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Microwave-induced crystallization of AC/TiO₂ for improving the performance of Rhodamine B dye degradation

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Titanium dioxide (TiO₂) deposition on activated carbon (AC) is widely used for pollutant photodegradation. In this study, a simple and efficient method for preparing AC/TiO₂ composites under microwave irradiation was developed for photocatalytic degradation of Rhodamine B (RhB) under UV light. Results of X-ray diffraction, scanning electron microscopy, and transmission electron microscopy revealed that TiO₂ nanoparticles are anatase and rutile, with a spherical shape and a particle size of 20–50 nm and are well distributed on the AC surface. The UV-vis spectrum of TiO₂ coated on AC showed an evident red-shift and exhibited stronger optical absorption capacity than pure TiO₂. The AC/TiO₂ nanoparticles prepared at a microwave power of 700 W for 15 min exhibited 98% efficiency in removing RhB dye under UV irradiation for 30 min. The high photocatalytic activity of AC/TiO₂-700 W could be mainly attributed to the high sorption capacity of the mesoporous carbon material and high TiO₂ content, which could produce higher quantity of ·OH. This study provides a rapid synthesis technique to prepare AC/TiO₂ and a novel method to improve photocatalytic efficiency via synergistic effect for other catalytic systems.

Keywords: anatase-rutile; microwave irradiation; mesoporous carbon; photocatalysis; adsorption.

1. Introduction

Water pollution has become one of the most serious problems of our society. Organic poisonous contaminants including xanthene dyes are of the most harmful water pollutants.

23 Rhodamine B (RhB) is an important xanthene dye used as a laser and colorant for textile materials
24 because of its good stability [1]. According to the International Agency for Research on Cancer,
25 RhB may cause acute and chronic poisoning through ingestion, inhalation, and skin contact. This
26 poisonous organic contaminant can be removed from water through various methods, such as
27 chemical precipitation, advanced oxidation, electrochemical techniques, and ion exchange [2-5].
28 As applications of these methods are limited because of technical difficulties or environment
29 hazards [6-7], an effective and optimal strategy to rapidly remove RhB from water and wastewater
30 must be developed.

31 Semiconductor photocatalysts are the most cost-optimal, effective, and environment friendly
32 material for applications directed toward energy and environmental concerns [8-10]. Among these
33 photocatalysts, titanium dioxide (TiO₂) is widely used in heterogeneous photocatalysis to degrade
34 organic pollutants in water and air because it features nontoxicity, chemical and biological
35 inertness, and low cost [11-16]. TiO₂ nanoparticles are generally synthesized through different
36 methods, such as hydrothermal, sol-gel, and electrochemical [17-18]. These methods involve a
37 conventional thermal treatment process using a high-temperature furnace for annealing [19-22].
38 Nevertheless, heating a furnace consumes a high amount of energy and time. In this regard,
39 microwave-hydrothermal technique, as a novel and fast method, has attracted much interest in
40 recent years [23]. Microwaves exhibit potential for various applications and the use of microwaves
41 provides a fast heating process, thereby saving energy and money and shortening synthesis time
42 [24, 25]. Chen et al. [26] reported that the reaction time for TiO₂ crystallization decreased from 16
43 h via the hydrothermal process to 80 min via microwave irradiation.

44 In most of the cases, the degradation efficiency of TiO₂ is relatively low in practical

45 application because of its small surface area and the poor adsorption of organic poisonous
46 contaminants onto it [27, 28]. TiO₂ supported on activated carbon that provided the crystalline
47 framework to support TiO₂ nanoparticles, has been adopted in removal of organic contaminants.
48 Pastravanu et al. [29] synthesized TiO₂-coated carbon samples that exhibited high photocatalytic
49 activity, such that 92% of methyl orange (MO) was degraded after 170 min of UV irradiation. The
50 studies showed that the microwave-assisted synthesis requires a shorter reaction time than
51 conventional methods. Nevertheless, to the best of our knowledge, limited studies have used
52 microwave radiation to synthesize AC/TiO₂ for rapid photocatalysis of RhB. Furthermore, no
53 studies have reported the effects of microwave conditions on the properties of TiO₂ loaded on AC
54 and on the catalytic performance of AC/TiO₂.

55 In this study, AC/TiO₂ was synthesized via a simple, fast, and efficient one-step method under
56 different microwave conditions. Brunauer–Emmett–Teller (BET) surface area, X-ray diffraction
57 (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray
58 photoelectron spectroscopy (XPS), Fourier-transform infrared (FTIR) spectroscopy, and UV-vis
59 diffusion reflection spectroscopy (DRS) were utilized to assess the photocatalytic performance of
60 the enhanced catalyst. In addition, photocatalytic degradation of RhB by AC/TiO₂ and bare TiO₂
61 was evaluated under different microwave powers.

62 **2. Materials and methods**

63 **2.1 Preparation of AC/TiO₂**

64 AC was prepared based on our previous study [30]. It was using a microwave oven
65 (MM823LA6-NS, Midea) at a frequency of 2.45 GHz. A mixture of solid KOH (10 g) and dried
66 coal at a ratio of 1:1 was placed in a quartzose tube in a microwave reactor and activated under

67 vacuum atmosphere at 693 W for 10 min. The KOH is intercalated to the carbon matrix
68 responsible for both stabilization and widening of the spaces between the carbon atomic layers.
69 Metallic potassium formed during redox reaction can be intercalated into the carbon walls
70 independently of the structural order responsible for separation and degradation of graphitic layers
71 thus develop the microporosity and mesoporosity. The obtained AC samples were pretreated by
72 adding into HNO₃ solution with 24 h. The mixture was filtered using distilled water until they
73 became neutral. The pretreated AC was then dried and stored until use.

74 The TiO₂ gel/sol was obtained by conventional sol-gel method. All reagents were of analytical
75 grade and used without further purification. In typical synthesis process, 30 mL of tetrabutyl
76 orthotitanate (TBOT) was dissolved in anhydrous alcohol (EtOH) in proportion of 1:1 (volume
77 ratio). This solution was thoroughly stirred for 40 min and named solution A. Solution B was
78 prepared by mixing 14 mL of glacial acetic acid and 7 mL of distilled water in 35 mL of absolute
79 alcohol. Solution B was added to solution A dropwise and continuously stirred for 1 h. Then it was
80 obtained pale yellow clear TiO₂ sol.

81 AC/TiO₂ nanoparticles were prepared as follows. Pretreated AC (10 g) was added into TiO₂
82 sol (100 g) [31]. The mixture was placed in an oven at 100 °C for 24 h. After solidification,
83 AC/TiO₂ was prepared under different microwave conditions: irradiation at 100 W for 30 min or at
84 300–900 W for 15 min based on results of preliminary experiment, the microwave oven followed a
85 working cycle of 6 s on and 24 s off (20% power). The resulted samples were noted as
86 AC/TiO₂-100 W, AC/TiO₂-300 W, AC/TiO₂-500 W, AC/TiO₂-700 W and AC/TiO₂-900 W.

87 **2.2 Catalyst characterization**

88 The prepared samples were characterized through XRD on a Rigaku D/Max-2500/PC powder

89 diffractometer. Each sample powder was scanned using Cu- $K\alpha$ radiation with an operating voltage
90 of 40 kV and an operating current of 200 mA. The scan rate of 5°/min was applied to record the
91 patterns in the range of 10-80° at a step of 0.02°. XPS analysis of samples was conducted using a
92 PHI5700 ESCA system equipped with a Mg $K\alpha$ X-ray source (1253.6 eV) under a vacuum
93 pressure $<10^{-6}$ Pa. Pass energy was set as 187.85 and 29.35 eV for the survey and high-resolution
94 spectra, respectively. The XPS spectra of the samples were calibrated by taking the graphitic
95 carbon peak as 284.6 eV. The surface micromorphologies of AC and AC/TiO₂ were characterized
96 through SEM (S4800, Hitachi LTD) at an accelerating voltage of 15 kV. TEM was performed on a
97 Tecnai G2 F20 microscope at 100 kV. FTIR spectra were recorded with a Bruker Vertex FTIR
98 spectrometer, resolution of 2 cm⁻¹, in the range of 4000-400 cm⁻¹ by KBr pellet technique. The
99 UV-vis DRS were obtained with a powder UV-vis spectrophotometer (U-4100, Hitachi LTD).
100 Specific surface area (SBET, m²·g⁻¹) was calculated using the BET equation, and total pore volume
101 (V_t , m³·g⁻¹) was evaluated by converting the adsorption amount at $P/P_0 = 0.95$ to the volume of
102 liquid adsorbate. Micropore volume, micropore surface area, and external surface area were
103 determined using t-plot method. Average pore size (r , Å) was estimated with the following
104 equation:

$$105 \quad r = \frac{4V_t}{SBET} \quad (2-1)$$

106 The formation rate of ·OH at photo-illuminated sample/water interface was detected by the
107 Photoluminescence (PL) technique using terephthalic acid (TA) as a probe molecule. PL
108 spectroscopy of synthesized products was taken at room temperature on a Hitachi F2500
109 spectrofluorometer using a Xe lamp with an excitation wavelength of 325 nm.

110 **2.3 Photocatalytic activity for RhB degradation**

111 Photocatalytic experiments were performed to investigate UV-assisted degradation of RhB
112 solution by AC/TiO₂ at room temperature by using a 1000 W UV lamp with 365 nm wavelength. In
113 a typical test, 0.01 g of catalyst was added to 50 mL of RhB solution (30 mg/L, pH=6.8). The
114 mixture was kept in the dark for 30 min to allow adsorption of RhB on the AC/TiO₂ surface. The
115 mixture was then irradiated under UV lamp to degrade RhB. The distance between the reactor and
116 lamp housing is 8.5 cm.

117 The removal rate (η) of RhB can be calculated as follows:

$$118 \quad \eta = \frac{C_o - C_t}{C_o} \times 100 \quad (2-2)$$

119 where C_o and C_t are the concentrations of RhB at initial and different irradiation times,
120 respectively.

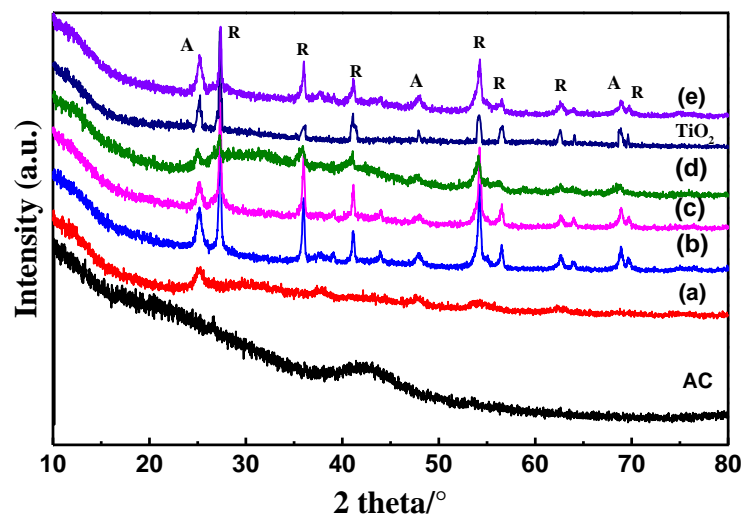
121 **3. Results and discussion**

122 **3.1 XRD spectra**

123 **Fig. 1** depicts the XRD patterns of neat AC as support and AC/TiO₂. No diffraction patterns
124 from carbon species were detected in all samples. All AC/TiO₂ composites exhibited peaks at $2\theta =$
125 25.281° , which is a characteristic of the anatase phase (101). The average crystallite sizes of the
126 anatase and rutile phase calculated from the Scherrer equation are listed in Table 1. The calculated
127 crystal sizes of the samples range from 10 nm to 50 nm. These results indicated that TiO₂ loaded
128 on the AC powder are nanoparticles.

129 **Fig. 1** shows that after 100 W of microwave radiation, the XRD peaks of the TiO₂ anatase
130 phase could be detected in the powder sample without other phase. When the microwave power
131 was increased, the mixed crystals of anatase [JCDPS No. 21-1272] and rutile [JCDPS No. 21-1276]
132 [11] were observed (**Fig. 1 (b)-(e)**). The anatase to rutile phase transformation is generally

133 considered as nucleation growth process during which the rutile nuclei are formed within the
134 anatase phase [4]. Thus, various crystallite size of anatase can be obtained in the formation process
135 of rutile under different prepared condition. With an increase of the microwave power from 300 W
136 to 900 W, the content of rutile increased see in Table 1. As the energy position of the anatase
137 conduction band edge is higher than that of rutile, the photogenerated electrons migrate from
138 anatase to rutile and the positive holes migrate from rutile to anatase. Hence, low electron–hole
139 recombination can enhance the photocatalytic activity of the mixed-phase TiO₂. When the
140 microwave power was increased, the degree of crystallinity in the structural order also increased
141 (narrower peaks) [8], while no further improvement was observed at power exceeding 700 W. As
142 photoreactivity requires a balance among crystallinity, specific surface area, and porosity, we
143 prepared amorphous TiO₂ gel through fast microwave crystallization and improved the crystallinity
144 of TiO₂ spheres with minimal loss in the SBET and porosity. Compared with as-synthesized TiO₂
145 (for 700 W with 15 min), AC/TiO₂-700 W show the same peaks. Thus, combination with AC does
146 not influence the crystal structure of the host TiO₂ material. The XRD results demonstrated that
147 microwave is a promising synthesis technique to enhance the crystallinity of AC/TiO₂.



148
149 Fig. 1 XRD patterns of AC, TiO₂ (for 700 W with 15 min) and AC/TiO₂: (a) AC/TiO₂-100 W, (b)

150 AC/TiO₂-300 W, (c) AC/TiO₂-500 W, (d) AC/TiO₂-700 W, (e) AC/TiO₂-900 W. A: anatase crystalline phase of
151 TiO₂ and R: rutile crystalline phase of TiO₂.

152 3.2 BET

153 Surface areas and pore size distribution of the samples were determined through N₂ sorption
154 measurements. SBET, V_t , and mean pore diameter (d_{mean}) obtained from N₂ adsorption/desorption
155 measurements are presented in [Table 1](#). Pure AC presented large SBET and V_t , whereas AC/TiO₂
156 demonstrated decreased SBET of more than 50% and decreased V_t . This phenomenon could be due
157 to the generated TiO₂ crystals and other solid matter that covered the AC surface and blocked the
158 pore structure. The BET surface of AC/TiO₂ evidently increased when the microwave power
159 increased from 100 to 700 W. This phenomenon is probably due to sublimation of the covered
160 solid matter which reduced the blocked surface of AC, thereby increasing the exposed surface area.
161 When the microwave power was increased to 900 W, the SBET of AC/TiO₂ decreased because the
162 reunion of titanium dioxide crystals and collapse of the AC structure induced by high temperatures.

163 [Fig. 2](#) shows the N₂ adsorption–desorption isotherms of uncoated and TiO₂-coated AC and the
164 pore size distribution (inset) calculated by BJH method. A unimodal distribution centralized at
165 3.8 nm was observed in AC and AC/TiO₂ (300–900 W) powders, whereas AC/TiO₂-100 W showed
166 very small mesopores of approximately 3.414 nm. This characteristic could be due to incomplete
167 crystal formation of TiO₂ sol at a low microwave power (100 W). Although AC and AC/TiO₂
168 showed similar peaks, the latter presented significantly lower intensity, indicating that the carbon
169 pore entrance was blocked by TiO₂ nanoparticles. Data on average pore diameter indicated that all
170 prepared photocatalysts are mesoporous materials. The mesoporosity of AC/TiO₂ was significantly
171 reduced when the microwave power was increased to 900 W, which could be due to the destroyed
172 AC pores.

173 According to IUPAC classification, the N₂ adsorption isotherms of the samples are essentially
 174 of type IV with a type-H₄ hysteresis loop (Fig. 2). This characteristic indicates that synthesized
 175 materials present mesoporous structure with slit-shaped pores, which is similar to the result
 176 obtained by Pastravanu et al. [29]. In the mesoporous carbon sample, AC/TiO₂ exhibited almost the
 177 same shape with a small difference in N₂ adsorbed volume. This characteristic is an indication of
 178 carbon mesopore filling with titania nanoparticles that resulted in reduced SBET (Table 1).
 179 However, during TiO₂ deposition, the hysteresis shape tended toward an H₂-type, suggesting the
 180 evolution of slit-shape into a complex pore structure. All isotherms showed a significant hysteresis
 181 at the relative pressure P/P_0 between 0.05 and 0.2, which indicates the existence of mesoporosity
 182 in the nanospheric samples [1].

183 Table 1 The characterization results of different samples

Samples	SBET ^a (m ² /g)	V _t ^b (cm ³ /g)	d _{pore} ^c (nm)	D _{hkl} ^d (nm)	d _{particle} ^e (nm)	A/R ^f	M ^g (%)
AC	1915	1.020	3.829	/	/	/	/
AC/TiO ₂ -100W	332	0.196	3.414	11.6	12	A	30.81
AC/TiO ₂ -300W	364	0.215	3.828	22.6/24.5	30	34/66	42.97
AC/TiO ₂ -500W	498	0.237	3.825	46.8/49.3	45	39/61	52.56
AC/TiO ₂ -700W	547	0.362	3.828	17.9/22.9	17	47/53	58.72
AC/TiO ₂ -900W	190	0.121	3.829	48.3/50.2	45	78/22	47.51

184 a BET specific surface area.

185 b Total pore volume taken at $P/P_0 = 0.98$.

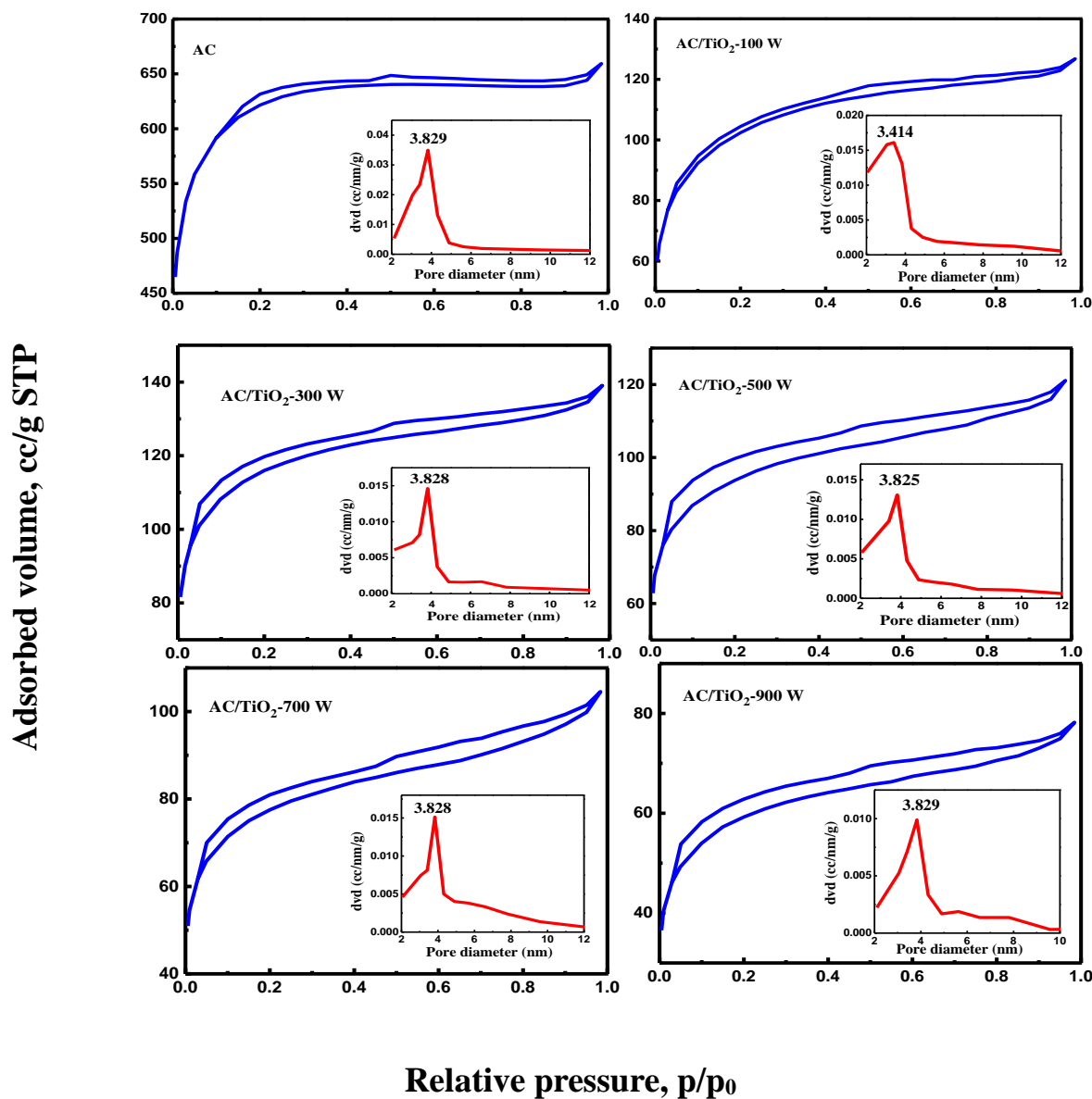
186 c Mean pore diameter calculated with BJH method.

187 d Crystallite size of anatase and rutile calculated with Scherrer equation.

188 e Mean particle size of TiO₂ determined from TEM.

189 f Phase ratio of anatase and rutile.

190 g Percentage composition of TiO₂ calculated by ash method



191

192 Fig. 2 Nitrogen adsorption-desorption BET isotherms and pore size distribution curves (inset) of AC and

193 AC/TiO₂.

194 3.3 SEM

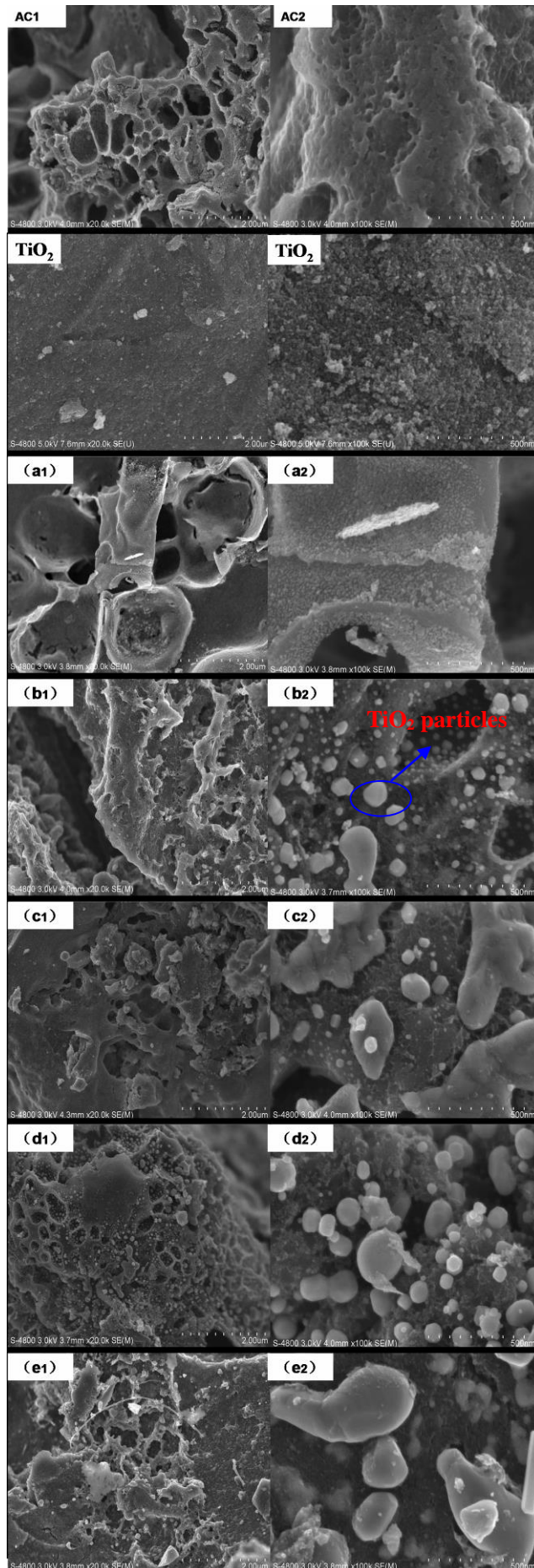
195 The morphology of the synthesized samples was examined through SEM, and the typical

196 SEM micrographs of AC, TiO₂, and AC/TiO₂ are shown in Fig. 3. The uncoated AC particle

197 surface was smooth. By contrast, for AC/TiO₂, TiO₂ particles were distributed on the AC surface

198 and no significant changes in the internal morphology of AC were observed as shown in the SEM

199 micrographs (Fig. 3 (a)–(e)). Changing the microwave power resulted in different distributions and
200 covered areas of TiO₂ on the AC surface, although a portion on the AC surface remained
201 unoccupied as shown in the lower magnification micrograph on the left side of Fig. 3; this finding
202 is consistent with BET results. The high-magnification images on the right side of Fig. 3 indicate
203 that the synthesized TiO₂ features 20 to 50 nm size and a spherical shape. When the microwave
204 power was increased from 100 to 700 W, more TiO₂ particles formed on the AC surface. Under
205 microwave preparation conditions of 700 W for 15 min, photocatalytic particles were relatively
206 uniform, spherical in shape, and better dispersed on AC. And compared with TiO₂, the coated-TiO₂
207 particles become pronounced and coarse by pitch treatment and the size of the particles is kept
208 large. While the microwave power rising to 900 W, the TiO₂ particle was highly agglomerated due
209 to the low stability of the small-sized particles, and leading to the TiO₂ gather on the surface of
210 AC.



212 Fig. 3 SEM of AC, TiO₂ and AC/TiO₂: (a) AC/TiO₂-100 W, (b) AC/TiO₂-300 W, (c) AC/TiO₂-500 W, (d)
213 AC/TiO₂-700 W, (e) AC/TiO₂-900 W.

214 3.4 TEM

215 Fig. 4 shows the TEM micrographs of AC/TiO₂ samples recorded under different
216 magnifications. Under low magnification, the TEM micrograph showed spherical TiO₂ particles
217 distributed on the AC surface, which was also observed in the SEM measurements. Under high
218 magnification, the particle sizes (nm) of the spherical-shaped TiO₂ crystals are distributed as
219 follows: (a) 10–15 nm, (b) 20–50 nm, (c) 40–50 nm, (d) 15–20 nm, and (e) 40–50 nm; these
220 findings are consistent with the XRD results. Only a small amount of TiO₂ particles formed on the
221 AC surface at a microwave power of 100 W for 30 min, and the particle size of TiO₂ is very small
222 with an unstable morphology and structure. Thus, a very low microwave power is not conducive to
223 the formation of the TiO₂ core-shell structure. The amount of TiO₂ particles loaded on AC
224 increased when the microwave power increased from 100 to 700 W (Table 1). The images showed
225 that TiO₂ nanoparticles are uniform in size and shape, free from aggregation, and well-dispersed on
226 AC when the preparation power was 700 W. However, when the microwave power was increased
227 to 900 W, TiO₂ spheres with close interconnection showed serious agglomeration. Thus, the
228 AC/TiO₂-700 W photocatalyst could provide the free surface of AC for dye adsorption on the
229 microspheres, and the transfer of the dye around TiO₂ resulted in enhanced dye degradation.

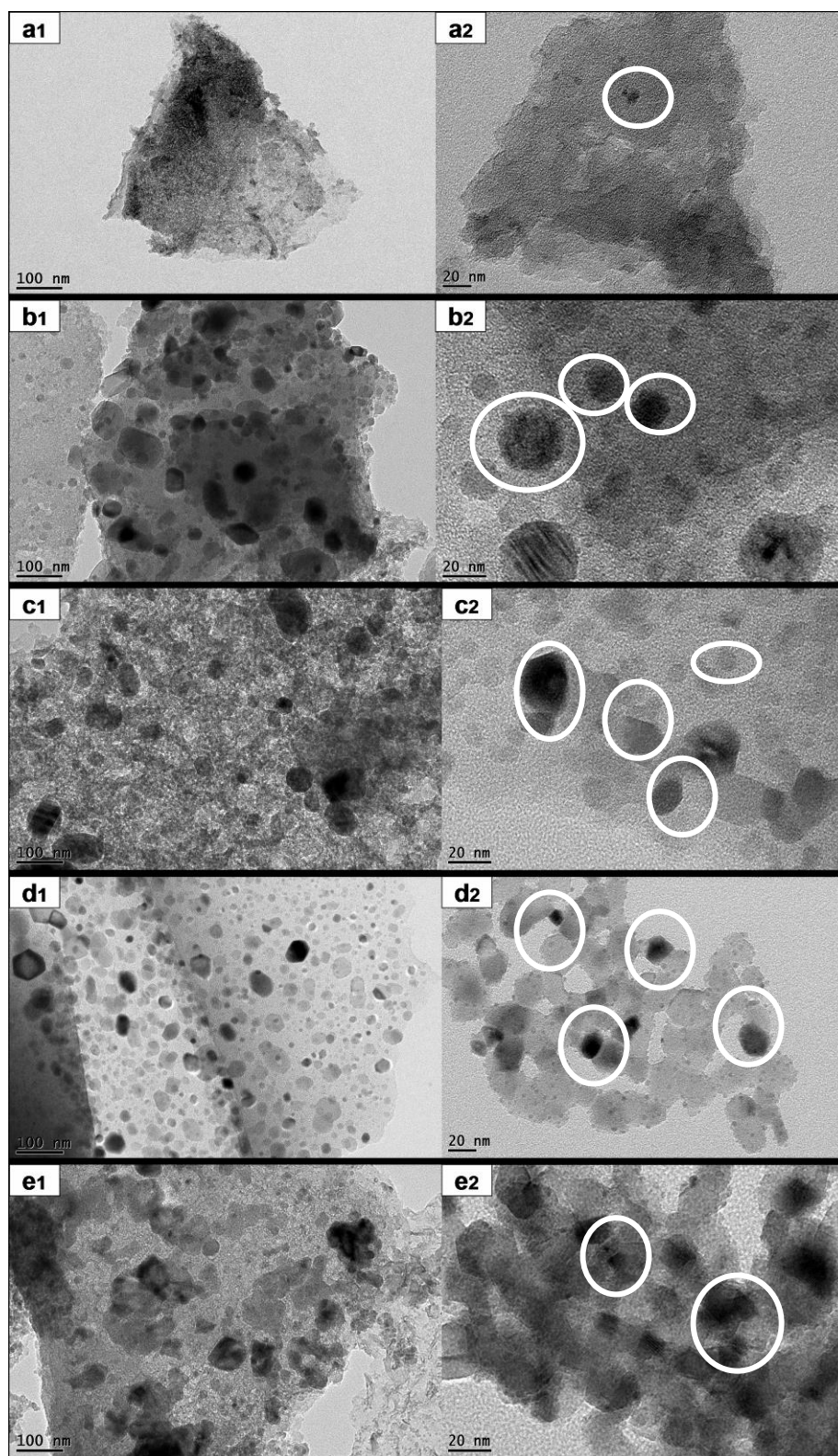


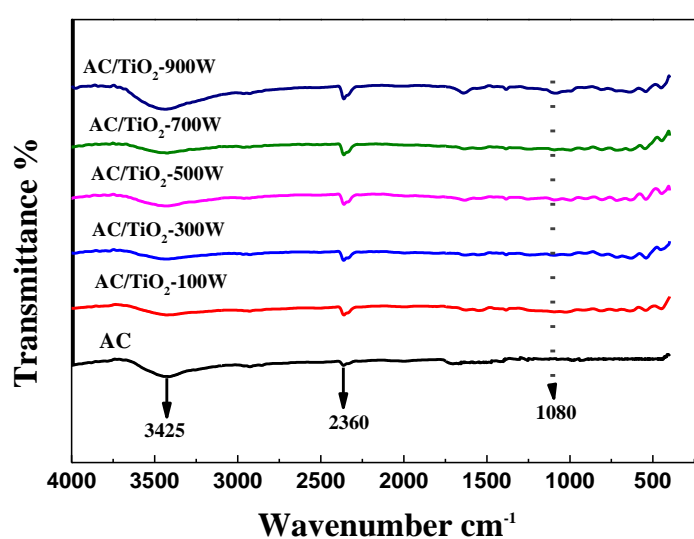
Fig. 4 TEM of AC/TiO₂: (a) AC/TiO₂-100 W, (b) AC/TiO₂-300 W, (c) AC/TiO₂-500 W, (d) AC/TiO₂-700 W, (e) AC/TiO₂-900 W.

230
231
232

233 3.5 FTIR

234 We performed FTIR experiments to determine the surface activity of the catalysts. Fig. 5

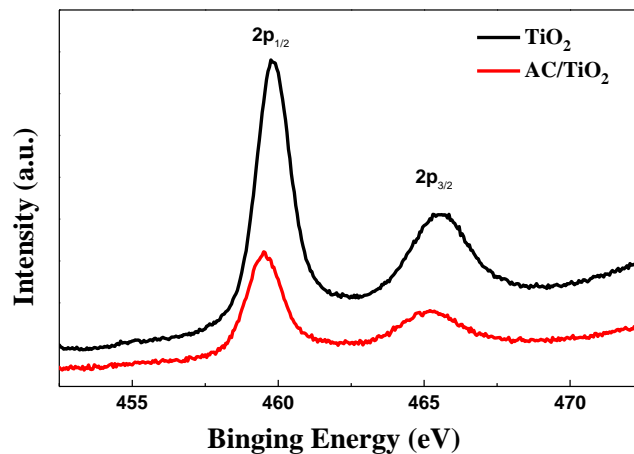
235 shows the FTIR spectra of AC and AC/TiO₂ nanocomposites in the spectral region from 450 to
236 4000 cm⁻¹. The strong peak of the AC/TiO₂ nanocomposites around 3425 and 2360 cm⁻¹ are
237 attributed to asymmetric stretching vibration of O–H, which are similar to those of the AC samples.
238 This finding indicates that no dehydroxylation occurred during formation of AC/TiO₂
239 nanocomposites. The improved hydrophilicity and wettability of the mesoporous carbon are
240 advantageous for organic adsorption from aqueous solutions [28]. The main reason for this benefit
241 may be that the very short heating time and the activity of rapid resolidification of molten phases,
242 in conjunction with the aqueous environment, avoids the dehydroxylation of AC. The comparison
243 of the curves of AC and AC/TiO₂ and FTIR results suggest that the formation of titania
244 nanoparticles in the AC/TiO₂ nanocomposites did not alter the structure or phase of the AC crystals.
245 The broad absorption band in the range of 400–800 cm⁻¹ characterizes the Ti–O and Ti–O–Ti
246 vibration of anatase, which confirms the formation of TiO₂. Moreover, the appearance of bands at
247 1080 cm⁻¹ indicates the clear formation of the Ti–O–C bonds, suggesting that TiO₂ binds to the
248 mesoporous carbon surface [29].



249
250 Fig. 5 FTIR spectra of AC and AC/TiO₂: (a) AC/TiO₂-100 W, (b) AC/TiO₂-300 W, (c) AC/TiO₂-500 W, (d)
251 AC/TiO₂-700 W, (e) AC/TiO₂-900 W.

252 3.6 XPS

253 To understand the oxidation states of Ti, we conducted XPS measurements of TiO₂ (prepared
254 for 700 W with 15 min) and AC/TiO₂-700 W (Fig. 6). Ti 2p 1/2 and Ti 2p 3/2 peaks were observed
255 in pure TiO₂, with binding energies of 465.3 and 459.75 eV, respectively, and the binding energies
256 of these peaks in the AC/TiO₂ samples shifted toward 465.2 and 459.5 eV, respectively. The
257 observed range of the 2p binding energy values for TiO₂ and AC/TiO₂ samples indicates that Ti is
258 in the +4 oxidation state [28]. Therefore, Ti in the AC/TiO₂ nanocomposites is the TiO₂ derived
259 from titania. The XPS results confirmed the formation of titania in the AC/TiO₂ nanocomposites
260 and indicated the stability of the TiO₂ nanocomposite under the reaction condition.



261

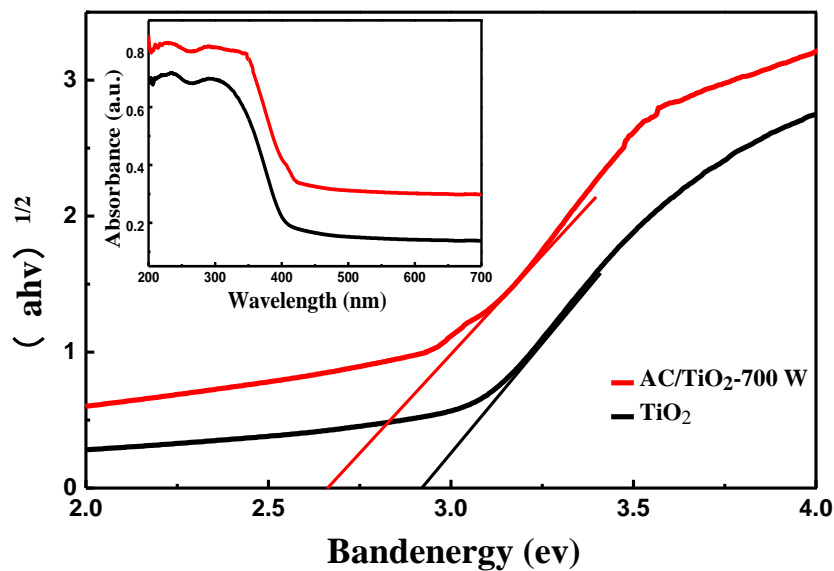
262

Fig. 6 XPS of Ti 2p in TiO₂ and AC/TiO₂-700 W.

263 3.7 UV-vis spectra

264 The UV-vis DRS of TiO₂ (prepared for 700 W with 15 min) and AC/TiO₂ samples are
265 shown in the inset Fig. 7. With TiO₂ loaded on AC, the absorbance in the visible region was
266 enhanced. Pure TiO₂ showed an intrinsic absorption with light wavelength shorter than 390 nm and
267 almost no absorption in visible light with wavelength ranging from 400 to 800 nm. This adsorption
268 is mainly attributed to the inter-band transition of TiO₂ [11]. The light absorption edge of

269 AC/TiO₂-700 W was 412 nm, with a remarkable red shift to the visible range compared with the
 270 spectrum of pure TiO₂. This change influenced the effective band gap of the photocatalyst. TiO₂ is
 271 known as an indirect semiconductor, for which the relation between absorption coefficient (α) and
 272 the incident photon energy ($h\nu$) can be written as $\alpha=B_i (h\nu-E_g)^2/h\nu$ [3], where B_i is the absorption
 273 constant for indirect transitions. Plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ from the spectral data are presented of
 274 Fig. 7. Thus, the sample AC/TiO₂ was found to have band gap 2.67 eV which was lower than the
 275 band gap of the initial titania powder (2.91 eV) and for this reason it is expected the AC-TiO₂ to be
 276 photocatalytically active under visible light. Moreover, Zhang [15] reported that absorbance in the
 277 presence of AC/TiO₂ was higher than that in the presence of AC.



278
 279 Fig. 7 Diffuse reflectance absorption spectra of TiO₂ and AC/TiO₂-700 W.

280 3.8 Photocatalytic activity

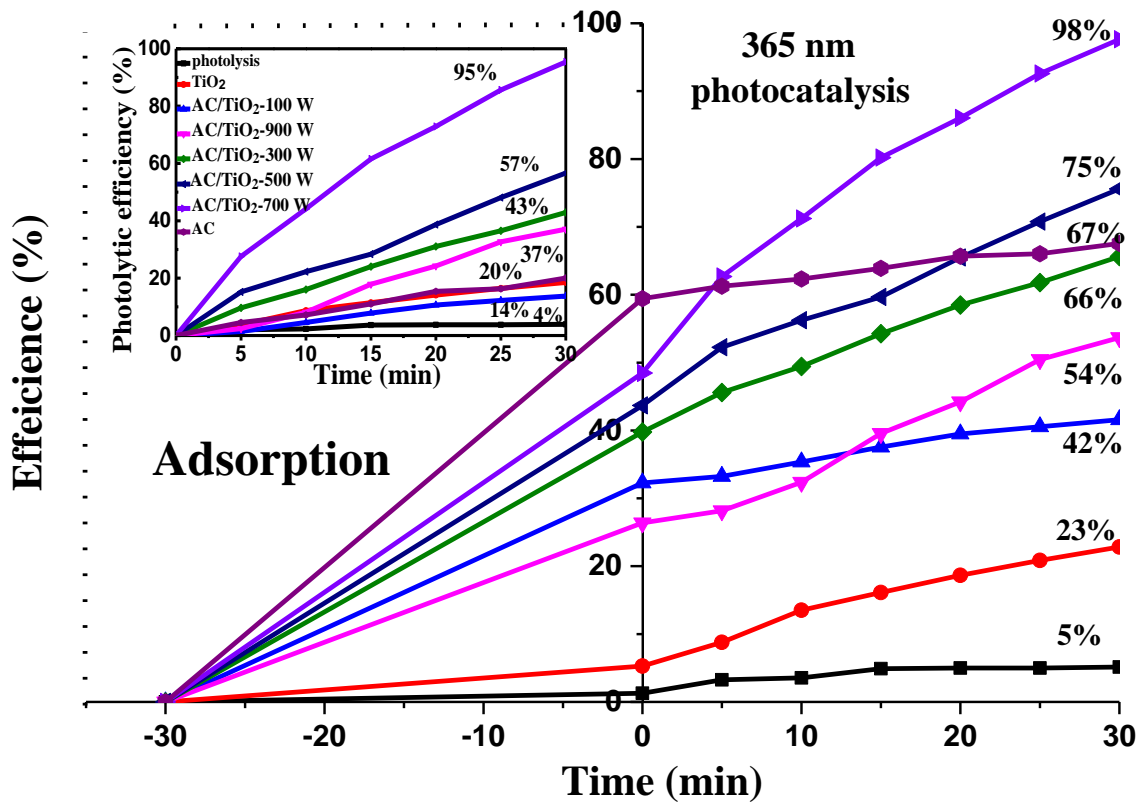
281 The activities of the synthesized nanocomposites were evaluated through photodegradation of
 282 RhB aqueous solution (30 mg/L) under UV irradiation at 365 nm (Fig. 8). A blank experiment
 283 without any photocatalyst (photolysis) was conducted for comparison. No evident
 284 photodegradation of RhB was observed after 30 min of irradiation in the absence of photocatalyst

285 (direct photolysis). The pure photolytic removal efficiency of the as-synthesized TiO₂ sample (for
286 700 W with 15 min) was 18.52%, and the adsorption efficiency of AC was 20%, exclusive of the
287 30 min dark reaction. The removal efficiency of AC/TiO₂ composite samples presented high
288 photolytic removal efficiency that ranged from 37 to 95% (Fig. 8 (inset)). TiO₂ loaded on AC
289 exhibited very high photocatalytic degradation efficiency compared with AC and pure TiO₂. The
290 substantially decrease in RhB concentration in the aqueous solution can occur in a
291 physical–chemical phenomenon, such as adsorption by AC and photocatalytic decomposition by
292 TiO₂. The activated carbon played a role of adsorption at the ratio 1:10 (AC and TiO₂-sel), and
293 most channel of active carbon was not dominated by the titanium dioxide [31]. The mesoporous
294 carbon with appropriate content may contribute to RhB molecules gather around TiO₂ particles in
295 low concentration solution of RhB, which improve the photocatalytic degradation process.
296 Therefore, the role of carbon pore structures is very important, which facilitate the diffusion of
297 RhB reactants and products on the TiO₂ active sites during the photocatalytic reaction. Similarly,
298 Pastravanu et al. [29] reported that even after 170 min of irradiation time, 92% MO was degraded
299 when the sample prepared through 7 min of microwave radiation was used as the photocatalyst;
300 nevertheless, only 42% of dye conversion was achieved in the case of pure TiO₂. The RhB removal
301 efficiencies followed the order of AC/TiO₂-700 W > AC/TiO₂-500 W > AC/TiO₂-300 W >
302 AC/TiO₂-900 W > AC/TiO₂-100 W. Nearly complete RhB photodegradation was further observed
303 when the microwave power was 700 W.

304 In a microwave oven, heat is generated from within the sample through the interaction of
305 microwaves with microwave-susceptible materials [25]. Therefore, the AC core was expected to
306 first interact with the microwaves to generate heat that will be transmitted to the TiO₂ shell,

307 resulting in the formation of the anatase phase (Fig. 1) at a relatively low power of 100 W. When
308 the microwave power exceeded 100 W, the phase of rutile gradually formed. Many studies
309 reported that the mixed-phase TiO₂ (anatase and rutile) exhibits higher photocatalytic activity than
310 the pure phase because of the charge trapping and transfer at the phase interfaces of the mixed
311 TiO₂ [5, 17, 23]. The anatase/rutile ratio is a more important factor in determining the
312 photocatalytic activity of the prepared AC/TiO₂ through the formation of ·OH [21, 32]. With the
313 increase of microwave power, the ratio of anatase/rutile decreased see in Table 1. When the power
314 increased to 700 W, the ratio of anatase/rutile was 47/53, which was beneficial to the formation of
315 ·OH. Lv et al. [22] reported the highest ·OH formation rate was observed when the two phase
316 structures of anatase and rutile phases with a ratio of 57:43. Moreover, all the AC/TiO₂ composites
317 exhibited higher PL intensity than pure TiO₂, suggesting that loading of TiO₂ on the surface of AC
318 was a good route to induce the transfer and separation of the photogenerated charge carriers, which
319 resulted in the increase of ·OH formation (Fig. 9). The following order was the generation rate of
320 ·OH radicals of the catalysts: AC/TiO₂-700 W > AC/TiO₂-500 W > AC/TiO₂-300 W AC/TiO₂-900
321 W > AC/TiO₂-100 W > TiO₂. The result is in accordance with the photocatalytic activities of the
322 photocatalysts in Fig. 8. So, the photocatalytic activity of the photocatalysts could be contributed
323 to amounts of ·OH induced in the reaction system to some extent. The degradation mechanism for
324 the AC/TiO₂ was similarly with the reported by Xiang et al. [23] that the activity of photocatalysts
325 depending on the ·OH. In addition, surface area is another important factor in determining the
326 photocatalytic activity of the prepared AC/TiO₂. The AC/TiO₂-100 W sample remained mostly
327 amorphous TiO₂ which covered on the surface of AC because the maximum temperature reached
328 was low with 30 min radiation. The amount of stable TiO₂ produced increased when the

329 microwave power was increased from 300 to 700 W, which resulted in an increase in TiO₂ loading
 330 on AC (Table 1). The rest of the amorphous TiO₂ detached from AC, thus increasing the exposed
 331 area of the carbon. Therefore, the photocatalytic effect of particles increased with increasing
 332 microwave power as evidenced by the synergistic relationship between AC and TiO₂. When the
 333 microwave power was increased to 900 W, the SBET significantly decreased because the high
 334 temperature induced TiO₂ agglomeration as shown in Fig. 3, resulting in decreased photolysis
 335 efficiency.



336
 337 Fig. 8 RhB remove efficiencies over catalysts under 365 nm UV light (RhB concentration of 30 mg/L).

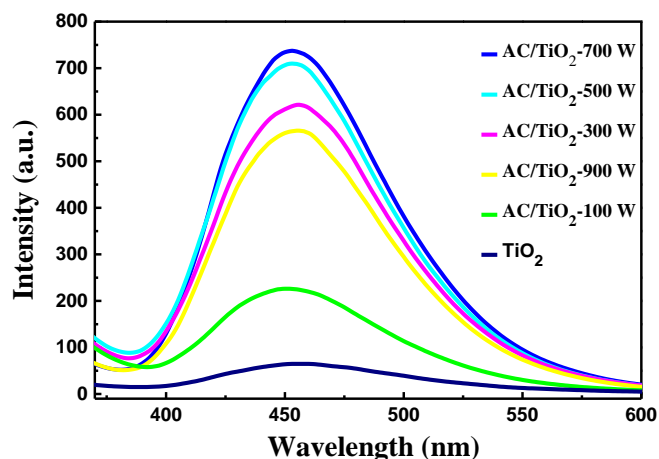
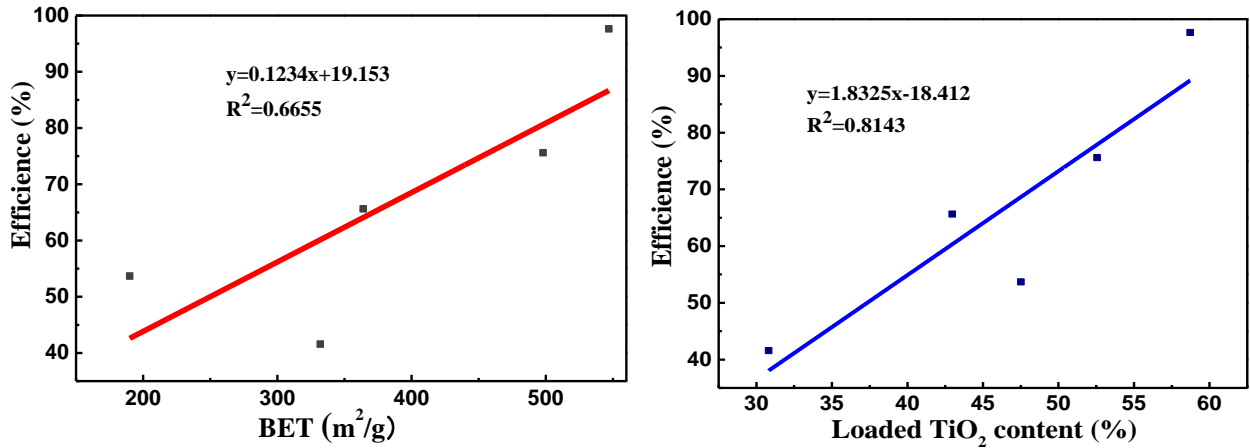


Fig. 9 PL spectra of pure TiO₂ and AC/TiO₂ prepared by different microwave conditions

3.9 Correlation analysis

The photocatalytic reaction process is complex and affected by several factors, such as TiO₂ content, morphology, and SBET. Correlation analysis was further conducted to study the effect of each factor on RhB removal efficiency. Fig. 10 shows that SBET and percentage composition of TiO₂ presented a good linear relationship to RhB removal efficiency in the tested AC/TiO₂ ($R^2=0.6655$ and $R^2=0.8143$). A high surface area of AC/TiO₂ with more TiO₂ content will generally result in high removal efficiency. Previous study showed that AC and TiO₂ has a synergetic effect on the photocatalytic RhB degradation, which could be ascribed to the enhanced adsorption of the pollutants on AC, followed by transfer from the interphase to titania, where the pollutants were photodegraded [19]. On the one hand, a large portion of the AC surface remained unoccupied, which shows that AC/TiO₂ still has very strong adsorptive capacity. Large SBET of the samples may dramatically enlarge the effective reaction surface areas between the photocatalysts and pollutants [5]. On the other hand, increased TiO₂ content could rapidly degrade RhB under irradiation. In addition, the correlation of microwave power (100-700 W) and removal efficiency has been shown in Fig.10 (c), which closed to the linear. So the AC/TiO₂-700 W sample was considered to own the highest photocatalytic activity, which was mainly attributed to the high

356 sorption properties of mesoporous carbon material and high amount of TiO₂. Thus, the surface area
 357 and TiO₂ content of AC/TiO₂ should be as high as possible to improve AC/TiO₂ performance for
 358 RhB photocatalytic degradation.

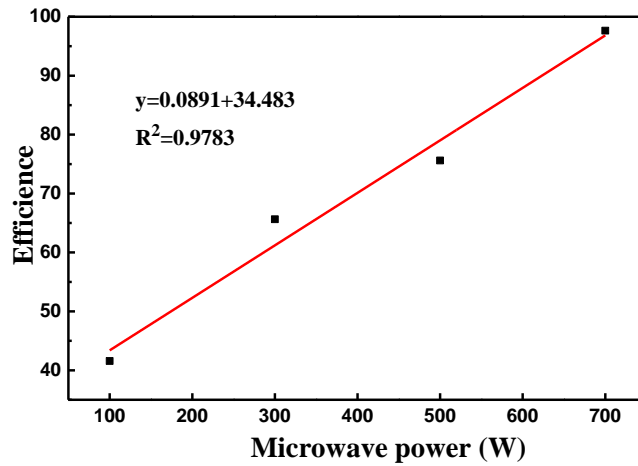


359

360

(a)

(b)



361

362

(c)

363 Fig.10. (a) BET surface area and remove efficiency of RhB (b) loaded TiO₂ content and remove efficiency
 364 of RhB (c) microwave power (100-700 W) and remove efficiency of RhB

365 4. Conclusions

366 In this study, AC/TiO₂ nanocomposites were efficiently prepared using microwave radiation
 367 technology. The proposed method features simplicity, flexibility, short reaction times, and high
 368 photocatalytic efficiency. XRD analysis confirmed that TiO₂ nanoparticles are anatase and rutile

369 with a particle size of 20–50 nm. The SEM and TEM analyses indicated that TiO₂ nanoparticles
370 are spherical in shape and well distributed on the AC surface. The SBETs of the AC/TiO₂
371 composites decreased with increasing TiO₂ loading, but a large portion of the AC surface remained
372 unoccupied. From the UV-vis spectrum, an obvious red-shift was observed when TiO₂ coated the
373 AC surface. The efficiency of the samples followed the order: AC/TiO₂-700 W > AC/TiO₂-500
374 W > AC/TiO₂-300 W > AC/TiO₂-900 W > AC/TiO₂-100 W > TiO₂, which was related to the
375 formation rate of ·OH. For AC/TiO₂-700 W, the removal efficiency of RhB reached to 98% after 30
376 min of UV irradiation. The high surface area with high TiO₂ content of AC/TiO₂ showed good RhB
377 photocatalytic degradation. The proposed method for preparation of photocatalysts with improved
378 structural features and excellent photocatalytic effect can be easily implemented and is economical,
379 and the resulting composite can be potentially applied in water pollution treatment.

380

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