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► **To cite this version:**

Guy Didier Fanou, Mamadou Traore, Benjamin Kouassi Yao, Andrei Kanaev, Khay Chhor. Photocatalytic activity of $\text{TiO}_2\text{-P25@n-TiO}_2\text{@HAP}$ 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

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

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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 $\text{P}_{25}\text{-TiO}_2$
13 nanoparticles and HAP obtained by co-precipitation of salts. The 5-nm oxo- 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:** 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 TiO₂ 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⁻) of the valence
32 band (BV) of the TiO₂ pass to the conduction band (BC), leaving a positive charge or hole
33 (noted h⁺) 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-TiO₂ 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 TiO₂ / 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 TiO₂ 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 TiO₂ 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 TiO₂ P25 and HAP components. The photocatalytic activity of the prepared TiO₂-P₂₅@ n-
62 TiO₂@HAP materials has been evaluated.

63

64 **2. Material and Methods**

65

66 **2.1 Elaboration of TiO₂-P₂₅@ n-TiO₂**

67 The general approach to synthesize the TiO₂-P₂₅@n-TiO₂ 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 cm³ of a TTIP/propan-2-ol
70 solution and 50 cm³ of a H₂O/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-TiO₂ 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 TiO₂-P25 powder under stirring. The ratio 66 % of TiO₂-
79 P25/ n-TiO₂ was the same for all prepared samples. A stable nanocoating, with a specific area
80 of 72 m²/g, was prepared by immobilization of nanoparticles on glass bed by dip-coating.

81

82 **2.2 Elaboration of TiO₂-P₂₅@ n-TiO₂@HAP**

83 Two types of composites were prepared by i) crystallization on the surface of the TiO₂-P25 @
84 n-TiO₂ of hydroxyapatite in a physiological solution SBF (CPS / HAP-SBF) ii) incorporation
85 of hydroxyapatite in the matrix TiO₂-P25 @ n-TiO₂ (CPS / HAP).

86

87 2.2.1 Co-precipitation method

88 The chemicals (Sigma Aldrich) involved in this experiment are calcium nitrate
89 Ca(NO₃)₂·4H₂O (purity 99%), ammonium dihydrogen phosphate NH₄H₂PO₄ (purity ≥ 98%)
90 and Ammonia (purity 99,5%). 125 ml of calcium nitrate (0.5 mol.L⁻¹) and 75 ml of
91 ammonium phosphate (0.5 mol.L⁻¹) 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 TiO₂-P₂₅@n-TiO₂ 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 TiO₂-P25 @ n-TiO₂
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 α 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⁻¹ and 5 μ 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 μ 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 2θ 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 (\AA), k is a constant (0.9), λ is the incident wavelength (\AA),
149 θ 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 TiO₂-P25 @ n-TiO₂ 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) TiO₂-P25 @ n-TiO₂ / 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⁻¹ characterizes the diffusion bands of the
169 (PO₄)³⁻ group. The peaks observed around 430 and 449 cm⁻¹ can be attributed to the
170 deformation vibration ν_2 . The Raman bands at 580, 592 and 610 cm⁻¹ correspond to the triple
171 degenerate vibrational mode ν_4 . The symmetrical elongation vibration mode ν_1 of the (PO₄)³⁻
172 group appears as a very intense peak located at 962 cm⁻¹. This diffusion band is characteristic
173 of the structure of hydroxyapatite (Smeulders, 2001). The antisymmetric vibration ν_3 can be
174 associated with the diffusion bands observed at 1032, 1048 and 1079 cm⁻¹. Figure 4 shows the

175 Raman spectra of the TiO₂-P25 @ n-TiO₂ / 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⁻¹ 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⁻¹ attributed to the vibrational mode ν_1 of the (PO₄)³⁻
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_N 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 η 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 OH° radicals is greater onto HAP / TiO_2 composite than TiO_2 alone. In the
211 same time, the band gap energy of HAP/ 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 η 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 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.

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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

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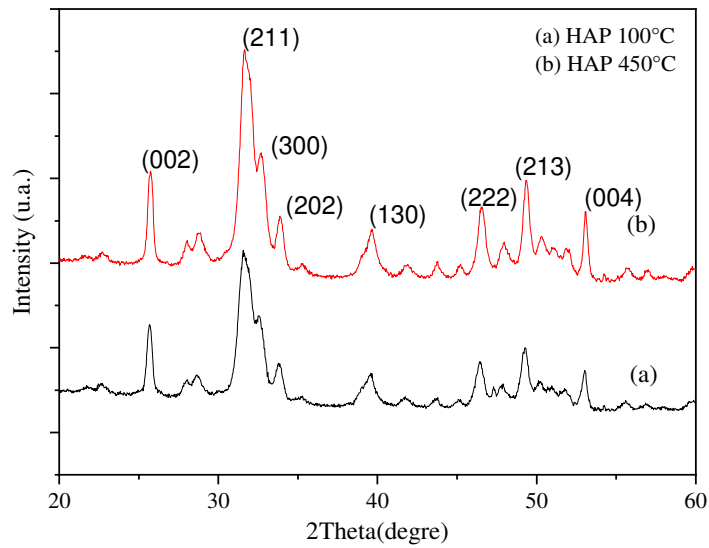
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406 **FIGURES**

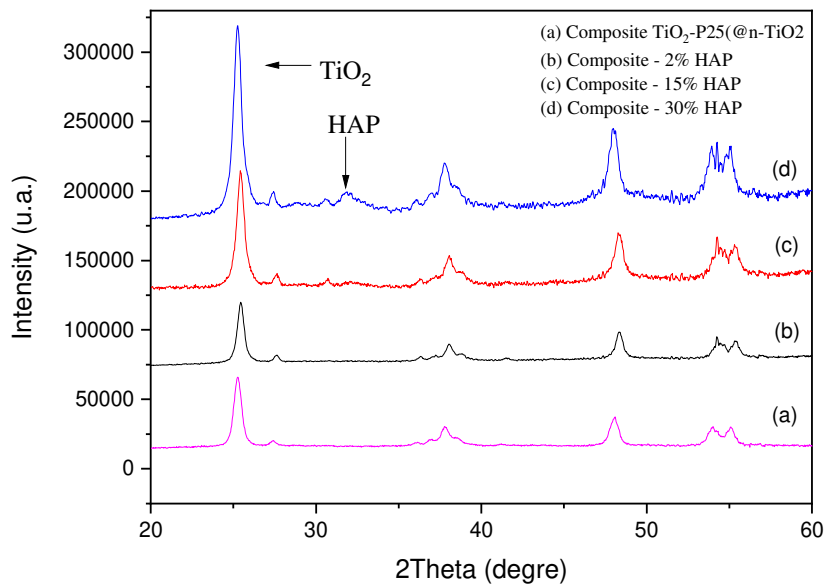
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409 *Fig. 1: Heat-treated hydroxyapatite diffraction patterns at 100°C (a) and 450°C (b).*

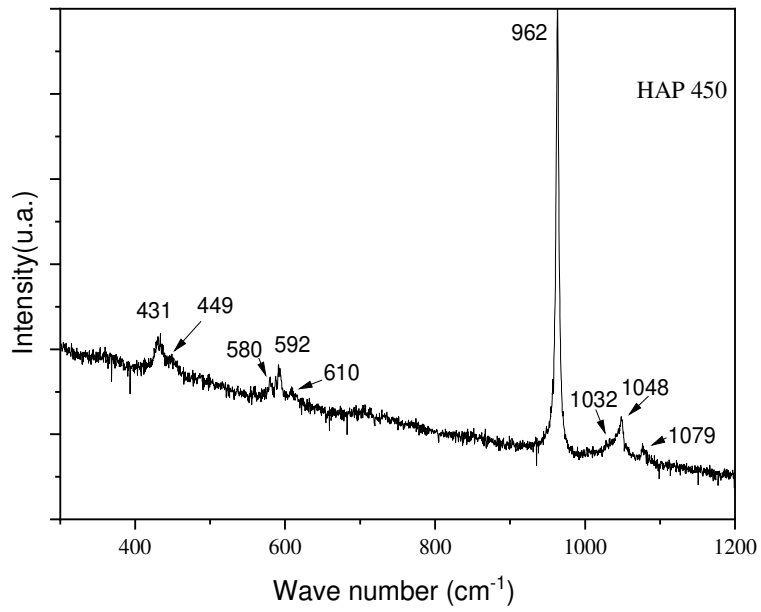
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412 *Fig. 2: X-ray diffractograms of samples of TiO₂-P25 @ n-TiO₂ / HAP composite treated with*
413 *different mass compositions of hydroxyapatite (a) 0% (b) 2% (c) 15% and (d) 30%.*

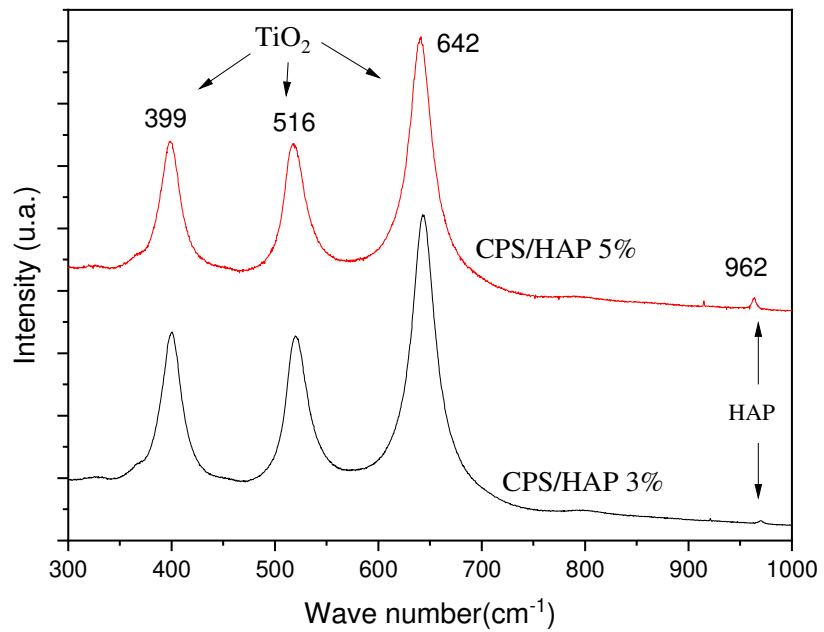
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416 *Fig. 3: Raman spectrum of hydroxyapatite treated at 450 ° C recorded with excitatory*

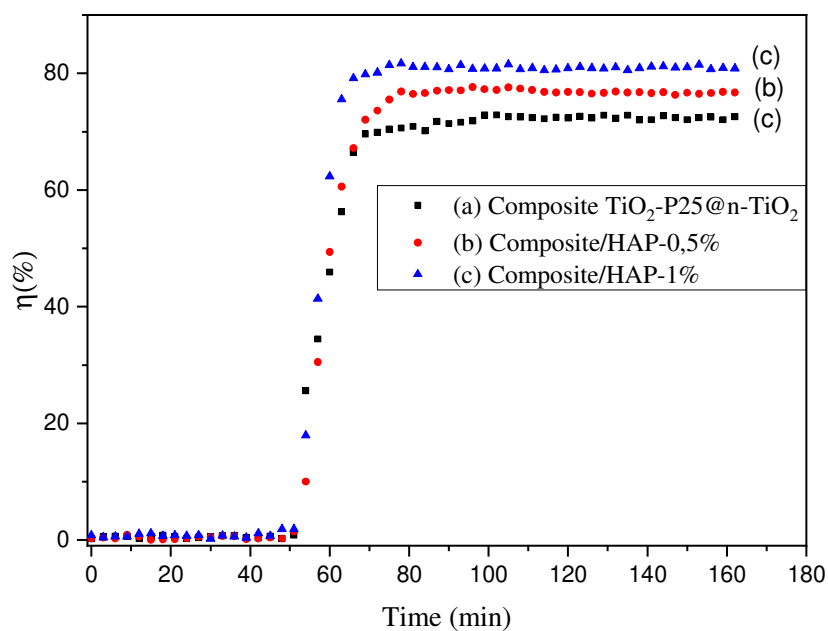
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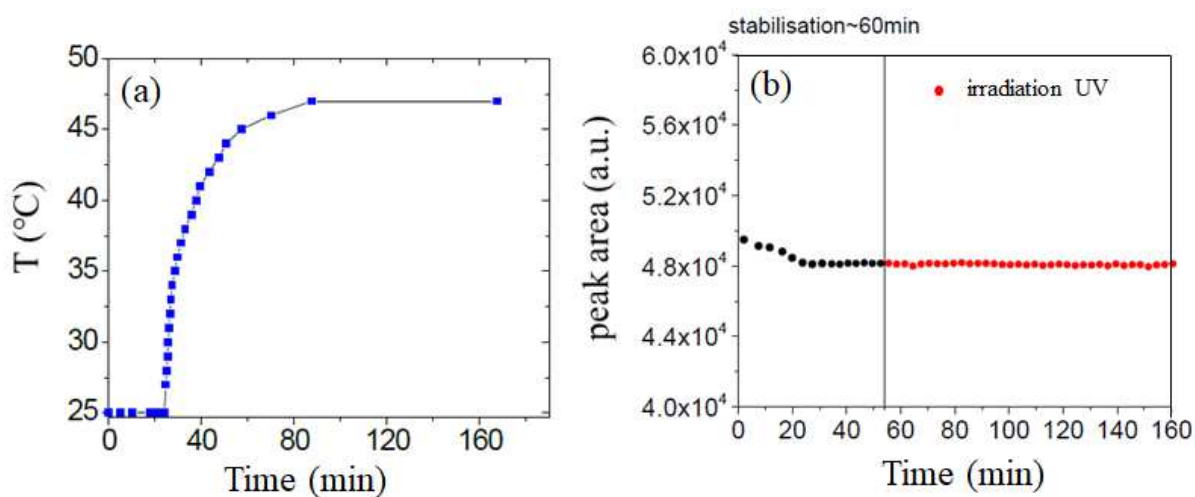
419 *Fig. 4: Raman spectra of two CPS / PAH samples loaded with 3 and 5% PAH and treated at*
 420 *450 ° C for 4 h.*

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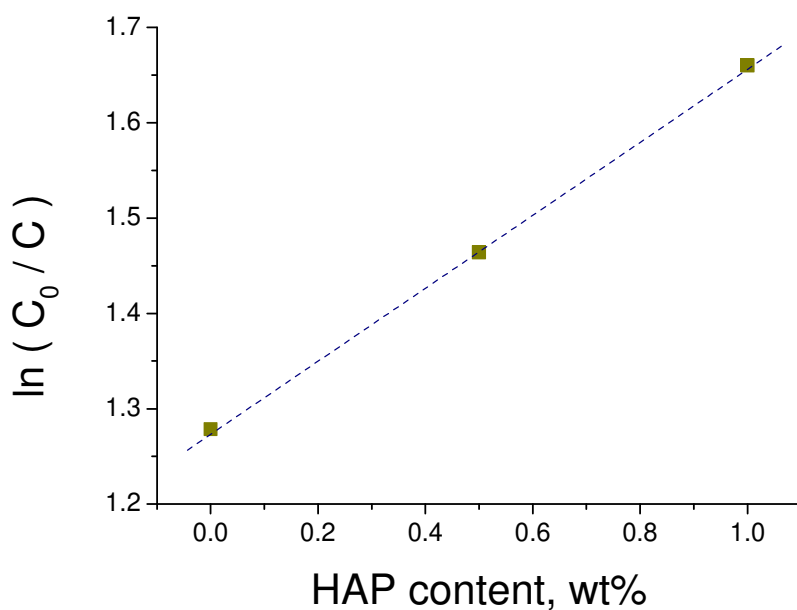
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 423 *Fig. 5: Evolution of the photodegradation of ethylene by CPS / HAP-0.5 and CPS / HAP-1 as*
 424 *a function of the irradiation time. The conversion rate of ethylene by the untreated composite*
 425 *is given for comparison. ($\lambda = 360 \text{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

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

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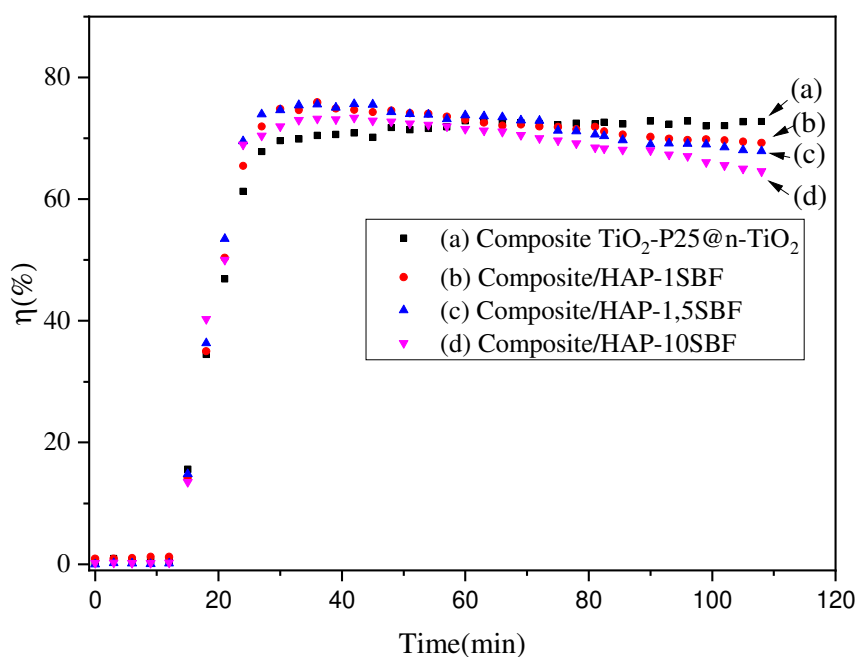


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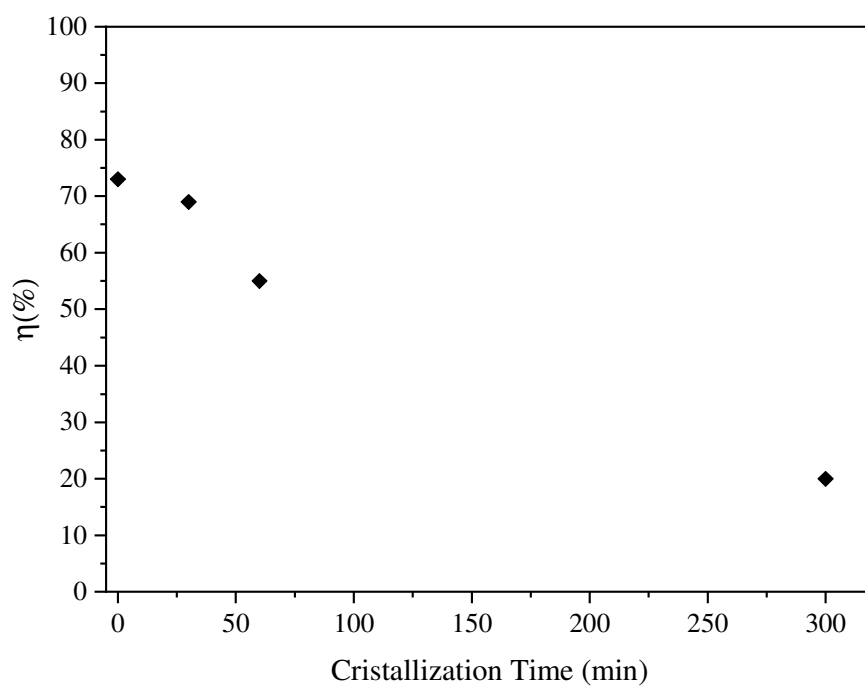
Fig. 7: Photocatalytic activity as a function of HAP doping.



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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 $10 \text{ mL}\cdot\text{min}^{-1}$).*