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Dear Editor,

I kindly ask you to consider for possible publication our research paper in “**Applied Catalysis B: Environmental**”.

The title of our paper is:

Enhanced visible light photocatalytic activity by up-conversion phosphors modified N-doped TiO₂

The manuscript is an original and novel contribution and relevant to topics of interest for this journal.

In this work, the photocatalytic activity of N-doped TiO₂ (NdT) under visible light irradiation has been strongly enhanced in presence of organic up-conversion phosphors (OP) in the catalyst formulation. At our knowledge, it is the first paper reporting the use of organic up-conversion phosphors in a photocatalytic system.

Such photocatalysts (NdT/OP) have been prepared, characterized and tested in the photocatalytic degradation of a wide range of organic dyes in the presence of visible light irradiation emitted by green or white LEDs. In all cases, the optimization of the use of light irradiation has been achieved because NdT was excited both by the emission spectrum of the white LEDs and by the blue emission of the phosphors (OP), excited by the green component emitted by white LEDs. The obtained results make NdT/OP photocatalysts a very suitable system to achieve high photocatalytic activity with solar light.

Sincerely,

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1 **Enhanced visible light photocatalytic activity by up-**
2 **conversion phosphors modified N-doped TiO₂**

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13 **Abstract**

14 The development of photocatalytic processes is strongly related to an efficient
15 irradiation of the catalyst surface. A chance to get a significant reactivity
16 enhancement is the promotion of the photocatalyst with up-conversion phosphors
17 able to convert low-energy into high-energy photons. In this work it was found that
18 the photocatalytic activity of visible active N-doped TiO₂ (NdT) can be strongly
19 enhanced when it is promoted by the presence of organic up-conversion phosphors
20 (OP) in the catalyst formulation. Such photocatalysts (NdT/OP) have been prepared
21 and tested in the photocatalytic degradation of a wide range of organic dyes in the
22 presence of visible light irradiation emitted by green or white LEDs. The
23 photocatalytic activity of NdT/OP in the presence of green LEDs is attributed to the
24 up-conversion property of OP phosphors that emit at 434 nm, wavelength suitable
25 for photoexciting NdT. Moreover, NdT/OP showed a dramatic enhancement of
26 photocatalytic activity when white LEDs were used as light source. In this case, the
27 NdT supported on OP surface is excited both by the emission spectrum of the white
28 LEDs and by the blue emission of the phosphors (OP), excited by the green
29 component emitted by white LEDs. The obtained results make NdT/OP
30 photocatalyst a very suitable system to achieve high photocatalytic activity with solar
31 light.

32 **Keywords:** N-doped TiO₂, up-conversion organic phosphors, white and green LEDs,
33 photocatalytic degradation of dyes.

34

35 **1. Introduction**

36 The search for a renewable and sustainable energy supply has been intensified in the
37 past years in response to the environmental problems caused by fossil fuels
38 exploitation. In this context, solar energy is clean and very abundant, but its
39 utilization is still very limited. So, it is necessary to develop a sustainable and cost-
40 effective manner for harvesting solar energy to satisfy the growing energy demand of
41 the world with a minimal environmental impact [1].

42 Photocatalysis can play an important role for the conversion of solar energy into
43 chemicals [2, 3] , fuels [4, 5], electricity [6], and in the removal of organic pollutants
44 both in wastewater [7-12] and in gaseous stream [13-15].

45 Since the discovery of the semiconducting properties of TiO₂ (band-gap energy: 3.2
46 eV) [16], great research efforts have been directed to a better exploitation of solar
47 energy in photocatalysis. However, despite the great number of photocatalyst
48 formulations proposed, most of them are only active under ultraviolet (UV)
49 radiation, which is only a little fraction (5%) of solar light. To be of practical use for
50 photocatalysis, the photo-response of the transition metal oxides should be within the
51 visible light (43%) of the electromagnetic radiation reaching the planet's surface.
52 Therefore, an appropriate photocatalyst should work in the visible-light region (420
53 nm < λ < 800 nm) with a band gap of less than 3 eV.

54 Different approaches to improve the exploitation of sun light in photocatalytic
55 processes have been proposed, especially oxide semiconductors doping [17] or
56 titania photosensitization [18]. However, both approaches still suffer from

57 disadvantages. For example, the introduction of impurities strongly affects the
58 lifetime of the photogenerated e^-h^+ pair, and doping can also decrease the corrosion
59 resistance of the material [19]. Moreover, titania photosensitization with organic
60 dyes still presents major limitations for applications in photocatalysis, due to the
61 poor stability of the dye, which can undergo desorption, photolysis and oxidative
62 degradation, and fast back electron transfer, resulting in low quantum yield for the
63 photocatalytic reaction [20].

64 Good visible photocatalytic activity results were found on N-doped TiO_2 , both under
65 visible irradiation and under solar simulated radiation (250W lamp) in the removal
66 of several pollutants such as emerging contaminants [21] and bacteria inactivation
67 [22]. In all cases, a main issue emerged, since the photocatalytic activity is related to
68 the light propagation inside the overall volume of photoreactors [8]. Therefore,
69 together with the insufficient performances of visible light photocatalysts, the main
70 issue to deal with in the development of photocatalytic processes is the limitation of
71 light propagation inside the photoreactor. Therefore, since the improving of the
72 photocatalytic reactivity is correlated to an efficient irradiation of the catalytic
73 surface, the chance to get this improvement by modifying a photocatalyst with light
74 carriers such as emitting phosphorescent particles (generally known as phosphors)
75 has been successfully verified to confer additional radiation emission or to decrease
76 the optical path of irradiation towards the photocatalyst [23, 24]. A reasonable
77 consequence of such an approach for the intensification of the photocatalytic process
78 seems to be the use of up-conversion phosphors able to convert low-energy into
79 high-energy photons [25]. Few examples report the use of inorganic up-conversion
80 phosphors in a photocatalytic system. To this purpose, active carbon supported
81 undoped TiO_2 catalyst (C- TiO_2) was modified with $Er^{3+}:YAlO_3$ up-conversion

82 phosphors that convert visible light into UV light able to photoexcite TiO₂ [26]. It is
83 worthwhile to highlight that the photocatalytic tests were carried out with a visible
84 light source that is not able to activate undoped TiO₂.

85 Moreover, in order to utilize visible light directly, C-TiO₂ catalyst was modified by
86 blue, green and red colour emitting inorganic up-conversion phosphors through
87 calcination assisted solvothermal method. The characterization data demonstrated
88 that such photocatalysts could be excited by UV, visible and NIR light
89 simultaneously [27]. In this case, all the composites exhibited excellent induced
90 rhodamine B degradation activity under the irradiation of 980 nm NIR laser,
91 although uncoupled phosphors and C-TiO₂ showed no destruction ability [27].
92 However, it is very important to underline that only 35 % of dye decolourization has
93 been achieved after 5 h of irradiation [27] .

94 Recently, triplet–triplet annihilation up-conversion luminescence has emerged as an
95 efficient process with anti-Stokes shift upon excitation by low power light intensity
96 [28]. When compared to rare-earth up-conversion phosphors, the organic ones have
97 several advantages including more intense absorption coefficient of sensitizer and
98 higher quantum yield [29].

99 In this work, a visible active N-doped TiO₂ photocatalyst, was modified by organic
100 up conversion phosphors and studied in the photocatalytic degradation of a wide
101 range of organic dyes in the presence of white LEDs visible light irradiation. At our
102 knowledge, it is the first paper reporting the use of organic up-conversion phosphors
103 in a photocatalytic system.

104

105

106

107 **2. Materials and methods**

108 *2.1 Materials*

109 Reagents and solvents for the preparation of blue-emissive up conversion organic
110 nanoparticles were: nonionic surfactant Pluronic F127, tetraethyl ortosilicate (TEOS,
111 99.99%), Pd complex octaethylporphyrin (PdOEP), 9,10-diphenylanthracene (DPA),
112 reagent grade toluene (Aldrich), and hydrochloric acid (fuming, $\geq 37\%$).

113 Reagents for the synthesis of N-doped TiO_2 catalyst were: titanium (IV)
114 isopropoxide (TTIP, >97 wt%, Sigma Aldrich) and ammonia aqueous solutions (30
115 wt%).

116 For the photocatalytic tests, methylene blue (MB), crystal violet (CV), eriochrome
117 black-T (EBT), Rhodamine B (RhB), red allura (RED) and tartrazine (TR) (Aldrich)
118 were used.

119

120 *2.2. N-doped TiO_2 preparation*

121 N-doped TiO_2 (NdT) was prepared by hydrolysis reaction between titanium
122 tetraisopropoxide and 30 wt% ammonia aqueous solution [10]. The preparation was
123 carried out at 0°C and under stirring until the formation of a gel. The obtained gel
124 was centrifuged and washed with distilled water and then placed in a furnace at 450°
125 C for 30 min. The molar ratio N/Ti is 18.6, the same as in the catalyst formulation
126 optimised in a previous work [22, 30]. The characterization of NdT catalyst, yellow
127 in colour, by different analytical techniques has been reported in our previous papers
128 [22, 30]. In particular, UV–vis spectra evidenced the ability of NdT to absorb visible
129 light, as shown by the band gap value (2.5 eV) [30].

130

131

132 *2.3 Blue-emissive up-conversion organic nanoparticles preparation*

133 Blue-emissive up-conversion organic nanoparticles (OP) (with a size ranging
134 between 10 and 22 nm [28]) were prepared following the method reported by Liu et
135 al. [28]. In particular, 2.0 g of Pluronic F127, 1.0 mg of PdOEP, and 10 DPA were
136 carefully solubilised in 20 mL of toluene. Toluene was evaporated from the
137 homogeneous organic solution by means of a gently nitrogen flow until to obtain a
138 pink solid residue (OP). The schematic picture of the preparation procedure is
139 reported in Fig. 1.

140

141 *2.4 Preparation of NdT/OP catalyst*

142 OP nanoparticles (0.4 g) were dissolved under magnetic stirring in 25 mL of HCl
143 (0.85 mol L^{-1}) aqueous solution. First TEOS (2 mL), and then NdT (0.12 g) were
144 added to the solution (Fig 2). The mixture was kept under stirring for 48 h at 25 °C
145 and then centrifuged to recover the final NdT/OP solid phase. The nominal loading
146 of NdT in the catalyst was 30 wt % [31].

147

148 *2.5 Samples characterization*

149 The samples were characterized with several techniques. Specific surface area of
150 catalysts were obtained by N₂ adsorption measurement at -196 °C with a Costech
151 Sorptometer 1040 after pretreatment at 60 °C for 120 min in He flow (99.9990 %).
152 UV-Vis reflectance spectra were recorded with a Perkin Elmer spectrometer Lambda
153 35. The TiO₂ content of the NdT/OP sample was determined by X-ray fluorescence
154 spectrometry (XRF) in a thermoFischer ARL QUANT'X EDXRF spectrometer
155 equipped with a rhodium standard tube as the source of radiation and with Si-Li
156 drifted crystal detector. X-ray diffraction (XRD) was carried out using an X-ray

157 microdiffractometer Rigaku D-max-RAPID (Cu-K α radiation). Raman spectra were
158 obtained at room temperature with a Dispersive MicroRaman spectrophotometer
159 (Invia, Renishaw), equipped with a 514 nm diode-laser, in the range 100–2500 cm⁻¹.
160 For the evaluation of photoluminescence spectrum (PL) of OP nanoparticles, a
161 suspension in distilled water was prepared in a magnetically-stirred cuvette. The
162 sample was irradiated with a 150 W Xe lamp and the excitation wavelength was
163 selected by the use of a LOT MSH-150 monochromator system. The excitation light
164 was guided through a focusing lens and PL was detected by a SM442 CCD
165 spectrometer placed at 45° to the incident light beam.

166

167 *2.6 Photocatalytic activity test*

168 Photocatalytic experiments were carried out with a pyrex tubular photoreactor (ID =
169 2.5 cm) equipped with an air distributor device ($Q_{\text{air}} = 150$ mL/min (STP)), a
170 magnetic stirrer to maintain the photocatalyst suspended in the aqueous solution and
171 a temperature controller [21]. The photoreactor was irradiated by a strip composed of
172 30 white light LEDs (nominal power: 6W) with wavelength emission in the range
173 400–800 nm or by the same number green light LEDs (nominal power: 6W) with
174 wavelength emission in the range 450–600 nm (with a maximum centered at about
175 532 nm) (Fig. 3). The LEDs strip was positioned around the reactor to assure
176 uniform illumination of the reaction volume.

177 In a typical photocatalytic test, 3 g/L of photocatalyst was suspended in 50 mL
178 solution. The system was kept in dark condition for 2 h to reach dye adsorption
179 equilibrium on the catalyst surface, and then the photocatalytic reaction was initiated
180 by the LEDs lighting. Liquid samples were taken at regular time intervals during the
181 test and centrifuged for 20 minutes at 4000 rpm for removing the photocatalyst

182 particles. The centrifuged samples were analyzed to determine the change of dye
183 concentration, measured with a Perkin Elmer UV-Vis spectrophotometer at $\lambda = 663,$
184 528, 426, 506, 583 and 553 for MB, EBT, TRZ, RED, CV and RhB respectively.
185 The initial concentration of dyes in the photocatalytic tests was equal to 10 mg/L.

186

187 **3. Results and Discussion**

188 *3.1. Characterization of the samples*

189 All the catalysts are listed in Table 1, together with nominal and measured NdT
190 loading, specific surface area (BET), equivalent band-gap energy, and NdT average
191 crystallites size.

192 The specific surface area (SSA) of pure NdT, after calcination in air at 450°C, is 30
193 m²/g, while a lower value (1 m²/g) was found for OP. It is worthwhile to note that the
194 SSA of NdT/OP catalyst increased up to 8 m²/g after the deposition of NdT on the
195 surface. The increase of surface area could be ascribed to the formation of NdT
196 coating on the OP surface.

197 The total amount of titania in NdT/OP catalyst, determined by XRF, well agrees with
198 the nominal TiO₂ amount, indicating that the preparation method is a suitable way to
199 couple NdT with OP phosphors.

200 Crystal phase composition and crystallinity of the materials were determined by
201 XRD (Fig.4). Anatase was the only TiO₂ crystalline phase detected for both NdT and
202 NdT/OP. This result suggests that the preparation method used for obtaining the
203 catalyst did not induce any change in the NdT crystalline structure, as also evidenced
204 by the same value of crystallite size, evaluated at diffraction plane (101) through the
205 Scherrer equation (Table 1). In the case of NdT/OP, a broad band with low intensity
206 centered at $2\theta = 23^\circ$ appears, attributed to silica obtained from the hydrolysis of

207 TEOS [32]. The main diffraction signals of OP disappeared in NdT/OP pattern, due
208 to the covering of OP surface by silica and NdT.

209 Raman spectra of NdT, OP and NdT/OP are shown in Fig. 5. In the range 100-1000
210 cm^{-1} (Fig. 5a), NdT showed bands at 144, 396, 514, 637 cm^{-1} and a weak shoulder at
211 195 cm^{-1} , due to the Raman-active fundamental modes of anatase [33].

212 The NdT/OP catalyst also shows the presence of some bands of NdT without any
213 shift in their positions. This indicates that the dispersion of NdT on the OP surface
214 did not cause modification in the crystalline structure of NdT catalyst, as shown by
215 XRD analysis.

216 In the range 100-1000 cm^{-1} , the spectrum of OP displayed signals at 281, 366, 536,
217 582, 847 and 926 cm^{-1} , less intensive than those ones of NdT. These signals
218 disappear when NdT is supported on the surface of OP. On the contrary, in the range
219 1000-2000 cm^{-1} (Fig. 5b), the OP spectrum displayed signals at 1065, 1146, 1233,
220 1280, 1455 and 1486 cm^{-1} , that are present also in NdT/OP, but with lower intensity
221 (Fig. 5b).

222 Figure 6 depicts the PL spectrum of OP excited at 532 nm wavelength, accordingly
223 with the spectral distribution of green LEDs employed to irradiate the photoreactor.
224 A wide emission band between 400 and 500 nm was detected, with a blue peak
225 centered at about 434 nm and two blunter peaks located at 418 and 450 nm, in good
226 agreement with the data previously published [28].

227

228 *3.2 Photocatalytic activity tests with green LEDs as light source*

229 To understand the influence of OP blue emission on NdT photoactivity, a
230 photocatalytic test was carried out with MB dye solution (initial concentration of 10
231 mg/L) and green LEDs as light source. As reported in the Fig. 7 (insert),

232 photocatalytic test on NdT showed that the MB concentration reached a maximum
233 value, likely due to MB desorption from the NdT surface, and then decreased. After
234 240 min of irradiation, the MB degradation reached a value of about 3 % indicating
235 that NdT has only a negligible photoactivity in the presence of green LEDs. It is
236 worthwhile to consider that at these operating conditions no photolysis of MB
237 occurred (not shown).

238 A dramatically different trend was found for the NdT/OP catalyst, which showed
239 MB degradation of about 20% after 4 hours of irradiation. These results clearly
240 indicate that the photocatalytic activity under green light is only due to the presence
241 of OP, that has up-conversion property and emits at 434 nm, wavelength able to
242 photoexcite the nitrogen-doped titania deposited on OP surface, as also confirmed by
243 the UV-vis DRS spectrum of NdT (Fig. 7). Indeed, the NdT catalyst evidenced a
244 reflectance value of about 27% at excitation wavelength of 434 nm, corresponding to
245 the blue emission of OP. On the contrary, with excitation wavelength of 532 nm
246 (corresponding to the maximum emission of green LEDs), the NdT catalyst showed
247 a very higher reflectance value with respect to that one at 434 nm.

248

249 *3.3 Photocatalytic activity tests with white LEDs as light source*

250 In order to verify that the dyes were converted in a heterogeneous photocatalytic
251 process, blank experiments were performed. In particular, tests carried out in dark
252 conditions with all the investigated dyes did not evidence any oxidation activity.
253 Moreover, additional control tests were carried out in the presence of each dye and
254 irradiating the photoreactor with white LEDs (photolysis reaction) and in the absence
255 of photocatalyst. Also in this case, no degradation of the target dye was detected.

256 The results of photocatalytic activity testing with NdT and NdT/OP for MB, CV,
257 RhB, EBT, TRZ and RED are reported in Figs. 8-10.

258 For all the dyes a very strong increase of photocatalytic activity was found with
259 NdT/OP with respect to NdT.

260 In particular, Fig. 8 gives a clear evidence of the dramatic enhancement of the
261 photocatalytic decolourization rate of MB due to the presence of OP; NdT/OP allows
262 to obtain 80 % MB degradation after only 30 min of irradiation time, while with the
263 NdT only 30 % degradation was achieved after the same irradiation time.

264 Moreover, while the photocatalyst NdT did not allow to reach an effective
265 degradation of CV dye, the NdT/OP catalyst improved the efficiency of the process
266 reaching 30% degradation after 180 min of irradiation, much higher than that
267 obtained with NdT (about 11%) after the same irradiation time.

268 The same trend was found for RhB, EBT, TRZ and RED dyes (Fig. 9 and Fig. 10).

269 The dramatic enhancement of photocatalytic activity obtained in this work is related
270 to the specific formulation of the NdT/OP photocatalyst. It is possible to retain that
271 NdT supported on the OP surface is excited both by the blue component of the
272 emission spectrum of the white LEDs, and by the blue emission of the phosphors
273 (OP), excited in turn by the green component emitted by the white LEDs. This
274 phenomenon contributes to strongly enhance the NdT/OP photoactivity when it is
275 irradiated with white LEDs.

276

277 **4. Conclusions**

278 In this work we have found that the photocatalytic activity of visible active N-doped
279 TiO₂ (NdT) can be strongly enhanced when it is promoted by the presence of organic
280 up-conversion phosphors (OP) in the catalyst formulation. A wide range of organic

281 dyes was photocatalytically degraded in the presence of visible light irradiation
282 emitted by green or white LEDs. It is possible to retain that the photocatalytic
283 activity of N-doped TiO₂ supported on up-conversion phosphors (NdT/OP) under
284 green light is due to the presence of the phosphors, that has up-conversion property
285 and emits at 434 nm, wavelength able to photoexcite the NdT deposited on the OP
286 surface. The NdT/OP catalyst shows high photocatalytic activity when white LEDs
287 are used as light source. In this case, the NdT supported on the OP surface is excited
288 both by the blue component of the emission spectrum of the white LEDs, and by the
289 blue emission of the phosphors (OP), excited by the green component emitted by
290 white LEDs. This phenomenon contributes to strongly enhance the photocatalytic
291 activity of NdT/OP photocatalyst in the decolourization process of all the tested dyes.
292 The obtained results make the visible active NdT photocatalyst modified with
293 organic up-conversion phosphors, a very suitable system to achieve high
294 photocatalytic activity with solar light.

295

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362
363

Table 1 List of the catalysts and their characteristics

Sample	TiO ₂ nominal loading wt/%	TiO ₂ measured loading (XRF) wt/%	Specific surface area m ² /g	TiO ₂ average crystallites size nm	Equivalent Band gap energy eV
NdT	100	100	30	17	2.5
OP	-	-	1	-	-
NdT/OP	30	28	8	17	-

Figure 1

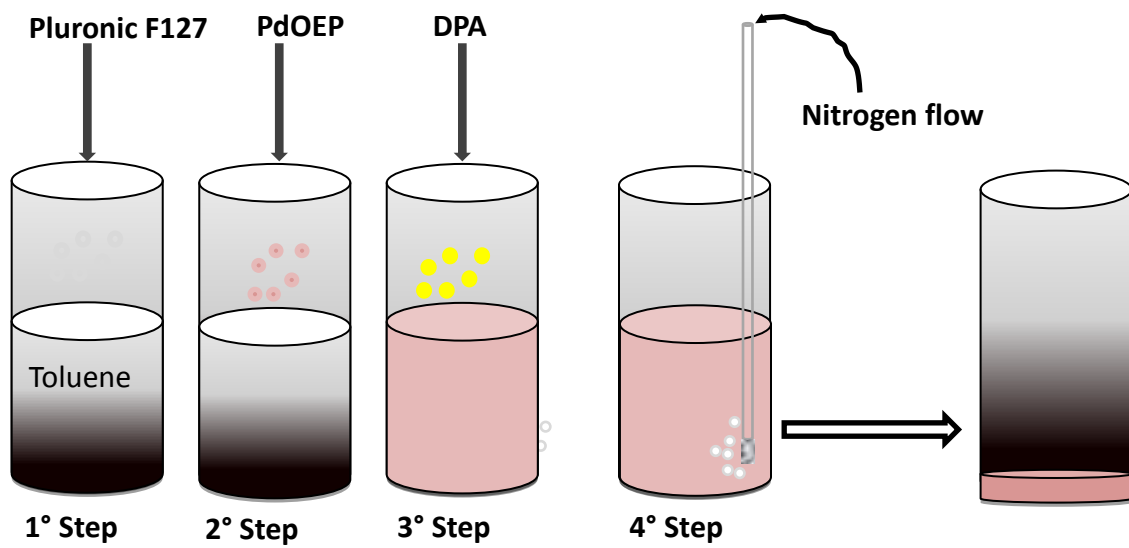


Figure 1

Figure 2

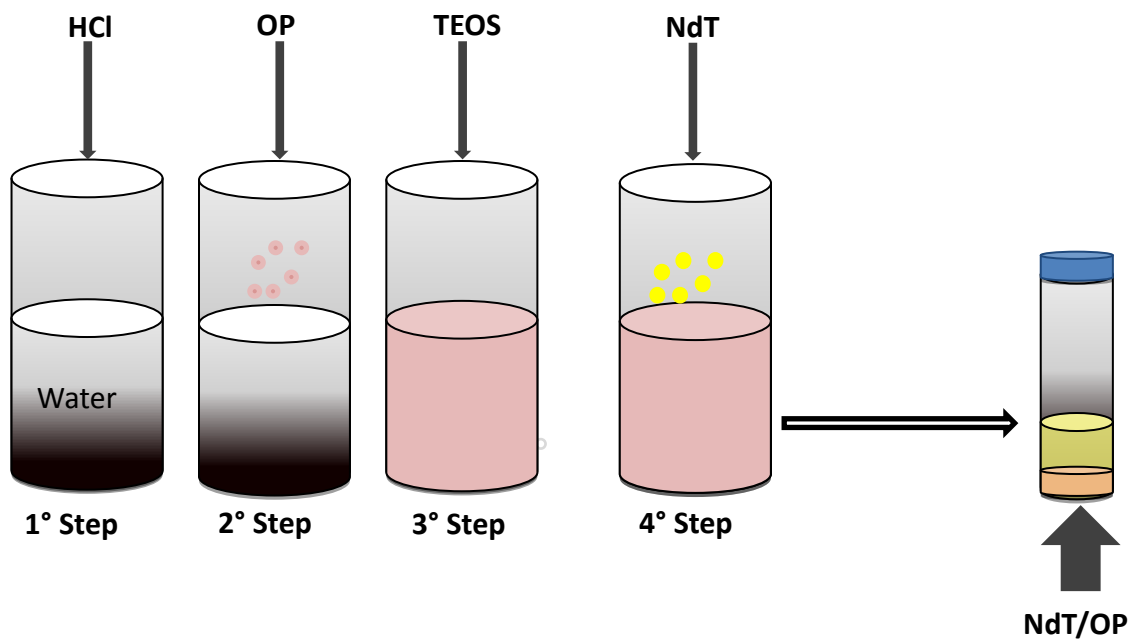


Figure 1

Figure 3

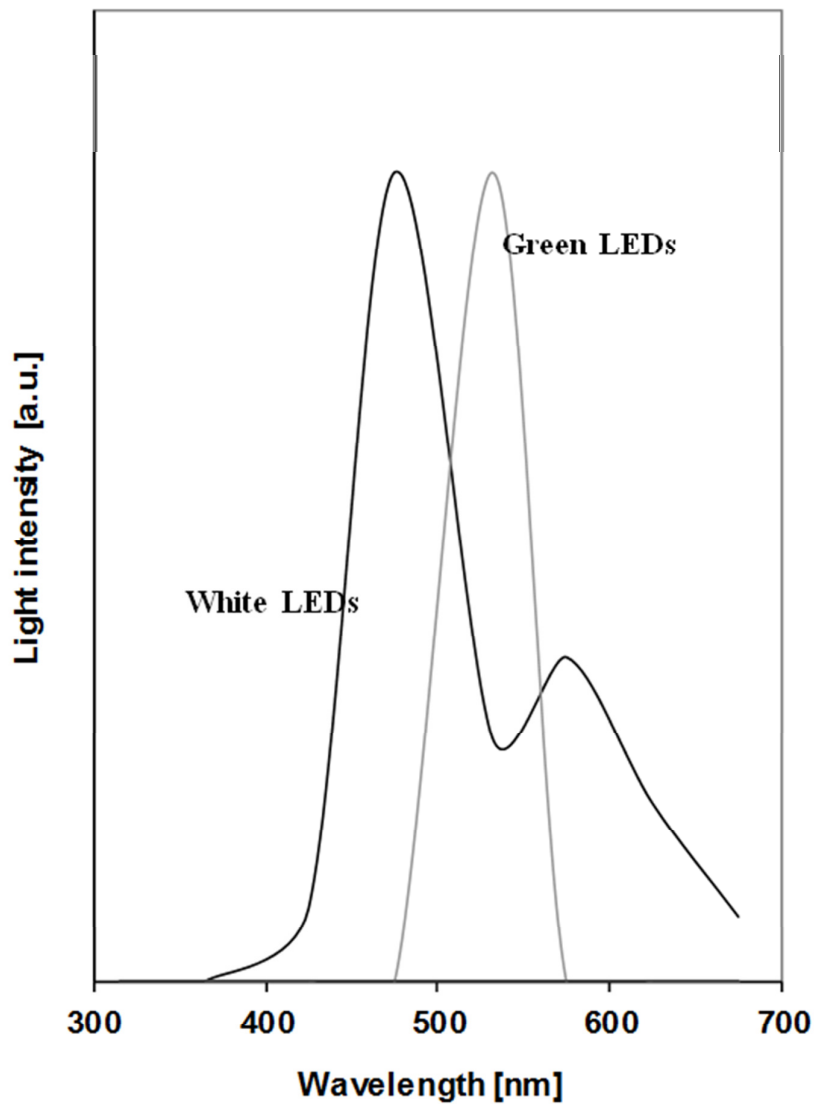


Fig. 3 Emission spectrum of the Green and White LEDs sources.

Figure 4

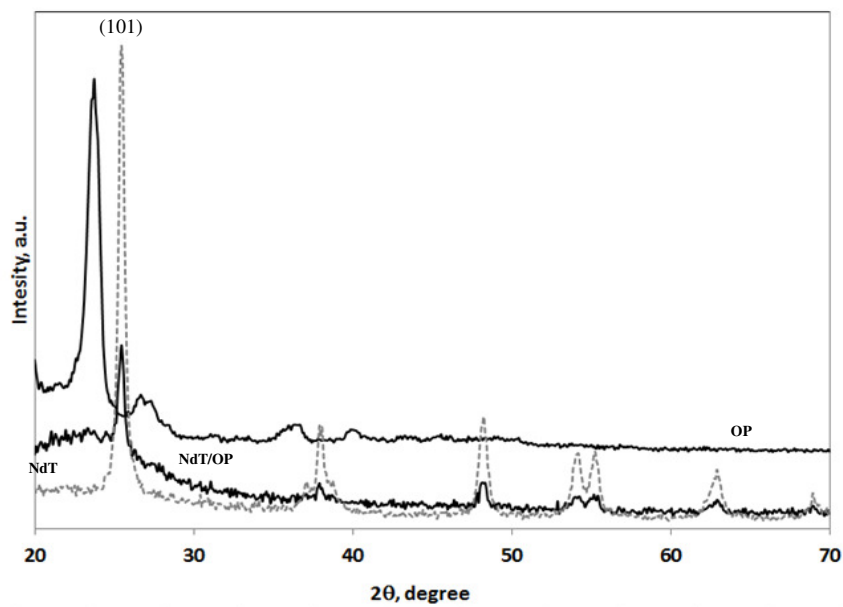


Fig. 4 XRD analysis of NdT, OP and NdT/OP

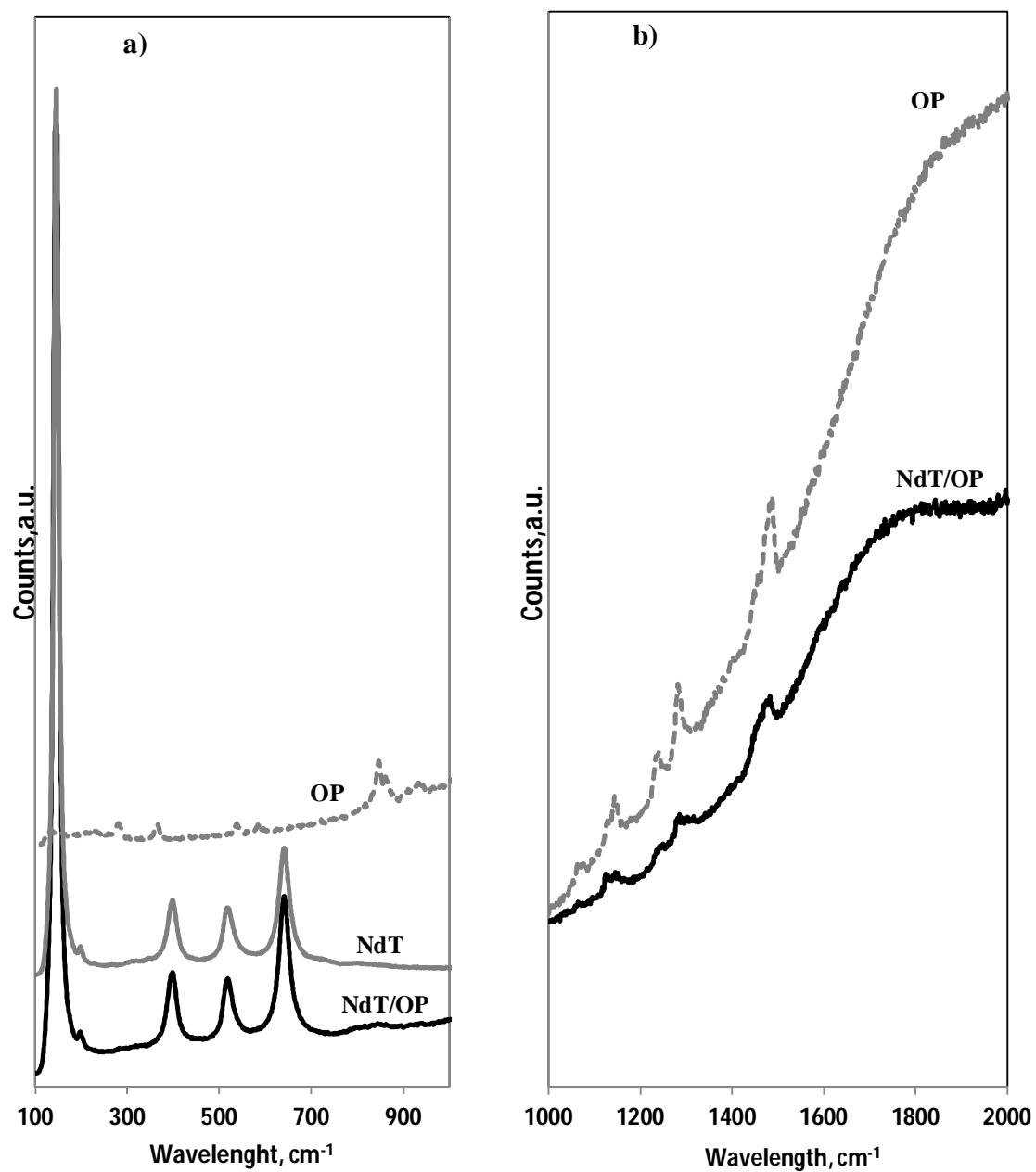


Fig. 5 Raman spectra of the samples OP, NdT and NdT/OP in the range: a) 100-1000cm⁻¹ and b) 1000-2000 cm⁻¹

Figure 6

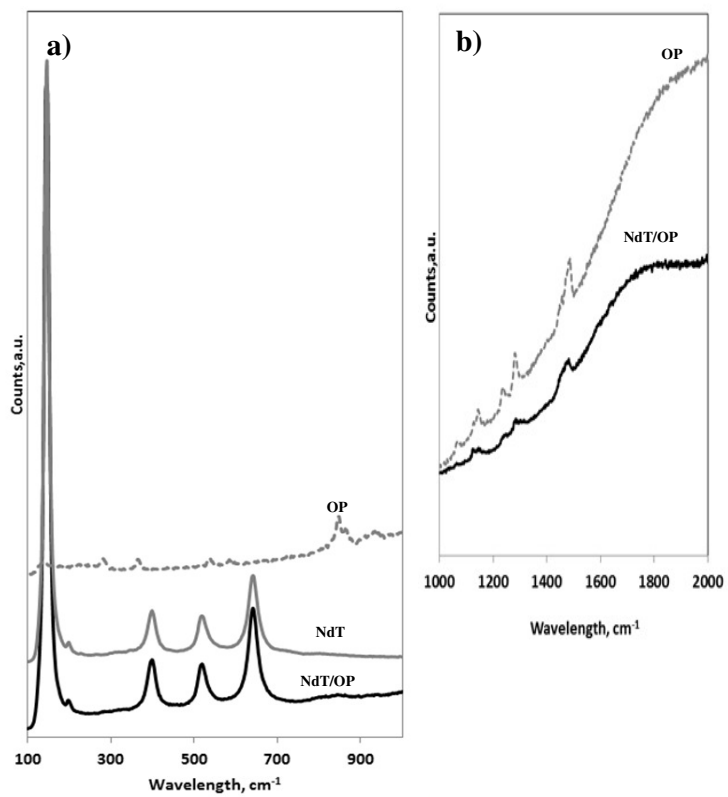


Fig. 6 Raman spectra of the samples OP, NdT and NdT/OP in the range: a) 100-1000 cm^{-1} and b) 1000-2000 cm^{-1}

Figure 7

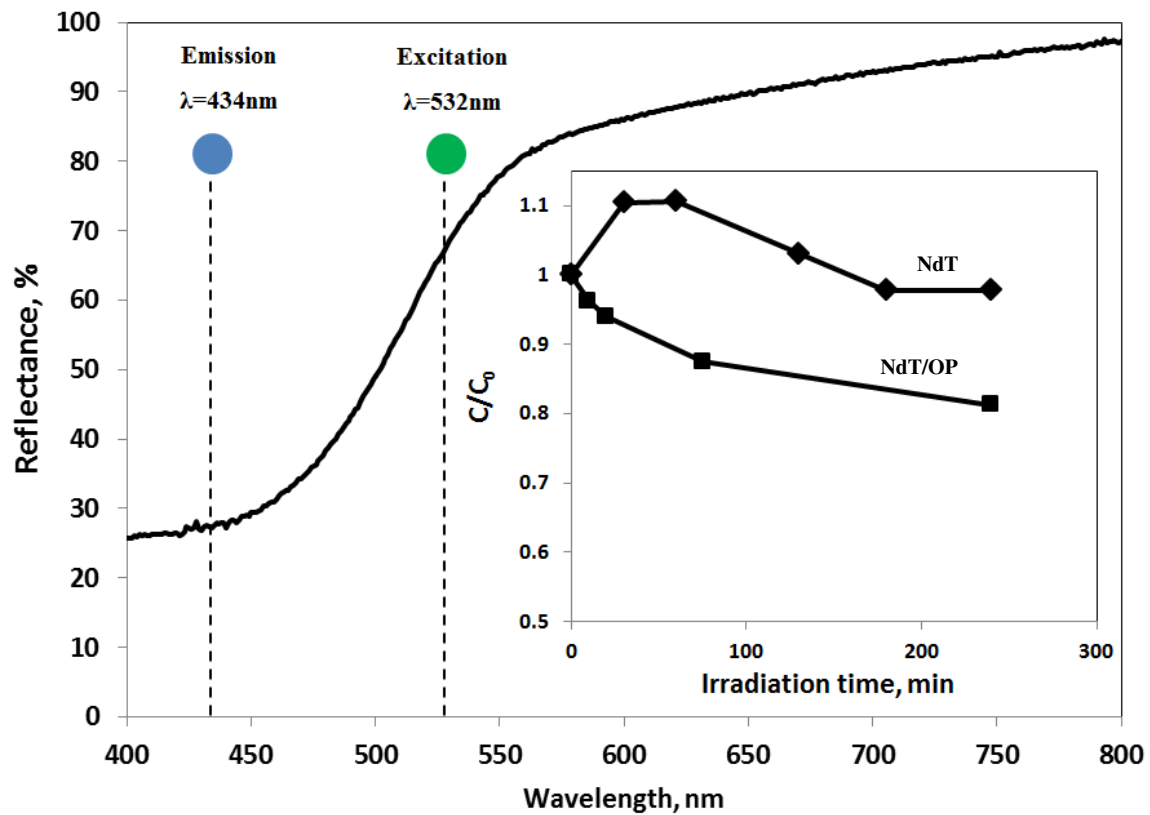


Fig. 7 Absorbance spectrum of NdT sample and behavior of MB concentration as a function of irradiation time on NdT and NdT/OP composite; light source: green LEDs.

Figure 8

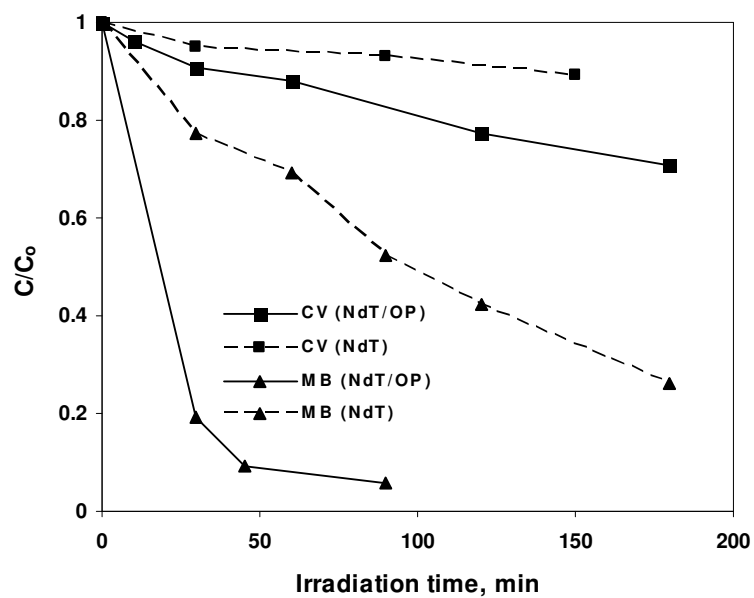


Fig. 8 Photocatalytic decolorization of MB and CV on NdT and NdT/OP.; light source: white LEDs. This phenomenon increases the activity of the catalyst when it is irradiated with the white LED.

Figure 9

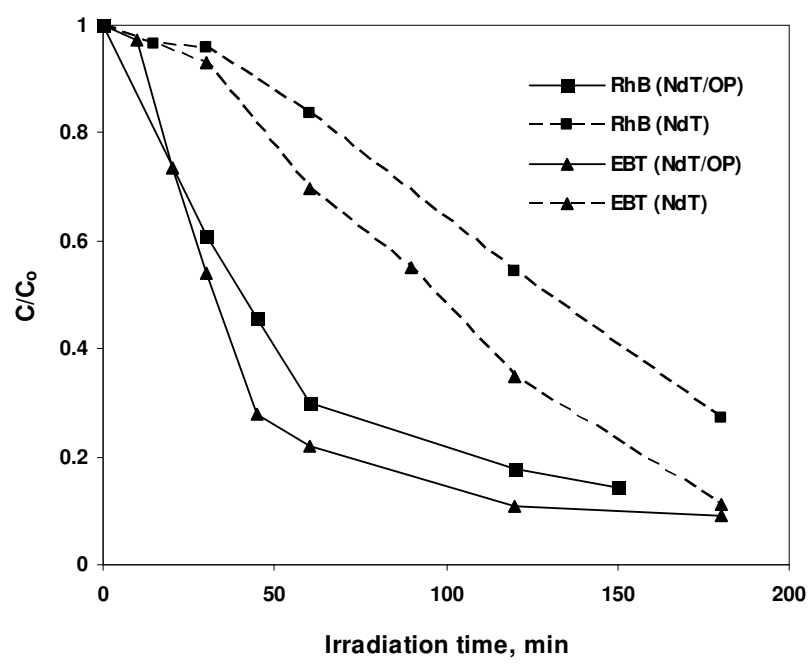


Fig. 9 Photocatalytic decolourization of RhB and EBT on NdT and NdT/OP.; light source: white LEDs.

Figure 10

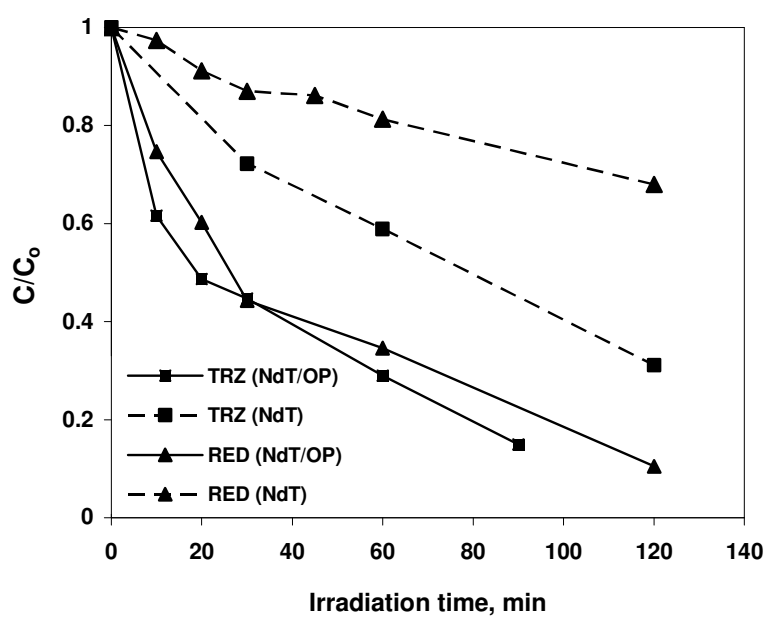
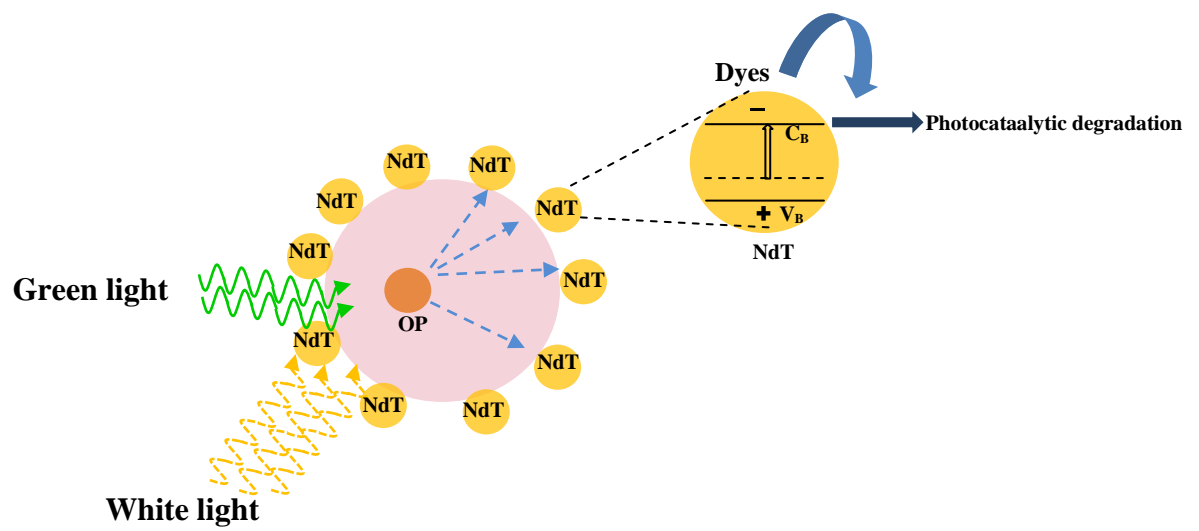


Fig. 10 Photocatalytic decolourization of TRZ and RED on NdT and NdT/OP.; light source: white LEDs.



- N-doped TiO₂ photocatalyst modified by organic up conversion phosphors (NdT/OP)
- Visible light irradiation emitted by green or white LEDs
- Dramatic enhancement of the photocatalytic activity on NdT/OP under visible light
- Under green light, OP emits at 434 nm, enhancing NdT photoactivity
- Photocatalytic degradation of a wide range of organic dyes