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# Microwave-induced crystallization of AC/TiO<sub>2</sub> for improving the performance of Rhodamine B dye degradation

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

## 20 1. Introduction

21 Water pollution has become one of the most serious problems of our society. Organic 22 poisonous contaminants including xanthene dyes are of the most harmful water pollutants.

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

31 Semiconductor photocatalysts are the most cost-optimal, effective, and environment friendly material for applications directed toward energy and environmental concerns [8-10]. Among these 32 photocatalysts, titanium dioxide (TiO<sub>2</sub>) is widely used in heterogeneous photocatalysis to degrade 33 34 organic pollutants in water and air because it features nontoxicity, chemical and biological inertness, and low cost [11-16]. TiO<sub>2</sub> nanoparticles are generally synthesized through different 35 methods, such as hydrothermal, sol-gel, and electrochemical [17-18]. These methods involve a 36 conventional thermal treatment process using a high-temperature furnace for annealing [19-22]. 37 Nevertheless, heating a furnace consumes a high amount of energy and time. In this regard, 38 microwave-hydrothermal technique, as a novel and fast method, has attracted much interest in 39 recent years [23]. Microwaves exhibit potential for various applications and the use of microwaves 40 provides a fast heating process, thereby saving energy and money and shortening synthesis time 41 [24, 25]. Chen et al. [26] reported that the reaction time for TiO<sub>2</sub> crystallization decreased from 16 42 43 h via the hydrothermal process to 80 min via microwave irradiation.

44 In most of the cases, the degradation efficiency of  $TiO_2$  is relatively low in practical

application because of its small surface area and the poor adsorption of organic poisonous 45 contaminants onto it [27, 28]. TiO<sub>2</sub> supported on activated carbon that provided the crystalline 46 47 framework to support TiO<sub>2</sub> nanoparticles, has been adopted in removal of organic contaminants. Pastravanu et al. [29] synthesized TiO<sub>2</sub>-coated carbon samples that exhibited high photocatalytic 48 49 activity, such that 92% of methyl orange (MO) was degraded after 170 min of UV irradiation. The studies showed that the microwave-assisted synthesis requires a shorter reaction time than 50 conventional methods. Nevertheless, to the best of our knowledge, limited studies have used 51 microwave radiation to synthesize AC/TiO<sub>2</sub> for rapid photocatalysis of RhB. Furthermore, no 52 53 studies have reported the effects of microwave conditions on the properties of TiO<sub>2</sub> loaded on AC and on the catalytic performance of AC/TiO<sub>2</sub>. 54

In this study, AC/TiO<sub>2</sub> was synthesized via a simple, fast, and efficient one-step method under different microwave conditions. Brunauer–Emmett–Teller (BET) surface area, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared (FTIR) spectroscopy, and UV-vis diffusion reflection spectroscopy (DRS) were utilized to assess the photocatalytic performance of the enhanced catalyst. In addition, photocatalytic degradation of RhB by AC/TiO<sub>2</sub> and bare TiO<sub>2</sub> was evaluated under different microwave powers.

62 **2. Materials and methods** 

### 63 2.1 Preparation of AC/TiO<sub>2</sub>

AC was prepared based on our precious study [30]. It was using a microwave oven (MM823LA6-NS, Midea) at a frequency of 2.45 GHz. A mixture of solid KOH (10 g) and dried coal at a ratio of 1:1 was placed in a quartzose tube in a microwave reactor and activated under vacuum atmosphere at 693 W for 10 min. The KOH is intercalated to the carbon matrix responsible for both stabilization and widening of the spaces between the carbon atomic layers. Metallic potassium formed during redox reaction can be intercalated into the carbon walls independently of the structural order responsible for separation and degradation of graphitic layers thus develop the microporosity and mesoporosity. The obtained AC samples were pretreated by adding into HNO<sub>3</sub> solution with 24 h. The mixture was filtered using distilled water until they became neutral. The pretreated AC was then dried and stored until use.

The TiO<sub>2</sub> gel/sol was obtained by conventional sol-gel method. All reagents were of analytical grade and used without further purification. In typical synthesis process, 30 mL of tetrabutyl orthotitanate (TBOT) was dissolved in anhydrous alcohol (EtOH) in proportion of 1:1 (volume ratio). This solution was thoroughly stirred for 40 min and named solution A. Solution B was prepared by mixing 14 mL of glacial acetic acid and 7 mL of distilled water in 35 mL of absolute alcohol. Solution B was added to solution A dropwise and continuously stirred for 1 h. Then it was obtained pale yellow clear TiO<sub>2</sub> sol.

AC/TiO<sub>2</sub> nanoparticles were prepared as follows. Pretreated AC (10 g) was added into TiO<sub>2</sub> sol (100 g) [31]. The mixture was placed in an oven at 100 °C for 24 h. After solidification, AC/TiO<sub>2</sub> was prepared under different microwave conditions: irradiation at 100 W for 30 min or at 300–900 W for 15 min based on results of preliminary experiment, the microwave oven followed a working cycle of 6 s on and 24 s off (20% power). The resulted samples were noted as AC/TiO<sub>2</sub>-100 W, AC/TiO<sub>2</sub>-300 W, AC/TiO<sub>2</sub>-500 W, AC/TiO<sub>2</sub>-700 W and AC/TiO<sub>2</sub>-900 W.

87 2.2 Catalyst characterization

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

diffractometer. Each sample powder was scanned using  $Cu-K\alpha$  radiation with an operating voltage 89 of 40 kV and an operating current of 200 mA. The scan rate of 5°/min was applied to record the 90 patterns in the range of 10-80° at a step of 0.02°. XPS analysis of samples was conducted using a 91 PHI5700 ESCA system equipped with a Mg  $K\alpha$  X-ray source (1253.6 eV) under a vacuum 92 pressure <10<sup>-6</sup> Pa. Pass energy was set as 187.85 and 29.35 eV for the survey and high-resolution 93 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/TiO<sub>2</sub> were characterized through SEM (S4800, Hitachi LTD) at an accelerating voltage of 15 kV. TEM was performed on a 96 97 Tecnai G2 F20 microscope at 100 kV. FTIR spectra were recorded with a Bruker Vertex FTIR spectrometer, resolution of 2 cm<sup>-1</sup>, in the range of 4000-400 cm<sup>-1</sup> by KBr pellet technique. The 98 UV-vis DRS were obtained with a powder UV-vis spectrophotometer (U-4100, Hitachi LTD). 99 Specific surface area (SBET,  $m^2 \cdot g^{-1}$ ) was calculated using the BET equation, and total pore volume 100  $(V_t, m^3 \cdot g^{-1})$  was evaluated by converting the adsorption amount at  $P/P_0 = 0.95$  to the volume of 101 liquid adsorbate. Micropore volume, micropore surface area, and external surface area were 102 determined using t-plot method. Average pore size (r, A) was estimated with the following 103 equation: 104

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

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

### 110 **2.3 Photocatalytic activity for RhB degradation**

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Photocatalytic experiments were performed to investigate UV-assisted degradation of RhB solution by AC/TiO<sub>2</sub> at room temperature by using a 1000 W UV lamp with 365 nm wavelength. In a typical test, 0.01 g of catalyst was added to 50 mL of RhB solution (30 mg/L, pH=6.8). The mixture was kept in the dark for 30 min to allow adsorption of RhB on the AC/TiO<sub>2</sub> surface. The mixture was then irradiated under UV lamp to degrade RhB. The distance between the reactor and lamp housing is 8.5 cm.

117 The removal rate  $(\eta)$  of RhB can be calculated as follows:

118 
$$\eta = \frac{C_{o} - C_{t}}{C_{o}} \times 100 \tag{2-2}$$

119 where  $C_0$  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**

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

Fig. 1 shows that after 100 W of microwave radiation, the XRD peaks of the TiO<sub>2</sub> anatase phase could be detected in the powder sample without other phase. When the microwave power was increased, the mixed crystals of anatase [JCDPS No. 21-1272] and rutile [JCDPS No. 21-1276] [11] were observed (Fig. 1 (b)-(e)). The anatase to rutile phase transformation is generally

considered as nucleation growth process during which the rutile nuclei are formed within the 133 anatase phase [4]. Thus, various crystallite size of anatase can be obtained in the formation process 134 135 of rutile under different prepared condition. With an increase of the microwave power from 300 W to 900 W, the content of rutile increased see in Table 1. As the energy position of the anatase 136 137 conduction band edge is higher than that of rutile, the photogenerated electrons migrate from anatase to rutile and the positive holes migrate from rutile to anatase. Hence, low electron-hole 138 recombination can enhance the photocatalytic activity of the mixed-phase TiO<sub>2</sub>. When the 139 microwave power was increased, the degree of crystallinity in the structural order also increased 140 141 (narrower peaks) [8], while no further improvement was observed at power exceeding 700 W. As photoreactivity requires a balance among crystallinity, specific surface area, and porosity, we 142 prepared amorphous TiO<sub>2</sub> gel through fast microwave crystallization and improved the crystallinity 143 144 of TiO<sub>2</sub> spheres with minimal loss in the SBET and porosity. Compared with as-synthesized TiO<sub>2</sub> (for 700 W with 15 min), AC/TiO<sub>2</sub>-700 W show the same peaks. Thus, combination with AC does 145 not influence the crystal structure of the host TiO<sub>2</sub> material. The XRD results demonstrated that 146 147 microwave is a promising synthesis technique to enhance the crystallinity of AC/TiO<sub>2</sub>.





Fig. 1 XRD patterns of AC, TiO<sub>2</sub> (for 700 W with 15 min) and AC/TiO<sub>2</sub>: (a) AC/TiO<sub>2</sub>-100 W, (b)

AC/TiO<sub>2</sub>-300 W, (c) AC/TiO<sub>2</sub>-500 W, (d) AC/TiO<sub>2</sub>-700 W, (e) AC/TiO<sub>2</sub>-900 W. A: anatase crystalline phase of TiO<sub>2</sub> and R: rutile crystalline phase of TiO<sub>2</sub>.

152 **3.2 BET** 

153 Surface areas and pore size distribution of the samples were determined through N<sub>2</sub> sorption measurements. SBET,  $V_t$ , and mean pore diameter ( $d_{mean}$ ) obtained from N<sub>2</sub> adsorption/desorption 154 155 measurements are presented in Table 1. Pure AC presented large SBET and Vt, whereas AC/TiO<sub>2</sub> demonstrated decreased SBET of more than 50% and decreased Vt. This phenomenon could be due 156 to the generated TiO<sub>2</sub> crystals and other solid matter that covered the AC surface and blocked the 157 pore structure. The BET surface of AC/TiO<sub>2</sub> evidently increased when the microwave power 158 159 increased from 100 to 700 W. This phenomenon is probably due to sublimation of the covered solid matter which reduced the blocked surface of AC, thereby increasing the exposed surface area. 160 When the microwave power was increased to 900 W, the SBET of AC/TiO<sub>2</sub> decreased because the 161 162 reunion of titanium dioxide crystals and collapse of the AC structure induced by high temperatures. Fig. 2 shows the N<sub>2</sub> adsorption–desorption isotherms of uncoated and TiO<sub>2</sub>-coated AC and the 163 pore size distribution (inset) calculated by BJH method. A unimodal distribution centralized at 164 165 3.8 nm was observed in AC and AC/TiO<sub>2</sub> (300–900 W) powders, whereas AC/TiO<sub>2</sub>-100 W showed very small mesopores of approximately 3.414 nm. This characteristic could be due to incomplete 166 crystal formation of TiO<sub>2</sub> sol at a low microwave power (100 W). Although AC and AC/TiO<sub>2</sub> 167 showed similar peaks, the latter presented significantly lower intensity, indicating that the carbon 168 pore entrance was blocked by TiO<sub>2</sub> nanoparticles. Data on average pore diameter indicated that all 169 prepared photocatalysts are mesoporous materials. The mesoporosity of AC/TiO<sub>2</sub> was significantly 170 171 reduced when the microwave power was increased to 900 W, which could be due to the destroyed AC pores. 172

173	According to IUPAC classification, the N <sub>2</sub> adsorption isotherms of the samples are essentially
174	of type IV with a type-H <sub>4</sub> 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/TiO <sub>2</sub> exhibited almost the
177	same shape with a small difference in N <sub>2</sub> 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 TiO <sub>2</sub> deposition, the hysteresis shape tended toward an H <sub>2</sub> -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].

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Table 1 The characterization results of different samples

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

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 TiO<sub>2</sub> determined from TEM.

189 f Phase ratio of anatase and rutile.

190 g Percentage composition of  $TiO_2$  calculated by ash method



**Relative pressure, p/p**<sub>0</sub>

Fig. 2 Nitrogen adsorption-desorption BET isotherms and pore size distribution curves (inset) of AC andAC/TiO<sub>2</sub>.

### 194 **3.3 SEM**

The morphology of the synthesized samples was examined through SEM, and the typical SEM micrographs of AC,  $TiO_2$ , and  $AC/TiO_2$  are shown in Fig. 3. The uncoated AC particle surface was smooth. By contrast, for  $AC/TiO_2$ ,  $TiO_2$  particles were distributed on the AC surface 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 covered areas of TiO<sub>2</sub> on the AC surface, although a portion on the AC surface remained 200 unoccupied as shown in the lower magnification micrograph on the left side of Fig. 3; this finding 201 is consistent with BET results. The high-magnification images on the right side of Fig. 3 indicate 202 203 that the synthesized TiO<sub>2</sub> features 20 to 50 nm size and a spherical shape. When the microwave 204 power was increased from 100 to 700 W, more TiO<sub>2</sub> particles formed on the AC surface. Under microwave preparation conditions of 700 W for 15 min, photocatalytic particles were relatively 205 uniform, spherical in shape, and better dispersed on AC. And compared with TiO<sub>2</sub>, the coated-TiO<sub>2</sub> 206 207 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 TiO<sub>2</sub> particle was highly agglomerated due to the low stability of the small-sized particles, and leading to the TiO<sub>2</sub> gather on the surface of 209 210 AC.



# Fig. 3 SEM of AC, TiO<sub>2</sub> and AC/TiO<sub>2</sub>: (a) AC/TiO<sub>2</sub>-100 W, (b) AC/TiO<sub>2</sub>-300 W, (c) AC/TiO<sub>2</sub>-500 W, (d) AC/TiO<sub>2</sub>-700 W, (e) AC/TiO<sub>2</sub>-900 W.

214 **3.4 TEM** 

Fig. 4 shows the TEM micrographs of AC/TiO<sub>2</sub> samples recorded under different 215 magnifications. Under low magnification, the TEM micrograph showed spherical TiO<sub>2</sub> particles 216 217 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 TiO<sub>2</sub> crystals are distributed as follows: (a) 10-15 nm, (b) 20-50 nm, (c) 40-50 nm, (d) 15-20 nm, and (e) 40-50 nm; these 219 findings are consistent with the XRD results. Only a small amount of TiO<sub>2</sub> particles formed on the 220 221 AC surface at a microwave power of 100 W for 30 min, and the particle size of TiO<sub>2</sub> is very small with an unstable morphology and structure. Thus, a very low microwave power is not conducive to 222 the formation of the TiO<sub>2</sub> core-shell structure. The amount of TiO<sub>2</sub> particles loaded on AC 223 224 increased when the microwave power increased from 100 to 700 W (Table 1). The images showed that TiO<sub>2</sub> nanoparticles are uniform in size and shape, free from aggregation, and well-dispersed on 225 AC when the preparation power was 700 W. However, when the microwave power was increased 226 227 to 900 W, TiO<sub>2</sub> spheres with close interconnection showed serious agglomeration. Thus, the AC/TiO<sub>2</sub>-700 W photocatalyst could provide the free surface of AC for dye adsorption on the 228 229 microspheres, and the transfer of the dye around TiO<sub>2</sub> resulted in enhanced dye degradation.





# **3.5 FTIR**

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

shows the FTIR spectra of AC and AC/TiO<sub>2</sub> nanocomposites in the spectral region from 450 to 235 4000 cm<sup>-1</sup>. The strong peak of the AC/TiO<sub>2</sub> nanocomposites around 3425 and 2360 cm<sup>-1</sup> are 236 attributed to asymmetric stretching vibration of O–H, which are similar to those of the AC samples. 237 This finding indicates that no dehydroxylation occurred during formation of AC/TiO<sub>2</sub> 238 239 nanocomposites. The improved hydrophilicity and wettability of the mesoporous carbon are advantageous for organic adsorption from aqueous solutions [28]. The main reason for this benefit 240 may be that the very short heating time and the activity of rapid resolidification of molten phases, 241 in conjunction with the aqueous environment, avoids the dehydroxylation of AC. The comparison 242 243 of the curves of AC and AC/TiO<sub>2</sub> and FTIR results suggest that the formation of titania nanoparticles in the AC/TiO<sub>2</sub> nanocomposites did not alter the structure or phase of the AC crystals. 244 The broad absorption band in the range of 400–800 cm<sup>-1</sup> characterizes the Ti–O and Ti–O–Ti 245 246 vibration of anatase, which confirms the formation of TiO2. Moreover, the appearance of bands at 1080 cm<sup>-1</sup> indicates the clear formation of the Ti–O–C bonds, suggesting that TiO<sub>2</sub> binds to the 247 mesoporous carbon surface [29]. 248



Fig. 5 FTIR spectra of AC and AC/TiO<sub>2</sub>: (a) AC/TiO<sub>2</sub>-100 W, (b) AC/TiO<sub>2</sub>-300 W, (c) AC/TiO<sub>2</sub>-500 W, (d)
 AC/TiO<sub>2</sub>-700 W, (e) AC/TiO<sub>2</sub>-900 W.

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252 **3.6 XPS** 

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



261

262

Fig. 6 XPS of Ti 2p in TiO<sub>2</sub> and AC/TiO<sub>2</sub>-700 W.

### 263 **3.7 UV-vis spectra**

The UV-vis DRS of TiO<sub>2</sub> (prepared for 700 W with 15 min) and AC/TiO<sub>2</sub> samples are shown in the inset Fig. 7. With TiO<sub>2</sub> loaded on AC, the absorbance in the visible region was enhanced. Pure TiO<sub>2</sub> showed an intrinsic absorption with light wavelength shorter than 390 nm and almost no absorption in visible light with wavelength ranging from 400 to 800 nm. This adsorption is mainly attributed to the inter-band transition of TiO<sub>2</sub> [11]. The light absorption edge of

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







Fig. 7 Diffuse reflectance absorption spectra of  $TiO_2$  and  $AC/TiO_2$ -700 W.

### 280 **3.8 Photocatalytic activity**

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

(direct photolysis). The pure photolytic removal efficiency of the as-synthesized TiO<sub>2</sub> sample (for 285 700 W with 15 min) was 18.52%, and the adsorption efficiency of AC was 20%, exclusive of the 286 30 min dark reaction. The removal efficiency of AC/TiO<sub>2</sub> composite samples presented high 287 photolytic removal efficiency that ranged from 37 to 95% (Fig. 8 (inset)). TiO<sub>2</sub> loaded on AC 288 exhibited very high photocatalytic degradation efficiency compared with AC and pure TiO<sub>2</sub>. The 289 290 substantially decrease in RhB concentration in the aqueous solution can occur in a physical-chemical phenomenon, such as adsorption by AC and photocatalytic decomposition by 291 TiO<sub>2</sub>. The activated carbon played a role of adsorption at the ratio 1:10 (AC and TiO<sub>2</sub>-sel), and 292 293 most channel of active carbon was not dominated by the titanium dioxide [31]. The mesoporous carbon with appropriate content may contribute to RhB molecules gather around TiO<sub>2</sub> particles in 294 low concentration solution of RhB, which improve the photocatalytic degradation process. 295 296 Therefore, the role of carbon pore structures is very important, which facilitate the diffusion of RhB reactants and products on the TiO<sub>2</sub> active sites during the photocatalytic reaction. Similarly, 297 Pastravanu et al. [29] reported that even after 170 min of irradiation time, 92% MO was degraded 298 when the sample prepared through 7 min of microwave radiation was used as the photocatalyst; 299 nevertheless, only 42% of dye conversion was achieved in the case of pure TiO<sub>2</sub>. The RhB removal 300 efficiencies followed the order of AC/TiO2-700 W > AC/TiO2-500 W > AC/TiO2-300 W > 301  $AC/TiO_2-900 \text{ W} > AC/TiO_2-100 \text{ W}$ . Nearly complete RhB photodegradation was further observed 302 when the microwave power was 700 W. 303

In a microwave oven, heat is generated from within the sample through the interaction of microwaves with microwave-susceptible materials [25]. Therefore, the AC core was expected to first interact with the microwaves to generate heat that will be transmitted to the  $TiO_2$  shell,

307 resulting in the formation of the anatase phase (Fig. 1) at a relatively low power of 100 W. When the microwave power exceeded 100 W, the phase of rutile gradually formed. Many studies 308 309 reported that the mixed-phase TiO<sub>2</sub> (anatase and rutile) exhibits higher photocatalytic activity than the pure phase because of the charge trapping and transfer at the phase interfaces of the mixed 310 311 TiO<sub>2</sub> [5, 17, 23]. The anatase/rutile ratio is a more important factor in determining the 312 photocatalytic activity of the prepared AC/TiO<sub>2</sub> through the formation of  $\cdot$ 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 structures of anatase and rutile phases with a ratio of 57:43. Moreover, all the AC/TiO<sub>2</sub> composites 316 exhibited higher PL intensity than pure TiO<sub>2</sub>, suggesting that loading of TiO<sub>2</sub> on the surface of AC 317 was a good route to induce the transfer and separation of the photogenerated charge carriers, which 318 319 resulted in the increase of ·OH formation (Fig. 9). The following order was the generation rate of ·OH radicals of the catalysts:  $AC/TiO_2$ -700 W >  $AC/TiO_2$ -500 W >  $AC/TiO_2$ -300 W  $AC/TiO_2$ -900 320 321  $W > AC/TiO_2-100 W > TiO_2$ . The result is in accordance with the photocatalytic activities of the photocatalysts in Fig. 8. So, the photocatalytic activity of the photocatalysts could be contributed 322 323 to amounts of ·OH induced in the reaction system to some extent. The degradation mechanism for the AC/TiO<sub>2</sub> was similarly with the reported by Xiang et al. [23] that the activity of photocatalysts 324 325 depending on the OH. In addition, surface area is another important factor in determining the photocatalytic activity of the prepared AC/TiO<sub>2</sub>. The AC/TiO<sub>2</sub>-100 W sample remained mostly 326 amorphous TiO<sub>2</sub> which covered on the surface of AC because the maximum temperature reached 327 was low with 30 min radiation. The amount of stable TiO<sub>2</sub> produced increased when the 328

microwave power was increased from 300 to 700 W, which resulted in an increase in  $TiO_2$  loading on AC (Table 1). The rest of the amorphous  $TiO_2$  detached from AC, thus increasing the exposed area of the carbon. Therefore, the photocatalytic effect of particles increased with increasing microwave power as evidenced by the synergistic relationship between AC and  $TiO_2$ . When the microwave power was increased to 900 W, the SBET significantly decreased because the high temperature induced  $TiO_2$  agglomeration as shown in Fig. 3, resulting in decreased photolysis efficiency.



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



Fig. 9 PL spectra of pure TiO<sub>2</sub> and AC/TiO<sub>2</sub> prepared by different microwave conditions

#### 340

**3.9 Correlation analysis** 

The photocatalytic reaction process is complex and affected by several factors, such as TiO<sub>2</sub> 341 content, morphology, and SBET. Correlation analysis was further conducted to study the effect of 342 each factor on RhB removal efficiency. Fig. 10 shows that SBET and percentage composition of 343 TiO<sub>2</sub> presented a good linear relationship to RhB removal efficiency in the tested AC/TiO<sub>2</sub> 344 345 ( $R^2$ =0.6655 and  $R^2$ =0.8143). A high surface area of AC/TiO<sub>2</sub> with more TiO<sub>2</sub> content will generally result in high removal efficiency. Previous study showed that AC and TiO<sub>2</sub> has a synergetic effect 346 on the photocatalytic RhB degradation, which could be ascribed to the enhanced adsorption of the 347 pollutants on AC, followed by transfer from the interphase to titania, where the pollutants were 348 photodegraded [19]. On the one hand, a large portion of the AC surface remained unoccupied, 349 which shows that AC/TiO<sub>2</sub> still has very strong adsorptive capacity. Large SBET of the samples 350 may dramatically enlarge the effective reaction surface areas between the photocatalysts and 351 pollutants [5]. On the other hand, increased TiO<sub>2</sub> content could rapidly degrade RhB under 352 irradiation. In addition, the correlation of microwave power (100-700 W) and removal efficiency 353 354 has been shown in Fig.10 (c), which closed to the linear. So the AC/TiO<sub>2</sub>-700 W sample was considered to own the highest photocatalytic activity, which was mainly attributed to the high 355

sorption properties of mesoporous carbon material and high amount of  $TiO_2$ . Thus, the surface area and  $TiO_2$  content of AC/TiO<sub>2</sub> should be as high as possible to improve AC/TiO<sub>2</sub> performance for



358 RhB photocatalytic degradation.



In this study, AC/TiO<sub>2</sub> nanocomposites were efficiently prepared using microwave radiation technology. The proposed method features simplicity, flexibility, short reaction times, and high photocatalytic efficiency. XRD analysis confirmed that  $TiO_2$  nanoparticles are anatase and rutile

with a particle size of 20-50 nm. The SEM and TEM analyses indicated that TiO<sub>2</sub> nanoparticles 369 are spherical in shape and well distributed on the AC surface. The SBETs of the AC/TiO2 370 composites decreased with increasing TiO<sub>2</sub> loading, but a large portion of the AC surface remained 371 unoccupied. From the UV-vis spectrum, an obvious red-shift was observed when TiO<sub>2</sub> coated the 372 373 AC surface. The efficiency of the samples followed the order:  $AC/TiO_2-700 \text{ W} > AC/TiO_2-500$  $W > AC/TiO_2-300 W > AC/TiO_2-900 W > AC/TiO_2-100 W > TiO_2$ , which was related to the 374 formation rate of ·OH. For AC/TiO<sub>2</sub>-700 W, the removal efficiency of RhB reached to 98% after 30 375 min of UV irradiation. The high surface area with high TiO<sub>2</sub> content of AC/TiO<sub>2</sub> showed good RhB 376 377 photocatalytic degradation. The proposed method for preparation of photocatalysts with improved structural features and excellent photocatalytic effect can be easily implemented and is economical, 378 and the resulting composite can be potentially applied in water pollution treatment. 379

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