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## **Adsorption and photocatalytic oxidation of ibuprofen using nanocomposites of TiO<sub>2</sub> nanofibers combined with BN nanosheets: Degradation products and mechanisms**

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1       **Adsorption and photocatalytic oxidation of ibuprofen using nanocomposites of TiO<sub>2</sub>**  
2       **nanofibers combined with BN nanosheets: degradation products and mechanisms**

3  
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20 **Abstract**

21 This study investigated the adsorption and photocatalytic activity of TiO<sub>2</sub>-boron nitride (BN)  
22 nanocomposites for the removal of contaminants of emerging concern in water using ibuprofen  
23 as a model compound. TiO<sub>2</sub> 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<sup>-</sup> and h<sup>+</sup>). The photocatalytic oxidation products and mechanisms of ibuprofen  
27 by the TiO<sub>2</sub>-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 TiO<sub>2</sub>-BN nanocomposites is a multi-step process and the interactions between ibuprofen  
32 molecules and the TiO<sub>2</sub>-BN nanocomposites govern the adsorption process. The increasing BN  
33 nanosheet content in the TiO<sub>2</sub> 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 TiO<sub>2</sub>-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<sup>-</sup>)-hole  
39 (h<sup>+</sup>) 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/H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub>, (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.,  $\text{TiO}_2$ ) 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 (TiO<sub>2</sub>) 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 TiO<sub>2</sub> 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), SiO<sub>2</sub> (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 TiO<sub>2</sub> 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 TiO<sub>2</sub> nanofibers with boron nitride  
105 (BN) nanosheets. Combining TiO<sub>2</sub> with BN nanosheets by electrospinning method is anticipated  
106 to enhance the separation of e<sup>-</sup>-h<sup>+</sup> pairs of TiO<sub>2</sub> 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 TiO<sub>2</sub>-  
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 TiO<sub>2</sub> nanofibers (0, 3%, 5%, 7%, and 10%, weight  
118 percentage of BN to the mass of Ti, referred as TiO<sub>2</sub>, 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<sup>-1</sup>) 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 TiO<sub>2</sub>-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 (UV<sub>254</sub>),  
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 UV<sub>254</sub> 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 TiO<sub>2</sub> 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<sup>-1</sup>) at time  $t$  (min),  
189  $k_{app}$  is the apparent pseudo-first-order rate constant (min<sup>-1</sup>).

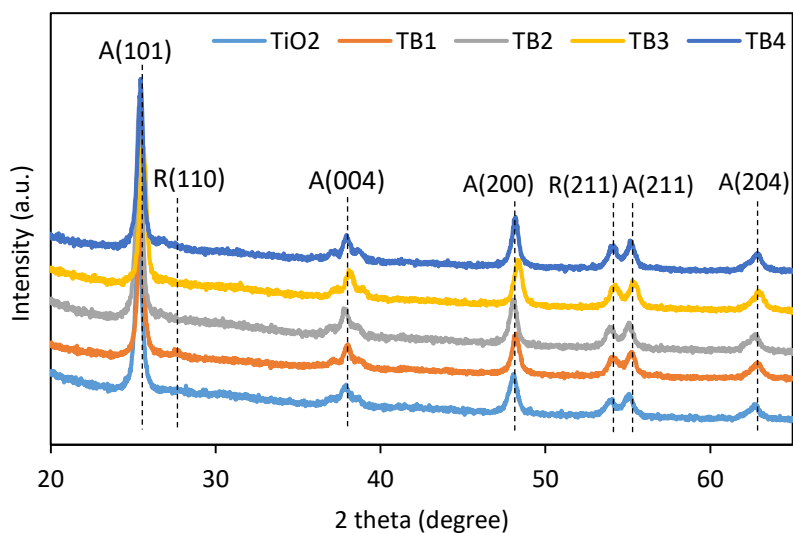
190

### 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 TiO<sub>2</sub> phase in  
194 the synthesized catalysts with presence of trace amount of rutile TiO<sub>2</sub> phase. Energy dispersive  
195 X-ray spectra (EDX) indicated the amounts of elements B and N increased with increasing BN  
196 dose in the TiO<sub>2</sub>-BN nanocomposites (Nasr et al., 2017a). However, the XRD patterns of TiO<sub>2</sub>-  
197 BN nanocomposites were similar to the pure TiO<sub>2</sub>, suggesting the doping of BN had marginal  
198 impact on TiO<sub>2</sub> 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 TiO<sub>2</sub>-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 TiO<sub>2</sub>-BN nanocomposites increased slightly with the increasing BN dose  
225 (24.3-28.7 nm), while the particle size of pure TiO<sub>2</sub> 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 TiO<sub>2</sub> nanofibers. Besides,  
230 previous XPS analysis of TiO<sub>2</sub>-BN nanocomposite suggested the formation of chemical B-O-Ti  
231 bond between a titanium atom of TiO<sub>2</sub> and a boron atom at the edge of BN in TiO<sub>2</sub>-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 m<sup>2</sup> g<sup>-1</sup> to 49.6  
217 m<sup>2</sup> g<sup>-1</sup> 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 TiO<sub>2</sub>,  
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 TiO<sub>2</sub>-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 TiO<sub>2</sub> 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 TiO<sub>2</sub>-BN nanocomposites in Section 3.3.

227

228 Table 1. Characterization of the synthesized nanocomposites

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

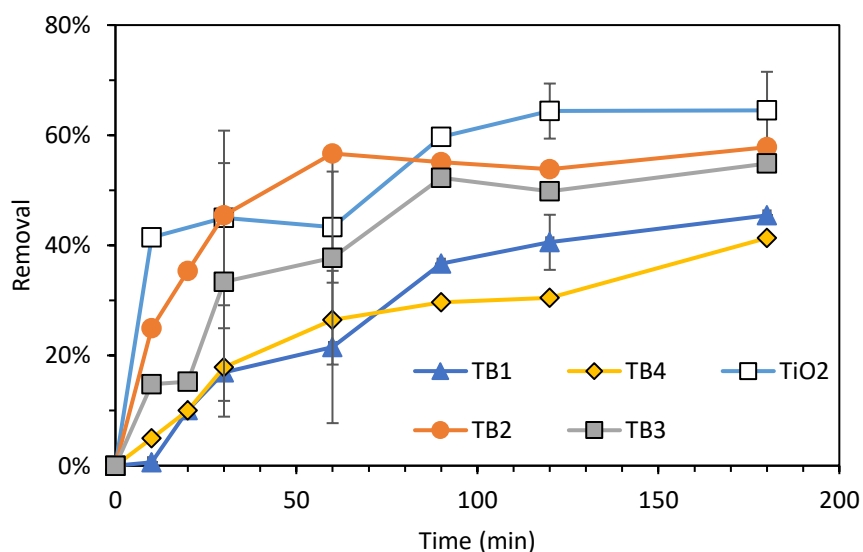
229

### 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 TiO<sub>2</sub>  
237 than with TiO<sub>2</sub>-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<sup>-1</sup> for all  
243 nanocomposites, except for TB4 (10.3 mg g<sup>-1</sup>). Pure TiO<sub>2</sub> 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 TiO<sub>2</sub> > 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 TiO<sub>2</sub> 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 TiO<sub>2</sub> 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-OH<sub>2</sub> (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<sub>a</sub> of 4.85 at neutral pH (Lin et al., 2017a). TiO<sub>2</sub> nanofibers are  
259 nearly neutral at pH 7 with the point of zero charge pH<sub>pzc</sub> 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 TiO<sub>2</sub> (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 TiO<sub>2</sub> and TiO<sub>2</sub>-  
266 BN nanocomposites

Catalyst	Adsorption			Photocatalysis	
	k <sub>1</sub> (min <sup>-1</sup> )	q <sub>e</sub> (mg g <sup>-1</sup> )	R <sup>2</sup>	k <sub>app</sub> (min <sup>-1</sup> )	R <sup>2</sup>

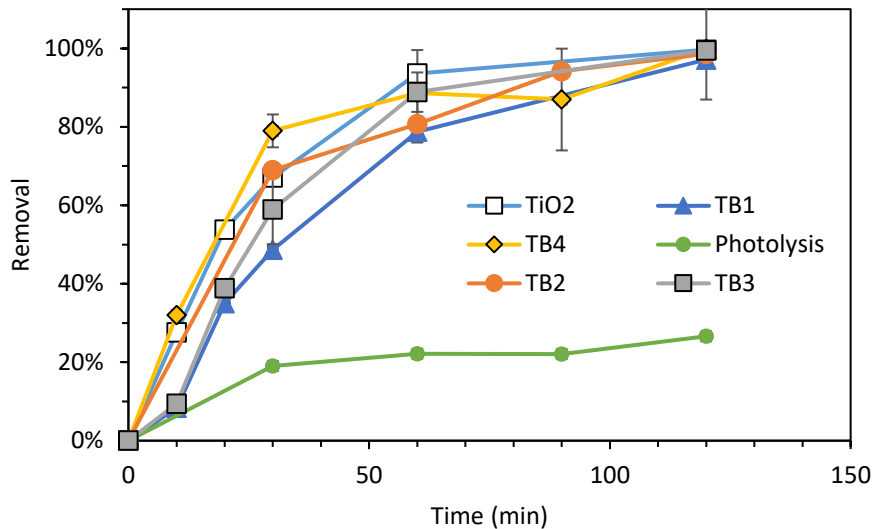
TiO <sub>2</sub>	0.106	14.13	0.836	0.047	0.994
TB1	0.010	13.95	0.974	0.028	0.985
TB2	0.052	14.1	0.996	0.033	0.979
TB3	0.024	13.77	0.964	0.041	0.975
TB4	0.015	10.28	0.974	0.054	0.952

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.





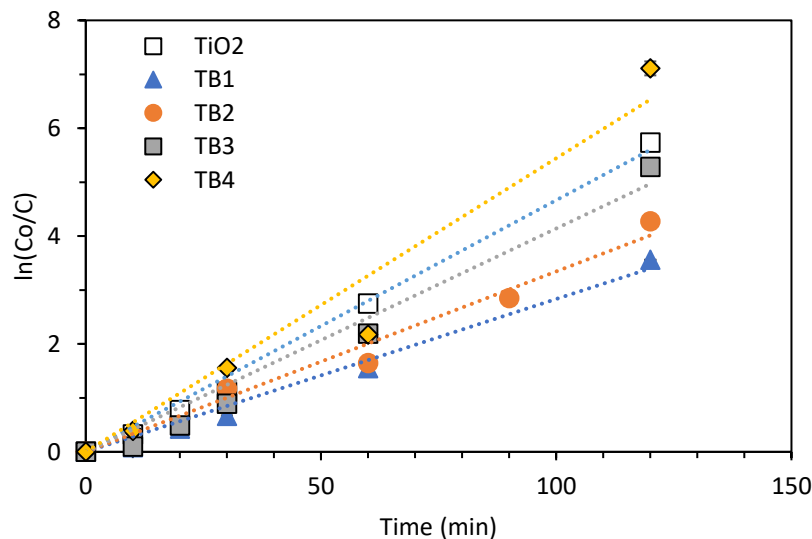
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277 Figure 3. Photocatalytic kinetics of ibuprofen onto different photocatalysts under UV light  
 278 irradiation. Error bars represent the standard deviation of duplicate experiments.

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  $\text{TiO}_2$ . As shown  
 285 in Table 2, the apparent photocatalysis rate of TB4 ( $0.054 \text{ min}^{-1}$ ) was higher than pure  $\text{TiO}_2$   
 286 ( $0.047 \text{ min}^{-1}$ ), while  $\text{TiO}_2$  had higher adsorption kinetics rate ( $\text{TiO}_2$   $0.059$  vs. TB4  $0.039 \text{ min}^{-1}$ ).  
 287 Hence, TB4 exhibits excellent photocatalytic activity for ibuprofen removal rather than  
 288 adsorption. The photocatalytic degradation rates of  $\text{TiO}_2$  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 TiO<sub>2</sub> 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<sup>-</sup>-h<sup>+</sup> pairs. The adsorbed ibuprofen may hinder  
302 the photocatalysis degradation by screening the light access to the catalysis, so photocatalytic  
303 degradation rate of TiO<sub>2</sub> was relatively low even with the highest adsorption rate. The  
304 photocatalytic degradation rate of TiO<sub>2</sub>-BN nanocomposite increased with the increasing BN  
305 content probably due to enhanced light absorption intensity (Section 3.1). Meanwhile, due to

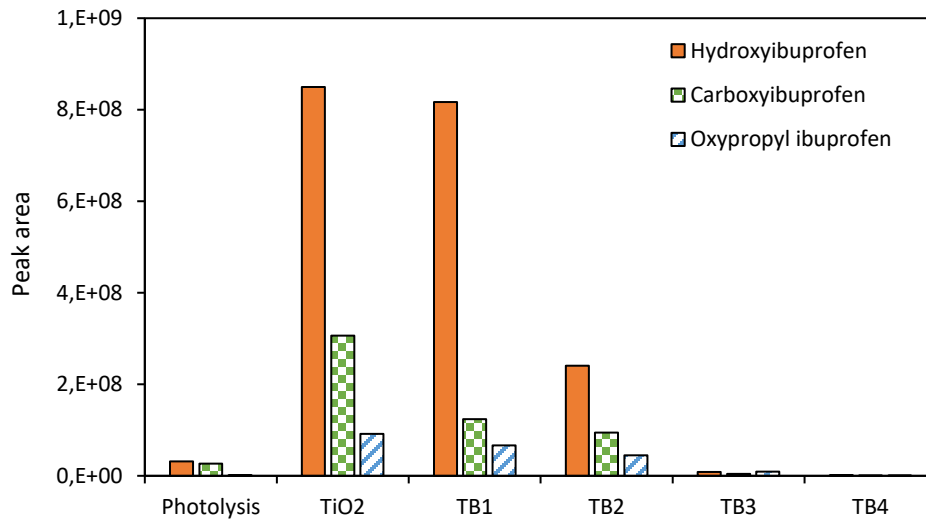
306 electrostatic interactions, the negatively charged BN nanosheets surface can lead to the transfer  
307 of  $h^+$  from the  $TiO_2$  particles to the BN nanosheets. As such, the recombination of  $e^-$  and  $h^+$  is  
308 inhibited with increasing BN dose, which was confirmed by previous photoluminescence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

310

### 311 3.4 Ibuprofen degradation intermediates and proposed pathway

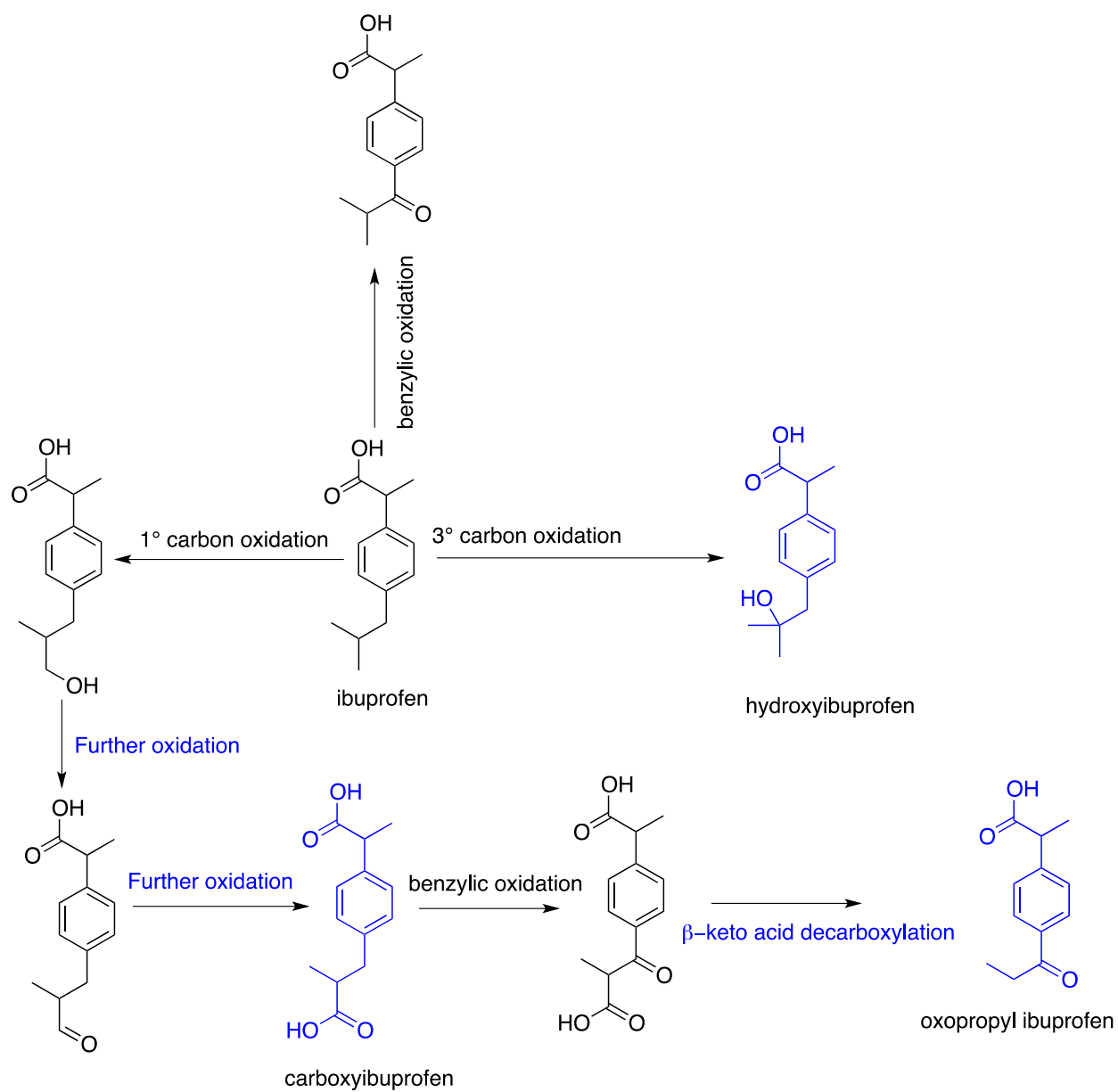
312 Aiming at identifying the degradation intermediates, (+) ESI LC-MS/MS was performed to  
313 detect the constituents in the ibuprofen solutions after photocatalytic treatment. Figure 5 showed  
314 extracted-ion chromatographic peak areas for ibuprofen degradation intermediates (including  
315 hydroxyibuprofen, 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 TiO<sub>2</sub>  
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 TiO<sub>2</sub>. 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 TiO<sub>2</sub>. 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 TiO<sub>2</sub>-BN photocatalysis. Indicated structures

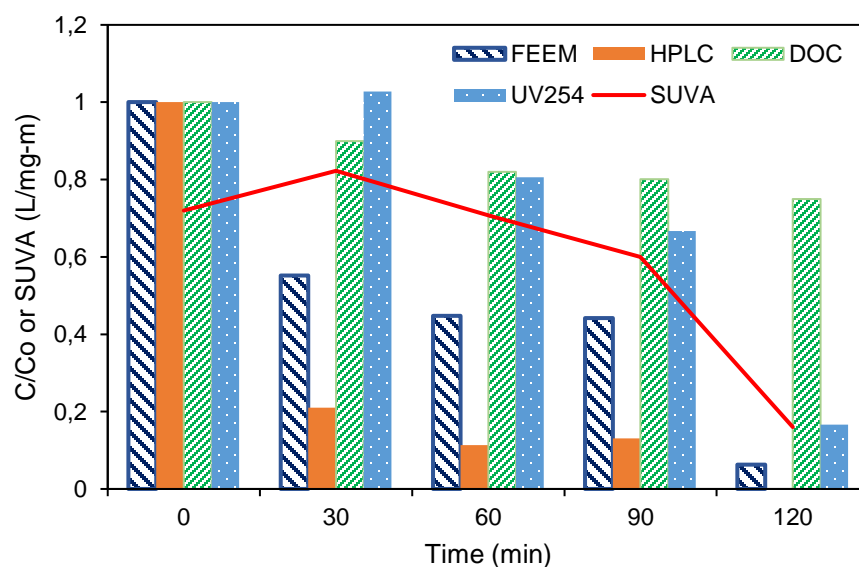
357

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 TiO<sub>2</sub>-BN nanocomposites. The  
362 photodegradation of ibuprofen was analyzed in terms of HPLC, FEEM, DOC, UV<sub>254</sub>, 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<sub>254</sub> 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<sub>254</sub> 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<sub>254</sub>, 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<sub>254</sub> 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<sub>254</sub>, 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



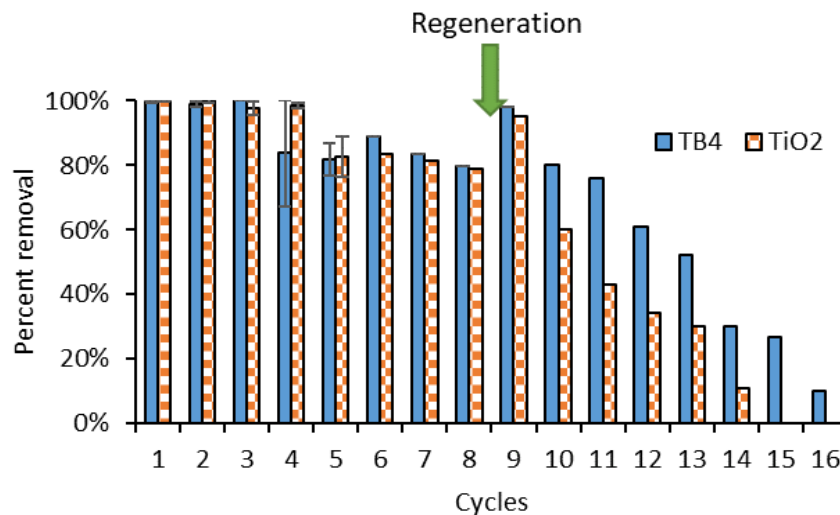
396 molecules by the synthesized nanofibers is a complex multi-step process, degradation of  
397 intermediates is probably a control step for the ibuprofen photocatalytic oxidation.

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 TiO<sub>2</sub> 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 TiO<sub>2</sub> and TB4 achieved 65% and 41% after 3-hour  
406 mixing (Figure 2), but the photocatalytic activity of TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub>.  
412 According to Section 3.4, more ibuprofen and intermediates were detected for TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub>-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 TiO<sub>2</sub> nanofibers improved light absorption efficiency and  
 428 specific surface area of TiO<sub>2</sub> nanofibers, and enhanced separation effectiveness of  
 429 photogenerated e<sup>-</sup>-h<sup>+</sup> pairs.

430 • Both adsorption and photocatalytic oxidation of ibuprofen by the TiO<sub>2</sub>-BN  
 431 nanocomposites followed the first-order kinetic models. The amount of adsorbed ibuprofen at

432 equilibrium reached approximately  $14 \text{ mg g}^{-1}$  for the  $\text{TiO}_2$ -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  $\text{TiO}_2$ . However, photocatalytic activity receded  
442 gradually, especially  $\text{TiO}_2$ , 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  $\text{TiO}_2$  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 TiO<sub>2</sub>-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 TiO<sub>2</sub> catalysts during multiple photocatalytic  
671 cycles under the irradiation of UV light

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