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1 **Adsorption and photocatalytic oxidation of ibuprofen using nanocomposites of TiO₂**
2 **nanofibers combined with BN nanosheets: degradation products and mechanisms**

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20 **Abstract**

21 This study investigated the adsorption and photocatalytic activity of TiO₂-boron nitride (BN)
22 nanocomposites for the removal of contaminants of emerging concern in water using ibuprofen
23 as a model compound. TiO₂ nanofibers wrapped by BN nanosheets were synthesized by
24 electrospinning method. Characterization of the nanocomposite photocatalysts indicated the BN
25 nanosheets improved the light absorbance and reduced the recombination of the photoexcited
26 charge carriers (e⁻ and h⁺). The photocatalytic oxidation products and mechanisms of ibuprofen
27 by the TiO₂-BN catalysts were elucidated using a multiple analysis approach by high
28 performance liquid chromatography, ultraviolet absorbance, dissolved organic carbon,
29 fluorescence excitation-emission matrices, and electrospray ionization–liquid chromatography–
30 tandem mass spectrometry. The experimental results revealed that the photocatalytic oxidation
31 by the TiO₂-BN nanocomposites is a multi-step process and the interactions between ibuprofen
32 molecules and the TiO₂-BN nanocomposites govern the adsorption process. The increasing BN
33 nanosheet content in the TiO₂ nanofibers facilitated the breakdown of ibuprofen degradation
34 intermediates (hydroxyibuprofen, carboxyibuprofen, and oxypropyl ibuprofen). Kinetic
35 modeling indicated both adsorption and photocatalytic oxidation of ibuprofen by the TiO₂-BN
36 nanocomposites followed the first-order kinetic model. The photocatalytic oxidation rate
37 increased with the increasing BN content in the nanocomposite catalysts, which was attributed to
38 the light absorption capacity and the separation efficiency of the photoexcited electron (e⁻)-hole
39 (h⁺) pairs. Multiple photocatalytic cycles were conducted to investigate the reusability and
40 regeneration of the nanofibers for degradation of ibuprofen.

41

- 42 **Keywords:** titanium dioxide boron-nitride nanocomposites; photocatalytic oxidation; adsorption;
- 43 degradation intermediates; photocatalytic degradation mechanisms

44 **1. Introduction**

45 Contaminants of emerging concerns such as pharmaceuticals and personal care products (PPCPs)
46 have been widely detected in water bodies around the world (Vieno et al., 2007). Many PPCPs
47 are of serious concerns even in trace amounts due to their toxicity to aquatic life and potential
48 risks to public health (Vieno et al., 2007; Christen et al., 2010). Conventional water and
49 wastewater treatment processes including coagulation, sedimentation, media filtration, and
50 biological processes are not effective to remove these recalcitrant organic contaminants (Vieno et
51 al., 2007; Xiang et al., 2016). Adsorption by activated carbon is an efficient technique to remove
52 hydrophobic PPCPs through hydrophobic interactions, however the adsorption capacity
53 gradually decreases as the carbon is saturated with the adsorbed chemicals. In addition, it is
54 ineffective to adsorb hydrophilic compounds such as atenolol, acetaminophen, and naproxen
55 (Vieno et al., 2007; Huerta-Fontela et al., 2011; Wang et al., 2015). Oxidation using chlorine,
56 chlorine dioxide, and ozone is typically effective to degrade PPCPs with electron-donating
57 functional groups (e.g., phenolic-and amine-containing compounds) (Lee and von Gunten, 2010).
58 Ultraviolet (UV) irradiation can degrade many PPCPs but treatment cost is inhibitive because of
59 high energy demand (Rosenfeldt and Linden, 2004).

60 To degrade the persistent organic contaminants, advanced oxidation processes (AOPs) are
61 typically needed (De la Cruz et al., 2012). AOPs generate hydroxyl radicals ($\cdot\text{OH}$) which react
62 non-selectively with most organic compounds (Andreozzi et al., 1999). Commonly used AOPs
63 for PPCPs removal from wastewater include UV/H₂O₂, UV/O₃, (photo)-Fenton, and
64 heterogeneous photocatalysis (De Witte et al., 2009; Homem and Santos, 2011; Prieto-Rodriguez
65 et al., 2012; Carbonaro et al., 2013; Van Doorslaer et al., 2015; Thagard et al., 2016). Complete
66 mineralization is usually not the goal of AOPs because it is energy intensive and not cost-

67 effective (Doll and Frimmel, 2004). Partial degradation of recalcitrant PPCPs is more
68 economically attractive to deactivate their biological activity or increase their biodegradability
69 (Van Doorslaer et al., 2015). But more concerns are raised regarding the intermediate
70 degradation products and their environmental toxicities.

71 Heterogeneous photocatalytic oxidation using metal oxides (e.g., TiO_2) has attracted
72 considerable attention particularly due to its potentially lower cost than other AOPs (Jing et al.,
73 2006; Dalrymple et al., 2007; Rubio et al., 2013; Lin et al., 2015; Arlos et al., 2016; Lin et al.,
74 2016; Lin et al., 2017b; Lin et al., 2017f; Li and Hu, 2018). More than 90 organic and 25
75 inorganic compounds catalogued on the US Environmental Protection Agency's (USEPA)
76 priority list of contaminants have been investigated using heterogeneous photocatalysis (Blake,
77 2001), such as acetone, aniline, atrazine, benzene, methyl tertiary butyl ether (MTBE),
78 trichloroethane. The process has also been successfully applied for the treatment of organic and
79 inorganic compounds at low concentrations in aqueous solutions (Wold, 1993; Nakajima et al.,
80 2005; Westerhoff et al., 2005; Le-Clech et al., 2006).

81 During heterogeneous photocatalysis, organic molecules adsorb onto a metal oxide catalyst
82 surface and react with the photoexcited charge carriers (e^- and h^+) or free radicals (e.g., $\cdot\text{OH}$)
83 (Ollis et al., 1984; Kormann et al., 1991). The photocatalytic reaction depends on the species of
84 organic molecules adsorbed onto the photocatalyst surface and in aqueous phase, which results in
85 different kinetics of photodegradation. As a critical step in heterogeneous photocatalysis, very
86 few studies investigated the kinetics of organics adsorption on a photocatalyst (Bauer et al., 2001;
87 Vautier et al., 2001; Hu et al., 2003; Yu et al., 2005; Lee et al., 2011; Zhang et al., 2013; Rioja et
88 al., 2014; Lv et al., 2016).

89 Titanium dioxide (TiO₂) is the most commonly used photocatalyst due to its relatively low cost,
90 high stability, and low toxicity (Fujishima et al., 2000; Kumar and Devi, 2011a; Nakata and
91 Fujishima, 2012). Substantial efforts have been devoted to improve the photocatalytic
92 degradation efficiency of TiO₂ through combination with metal ions, non-metal ions, and some
93 2D nanomaterials (Liqiang et al., 2006; Rubio et al., 2013; Lin et al., 2015; Arlos et al., 2016;
94 Lin et al., 2016; Lin et al., 2017b; Lin et al., 2017f; Li and Hu, 2018; Yi et al., 2018; Merenda et
95 al., 2019). These dopants, such as Ag (Harifi and Montazer, 2014), Fe (Asiltürk et al., 2009; Lin
96 et al., 2016), P (Zhang et al., 2012), SiO₂ (Tawkaew and Supothina, 2008), and graphene (oxide)
97 (Lin et al., 2017c; Lin et al., 2017d; Yi et al., 2018), have been proven to be effective to improve
98 the photocatalytic activity. A recent study reported that the boron nitride (BN) nanosheets exhibit
99 unique properties due to the high surface area and the reactive edge structure (Biscarat et al.,
100 2015). Previous study demonstrated that the introduction of BN nanosheets enhanced the
101 separation of electron–hole pairs of TiO₂ and dramatically improved photocatalytic activity of
102 methyl orange under ultraviolet (UV) irradiation (Nasr et al., 2017b).

103 This study aims to investigate the mechanisms and kinetics of adsorption and photocatalytic
104 oxidation of PPCPs using novel photocatalytic composite TiO₂ nanofibers with boron nitride
105 (BN) nanosheets. Combining TiO₂ with BN nanosheets by electrospinning method is anticipated
106 to enhance the separation of e⁻-h⁺ pairs of TiO₂ thus to improve the photocatalytic activity.
107 Ibuprofen, a nonsteroidal anti-inflammatory drug that has been found extensively in wastewater
108 effluents, was used as the target recalcitrant PPCP. The adsorption and degradation of ibuprofen
109 by photolysis and photocatalysis was characterized by a series of analytical methods.
110 Degradation intermediates of ibuprofen were analyzed by a positive ion electrospray ionization–
111 liquid chromatography–tandem mass spectrometry [(+) ESI LC-MS/MS]. Multiple

112 photocatalytic cycles were conducted to evaluate the recyclability and regeneration of the TiO₂-
113 BN nanocomposites for the degradation of ibuprofen.

114

115 **2. Materials and methods**

116 2.1 Materials and characterization

117 A series of BN nanosheets incorporated TiO₂ nanofibers (0, 3%, 5%, 7%, and 10%, weight
118 percentage of BN to the mass of Ti, referred as TiO₂, TB1, TB2, TB3, and TB4, respectively)
119 were synthesized using electrospinning technique as described by Nasr et al. (2017b). UV-Vis
120 absorbance of the nanofibers was measured by a spectrophotometer (DR6000; Hach Company,
121 CO). X-ray diffraction (XRD) measurements were conducted using a PANalytical Xpert-PRO
122 diffractometer equipped with an X'celerator detector using Ni-filtered Cu-radiation. The specific
123 surface area of the nanocomposites was determined from the nitrogen adsorption-desorption
124 isotherms measured at liquid nitrogen temperature using a Micromeritics ASAP 2010
125 (outgassing conditions: 200 °C and 12 h). The structure and morphology of the nanocomposite
126 catalysts was characterized by an H-7650 transmission electron microscope (TEM; Hitachi High-
127 Technologies Corp., Pleasanton, CA). The elemental mapping images were taken with a Zeiss
128 EVO HD15 microscope coupled with an Oxford X-MaxN EDX detector.

129

130 2.2 Adsorption and photodegradation experiments

131 Ibuprofen (Analytical grade; Acros Organics Co, NJ) was used as a model compound
132 representative of PPCPs to evaluate the adsorption and photocatalytic activity of the synthesized
133 nanocomposites. The pH of the tested ibuprofen solution was neutral throughout the experiments.

134 Batch experiments were conducted in 100 mL beakers containing a suspension of 10 mg
135 nanofibers and 50 mL ibuprofen solution (5 mg L⁻¹) under dark (adsorption), UV light
136 irradiation with nanofibers (photocatalysis) or without nanofibers (photolysis) conditions. The
137 irradiance of UV lamp (160W PUV-10, Zoo Med Laboratories, San Luis Obispo, CA) included
138 both UV (365 nm, minor peaks at 290, 315, 335 nm) and visible light (405, 435, and 545 nm)
139 wavelength spectrum. The solution mixtures were magnetically stirred for 2 to 3 hours, and 1 mL
140 water samples were taken at 0, 10, 20, 30, 60, 90, 120, and 180 min. The suspensions were then
141 filtered through 0.45 µm cellulose acetate membrane to separate nanofibers for analysis. All
142 adsorption, photolysis, and photocatalytic degradation experiments under each condition were
143 conducted at least two times to ensure the reproducibility of the results.

144 Repeated ibuprofen degradation experiments were conducted for 16 cycles to evaluate the
145 recyclability of the TiO₂-BN nanocomposites under 3-hour UV light irradiation. Because the
146 filtration and the centrifugation were not effective to collect all the nanocomposites from the
147 solution, the suspensions were dried at 80 °C overnight after each degradation experiment to
148 evaporate water from the ibuprofen and nanofibers mixture solution. Fresh ibuprofen solution
149 was then added to the dried nanocomposites to repeat the photocatalytic experiment.

150

151 2.3 Analytical methods

152 The adsorption and degradation of ibuprofen were characterized by a high-performance liquid
153 chromatography (HPLC; PerkinElmer Series 200, CT, USA), UV absorbance at 254 nm (UV₂₅₄),
154 and dissolved organic carbon (DOC) quantified through a carbon analyzer (Shimadzu TOC-L,
155 Kyoto, Japan). Specific UV absorbance (SUVA) was quantified by dividing the UV₂₅₄ by the
156 corresponding DOC concentration of ibuprofen samples, which indicates the change of aromatic

157 structure of ibuprofen molecules. Fluorescence excitation-emission matrix (FEEM) spectroscopy
158 was used to obtain information on characteristics of ibuprofen and potential degradation
159 products in water samples (Aqualog-UV-800-C; Horiba Instruments Inc., NJ).

160 The intermediate products of the ibuprofen degradation were further investigated using a (+) ESI
161 LC-MS/MS method with an Ultimate 3000 nano-flow LC system coupled to an Orbitrap Fusion
162 mass spectrometer equipped with an Adivon NanoMate nano-electrospray ionization source.
163 The LC solvent system consisted of water with 0.1% formic acid (A) and acetonitrile with 0.1%
164 formic acid (B). The gradient was 2% B at 0 min to 95% B at 60 min with a 10 min 95% B flush
165 and 20 min equilibration between samples. Data-dependent Orbitrap MS2 mass spectra (HCD
166 Energy = 27%, RP = 30000) were collected with a 3-sec cycle time between parent scans (m/z
167 100-1000, RP = 120000). Easy-IC lock mass calibration was used for parent scans. Background
168 ion signals were excluded from tandem mass spectrometry. Accurate mass measurement for
169 parent ions (e.g. <1 part per million, ppm) was used to constrain tandem mass spectral library
170 matching and impart high confidence to the matched results. Tandem mass spectra were searched
171 against the 2017 NIST tandem MS library and only matches within 1 ppm precursor mass
172 tolerance, 0.5 m/z product ion mass tolerance, a reverse match factor > 700, and C# < 13 were
173 considered robust matches.

174

175 2.4 Adsorption and photocatalytic kinetic models

176 Adsorption kinetics are usually governed by film diffusion and intra-particle diffusion (Lu Lin,
177 2014; Xuesong Xu, 2015; Lin et al., 2017g). However, the adsorption kinetics in this study are
178 complex due to the desorption of ibuprofen molecules from nanofibers with weak adsorption

179 bonding energy. Thus, the adsorption capacity and the rate to reach the equilibrium
180 concentration were investigated using a commonly used kinetic model: the pseudo first-order
181 kinetic model.

182 Typically, the performance of TiO₂ photocatalysis is usually characterized by Langmuir–
183 Hinshelwood kinetic model (Turchi and Ollis, 1990; Ollis et al., 1991; Coleman et al., 2000;
184 Tanaka et al., 2000; Houas et al., 2001; Li et al., 2006; Kumar and Devi, 2011b). It describes a
185 pseudo-first-order kinetics when the initial concentration of ibuprofen is low (millimolar) (Houas
186 et al., 2001; Konstantinou and Albanis, 2004) (Eq. 1):

$$187 \quad \ln\left(\frac{C_0}{C}\right) = k_{app}t \quad (1)$$

188 where C_0 and C are the initial and real-time ibuprofen concentrations (mg L⁻¹) at time t (min),
189 k_{app} is the apparent pseudo-first-order rate constant (min⁻¹).

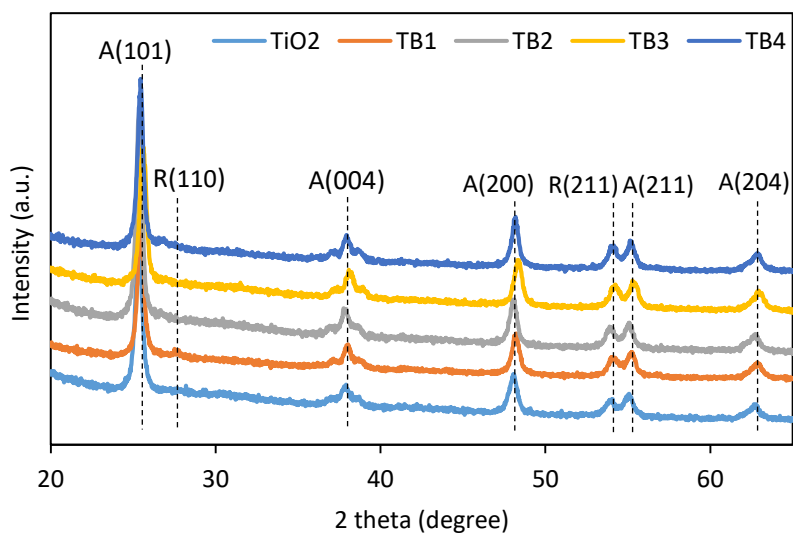
190

191 **3. Results and discussion**

192 3.1 Characterization of the synthesized catalysts

193 As shown in Figure 1, the peaks in XRD spectra were referred to primary anatase TiO₂ phase in
194 the synthesized catalysts with presence of trace amount of rutile TiO₂ phase. Energy dispersive
195 X-ray spectra (EDX) indicated the amounts of elements B and N increased with increasing BN
196 dose in the TiO₂-BN nanocomposites (Nasr et al., 2017a). However, the XRD patterns of TiO₂-
197 BN nanocomposites were similar to the pure TiO₂, suggesting the doping of BN had marginal
198 impact on TiO₂ crystallization during electrospinning process.

219 The elemental mapping images revealed that Ti, O, B and N elements were evenly distributed
220 over the entire area of the synthesized materials (Nasr et al., 2017a). The morphological and
221 structural features of the synthesized materials were examined by TEM as shown in Figure S1.
222 The TiO₂-BN nanocomposites with different BN doses all displayed in a similar fiber form. The
223 crystallite size of the nanofibers can be determined by Scherrer equation (Lin et al., 2017e). The
224 crystallite sizes of the TiO₂-BN nanocomposites increased slightly with the increasing BN dose
225 (24.3-28.7 nm), while the particle size of pure TiO₂ was the smallest of 16.4 nm (Table 1). The
226 increasing trend of grain sizes was also observed by scanning electron microscopy (SEM)
227 images in previous study (Nasr et al., 2017a). This can be attributed to the increase of the
228 solution viscosity induced by inclusion of BN in the electrospinning solution (Nalbandian et al.,
229 2015). This increase revealed the successful incorporation of BN in TiO₂ nanofibers. Besides,
230 previous XPS analysis of TiO₂-BN nanocomposite suggested the formation of chemical B-O-Ti
231 bond between a titanium atom of TiO₂ and a boron atom at the edge of BN in TiO₂-BN
232 nanocomposite (Liu et al., 2017).



213

214

Figure 1. XRD patterns of synthesized catalysts. A: anatase; R: rutile.

215

216 The specific surface area of the synthesized nanocomposites increased from 19.7 m² g⁻¹ to 49.6
217 m² g⁻¹ with the increasing dose of BN nanosheets in the composites (Table 1). In general,
218 materials with a large surface area can accelerate adsorption process due to more active
219 adsorption sites available (Lin et al., 2017a). In addition, the UV-Vis absorption spectra of TiO₂,
220 TB1, TB2, TB3, and TB4 measured in previous study (Nasr et al., 2017a) demonstrated that the
221 incorporation of BN nanosheets improved the light absorbance of the TiO₂-BN nanocomposites
222 in the range of 350-550 nm, which corresponds to the irradiance peak of the UV lamp used in the
223 present work. As such, a higher photocatalytic performance could be expected by combining
224 TiO₂ nanofibers with BN nanosheets. The increased light absorption efficiency resulted in an
225 enhanced photocatalytic activity, which was further evidenced by the degradation of ibuprofen
226 using TiO₂-BN nanocomposites in Section 3.3.

227

228 Table 1. Characterization of the synthesized nanocomposites

Photocatalysts	TiO ₂	TB1	TB2	TB3	TB4
Specific surface area (m ² g ⁻¹)	19.7	31.8	34.4	48.3	49.6
Crystalline size (nm)	16.4	24.3	25.2	26.3	28.7

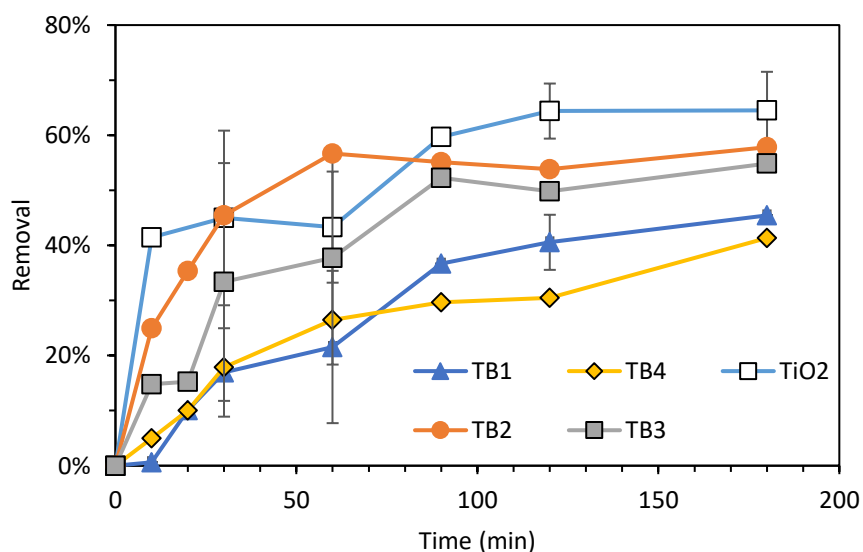
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230 3.2 Adsorption kinetics of the synthesized catalysts

231 The adsorption kinetics for ibuprofen onto different photocatalysts are shown in Figure 2.
232 Ibuprofen molecules adsorbed onto photocatalysts from the aqueous solution increased quickly

233 over time, and the equilibrium was achieved within 90 min for all photocatalysts. Adsorption
234 onto synthesized nanocomposites showed the same inverted “L” shape, indicating a similar
235 kinetic adsorption process. The adsorption capacity of these catalysts varied in the range of 40-
236 65% after 3-hour adsorption. Ibuprofen had better affinity and higher adsorption with pure TiO₂
237 than with TiO₂-BN nanocomposites.

238 The model parameters and the coefficients of determination (R^2) of the pseudo first-order kinetic
239 equation were calculated based on the experimental data, and the results are summarized in
240 Table 2 (modeling curves are presented in Supporting Information Figure S2). The kinetic model
241 fitted well to the experimental data with the coefficients of determination (R^2) higher than 0.8.
242 The amount of adsorbed ibuprofen at equilibrium (q_e) was approximately 14 mg g⁻¹ for all
243 nanocomposites, except for TB4 (10.3 mg g⁻¹). Pure TiO₂ achieved the highest adsorption kinetic
244 rate constant ($k_1 = 0.106 \text{ min}^{-1}$), which was 10 times larger than that of TB1. The adsorption
245 kinetic rate constants followed the order of TiO₂ > TB2 > TB3 > TB4 > TB1, which was similar
246 to the tendency observed in Figure 2.



247

248 Figure 2. Adsorption kinetics of ibuprofen onto different photocatalysts. Error bars represent the
249 standard deviation of duplicate experiments.

250
251 Generally, wrapping BN nanosheet onto TiO₂ nanofibers is expected to raise the ibuprofen
252 adsorption onto the photocatalyst due to the larger specific surface area (Table 1). However, the
253 interactions between ibuprofen and the nanocomposite catalysts also govern the adsorption
254 process. Lee *et al.* proposed that the adsorption mechanism between TiO₂ and organics involved
255 the electrostatic (H-bonding) and the covalent (bidentate-bridging mode) bonding (Lee et al.,
256 2011). The surface complex was formed via H-bonding with TiOH/Ti-OH₂ (Ti-O) and COO-
257 (COOH) groups (Lee et al., 2011). Besides, ibuprofen is negatively charged with the acid-base
258 logarithmic ionization constant pK_a of 4.85 at neutral pH (Lin et al., 2017a). TiO₂ nanofibers are
259 nearly neutral at pH 7 with the point of zero charge pH_{pzc} of 6.4, while the BN nanosheets are
260 hydrophilic and negatively charged (Lin et al., 2010). As such, the introduction of BN increased
261 the electrical repulsion between ibuprofen and the catalysts, resulting in lower adsorption. In
262 addition, smaller particle size of pure TiO₂ (Table 1) may contribute to higher ibuprofen
263 adsorption because smaller dimension often facilitates adsorption (Yean et al., 2005).

264
265 Table 2. Kinetic parameters for adsorption and photocatalytic activity of the pure TiO₂ and TiO₂-
266 BN nanocomposites

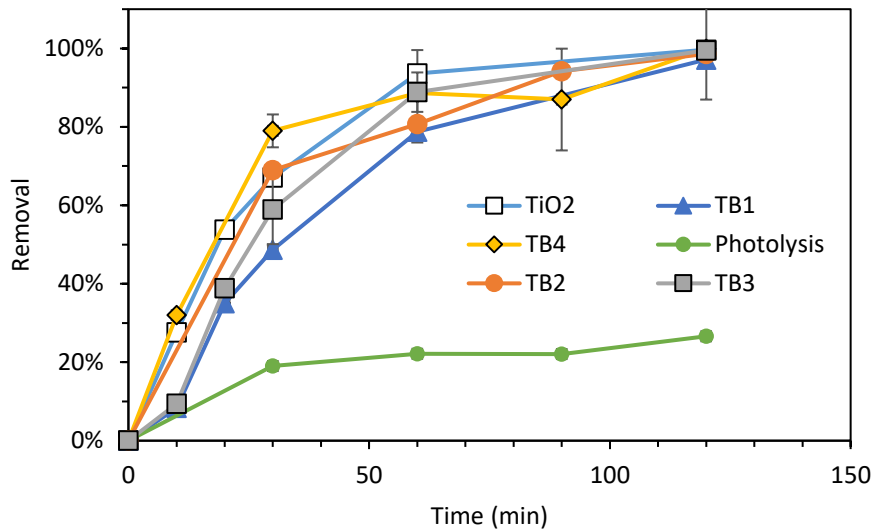
Catalyst	Adsorption			Photocatalysis	
	k ₁ (min ⁻¹)	q _e (mg g ⁻¹)	R ²	k _{app} (min ⁻¹)	R ²

TiO ₂	0.106	14.13	0.836	0.047	0.994
TB1	0.010	13.95	0.974	0.028	0.985
TB2	0.052	14.1	0.996	0.033	0.979
TB3	0.024	13.77	0.964	0.041	0.975
TB4	0.015	10.28	0.974	0.054	0.952

267

268 3.3 Photocatalytic kinetics of the synthesized catalysts

269 The photodegradation of ibuprofen under UV irradiation is shown in Figure 3. The degradation
 270 efficiency of direct photolysis (no catalyst) was measured under the same conditions for
 271 photocatalysis (with catalyst). After 120 min of UV light exposure, there was 27% degradation
 272 of ibuprofen without catalyst. It suggests that ibuprofen molecules can absorb UV light in the
 273 region of lamp emission. On the other hand, photodegradation of ibuprofen remarkably improved
 274 due to the enhancing effect of the nanocomposites under the UV irradiation. After 2 h of UV
 275 light exposure, ibuprofen was almost completely degraded in the presence of photocatalysts.



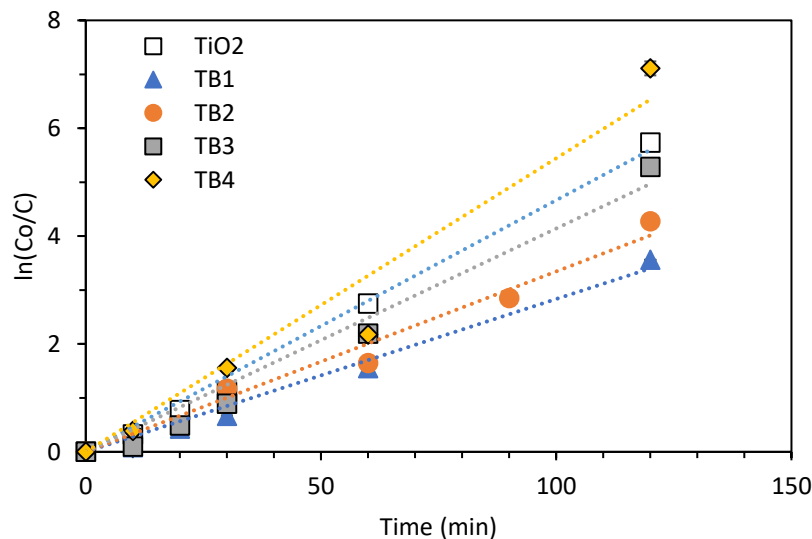
276

277 Figure 3. Photocatalytic kinetics of ibuprofen onto different photocatalysts under UV light
 278 irradiation. Error bars represent the standard deviation of duplicate experiments.

279

280 Langmuir-Hinshelwood kinetic model (Eq. 1) was applied to the photocatalytic data. A plot of
 281 $\ln(C_0/C)$ versus time t for ibuprofen degradation is presented in Figure 4, and the kinetic
 282 parameters are listed in Table 2. The Langmuir–Hinshelwood kinetic model fitted well the
 283 experimental data and the coefficients of determination (R^2) obtained were greater than 0.9. The
 284 photocatalytic activity presented a similar trend as BN content, except for pure TiO_2 . As shown
 285 in Table 2, the apparent photocatalysis rate of TB4 (0.054 min^{-1}) was higher than pure TiO_2
 286 (0.047 min^{-1}), while TiO_2 had higher adsorption kinetics rate (TiO_2 0.059 vs. TB4 0.039 min^{-1}).
 287 Hence, TB4 exhibits excellent photocatalytic activity for ibuprofen removal rather than
 288 adsorption. The photocatalytic degradation rates of TiO_2 and TB2 were lower than adsorption
 289 rates, inferring that their adsorption rate is faster than the photocatalytic oxidation rate, so
 290 oxidation is the control step for the photocatalytic reaction. On the contrary, adsorption is the

291 control step for TB1, TB3, and TB4 photocatalysis. This was further demonstrated by the
292 multiple photocatalysis cycles discussed in Section 3.6.



293

294 Figure 4. Langmuir-Hinshelwood kinetic modeling curves of ibuprofen degradation by the
295 synthesized nanocomposites

296

297 Adsorption has both positive and negative impacts on photocatalysis. On the one hand, more
298 adsorbed ibuprofen molecules on the catalyst surface improve the transfer of photogenerated
299 radicals, which explained why the photocatalytic degradation rate of TiO₂ was slightly higher
300 than TB1 and TB2. On the other hand, the photocatalytic activity is mainly affected by light
301 absorption capacity and separation efficiency of e⁻-h⁺ pairs. The adsorbed ibuprofen may hinder
302 the photocatalysis degradation by screening the light access to the catalysis, so photocatalytic
303 degradation rate of TiO₂ was relatively low even with the highest adsorption rate. The
304 photocatalytic degradation rate of TiO₂-BN nanocomposite increased with the increasing BN
305 content probably due to enhanced light absorption intensity (Section 3.1). Meanwhile, due to

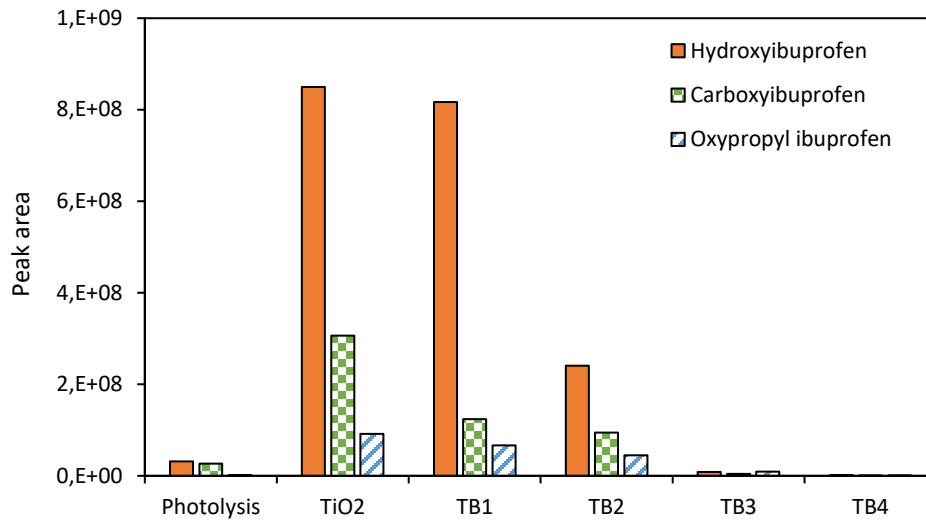
306 electrostatic interactions, the negatively charged BN nanosheets surface can lead to the transfer
307 of h^+ from the TiO_2 particles to the BN nanosheets. As such, the recombination of e^- and h^+ is
308 inhibited with increasing BN dose, which was confirmed by previous photoluminescence study
309 (Nasr et al., 2017a).

310

311 3.4 Ibuprofen degradation intermediates and proposed pathway

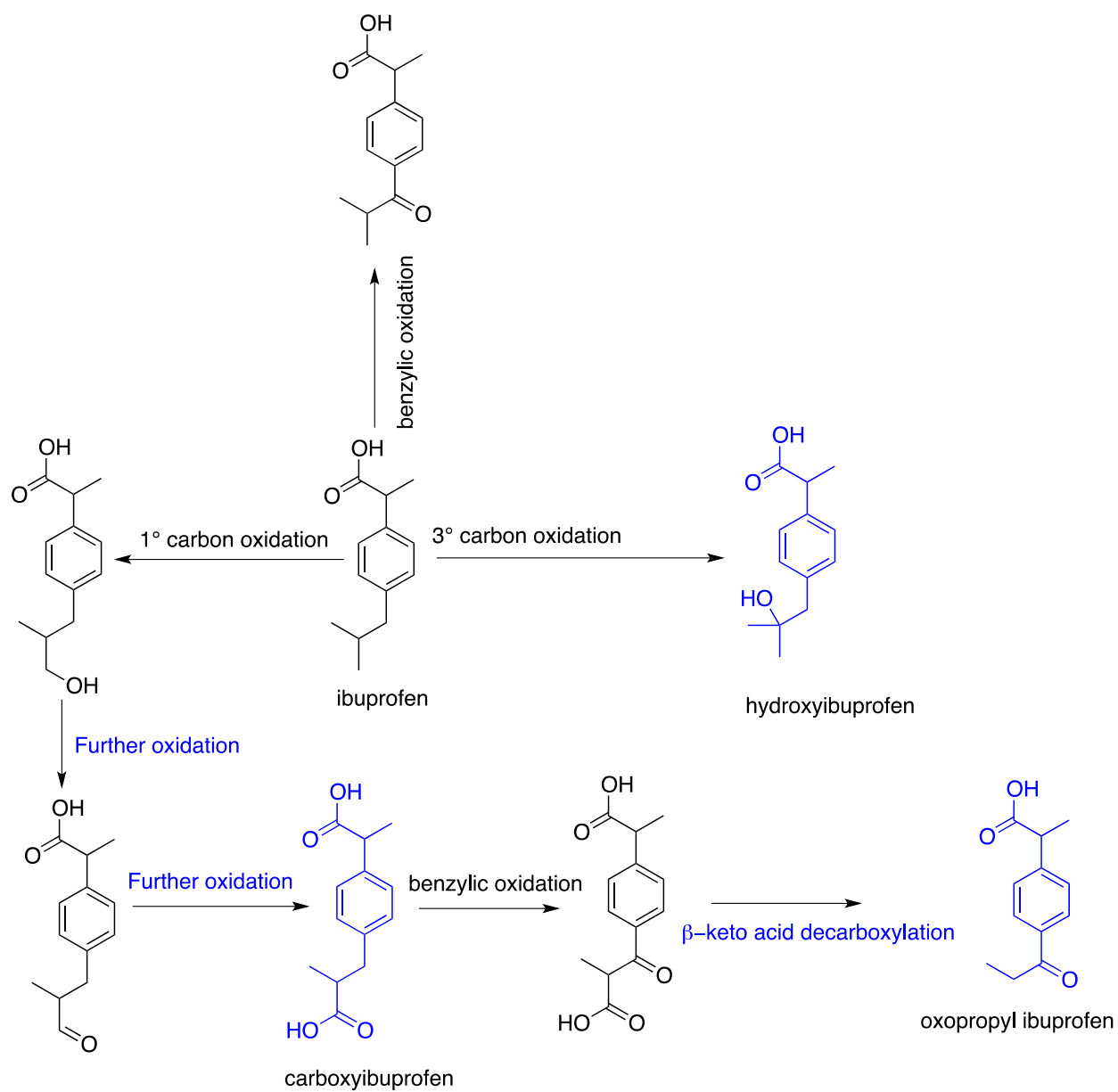
312 Aiming at identifying the degradation intermediates, (+) ESI LC-MS/MS was performed to
313 detect the constituents in the ibuprofen solutions after photocatalytic treatment. Figure 5 showed
314 extracted-ion chromatographic peak areas for ibuprofen degradation intermediates (including
315 hydroxyibuprofen, carboxyibuprofen, and oxypropyl ibuprofen) after 2-hour UV irradiation. The
316 proposed photocatalytic degradation pathway of ibuprofen is present in Figure 6. All compounds
317 shown were confirmed by high resolution mass spectrometry, where elemental composition of
318 the parent ions was determined from accurate m/z measurement and tandem mass spectrometry
319 indicates molecular structure. For simplicity, only one isomer among several possible is shown at
320 each step. Some intermediates are proposed to be formed by successive free radical
321 hydroxylation followed by oxidation to yield the carbonyl compounds (aldehyde and ketone).
322 The primary carbon oxidation to carboxylic acid is a facile process and that product is confirmed
323 by our mass spectrometry results. The most reactive site of the ibuprofen molecule in the
324 presence of free radical ($\cdot OH$) is the benzylic carbon, which gives monohydroxylated ibuprofen
325 (confirmed by mass spectrometry). Once the benzylic hydroxyl ibuprofen is formed, it undergoes
326 further oxidation to give the beta-keto acid. Beta keto acids are susceptible for decarboxylation
327 and results the formation of oxypropyl ibuprofen. A similar oxidation decarboxylation route for
328 the degradation of ibuprofen has been reported in the literature (Skoumal et al., 2009).

329 As presented in Figure 3, the sample under direct photolysis (no catalyst) displayed the lowest
330 removal of ibuprofen (27% in 2-hour UV irradiation) and relatively low amounts of degradation
331 intermediates (Figure 5). It suggested only a small fraction of ibuprofen was oxidized and the
332 degradation process was limited to the initial degradation levels. Degradation in the existence of
333 photocatalysts is more complete since both ibuprofen and its degradation products can be
334 adsorbed onto the catalysts. From Figure 3, ibuprofen was almost completely degraded in the
335 presence of photocatalysts after 2-hour UV light exposure, but the amounts of degradation
336 intermediates varied remarkably (Figure 5). Comparing to direct photolysis, the pure TiO₂
337 catalyst showed 27 times, 12 times, and 76 times increase in hydroxyibuprofen,
338 carboxyibuprofen, and oxypropyl ibuprofen, respectively, owing to the degradation of parent
339 compound (ibuprofen). When the BN content increased to 3% (TB1), the amount of degradation
340 intermediates showed 4%, 60%, and 28% reduction relative to the pure TiO₂. The catalysts with
341 5% BN (TB2) also showed a similar increase in degradation intermediates. However, when the
342 BN content increased to 7% (TB3) and 10% (TB4), the degradation intermediates decreased by
343 over 99%, 99%, and 90% for hydroxyibuprofen, carboxyibuprofen, and oxypropyl ibuprofen,
344 respectively, comparing to the pure TiO₂. Hence, the increasing BN content of the catalyst
345 facilitated the breakdown of ibuprofen degradation intermediates. However, the further
346 degradation products were not detected with (+) ESI LC-MS/MS probably due to the low
347 concentration of these compounds. These degradation products with smaller carbon chains might
348 be adsorbed onto the catalysts surface and degraded much faster than ibuprofen and its initial
349 degradation intermediates. More analysis of degradation mechanism was discussed in the
350 following Section 3.5.



351

352 Figure 5. Extracted-ion chromatographic peak areas for the precursor masses of ibuprofen
 353 degradation intermediates derived from (+) ESI LC-MS/MS chromatograms from different
 354 catalyst conditions.



355

356 Figure 6. Proposed degradation of ibuprofen by TiO₂-BN photocatalysis. Indicated structures

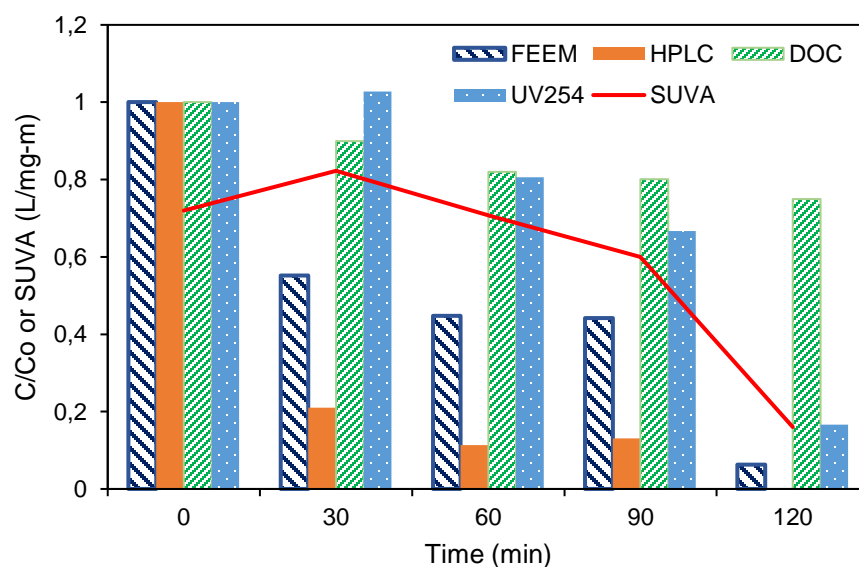
357

were confirmed by mass spectrometry as described.

358

359 3.5 Photocatalytic oxidation mechanisms of ibuprofen

360 The nanocomposite TB4 was chosen to investigate the photocatalytic degradation mechanism of
361 ibuprofen because of its highest photocatalytic activity among the TiO₂-BN nanocomposites. The
362 photodegradation of ibuprofen was analyzed in terms of HPLC, FEEM, DOC, UV₂₅₄, and SUVA
363 measurements (Figure 7). The concentration measured by HPLC was the exact concentration of
364 ibuprofen (parent compound); its concentration reduced rapidly and almost completely
365 disappeared after 2-hour reaction. DOC includes all organic carbons in parent compounds,
366 degradation intermediates and products, serving as an indicator for mineralization degree.
367 Compared with the ibuprofen removal results from the HPLC analysis, the DOC reduction was
368 much slower, with only 25% after 2-h reaction. Although the TB4 was effective to oxidize
369 ibuprofen at a fast rate, the organic intermediates from the ibuprofen oxidation need longer time
370 to be mineralized.



371
372 Figure 7. Reduction of DOC, FEEM peak values, and SUVA values during photocatalytic
373 oxidation of ibuprofen using TB4 under UV irradiation

374

375 The UV_{254} and SUVA are used to determine the removal of aromatic fractions of ibuprofen
376 (Stoll et al., 2015). As shown in Figure 7, the SUVA and UV_{254} results exhibited a similar
377 removal trend suggesting aromatic fraction of ibuprofen was degraded. Even though ibuprofen
378 concentration reduced by 79% for the first 30 min, there were 14% and 3% increases in terms of
379 SUVA and UV_{254} , respectively. The degradation of ibuprofen was further characterized by the
380 FEEM spectroscopy. The fluorescence peak disappeared after 2-hour of treatment (Figure S3).
381 The excitation-emission peak observed at 220 nm/285 nm corresponds to aromatic compounds
382 (Chen et al., 2003). The fluorescence peak volume was used to compare the aromatic fractions in
383 the tested ibuprofen solution at different reaction time (Figure 7). The peak volume reduced by
384 94% after 2-hour reaction, supporting the decrease in aromatic compounds, consistent with the
385 results of UV_{254} and SUVA that aromatic organic carbon was removed from the solution.

386 The results implied that the intermediates become more aromatic than the parent compound after
387 a partial oxidation. As discussed in Section 3.4, intermediates with more complex structure were
388 detected after photocatalytic treatment. Interestingly, there was only 13% reduction of ibuprofen
389 concentration in the last 30 min of reaction (from 90 to 120 min), but SUVA, UV_{254} , and FEEM
390 decreased by 61%, 50%, and 38%, respectively. It suggested that decomposition from parent
391 compounds to intermediates happened mainly during the initial 90 min, while degradation of
392 intermediates into shorter carbon chains occurred mainly after decomposition. Besides, the DOC
393 reduction in the first 30 min probably attributed to the adsorption of ibuprofen onto TB4 (Figure
394 3), the mineralization of ibuprofen was a slow process in the following 90 min due to the tardy
395 reduction of DOC. These results demonstrated that photocatalytic oxidation of ibuprofen

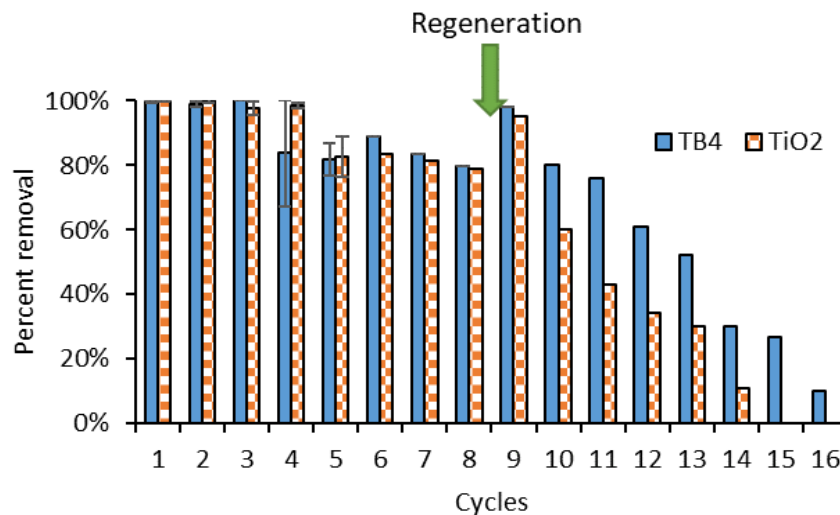
396 molecules by the synthesized nanofibers is a complex multi-step process, degradation of
397 intermediates is probably a control step for the ibuprofen photocatalytic oxidation.

398

399 3.6 Recyclability of the synthesized catalysts

400 The recyclability of the photocatalysts by reusing the catalysts in multiple treatment cycles is
401 crucial in accessing the practical application of a catalyst, because the catalyst may be poisoned
402 by some species (e.g., reaction intermediates) during the reaction process, or may otherwise
403 decompose. In the present work, the recyclability of the pure TiO₂ and TB4 was investigated by
404 performing 16 UV irradiation cycles. In each cycle, UV light was irradiated for 3-hour at room
405 temperature. The adsorption of ibuprofen by TiO₂ and TB4 achieved 65% and 41% after 3-hour
406 mixing (Figure 2), but the photocatalytic activity of TiO₂ and TB4 still remained 80% and 79%
407 after eight cycles of photocatalytic reaction (Figure 8).

408 After eight cycles, the used nanofibers were irradiated by the UV lamp for 3-hour in deionized
409 water. The treatment efficiency was recovered to 98% and 95% for TB4 and TiO₂ after 3-hour
410 regeneration by UV irradiation. However, the degradation efficiency of ibuprofen receded
411 gradually in the following eight cycles, although the TB4 remarkably outperformed TiO₂.
412 According to Section 3.4, more ibuprofen and intermediates were detected for TiO₂ than TB4,
413 hence, weaker photocatalytic activity is probably attributed to the generation and accumulation
414 of intermediates during the catalytic process, which remained on the catalyst and may restrain
415 the further adsorption and degradation of ibuprofen. In addition to the UV irradiation as an
416 effective method for the regeneration of exhausted nanofibers, chemical regeneration should also
417 be studied to fully restore the photocatalysts.



418

419 Figure 8. Ibuprofen removal efficiency of TB4 and TiO₂ catalysts during multiple photocatalytic
 420 cycles under the irradiation of UV light

421

422 4. Conclusions

423 The adsorption, photolysis, and photocatalytic oxidation of ibuprofen by TiO₂-BN
 424 nanocomposites were studied using a multiple analysis approach. The degradation kinetics,
 425 mechanisms, and intermediate products were elucidated. The primary conclusions of the study
 426 are summarized as follows.

427 • Wrapping BN nanosheets onto TiO₂ nanofibers improved light absorption efficiency and
 428 specific surface area of TiO₂ nanofibers, and enhanced separation effectiveness of
 429 photogenerated e⁻-h⁺ pairs.

430 • Both adsorption and photocatalytic oxidation of ibuprofen by the TiO₂-BN
 431 nanocomposites followed the first-order kinetic models. The amount of adsorbed ibuprofen at

432 equilibrium reached approximately 14 mg g^{-1} for the TiO_2 -BN photocatalysts. The
433 photocatalytic degradation rate increased with the increasing BN content.

434 • Analysis of degradation intermediates suggested that the increasing BN content of the
435 catalyst facilitated the breakdown of ibuprofen degradation intermediates (hydroxyibuprofen,
436 carboxyibuprofen, and oxypropyl ibuprofen). No further degradation intermediates were detected
437 by the (+) ESI LC-MS/MS chromatograms likely due to lower concentrations of these
438 compounds.

439 • Multiple photocatalytic cycles were conducted to investigate the reusability of the
440 photocatalysts. UV irradiation of the catalysts in clean water could recover the degradation
441 efficiency to 98% and 95% for TB4 and TiO_2 . However, photocatalytic activity receded
442 gradually, especially TiO_2 , as a result of the accumulation of intermediates during the catalytic
443 process. Further chemical regeneration should be investigated to fully recover the photocatalysts.

444 • Combining TiO_2 nanofibers with BN nanosheets provides an innovative method to
445 improve the photocatalytic performance for the degradation of organic contaminants. Further
446 studies on photocatalytic oxidation of organic contaminants of emerging concerns should be
447 conducted using solar light in environmental conditions (e.g., wastewater).

448

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453

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655 **List of the Figure Captions**

656 Figure 1. XRD patterns of synthesized catalysts. A: anatase; R: rutile.

657 Figure 2. Adsorption kinetics of ibuprofen onto different photocatalysts. Error bars represent the
658 standard deviation of duplicate experiments.

659 Figure 3. Photocatalytic kinetics of ibuprofen onto different photocatalysts under UV light
660 irradiation. Error bars represent the standard deviation of duplicate experiments.

661 Figure 4. Langmuir-Hinshelwood kinetic modeling curves of ibuprofen degradation by the
662 synthesized nanocomposites

663 Figure 5. Extracted-ion chromatographic peak areas for the precursor masses of ibuprofen
664 degradation intermediates derived from (+) ESI LC-MS/MS chromatograms from different
665 catalyst conditions.

666 Figure 6. Proposed degradation of ibuprofen by TiO₂-BN photocatalysis. Indicated structures
667 were confirmed by mass spectrometry as described.

668 Figure 7. Reduction of DOC, FEEM peak values, and SUVA values during photocatalytic
669 oxidation of ibuprofen using TB4 under UV irradiation

670 Figure 8. Ibuprofen removal efficiency of TB4 and TiO₂ catalysts during multiple photocatalytic
671 cycles under the irradiation of UV light

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