is the Bragg angle (degree) and  $b$  is the half width. recorded peak height expressed in  
150 radians.

151 The calculated value of  $d$  is close to 21 nm for the sample treated at 100 ° C. and 22.5 nm for  
152 that calcined at 450 ° C.

153 The X-ray diffraction patterns of the samples of the TiO<sub>2</sub>-P25 @ n-TiO<sub>2</sub> composite containing  
154 a dispersion of HAPs are shown in Figure 2.

155

156 The spectra show a presence of crystallized HAP in the material. The intensity of the most  
157 intense HAP peaks around 31.5 ° increases with the increase in its mass content in the  
158 material. They appear clearly in the sample diagram with 30% PAH.

159

### 160 **3-2. Raman spectroscopy**

161 The vibrational study by Raman scattering was recorded on the powders of the following  
162 samples:

163 i) Pure hydroxyapatite treated at 450 ° C.

164 ii) TiO<sub>2</sub>-P25 @ n-TiO<sub>2</sub> / PAH noted CPS / HA with a mass content equal to 3 and 5% of  
165 incorporated PAH.

166 The spectrum of hydroxyapatite is shown in Figure 3.

167

168 The frequency range between 400 and 1200 cm<sup>-1</sup> characterizes the diffusion bands of the  
169 (PO<sub>4</sub>)<sup>3-</sup> group. The peaks observed around 430 and 449 cm<sup>-1</sup> can be attributed to the  
170 deformation vibration  $\nu_2$ . The Raman bands at 580, 592 and 610 cm<sup>-1</sup> correspond to the triple  
171 degenerate vibrational mode  $\nu_4$ . The symmetrical elongation vibration mode  $\nu_1$  of the (PO<sub>4</sub>)<sup>3-</sup>  
172 group appears as a very intense peak located at 962 cm<sup>-1</sup>. This diffusion band is characteristic  
173 of the structure of hydroxyapatite (Smeulders, 2001). The antisymmetric vibration  $\nu_3$  can be  
174 associated with the diffusion bands observed at 1032, 1048 and 1079 cm<sup>-1</sup>. Figure 4 shows the

175 Raman spectra of the TiO<sub>2</sub>-P25 @ n-TiO<sub>2</sub> / HAP (CPS / HAP) composite with a mass  
176 content of 3 and 5% PAH.

177

178 The spectra obtained clearly show three Raman bands at 399, 516 and 642 cm<sup>-1</sup> of the anatase  
179 of the composite. As for the hydroxyapatite, because of its low concentration in the matrix (3  
180 and 5%) the intensity of the diffusion bands is very weak making the observation difficult.

181 The only detectable peak is 962 cm<sup>-1</sup> attributed to the vibrational mode  $\nu_1$  of the (PO<sub>4</sub>)<sup>3-</sup>  
182 group.

183

#### 184 **4. Photocatalytic activity**

185

##### 186 **4-1. Co-precipitation method**

187 The photocatalytic tests were measured on the samples of 0.5% and 1% by weight of  
188 hydroxyapatite with the references CPS / HAP-0.5 and CPS / HAP-1 respectively. Figure 5  
189 shows the evolution of photocatalytic activity of ethylene degradation.

190

191 The conversion of ethylene to CPS / HAP-0.5, CPS / HAP-1 shows a rapid increase for 20  
192 min under UV radiation. As Tieng et al have already observed (2011), the warm up time of  
193 UV lamps was too short (Figure 6a) to account for this behavior. The temperature increases  
194 from 25 °C to 46 ± 2 °C in about 3 min. Moreover no photolysis of ethylene is observed  
195 (Figure 6b). The delay in the achievement of the asymptotic ethylene conversion has been  
196 previously explained by the formation of non-volatile intermediate reaction products, assigned to the  
197 oxidized polymeric hydrocarbons: furan and furfural oligomers Ol<sub>N</sub> with N=6÷8 (Tieng et al. 2019).  
198 After this step, the photocatalytic yield reaches a stable steady state corresponding to a  
199 conversion value  $\eta$  greater than that of the reference composite: 12% for CPS / HAP-1 and

200 6% for CPS / HAP-0.5. The first order rates of the pollutant decomposition in Figure 7, which  
201 reflects the intrinsic photocatalyst activity (Fanou et al. 2016), showed a linear proportionality  
202 to the HAP content. It begins however from a non-zero value, characteristic of the pure titania  
203 activity, increasing by ~50% at 1wt% of HAP.

204  
205 This enhancement might be associated with: i) strong adsorption capacity of hydroxyapatite  
206 with respect to the pollutant and the secondary reaction products likely to form during the  
207 photocatalytic reactions (Hauchecorne et al. 2011), ii) better availability of active sites  
208 because of elimination of poisons by adsorbance on the composite surface , and iii) charge  
209 separation efficiency enhancement in the composite. Mitsionis et al. (2011) have reported that  
210 the formation of  $\text{OH}^\circ$  radicals is greater onto HAP /  $\text{TiO}_2$  composite than  $\text{TiO}_2$  alone. In the  
211 same time, the band gap energy of HAP/ $\text{TiO}_2$  composite  $E_g=3.08$  eV (Kamat 2002) has been  
212 reported to be insignificantly lower compared with pure titania (3.12 eV), whereas that of  
213 HAP reported by Feldbach et al. (2015) and Lopez et al. (2013) was significantly larger: 7.7  
214 eV and >6 eV respectively. Accordingly, synergistic effect between adsorbing and active sites  
215 could be responsible for the enhanced activity of the composite. The following scenario  
216 highlighting the synergistic action of these two components, composite and adsorbent, can be  
217 described as follows: the molecules of the pollutant are additionally adsorbed by HAP and  
218 then migrate along the composite surface to the active nanoparticles where they react. The  
219 secondary products, if formed, can be advantageously captured by HAP discharging active  
220 sites to be decomposed on a later stage.

221

#### 222 **4-2. SBF method**

223 Figure 8 shows the results of the photocatalytic activity of the films prepared with a  
224 crystallization time of 30 min.

225 The obtained results indicate that the ethylene conversion  $\eta$  increases rapidly for about 20  
226 minutes of irradiation to reach a maximum of 3% to 5% higher than that of the reference  
227 ( $\text{TiO}_2\text{-P25 @ n-TiO}_2$ ). We also explained this behavior by the thermal activation of the  
228 material following the rise of temperature. It then shows a slow decrease to a lower value than  
229 that of the untreated sample after about 40 minutes. This behavior is fairly reproducible for  
230 the three samples. Different reasons can explained this behavior : (i) scattering of the incident  
231 light by the surface particles (ii)  $e^-/h^+$  charge transfer blocking at the composite-  
232 hydroxyapatite interface of the composite to the adsorbed ethylene (Feldbach et al. 2015;  
233 Tsukada et al. 2011), iii) poisoning of sites material assets by the presence of products from  
234 the elaboration stage.

235 In order to confirm these hypotheses, we studied the influence of the crystallization  
236 time on the photocatalytic activity shown in Figure 9. The results show the similar behavior  
237 observed on Figure 8 and the maximum ethylene conversion is also obtained at the same time  
238 (30-40 min).

239  
240 We observe that the prolonged crystallization time decreases the photocatalytic  
241 activity of the composite material. This reduction in photocatalytic performance is important  
242 and varies from 5% (30 min) to 75% for a crystallization time of 5 h. These results support the  
243 explanations we have advanced above: hydroxyapatite on the surface, increase the scattering  
244 of the incident light and reduce the charges transfer at the interface and the crystallization  
245 products can poison the photocatalyst.

246 The different performances of the two prepared  $\text{TiO}_2\text{-P}_{25}\text{@ n-TiO}_2\text{@HAP}$  materials  
247 (Figures 5 and 8) can be explained by their probable structure. Hydroxyapatite crystals  
248 deposited on the surface of  $\text{TiO}_2\text{-P}_{25}\text{@ n-TiO}_2$  is obtained by the SBF method. In this case, an  
249 increase of crystallization time causes a decrease of the photocatalytic activity. Whereas,

250 when hydroxyapatite crystals are incorporated in the  $\text{TiO}_2\text{-P}_{25}\text{@ n-TiO}_2$  matrix, it is dispersed  
251 in the composite and can create a synergistic effect of hydroxyapatite on the photooxidation  
252 properties of the photocatalyst.

253

#### 254 **4. Conclusion**

255 Two families of new composite photocatalysts were prepared by crystallization on the surface  
256 of the  $\text{TiO}_2\text{-P}_{25}\text{@ n-TiO}_2$  of the hydroxyapatite in a physiological solution SBF and by  
257 incorporation of hydroxyapatite in  $\text{TiO}_2\text{-P}_{25}\text{@ n-TiO}_2$  matrix. Both HAP and  $\text{TiO}_2$  conserve  
258 own crystallinity in the material. The photocatalytic yield (gas phase conversion of ethylene)  
259 of the material obtained by co-precipitation was increased with an increase of the HAP  
260 content, indicating the synergy between two components. On the other hand, the prolonged  
261 crystallization time of the composite in SBF has a negative effect on the photocatalytic yield.

262

263

264

265

266

267

268

269

270

271

272

273

274

275 **Declarations**

276 Ethics approval and consent to participate :

277 Not applicable

278 Consent for publication :

279 Not applicable

280 Availability of data and materials :

281 The datasets used and/or analysed during the current study are available from the  
282 corresponding author on reasonable request.

283 Competing interests :

284 The authors declare that they have no competing interests

285 Funding :

286 Not applicable

287 Authors' contributions :

288 All authors (Guy Didier FANOUE, Mamadou TRAORE, Benjamin Kouassi YAO, Andrei  
289 KANAIEV and Khay CHHOR) contributed to the study conception and design. Material  
290 preparation, data collection and analysis were performed by Guy Didier FANOUE. The first  
291 draft of the manuscript was written by Mamadou TRAORE and other authors (Guy Didier  
292 FANOUE, Benjamin Kouassi YAO, Andrei KANAIEV and Khay CHHOR) commented on  
293 previous versions of the manuscript. All authors (Guy Didier FANOUE, Mamadou TRAORE,  
294 Benjamin Kouassi YAO, Andrei KANAIEV and Khay CHHOR) read and approved the final  
295 manuscript.

296 Acknowledgements :

297 Not applicable

298 **References**

299 -Atkinson R. (2000), Atmospheric chemistry of VOCs and NO<sub>x</sub>, Atmos. Environ. 34 : 2063–  
300 2101.

301 -Azouani R., Michau A., Hassouni K., Chhor K., Bocquet J.-F., Vignes J.-L., Kanaev A.  
302 (2010), Elaboration of pure and doped TiO<sub>2</sub> nanoparticles in sol–gel reactor with turbulent  
303 micromixing: Application to nanocoatings and photocatalysis, Chem. Eng. Res. Des. 88 :  
304 1123–1130.

305 -Azouani R., Soloviev A., Benmami M., Chhor K., Bocquet J.-F., Kanaev A. (2007), Stability  
306 and growth of titanium-oxo-alkoxy Ti<sub>x</sub>O<sub>y</sub>(OiPr)<sub>z</sub> clusters, J. Phys. Chem. C. 111 : 16243–  
307 16248.

308 -Azouani R., Tieng S., Chhor K., Bocquet J.-F., Eloy P., Gaigneaux E. M., Klementiev K.,  
309 Kanaev A. (2010), TiO<sub>2</sub> doping by hydroxyurea at the nucleation stage: towards a new  
310 photocatalyst in the visible spectral range, Phys. Chem. Chem. Phys. 12 : 11325–11334.

311 -Bahdod A., El Asri S., Saoiabi A., Coradin T., Laghzizil A. (2009), Adsorption of phenol  
312 from an aqueous solution by selected apatite adsorbents: Kinetic process and impact of the  
313 surface properties, Water Res. 43 : 313–318.

314 -Benmami M., Chhor K. and Kanaev A. (2005) Supported nanometric titanium oxide sols as a  
315 new efficient photocatalyst, J Phys Chem B, 109: 19766- 19771.

316 -Benmami M., Chhor K. and Kanaev A. (2006), High photocatalytic activity of monolayer  
317 nanocoatings prepared from non-crystalline titanium oxide sol nanoparticles, Chem. Phys.  
318 442 : 552–557.

319 -Bett J.A., Hall W.K. (1968), The microcatalytic technique applied to a zero order reaction:  
320 The dehydration of 2-butanol over hydroxyapatite catalysts, J. Catal. 10 : 105–113.

321 -Byrne J.A., Eggins B. R., Brown N.M.D., McKinney B., Rouse M. (1998), Immobilisation  
322 of TiO<sub>2</sub> powder for the treatment of polluted water, *Appl. Catal. B Environ.* 17 : 25–36.

323 -Chlala D., Labaki M., Giraudon J., Lamonier J. (2016), Toluene total oxidation over Pd and  
324 Au nanoparticles supported on hydroxyapatite, *Comptes Rendus Chimie*, 19 : 525-537.

325 -Fanou G.D., Yao B., Cheng K., Brinza O., Traore M., Kanaev A., Chhor K. (2016),  
326 “Elaboration of novel nanoparticulate TiO<sub>2</sub>-P25@nTiO<sub>2</sub> composite for Catalysis”,  
327 *International Journal of Advanced Applied Physics Research* 3 : 19-25.

328 -Feldbach E., Kirm M., Kotlov A., Mägi H. (2015), Luminescence Spectroscopy of Ca-  
329 apatites under VUV Excitation, *User Rep. Mater. Sci. Httpphoton-Sci. Desy* . 17 : 122–123.

330 -Fujishima A., Honda K. (1972), TiO<sub>2</sub> photoelectrochemistry and photocatalysis, *Nature*. 238  
331 : 37–38.

332 -Giwa A., Yusuf A., Balogun H. A, Sambudi N. S., Bilad M. R., Adeyemi I., Chakraborty S.  
333 Curcio S. (2021), Recent advances in advanced oxidation processes for removal of  
334 contaminants from water: A comprehensive review, *Process Safety and Environmental*  
335 *Protection*, 146 : 220-256

336 -Guo F.Q., Okamoto M., Crawford N. M. (2003), Identification of a plant nitric oxide  
337 synthase gene involved in hormonal signaling, *Science*. 302 : 100–103.

338 -Hauchecorne B., Tytgat T., Verbruggen S.W., Hauchecorne D., Terrens D., Smits M.,  
339 Vinken K., Lenaerts S. (2011), Photocatalytic degradation of ethylene: An FTIR in situ study  
340 under atmospheric conditions, *Appl. Catal. B Environ.* 105 : 111–116.

341 -Iliev V., Tomova D., Bilyarska L., Tyuliev G. (2007), Influence of the size of gold  
342 nanoparticles deposited on TiO<sub>2</sub> upon the photocatalytic destruction of oxalic acid, *J. Mol.*  
343 *Catal. Chem.* 263 : 32–38.

344 -Jacobson M.Z. (2002), Atmospheric pollution: history, science, and regulation, Cambridge  
345 University Press.

346 -Jia Z. (2013), Elaboration des matériaux composites nanostructurés Ag, Au/TiO<sub>2</sub> pour la  
347 dépollution des effluents gazeux avec une activation par plasma, Université Paris 13.

348 -Joris S. J., Amberg C. H. (1971), J. Phys. Chem. , 75 : 316

349 -Kamat P.V. (2002), Photophysical, photochemical and photocatalytic aspects of metal  
350 nanoparticles, J. Phys. Chem. B. 106 : 7729–7744.

351 -Kibby C.L., Lande S.S., Hall W.K. (1972), Tracer studies of acid-catalyzed reactions. XI.  
352 Stereoselectivity in alcohol dehydration over hydroxyapatite and alumina catalysts, J. Am.  
353 Chem. Soc. 94 : 214–220.

354 -Krestou A., Xenidis A., Papias D. (2004), Mechanism of aqueous uranium (VI) uptake by  
355 hydroxyapatite, Miner. Eng. 17 : 373–381.

356 -Li P., Nakanishi K., Kokubo T., de Groot K. (1993), Induction and morphology of  
357 hydroxyapatite, precipitated from metastable simulated body fluids on sol-gel prepared silica,  
358 Biomaterials. 14 : 963–968.

359 -Lopez L., Daoud W.A., Dutta D., Panther B.C., Turney T.W. (2013), Effect of substrate on  
360 surface morphology and photocatalysis of large-scale TiO<sub>2</sub> films, Appl. Surf. Sci. 265 : 162–  
361 168.

362 -Ma Q.Y., Traina S.J., Logan T.J., Ryan J.A. (1994), Effects of aqueous Al, Cd, Cu, Fe (II),  
363 Ni, and Zn on Pb immobilization by hydroxyapatite, Environ. Sci. Technol. 28 : 1219–1228.

364 -Matsumura Y., Kanai H., Moffat J.B (1997), Catalytic oxidation of carbon monoxide over  
365 stoichiometric and non-stoichiometric hydroxyapatites, J. Chem. Soc. Faraday Trans. 93 :  
366 4383–4387.

367 -Matsumura Y., Moffat J.B. (1994), Partial Oxidation of Methane to Carbon-Monoxide and  
368 Hydrogen with Molecular-Oxygen and Nitrous-Oxide over Hydroxyapatite Catalysts, *J. Catal.*  
369 148 : 323–333.

370 -Matsumura Y., Moffat J.B. (1996), Methanol adsorption and dehydrogenation over  
371 stoichiometric and non-stoichiometric hydroxyapatite catalysts, *J Chem Soc Faraday Trans.*  
372 92 : 1981–1984.

373 -Mitsionis A., Vaimakis T., Trapalis C., Todorova N., Bahnemann D., Dillert R. (2011),  
374 Hydroxyapatite/titanium dioxide nanocomposites for controlled photocatalytic NO oxidation,  
375 *Appl. Catal. B Environ.* 106 : 398–404.

376 -Monma H. (1982), Catalytic behavior of calcium phosphates for decompositions of 2-  
377 propanol and ethanol, *J. Catal.* 75 : 200–203.

378 -Nasr-Esfahani M., Fekri S. (2012), Alumina/TiO<sub>2</sub>/hydroxyapatite interface nanostructure  
379 composite filters as efficient photocatalysts for the purification of air, *React. Kinet. Mech.*  
380 *Catal.* 107 : 89–103.

381 -Nathanael A. J., Mangalaraj D., Chen P.C., Ponpandian N. (2010), Mechanical and  
382 photocatalytic properties of hydroxyapatite/titania nanocomposites prepared by combined  
383 high gravity and hydrothermal process, *Compos. Sci. Technol.* 70 : 419–426.

384 -Nishikawa H., Omamiuda K. (2002), Photocatalytic activity of hydroxyapatite for methyl  
385 mercaptane, *J. Mol. Catal. Chem.* 179 : 193–200.

386 -Nonami T. (2004), Apatite-Coated Titanium Dioxide Photocatalyst for Air Purification,  
387 *Catal. Today.* 96 : 113–118.

388 -Qian G., Li M., Wang F., Liu X. (2014), Removal of Fe<sup>3+</sup> from Aqueous Solution by  
389 Natural Apatite, *J. Surf. Eng. Mater. Adv. Technol.*

390 -Smeulders D. E., Wilson M.A., Armstrong L. (2001), Insoluble organic compounds in the  
391 Bayer process, *Ind. Eng. Chem. Res.* 40 : 2243–2251

392 -Smith K. (1989), *Modern Powder Diffraction*”; in *Review in Mineralogy*, Edited by D. L.  
393 Bish and J. E. Post. Mineralogical Society of America, Washington, DC, 20 : 183.

394 -Tanaka H., Tsuda E., Nishikawa H., Fuji M. (2012), FTIR studies of adsorption and  
395 photocatalytic decomposition under UV irradiation of dimethyl sulfide on calcium  
396 hydroxyapatite, *Adv. Powder Technol.* 23 : 115–119.

397 -Tieng S, Kanaev A and Chhor K. (2011) New homogeneously doped Fe(III)-TiO<sub>2</sub>  
398 photocatalyst for gaseous pollutant degradation, *J Appl Catal A* 399: 191-197.

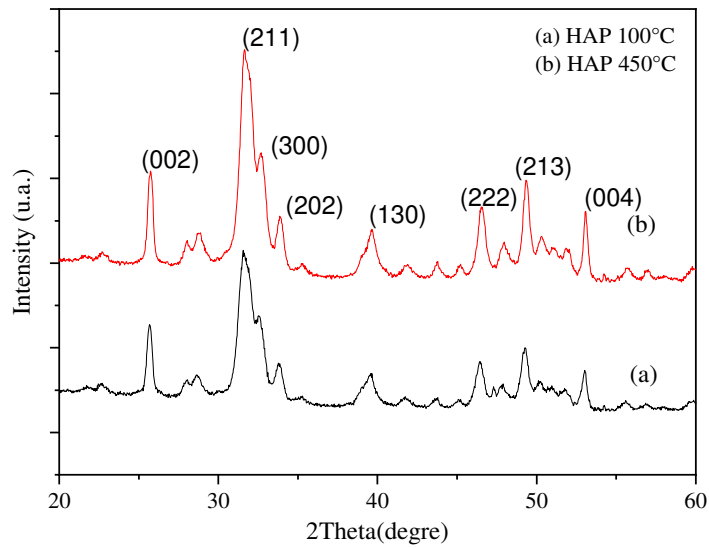
399 -Tieng S, Jia Z., Diaz-Gomez Trevino A. P., Eloy P., Giagneaux E. M., Chhor K., Kanaev A.  
400 (2019) Major non-volatile intermediate products of photo-catalytic decomposition of  
401 ethylene, *Journal of Catalysis* 374: 328-334.

402 -Tsukada M., Wakamura M., Yoshida N., Watanabe T. (2011), Band gap and photocatalytic  
403 properties of Ti-substituted hydroxyapatite: comparison with anatase-TiO<sub>2</sub>, *J. Mol. Catal.*  
404 *Chem.* 338 : 18–23.

405

406 **FIGURES**

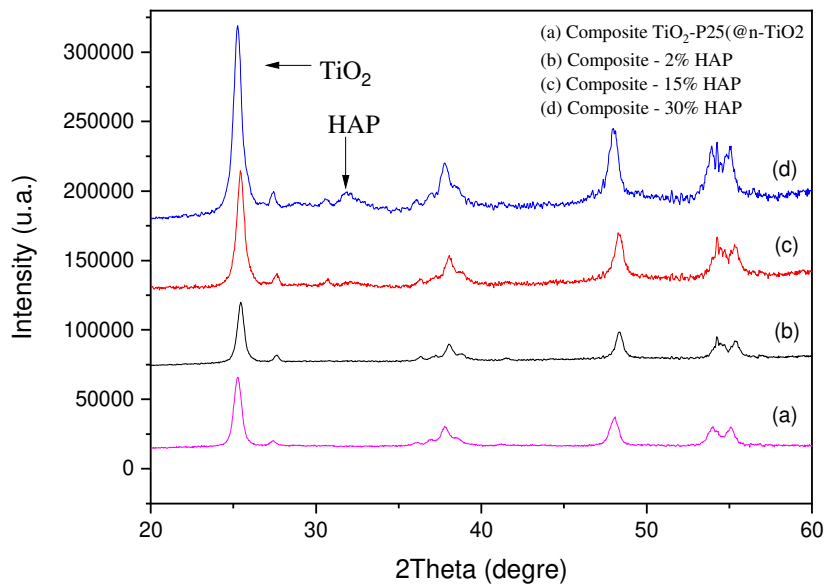
407



408

409 *Fig. 1: Heat-treated hydroxyapatite diffraction patterns at 100°C (a) and 450°C (b).*

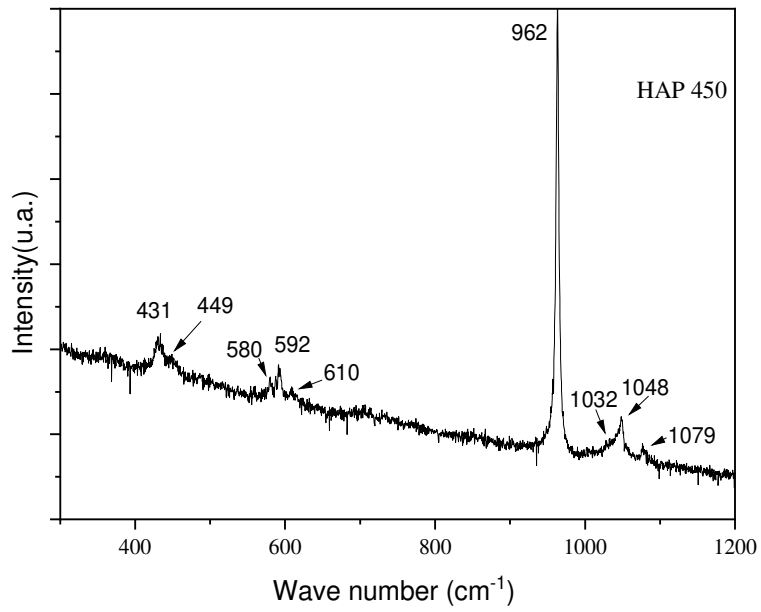
410



411

412 *Fig. 2: X-ray diffractograms of samples of TiO<sub>2</sub>-P25 @ n-TiO<sub>2</sub> / HAP composite treated with*  
413 *different mass compositions of hydroxyapatite (a) 0% (b) 2% (c) 15% and (d) 30%.*

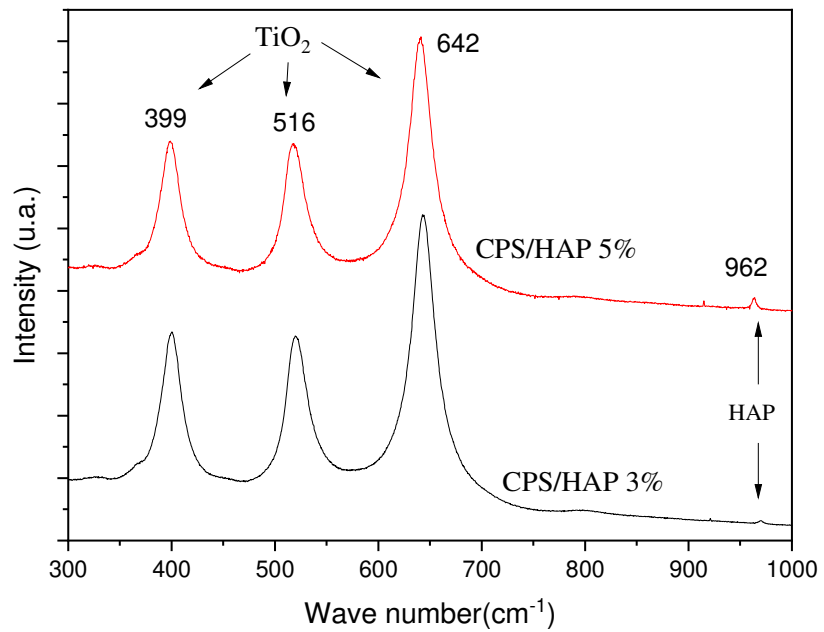
414



415

416 *Fig. 3: Raman spectrum of hydroxyapatite treated at 450 ° C recorded with excitatory*

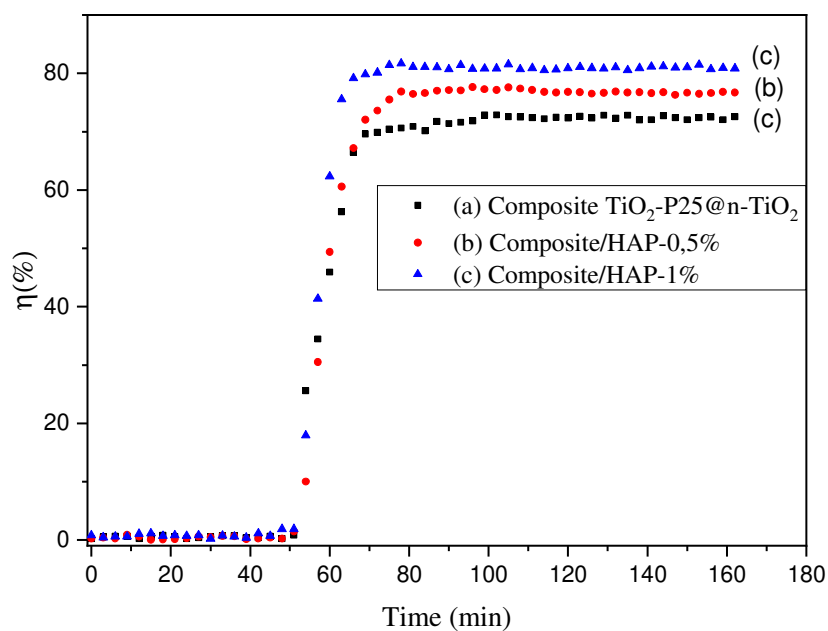
417



418

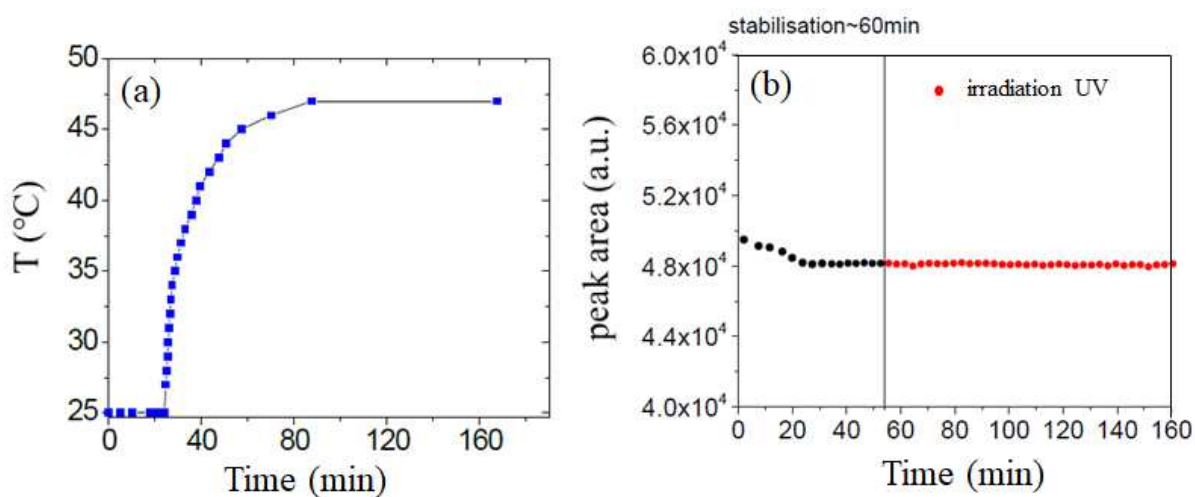
419 *Fig. 4: Raman spectra of two CPS / PAH samples loaded with 3 and 5% PAH and treated at*  
 420 *450 ° C for 4 h.*

421



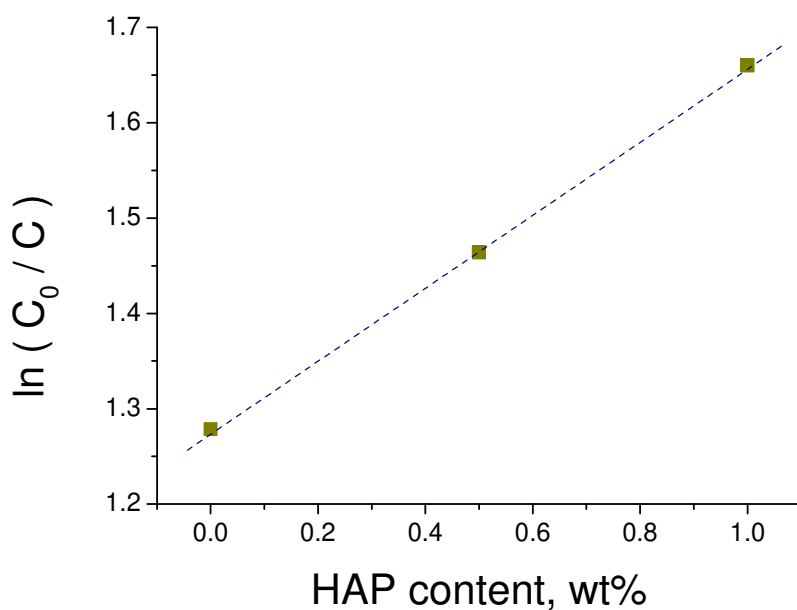
422  
 423 *Fig. 5: Evolution of the photodegradation of ethylene by CPS / HAP-0.5 and CPS / HAP-1*  
 424 *as a function of the irradiation time. The conversion rate of ethylene by the untreated composite*  
 425 *is given for comparison. (  $\lambda = 360 \text{ nm}$ , ethylene 150 ppm, flow rate  $10 \text{ mL}\cdot\text{min}^{-1}$  ).*

426  
 427



428  
 429 *Fig. 6: Temperature evolution during photocatalytic tests (a) and Ethylene concentration*  
 430 *evolution under UV irradiation without photocatalysts (b).*

431

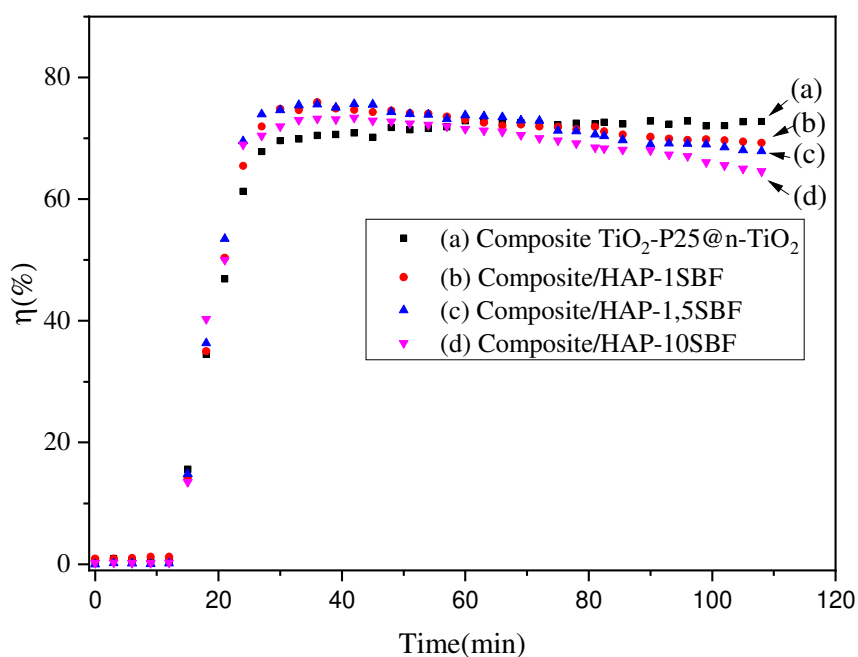


432

433

434

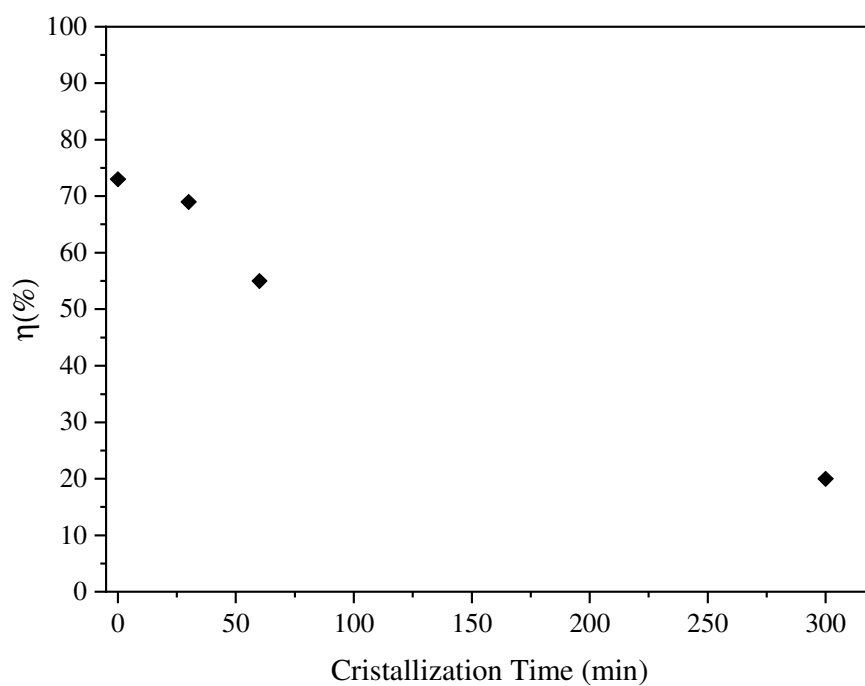
Fig. 7: Photocatalytic activity as a function of HAP doping.



435

436 Evolution of the photodegradation of ethylene by different CPS / HAP-SBF as a function of  
 437 the irradiation time. The conversion rate of ethylene by the untreated composite is given for  
 438 comparison. ( $\lambda = 360 \text{ nm}$ , ethylene 150 ppm, flow rate  $10 \text{ mL}\cdot\text{min}^{-1}$ ).

439



440

441 *Fig. 9: Photodegradation of ethylene by CPS / HAP-1SBF as a function of the crystallization*

442 *time. ( $\lambda = 360 \text{ nm}$ , ethylene 150 ppm, flow rate  $10 \text{ mL}\cdot\text{min}^{-1}$ ).*