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Comparative assessment of visible light and UV active photocatalysts by hydroxyl radical quantification

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1 **Comparative assessment of visible light and UV active photocatalysts by hydroxyl**
2 **radical quantification**

3 Sanjay Nagarajan^{1*}, Nathan C. Skillen¹, Federica Fina², Guan Zhang², Chamnan
4 Randorn², Linda A. Lawton³, John T.S. Irvine² and Peter K.J. Robertson^{1*}

5 ¹ Centre for the Theory and Application of Catalysis (CenTACat), School of Chemistry
6 and Chemical Engineering, Queen's University Belfast, David Keir Building, Stranmillis
7 Road, Belfast, BT9 5AG, United Kingdom;

8 ² JTSI Group, University of St. Andrews, School of Chemistry, Purdie Building, North
9 Haugh, St Andrews, KY16 9ST, United Kingdom;

10 ³ School of Pharmacy and Life sciences, Sir Ian Wood Building
11 Robert Gordon University, Garthdee Road, Aberdeen, AB10 7GJ, United Kingdom

12 *Corresponding authors, *p.robertson@qub.ac.uk*; *snagarajan01@qub.ac.uk*, Tel: +44
13 (0) 28 9097 4627

14

15 **ABSTRACT**

16 A simple method for determining hydroxyl radical yields on semiconductor
17 photocatalysts is highly desirable, especially when comparing different photocatalyst
18 materials. This paper reports the screening of a selection of visible light active
19 photocatalysts such as Pt-C₃N₄, 5% LaCr doped SrTiO₃, Sr_{0.95}Cr_{0.05}TiO₃ and Yellow
20 TiO₂ and compares them against WO₃ and ultra violet (UV) light activated TiO₂ P25
21 (standard commercial catalysts) based on their oxidative strengths (OH radical
22 producing capability) using a well-studied chemical probe – coumarin. 7-
23 hydroxycoumarin, the only fluorescent hydroxylation product of this reaction can then
24 be measured to indirectly quantify the OH radicals produced. P25 under UV light
25 produced the highest concentration of OH radicals (16.9 μM), followed by WO₃ (0.56
26 μM) and Pt-C₃N₄ (0.25 μM). The maximum OH radical production rate for P25, WO₃

27 and Pt-C₃N₄ were also determined and found to be 35.6 μM/hr, 0.28 μM/hr and 0.88
28 μM/hr respectively. The other visible light activated photocatalysts did not produce any
29 OH radicals primarily as a result of their electronic structure. Furthermore, it was
30 concluded that, if any visible light absorbing photocatalysts are to be fabricated in
31 future for the purpose of photocatalytic oxidation, their OH radical producing rates (and
32 quantities) should be determined and compared to P25.

33 **Keywords:** Photocatalyst, visible light photocatalysts, OH radical, coumarin, P25.

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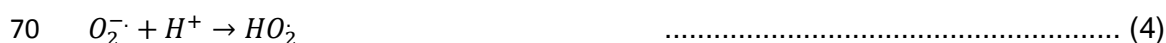
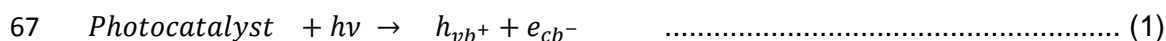
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50 1. INTRODUCTION

51 Photocatalysis has gained significant interest since the early publication by
52 Fujishima and Honda in 1972, demonstrating the potential of splitting water over TiO₂
53 [1]. Since this publication, photocatalysis has been applied to a broad range of fields
54 including waste water treatment, microbe destruction, toxin removal, energy production
55 and air treatment. [2-8]. The mechanism of photocatalysis has been well documented
56 and can be generally represented by the equations shown in reactions 1-9 [9,10]. The
57 formation of surface radical species such as superoxide (O₂⁻) and hydroxyl radicals
58 (OH·) play a key role in a number of photocatalytic pathways and as such their
59 identification and quantification is a key consideration. As shown in reaction 2, OH
60 radicals are primarily generated from the reaction between valence band holes (h_{vb+})
61 and hydroxyl ions on the catalyst surface. An indirect pathway, via O₂⁻, also results in
62 OH radical formation, as shown in reactions 3-6. The efficiency of OH radicals in
63 photocatalytic reactions is predominantly based on their strong oxidising potential of
64 2.8 V (vs NHE) [11]. The non-selective nature of these reactive oxygen species also
65 aids rapid degradation of various pollutants and organic contaminants [3,7,11-16].

66





76 where, h_{vb}^+ represents VB holes and e_{cb}^- means CB electrons.

77

78 Newly developed photocatalytic technologies and materials have often utilised
79 model compounds and screening methods to assess their performance [17-20].
80 Common evaluation methods reported in the literature include the decomposition of
81 dyes such as methylene blue (ISO test 10678:2010), or degradation of organic
82 pollutants such as 4-chlorophenol or toluene [17-20]. These procedures are often
83 coupled with the corresponding calculated photonic efficiencies and quantum yields to
84 evaluate overall efficiency. While these methods can be effective in identifying the
85 specific photocatalytic performance of a material in relation to a fingerprint compound,
86 they provide little information regarding the production of OH radicals involved within
87 the mechanism. Therefore, the requirement for a simple and robust method of radical
88 quantification for screening the oxidative potential of catalysts has significantly
89 increased. The challenge in OH radical quantification lies in both the non-selective
90 nature and short lifetime (~ 1 nanosecond) of the radical, which restricts the possibility
91 of direct quantification [21]. Consequently, a range of methods have been developed
92 such as emission spectroscopy, laser induced fluorescence, electron spin resonance,
93 spin trap and chemical probes or quencher based methods to quantify OH radicals [21-
94 37].

95

96 The use of a chemical probe to capture OH radicals presents a potentially efficient
97 way to measure the radical due to the low cost, rapid analysis time and reproducibility
98 of the method. Monitoring a probe compound through spectroscopy allows the
99 concentration of OH radicals to be calculated based on stoichiometric ratios of products
100 formed. A recently reported *in vivo* technique utilised a nanoprobe comprising of a
101 nanoparticle and azo dye in order to quantify OH radicals in the femtomolar range [37].

102 Here the nanoparticle was used as an energy donor and the modified orange was used
103 as an OH radical capturing ligand molecule (and the energy acceptor).

104

105 Dimethyl sulfoxide (DMSO) based methods for OH radical capture have also been
106 utilised in the past to quantify these species via the formation of formaldehyde
107 [28,29,31]. The formation of CH₄ in a closed system coupled with O₂ bubbling however
108 reduces the suitability of utilising DMSO as a probe molecule.

109

110 In the past, OH radical quantification has been carried out for various commercially
111 available photocatalysts, photo-Fenton's reaction and other modified TiO₂ based visible
112 light photocatalysts with either coumarin or terephthalic acid as probe molecules
113 [21,23,31-36,38,39]. Both compounds are capable of acting as OH radical traps by
114 forming fluorescent products as result of reacting with the radical species. Terephthalic
115 acid has been investigated in a study by Ishibashi *et al.* which achieved an OH radical
116 concentration of 7×10^{-5} M based on the measurement of 2-hydroxyterephthalic acid
117 [35]. In addition to the use of terephthalic acid as a probe molecule, coumarin has been
118 used in a number of studies to determine the concentration of OH radicals produced
119 from TiO₂ at relatively high loadings of 1 to 5 g/L [21,23,40]. For instance, Czili *et al.*
120 used 100 μM coumarin as the probe molecule to capture OH radicals under a 40 W UV
121 lamp. They determined a maximum OH radical production rate of 23.39 μM/g/hr
122 (calculated from their reported 7-hydroxycoumarin rates) with 1 g/L TiO₂ P25
123 photocatalyst.

124

125 This paper utilises coumarin as a hydroxyl radical trap and reports the screening of
126 a selection of visible light responsive photocatalysts under low power illumination
127 based on their OH radical producing capability. In contrast to previous reports, which
128 concentrated on quantifying the OH radicals produced from TiO₂, other commercially

129 available and a few synthesised photocatalysts [21,23,31,40], this work focusses on
130 assessing the oxidative strength of visible light photocatalysts Pt-C₃N₄, 5% LaCr
131 doped SrTiO₃, Sr_{0.95}Cr_{0.05}TiO₃ (referred to as Cr-SrTiO₃ from here on) and yellow TiO₂
132 and compares them against commercial TiO₂ P25 and WO₃ for evaluation. In addition,
133 a low catalyst loading was used to highlight efficient OH radical formation can be
134 achieved without requiring large quantities of powdered catalyst.

135

136 **2. EXPERIMENTAL PROCEDURE**

137 **2.1 Materials**

138 Coumarin and 7-hydroxycoumarin were purchased from Tokyo Chemical Industry
139 UK Ltd, while TiO₂ P25 was purchased from Degussa (now Evonik industries) and WO₃
140 nano powders were purchased from Sigma Aldrich. All commercial chemicals were
141 used as received. The catalysts Pt-C₃N₄ [41], 5% LaCr doped SrTiO₃, Cr-SrTiO₃ and
142 yellow TiO₂ [42] were synthesised at the school of chemistry, University of St. Andrews,
143 using methods cited in the literature [41-43].

144

145 **2.2 Characterisation of Photocatalysts**

146 WO₃, LaCr-SrTiO₃ and Cr-SrTiO₃ were characterised by X-Ray diffraction (XRD)
147 and UV-Visible absorption. XRD analysis of powders was examined on a SToe
148 STADI/P powder diffractometer. Incident radiation was generated using a Cu k_α source
149 (λ=1.54056 Å). Diffuse reflectance spectra were collected on a JASCO-V550 UV-
150 visible spectrophotometer. The characterisation of Pt-C₃N₄ and yellow TiO₂ has been
151 reported elsewhere in literature [41,42].

152

153 **2.3 Photocatalytic experiments**

154 All photocatalytic experiments were performed in closed screw cap bottles. The
155 reaction solution was composed of 100 ml of 100 μM coumarin along with 10 mg of

156 photocatalyst (0.1 g/L). A magnetic stirrer bar was placed inside the bottle and the
157 bottle was then placed on a magnetic stirrer at a distance of 11 cm from a 36 W
158 compact fluorescent non-integrated visible lamp (Philips, colour code 830) or a 36 W
159 UV lamp (Philips, Cleo lamps). The spectral outputs of the lamps were measured by a
160 StellaNet spectrometer and the spectra are shown in the supplementary material
161 (Figure S1). Prior to illumination, the reaction solution was stirred in the dark to allow a
162 state of equilibrium to be reached. The length of time required in the dark was
163 calculated from the control experiments conducted in the absence of light. During
164 irradiation, samples (3 mL) were taken at dedicated time intervals for a maximum of
165 120 mins. Samples were filtered through a 0.22 μm Millex syringe filter prior to
166 analysis. Coumarin absorbance was monitored using a Cary 300 Scan, UV-Visible
167 Spectrophotometer at 277 nm, with a scan rate of 400 nm/min. 7-hydroxycoumarin
168 fluorescence was measured in a PerkinElmer LS 50B luminescence
169 spectrophotometer, using an excitation wavelength of 332 nm and emission
170 wavelength at 456 nm [21]. The excitation and emission slit width was 4 mm and the
171 scan rate was 200 nm/min. A sample UV/Visible and fluorimeter spectra, with peaks at
172 277 nm and 456 nm respectively, are shown in the supplementary material Figure S2
173 and Figure S3. All experiments were performed in triplicate.

174

175 **2.4 OH radical quantification**

176 OH radicals were quantified based on a modified method described by Zhang *et al.*
177 [38] and according to equation 1. The concentration of OH radicals was calculated by
178 assuming that 6.1 % of total OH radicals were captured as 7-hydroxycoumarin. The
179 stoichiometric ratio of one mole of OH radical consumed for the production of one mole
180 of 7-hydroxycoumarin was used [23]. The total number of OH radicals produced over
181 time during this photocatalytic process was calculated using the following equation.

182

183 $X = \left\{ \frac{A}{6.1\%} - B \right\}$ Equation 1

184

185 Where, X is the total OH radical concentration (μM) produced during photocatalysis, A
186 is the mean 7-hydroxycoumarin concentration (μM) and B is the amount of OH radicals
187 (μM) produced during the light control experiments. The concentration of coumarin and
188 7-hydroxycoumarin was calculated using a standard curve of known concentrations as
189 shown in the supplementary material (Figure S4, Figure S5 and Figure S6).

190

191 **3. RESULTS AND DISCUSSION**

192 **3.1 Characterisation of Photocatalysts**

193 XRD patterns of WO_3 , Cr-SrTiO_3 and LaCr-SrTiO_3 samples were determined as
194 shown (Figure 1). The commercial WO_3 nanoparticles exhibited a typical crystallized
195 monoclinic phase structure, and the Cr-doped and La,Cr-co-doped SrTiO_3 samples
196 possessed homogeneous crystallized cubic perovskite structures, with no impurity
197 phase found for either of the doped samples and these results were consistent with
198 literature [44,45]. In the co-doped samples, since La and Cr substitute the Sr and Ti,
199 respectively, and the radius of La is similar with that of Sr while the radius of Cr was
200 similar to that of Ti, the peak positions of the Cr-SrTiO_3 and LaCr-SrTiO_3 samples are
201 not shifted compared to those of pure SrTiO_3 .

202

203 **Figure 1.**

204

205 In the UV-visible absorption spectra of WO_3 , Cr-SrTiO_3 and LaCr-SrTiO_3 (Figure
206 2), WO_3 exhibited visible light absorption up to 470 nm, which corresponds to the band-
207 gap energy of ca. 2.64 eV. SrTiO_3 , however, has no absorption in the visible light
208 region (bandgap of 3.75 eV) and metal-doping has been shown to be a feasible
209 method for extending the light absorption of SrTiO_3 into the visible region [46]. Doping

210 of Cr into the A-site of SrTiO₃ induces an absorption band in the visible region centred
211 at around 450 nm (Figure 2). The visible light absorption is ascribed to the electron
212 excitation from the Cr doping levels formed above the valence band of SrTiO₃ to the
213 conduction band of SrTiO₃ [43]. It was reported that La, Cr- co-doped SrTiO₃ showed
214 enhanced photocatalytic performance compared to the single Cr-doped SrTiO₃ due to
215 the inhibition of the formation of Cr⁶⁺ species in the B site [43]. Therefore, a co-doped
216 sample, LaCr-SrTiO₃ was prepared by the same method. The visible light absorption of
217 LaCr-SrTiO₃ was significantly enhanced compared to the Cr-SrTiO₃, with two strong
218 absorption peaks centred at around 450 nm and 650 nm in the visible light region. In
219 the case of co-doping, more intermittent doping levels are formed within the band-gap
220 of SrTiO₃ compared to the single Cr doped SrTiO₃, which results in the visible light
221 absorption.

222

223 **Figure 2.**

224

225 **3.2 Photocatalytic OH radical production**

226 **3.2.1 UV light photocatalysis on P25**

227 P25 has been one of the most extensively investigated and most active
228 commercially available photocatalysts under UV irradiation and therefore was used as
229 a benchmark for comparison in this study. Although, recent studies have reported that
230 nano-spherical InCrO₄-loaded TiO₂ and TiO₂ nanospheres deposited on graphene
231 performed better than P25 for OH radical production and dye degradation upon UV
232 irradiation [47,48], to date P25 is still regarded as the benchmark. The photocatalytic
233 hydroxylation of coumarin over P25 under UV light and subsequent formation of 7-
234 hydroxycoumarin is shown in Figure 3. The production of 7-hydroxycoumarin under
235 these conditions equates to a peak OH radical concentration of 16.9 μM after 45 mins.
236

237 **Figure 3.**

238 As shown in the figure, near complete degradation (97 %) of coumarin was
239 achieved after 120 mins irradiation. This level of degradation was likely to result from
240 the increased adsorption of coumarin onto the catalyst, which facilitated the reaction
241 with surface bound OH radicals. The role of surface bound radicals and those that are
242 present in bulk has been highlighted in a previous publication by Li *et al.* [49], who
243 investigated acid orange oxidation over TiO₂ P25 and AgBr. This group investigated
244 the quenching of OH radicals at the catalyst surface and in bulk in order to demonstrate
245 that surface bound species were the predominant radicals in the oxidation pathway.
246 This observation confirmed that increased adsorption of the substrate on the catalyst
247 surface can significantly increase the degradation efficiency.

248

249 Figure 3 also shows the profile of 7-hydroxycoumarin production and
250 decomposition which indirectly indicates the quantity of OH radicals generated. 7-
251 hydroxycoumarin concentration peaked at 45 minutes, with a maximum concentration
252 of 1.045 μM , which was equivalent to 16.9 μM OH radicals (as calculated from
253 equation 1). It was observed that an average production rate of 1.8 $\mu\text{M/hr}$ was
254 achieved during the first 45 mins, followed by an average degradation rate of 0.46
255 $\mu\text{M/hr}$ during the latter stages of irradiation. The decrease in concentration of 7-
256 hydroxycoumarin could also be attributed to the presence of superoxide radicals as
257 reported by Czili and Horvath [23].

258

259 Several reports have suggested the kinetics for 7-hydroxycoumarin generation
260 from coumarin with P25 under UV irradiation are zero order [21,23,38,50-52], however,
261 a number of these investigations also used a high concentration of both catalyst and
262 coumarin. Furthermore, it has been suggested that at higher concentrations of
263 coumarin (>100 μM), more UV light is absorbed by this probe and not the catalyst,

264 which results in a low 7-hydroxycoumarin and OH radical production rate [23]. In the
265 present study, K_{app} which is the rate constant for the formation of 7-hydroxycoumarin
266 was calculated to be 0.0234 $\mu\text{M}/\text{min}$ whereas K_{dis} , the rate constant for the
267 disappearance of 7-hydroxycoumarin was calculated to be 0.0135 $\mu\text{M}/\text{min}$. In this study
268 we have established that both, production and degradation of 7-hydroxycoumarin
269 followed zero order kinetics, which is agreement with previous studies.

270

271 **3.2.2 Visible light photocatalysis**

272 A number of visible light catalysts were also selected for comparison against P25
273 TiO_2 . While the synthesised catalysts all possessed energy band gaps that supported
274 visible light activation, only WO_3 and $\text{Pt-C}_3\text{N}_4$ had energy band potentials (valence
275 band at 3.2 V and 1.4 V respectively and conduction band at 0.2 V and -1.3 V
276 respectively) that would facilitate OH radical formation either directly or indirectly as
277 mentioned in reactions 2–6. Catalysts LaCr-SrTiO_3 , Cr-SrTiO_3 and yellow TiO_2 (valence
278 bands at 2.7 V, 2.7 V and 2.6 V respectively and conduction bands at -0.1 V for all the
279 three photocatalysts) were selected to monitor if 7-hydroxycoumarin was formed even
280 when the electronic structure of the catalyst was not suited to the redox potential of the
281 reaction.

282

283 The photocatalytic hydroxylation of coumarin to 7-hydroxycoumarin over WO_3 and
284 $\text{Pt-C}_3\text{N}_4$ under visible light is shown in Figure 4. As can be seen, minimal conversion of
285 coumarin was observed over both $\text{Pt-C}_3\text{N}_4$ and WO_3 , which was also supported by the
286 low formation of 7-hydroxycoumarin (Figure 5). $\text{Pt-C}_3\text{N}_4$ displayed a slow yet steady
287 conversion rate, reaching a 0.91 % drop in coumarin after 120 mins of irradiation
288 whereas, a varying coumarin concentration pattern was seen over time on WO_3 . It is
289 interesting to note that there was an initial decrease in coumarin concentration followed
290 by an increase which may be attributed to coumarin desorption from the surface of

291 WO₃. This desorption could be a result of the alteration in equilibrium in the closed
292 system due to the possible evolution of O₂ from water on WO₃ under visible light.

293

294 **Figure 4.**

295

296 While the decrease in coumarin concentration is low, production of OH radicals
297 over Pt-C₃N₄ and WO₃ was supported by the detection of 7-hydroxycoumarin upon
298 photocatalysis (Figure 5). When WO₃ was used as the photocatalyst, there was no 7-
299 hydroxycoumarin production until 30 minutes of irradiation which could be due to the
300 rapid recombination of the electrons and the photo generated holes. After 30 minutes,
301 OH radical production was steady with a gradual generation of 7-hydroxycoumarin
302 being observed. In the case of Pt-C₃N₄ however, 7-hydroxycoumarin production was
303 seen from 15 minutes. The initial increase in the 7-hydroxycoumarin concentration
304 correlates to a rapid degradation of coumarin during the first 60 mins of irradiation.

305

306 **Figure 5.**

307

308 In contrast to Pt-C₃N₄ and WO₃, the catalysts LaCr-SrTiO₃, Cr-SrTiO₃ and yellow
309 TiO₂ displayed no activity towards coumarin conversion to 7-hydroxycoumarin, which
310 indicates no OH radical formation. Furthermore, under prolonged visible light irradiation
311 no detectable 7-hydroxycoumarin was recorded.

312

313 **3.2.3 Influence of photocatalysts' electronic structure and particle size on OH** 314 **radical formation**

315 In order to evaluate and discuss the performance of the catalysts, it is essential to
316 consider the primary contributing factors; electronic structure and particle size. The
317 electronic structure of the catalysts dictates the initial photo-excitation of electrons to

318 higher energy levels, while the particle size dictates the concentration of photons
319 absorbed and surface reactions between coumarin and OH radicals. As shown in
320 reactions (2) – (6), OH radicals can occur via two routes in photocatalysis. The direct
321 formation at the valence band requires a redox potential of 2.8 V vs NHE, while the
322 indirect method occurs via the intermediate radical, $O_2^{\cdot-}$ and requires a redox potential
323 of -0.33 V vs NHE [53]. The electronic structure of the catalysts tested in this study, in
324 relation to the redox potentials required for radical formation, are shown in Figure 6.

325

326 **Figure 6**

327

328 As Figure 6 shows, catalysts TiO_2 P25, $Pt-C_3N_4$ and WO_3 possess an electronic
329 structure which corresponds to the redox potential of OH radical formation via either
330 direct or indirect mechanisms. The favourable electronic structure of TiO_2 for OH
331 radical formation has been well documented and is evident from the results highlighted
332 here. The performance of $Pt-C_3N_4$ and WO_3 for OH radical formation, however, has not
333 been as well reported. The structure of WO_3 with a more positive valence band
334 suggests it is capable of generating surface OH radicals, however, the results obtained
335 indicate minimal 7-hydroxycoumarin production within 2 hours. Based on the structure,
336 it was likely an increased rate of recombination preventing OH radical formation via the
337 valence band hole, due to insufficient energy to initiate a reduction reaction at the
338 conduction band [21]. To prevent recombination and to increase the OH radical
339 production, Kim *et al.* synthesised Pt-doped WO_3 and found that the OH radical
340 production from Pt- WO_3 was significantly higher than un-doped WO_3 [20]. Furthermore,
341 the large particle size of approximately 100 nm for WO_3 indicates a smaller surface
342 area, which leads to minimum absorption of light.

343

344 The electronic structure of Pt-C₃N₄ as seen from Figure 6 clearly indicates a
345 reducing catalyst, which is also supported by its application in water reduction
346 investigations [54]. Therefore, the hydroxylation of coumarin and subsequent formation
347 of 7-hydroxycoumarin, as indicated by the earlier results, is likely via the indirect O₂^{•-}
348 pathway. Based upon this observation, it is likely the low yield of OH radicals is a result
349 of competition for the conduction band electron between superoxide formation and H⁺
350 reduction to form H₂ (0 V vs NHE). In addition, since all these experiments were
351 performed in a closed system with limited O₂, a reducing catalyst such as Pt-C₃N₄ is
352 expected to produce less OH radicals than an open system. Furthermore, despite a
353 favourable particle size of 20-40 nm, Pt-C₃N₄ was observed to agglomerate to form
354 larger aggregates leading to a decrease in surface area and in turn light absorption.

355

356 In the case of LaCr-SrTiO₃, Cr-SrTiO₃ and yellow TiO₂, the electronic structures
357 showed both the valence band and conduction band of all these catalysts to be lower
358 than the redox potentials to facilitate radical formation as seen in Figure 6. These
359 catalysts were primarily used as a control parameter to ensure no 7-hydroxycoumarin
360 formation was observed.

361

362 The calculated OH radical concentrations and production rates produced over all
363 catalysts screened are summarised in Table 1. The results show that the activity of the
364 visible light activated photocatalysts studied were significantly lower than commercial
365 P25 under UV light. This further emphasises that although there are numerous visible
366 light absorbing photocatalysts, their ability to produce OH radicals is significantly lower
367 than P25. In future, if any visible light absorbing photocatalysts are to be fabricated for
368 the purpose of photocatalytic oxidation, their OH radical producing rates (and
369 quantities) should be determined and compared to P25 as demonstrated here.

370

371 **Table 1**

372

373 **4. CONCLUSION**

374 The aim of screening UV and visible light absorbing photocatalysts to assess their
375 oxidative strength was accomplished successfully by trapping OH radicals produced by
376 the photocatalysts in 7-hydroxycoumarin. The OH radical production capabilities of
377 various photocatalysts covering a range of band gaps and particle sizes were assessed
378 by comparing and discussing their differences with the commercial UV light activated
379 P25. To conclude, visible light activated photocatalysts such as LaCr-SrTiO₃, Cr-
380 SrTiO₃ and yellow TiO₂ did not produce any OH radicals and this could be attributed to
381 their electronic structure. Whereas, the (pseudo) maximum OH radical production rates
382 of other visible light activated photocatalysts namely, WO₃ (0.28 μM/hr) and Pt-C₃N₄
383 (0.886 μM/hr) were found to be significantly lower when compared to the commercial
384 UV light activated P25 photocatalyst (35.654 μM/hr). This method could be further
385 exploited as novel photocatalysts are developed and to compare a range of P25
386 concentrations for OH radical production. This study further emphasises the challenges
387 faced by the visible light photocatalysts for photocatalytic oxidation.

388

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397

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550 **List of Captions for figures and tables.**

551 Figure 1: XRD profiles of photocatalysts representing the plane indices [44,45].

552 Figure 2: UV-Visible absorption spectra of photocatalysts

553 Figure 3: Coumarin and 7-hydroxycoumarin profiles of 100 ml of 100 μ M coumarin with
554 0.1 g/L P25 under 36 W UV light

555 Figure 4: Coumarin profiles of 100 ml of 100 μ M coumarin with 0.1 g/L visible light
556 photocatalysts; Inset: coumarin profiles of WO_3 and Pt- C_3N_4

557 Figure 5: 7-hydroxycoumarin production profiles of 100 ml of 100 μ M coumarin with 0.1
558 g/L visible light photocatalysts

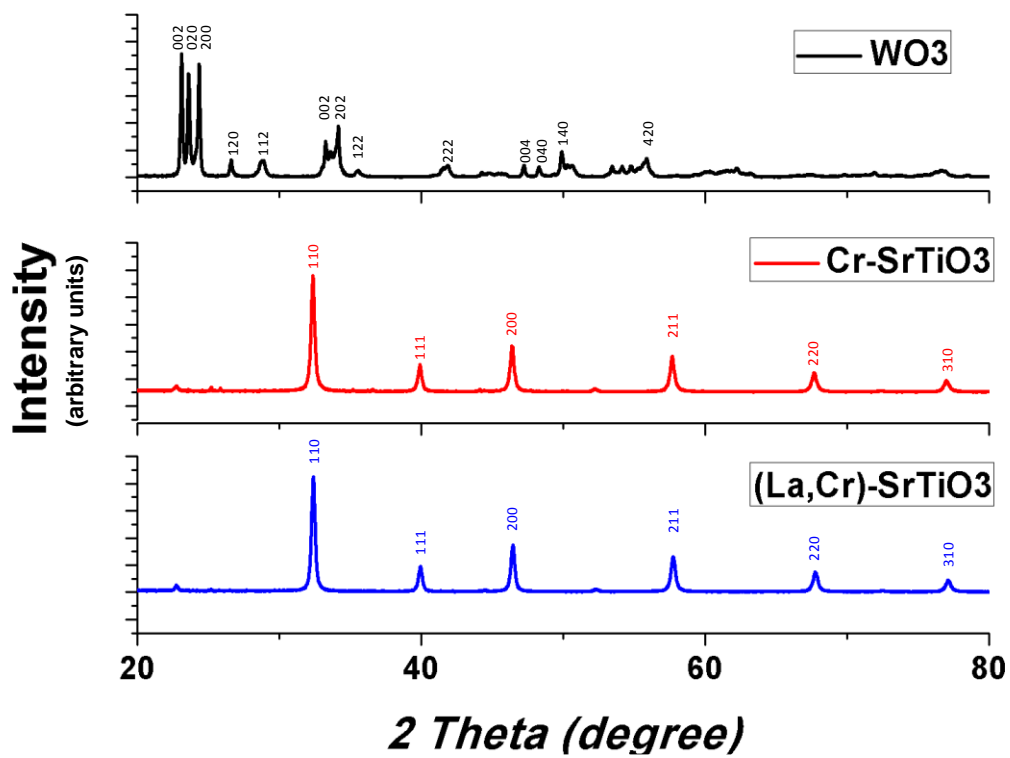
559 Figure 6: Electronic structure of the photocatalysts used

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561 Table 1: Pseudo maximum OH radical production rates and quantities.

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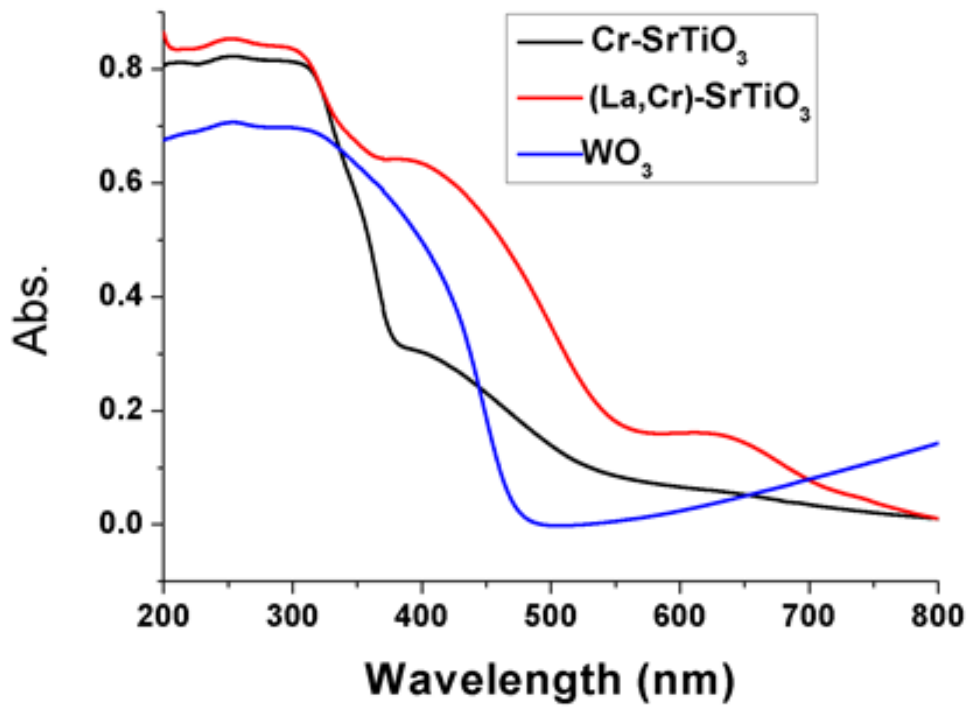
565 **Figure 1**

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571 **Figure 2**

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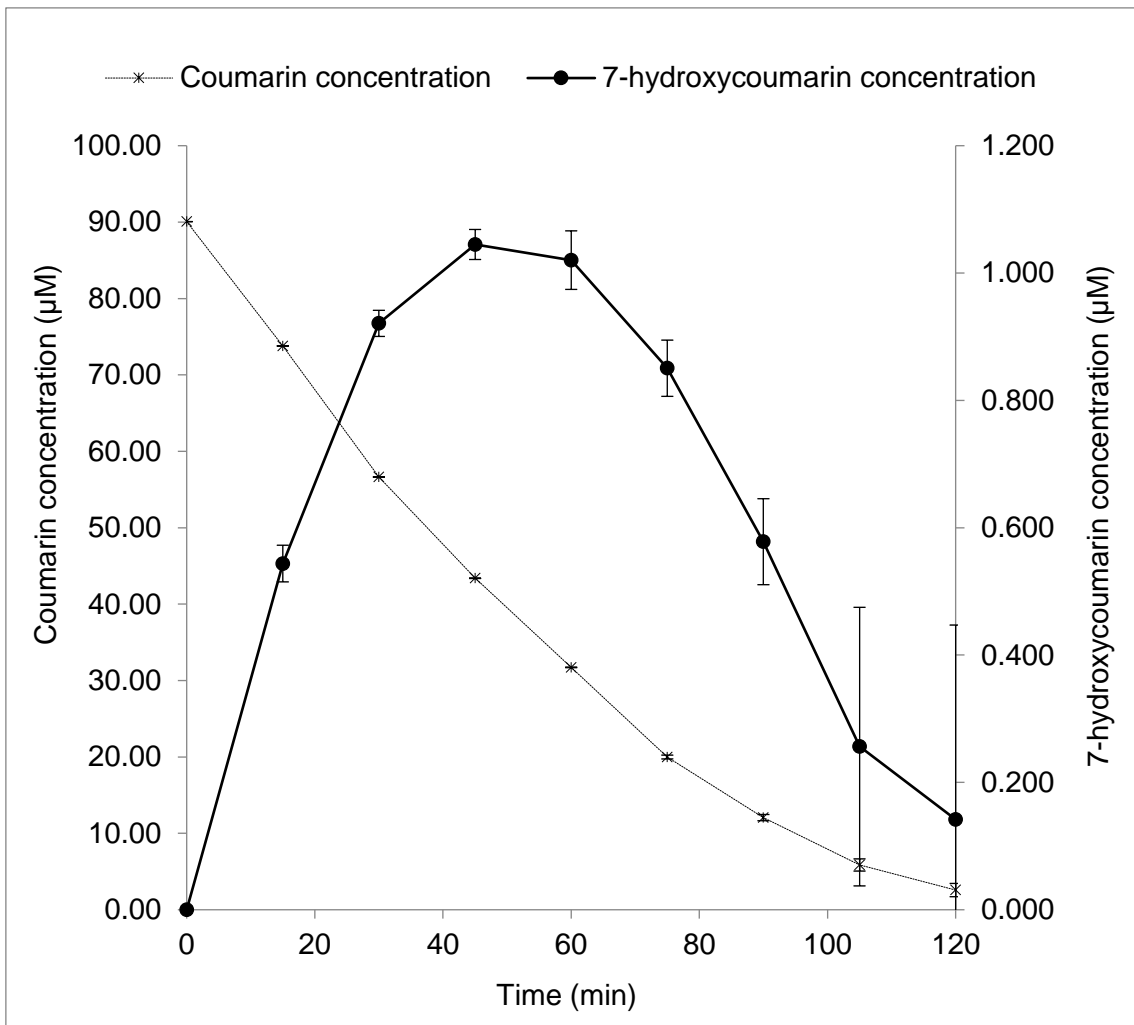
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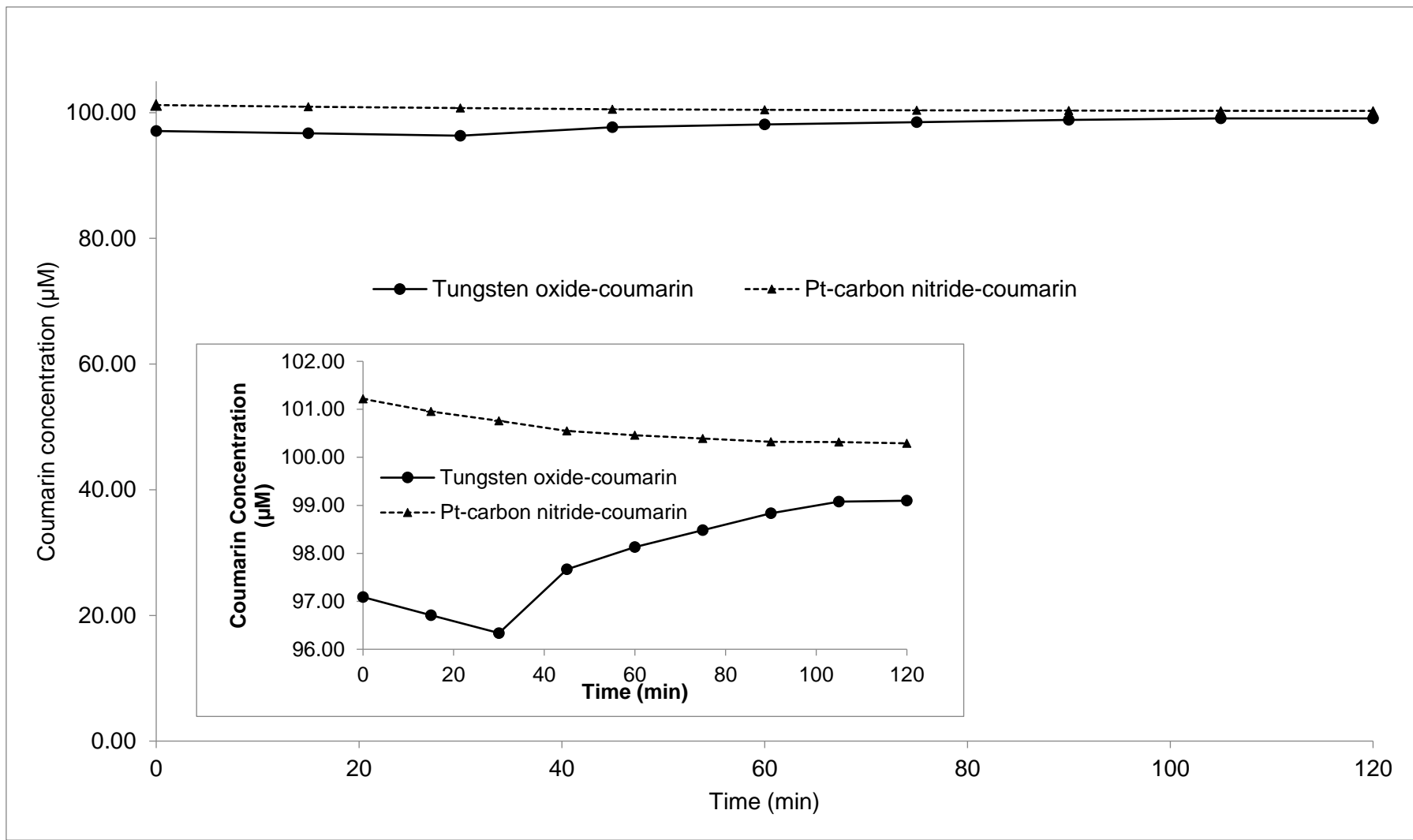
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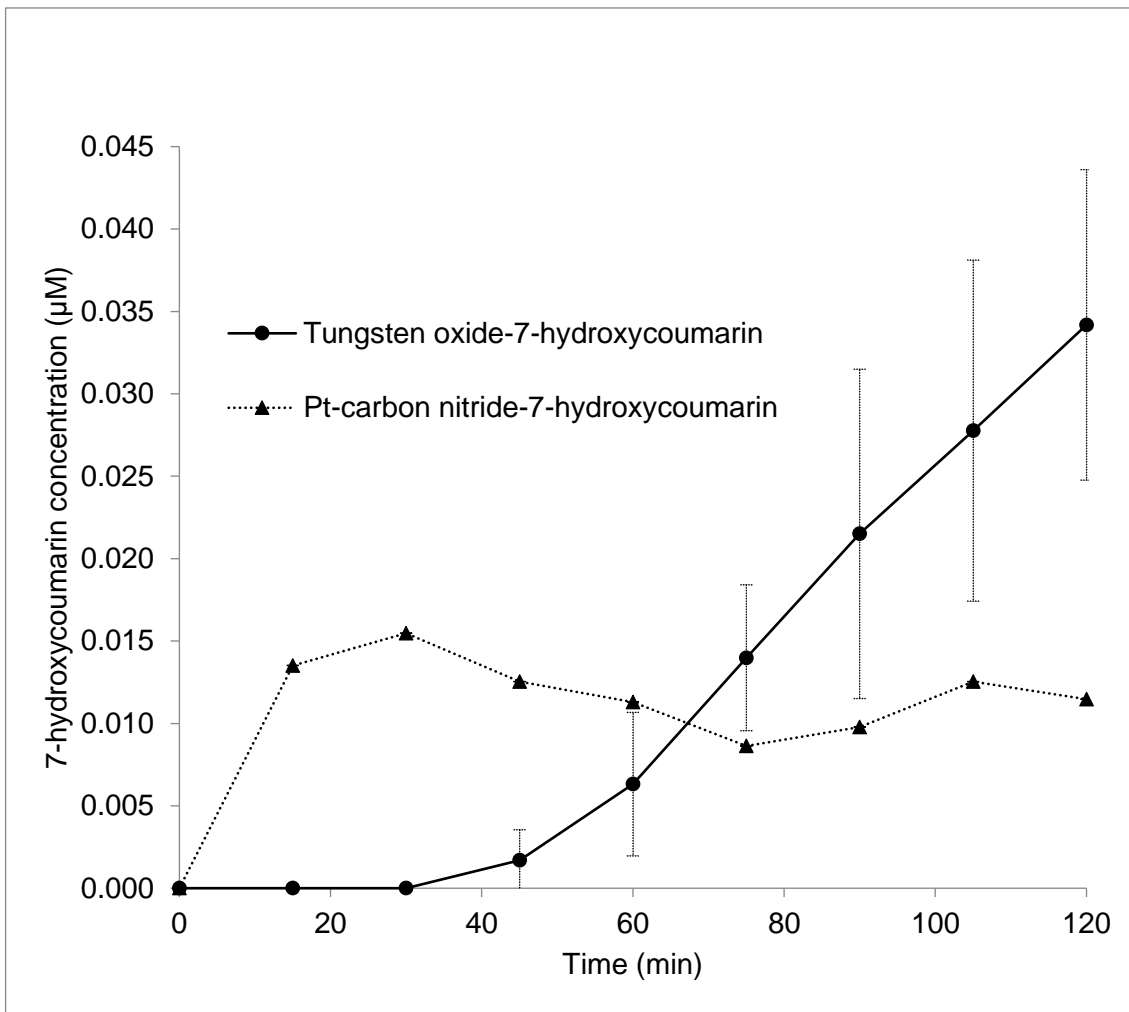
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579 **Figure 3**



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581 **Figure 4**



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583 **Figure 5**

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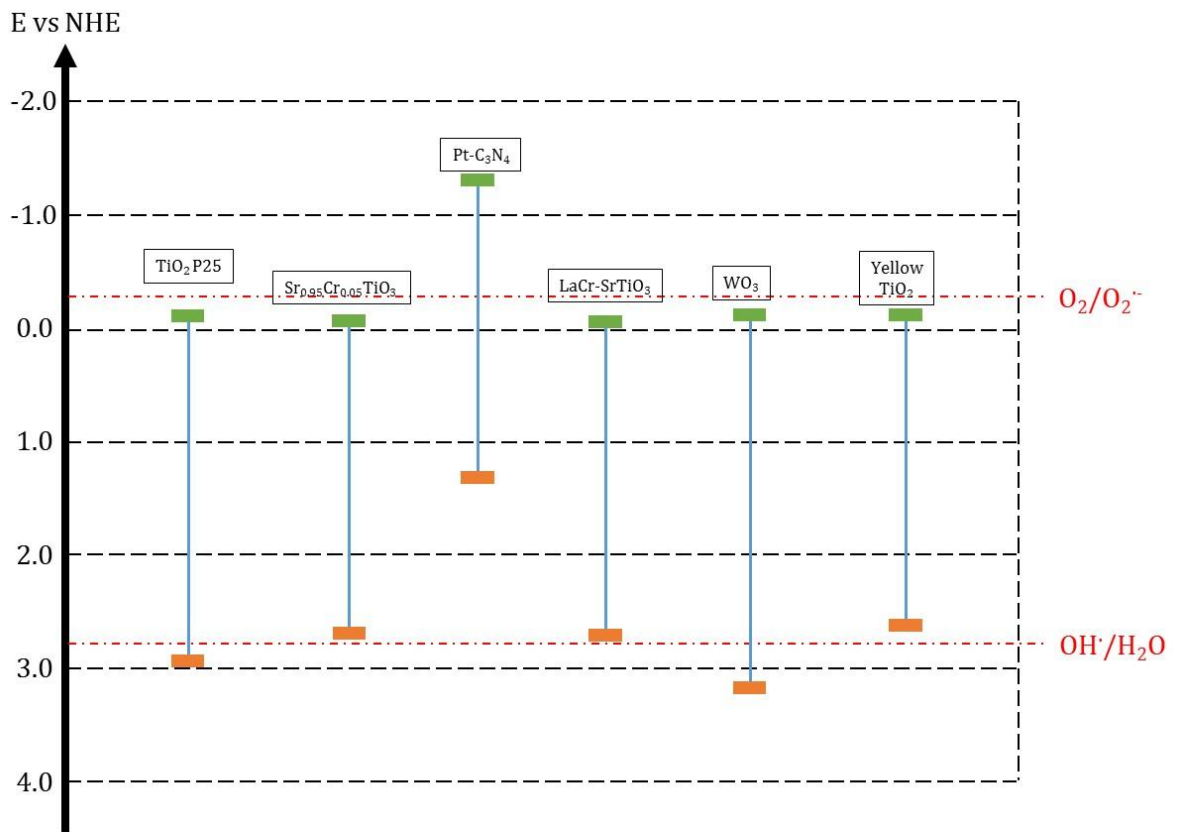
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598 **Figure 6**

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Photocatalyst	Light Source	Maximum OH radical concentration (μM)	Time at which maximum concentration of OH radical was produced (min)	Maximum OH radical production rate ($\mu\text{M/hr}$)
P25	UV	16.9	45	35.654
WO ₃	visible	0.560	120	0.280
Pt-C ₃ N ₄	visible	0.254	30	0.886

609

610 **Table 1**