

## Electronic Supplementary Material (ESI)

### Enhanced photocatalytic activity of porous TiO<sub>2</sub> containing C/P/K derived from grapefruit peel

Ruixiang Wu, <sup>a, b</sup> Wenhua Liu, <sup>\*a</sup> Renao Bai, <sup>b</sup> Xiufang Tian, <sup>b</sup> Weikai Lin, <sup>b</sup> Lejian Li, <sup>b</sup> Qianwei Ke<sup>b</sup>

<sup>a</sup> Guangdong Provincial Laboratory of Marine Biotechnology, Institute of Marine Sciences, Shantou University, Guangdong 515063, P.R. China

<sup>b</sup> College of Construction and Ecology, Shantou Polytechnic, Guangdong 515078, P.R. China

\*Corresponding authors: Wenhua Liu, <sup>\*a</sup>

E-mail address: [whliu@stu.edu.cn](mailto:whliu@stu.edu.cn)

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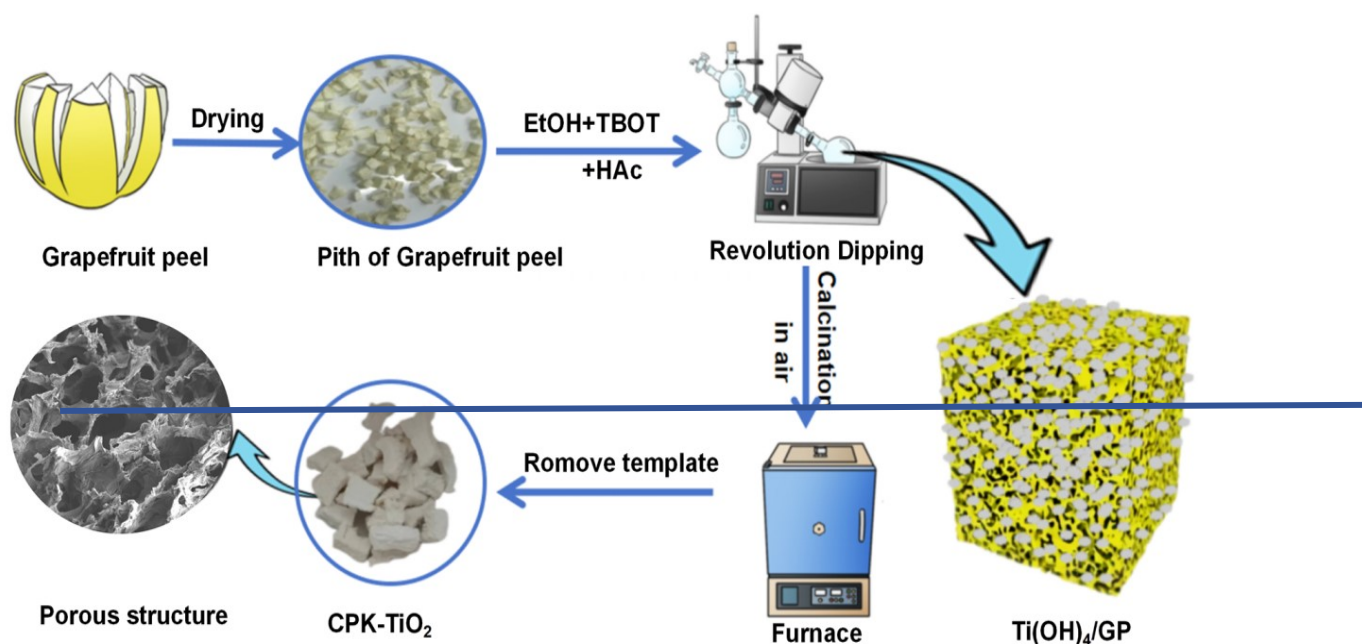
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#### 1. Instrument and equipment

Thermal gravimetric analyzer (TG209F3, NETZSCH Scientific Instruments Trading Ltd); The waring blender (JJ-2; Changzhou Jintan Jingda Instrument Manufacturing Co., Ltd) was utilized in this research. Electronic balance (LC-JA11003), freeze drier (LC-10N), ceramic fiber muffle furnace (LC-RF16-14TP), magnetic stirrer hotplate (LC-MSA-H), desk centrifuge (TGL-LX185C) were acquired from Shanghai LiChen Instrument Technology Co., Ltd. Rotary evaporator (RE-52; Yarong Biochemical Instrument Co., Ltd); UV-Vis spectrophotometer (UV-2500 model; Shimadzu, Japan); UV diffuse reflectance spectrophotometer (UV-3600i Plus; Shimadzu, Japan); X-ray diffractometer

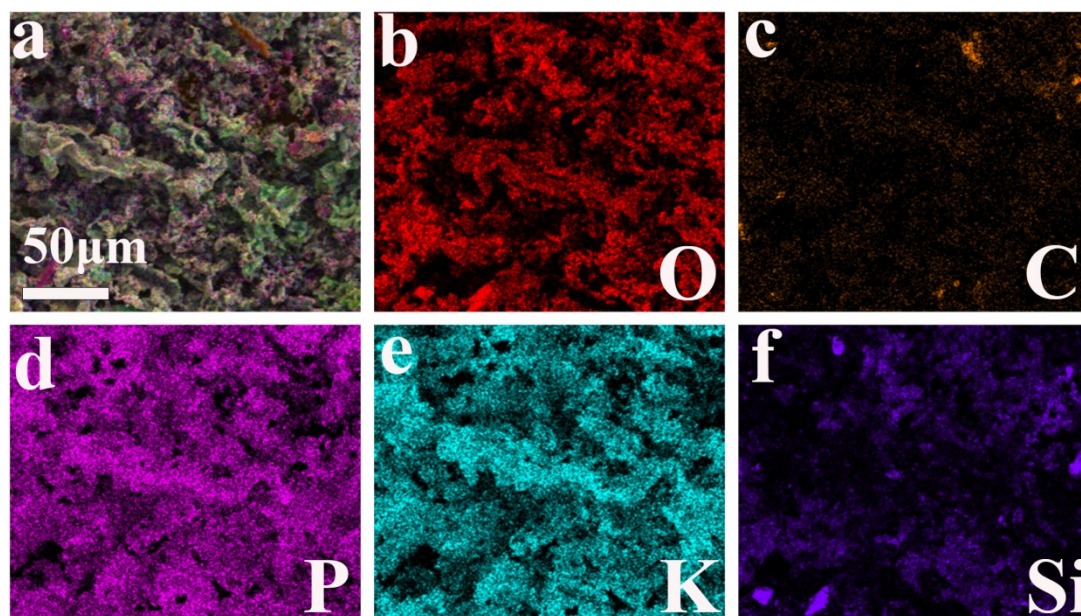
(Ultima VI model; Rigaku Corporation, Japan); Field emission scanning electron microscope (SEM; Gemini SEM450; Carl Zeiss AG, Germany); Field emission transmission electron microscope (TEM; JEM-F200; JEOL, Japan); X-ray photoelectron spectrometer (Thermo Scientific K-Alpha; Thermo Fisher Scientific); Brunauer-Emmett-Teller (BET) surface area analyzer (ASAP 2460; Micromeritics, USA); and mercury lamp (CME-M300, China Microenergy (Beijing) Technology Co., Ltd); Fourier-transform infrared spectroscopy (FTIR, Nicolet iS50, USA); TOC analysis instrument (TOC-L, Shimadzu, Japan); Electron paramagnetic resonance (Bruker EMXnano, Bruker Corporation).

## 2. Diagram of the preparation procedure of the CPK-TiO<sub>2</sub>



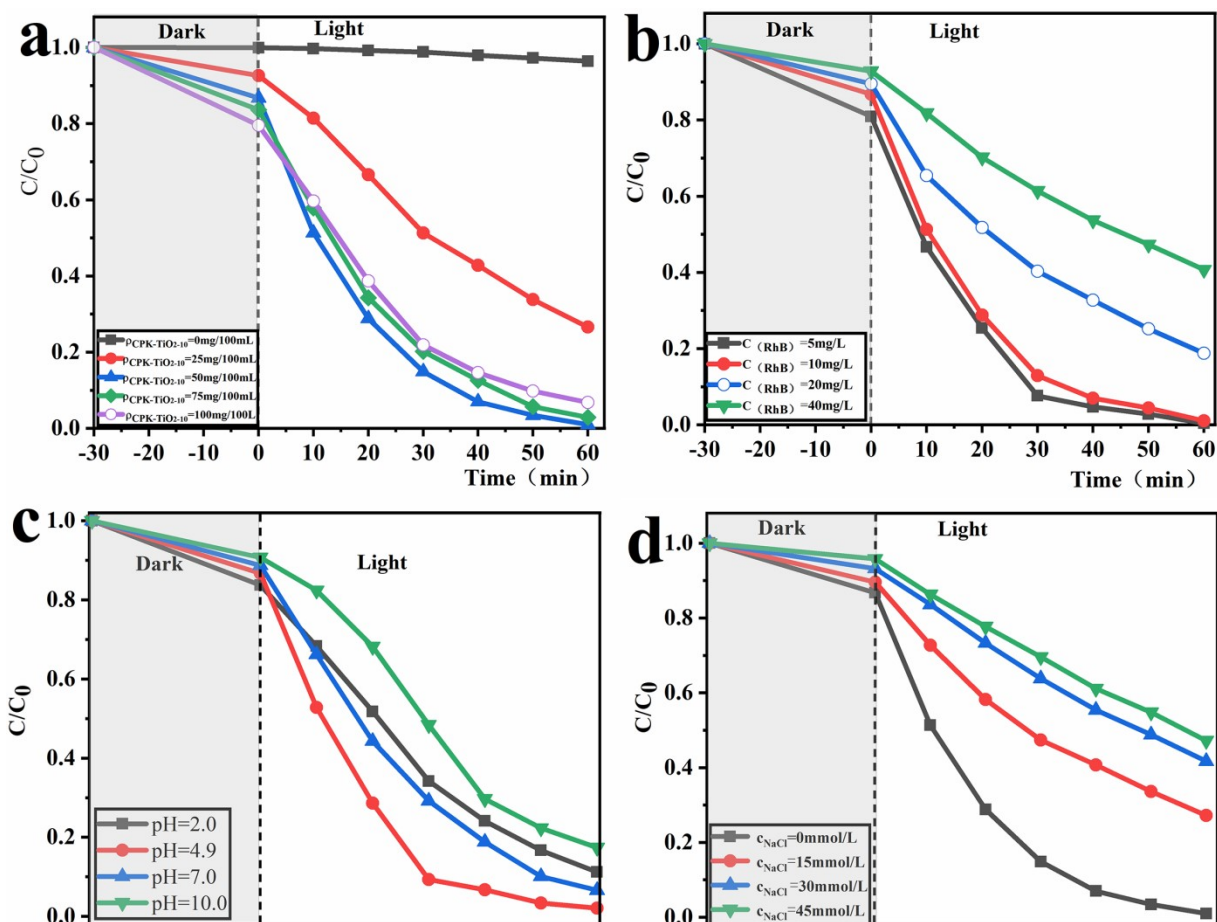
**Schematic. S1.** Diagram of the preparation procedure of the CPK-TiO<sub>2</sub>

peel ash are distributed in the whole area. The EDS energy spectrum of grapefruit peel ash (Fig. S1g) reveals that the weight percent contents of O, C, P and K in this sample are 42.9%, 15.5%, 11.9%, and 11.7%, respectively.



### 3. Analysis of factors affecting photocatalytic degradation of RhB by CPK-TiO<sub>2</sub>-10 sample

To study the impact of reaction parameters on the effect of CPK-TiO<sub>2</sub>-10 photocatalytic degradation of RhB, an examination was conducted on variables such as catalyst addition, initial concentration of RhB solution, initial pH, and salt effect.



### 3.1 Influence of CPK-TiO<sub>2</sub>-10 dosage on photocatalytic performance

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The RhB solution had an initial concentration of 10 mg/L, a volume of 100mL and a pH of approximately 4.9 (original). After dark adsorption at 25 °C for 30 minutes, the reaction system underwent irradiation with a 300 W mercury lamp for 60 minutes. The investigation focused on the impact of different CPK-TiO<sub>2</sub>-10 dosages (0 mg/100mL, 25mg/100mL, 50mg/100mL, 75mg/100mL, 100mg/100mL) on the RhB removal rate. The findings are illustrated in Fig.S2(a). The figure illustrates that the degradation rate of the RhB solution was only 3.8% after 60 minutes of irradiation with a mercury lamp when the dosage of CPK-TiO<sub>2</sub> was 0, indicating the relatively stable nature of the RhB solution. The adsorption rate of RhB escalated from 7.4% to 20.4% as the CPK-TiO<sub>2</sub>-10 dosage increased from 25mg/100mL to 100mg/100mL after 30 minutes adsorption in dark. Furthermore, the degradation rate of RhB first increases and then decreases as the CPK-TiO<sub>2</sub>-10 dosage increased. The degradation rate of RhB escalated from 73.4% to 100% as the CPK-TiO<sub>2</sub>-10 dosage increased from 25mg/100mL to 50mg/100mL after 60 minutes of mercury lamp irradiation. This phenomenon can be ascribed to the substantial increase in active sites on the surface of the catalyst with the elevated CPK-TiO<sub>2</sub>-10 dosage. The notable rise in the generation of photogenerated carriers and active radicals with oxidizing potential on the surface of the catalyst [1] led to a more effective photocatalytic reaction with RhB molecules. Upon increasing the CPK-TiO<sub>2</sub>-10 dosage to 100mg/100mL, the RhB degradation rate decreased to 93.2%. This decline may be attributed to the elevated CPK-TiO<sub>2</sub>-10 dosage leading to increased system turbidity and a subsequent deterioration in light transmittance. This phenomenon weakened the light absorption by CPK-TiO<sub>2</sub>-10, causing a relative reduction in the number of photons reaching the surface of the catalyst, thereby leading to a reduction in the system's photocatalytic activity. Therefore, for the optimal balance between photocatalytic effectiveness and economic benefit, the ideal dosage of CPK-TiO<sub>2</sub>-10 was determined to be 50mg/100mL.

### 3.2 Effect of initial concentration of RhB solution on photocatalytic performance

The volume of RhB solution was 100 mL, the dosage of CPK-TiO<sub>2</sub>-10 was 100mg/100mL, and the

pH was approximately 4.9 (original). After dark adsorption at 25 °C for 30 minutes, the reaction system underwent irradiation with a 300 W mercury lamp for 60 minutes to explore the impact of the initial concentration of RhB solution (5 mg/L, 10 mg/L, 20 mg, and 40 mg/L) on the degradation rate. The selection of RhB concentration was based on the concentration of dyes in the dyeing wastewater at each stage of the plant. After the printing and dyeing process, the concentration of dyes in the wastewater flowing directly from the dye vat was approximately 40 mg/L. The concentration of dyes in the printing and dyeing wastewater, resulting from mixing pretreatment wastewater and other wastewater from the dye-free process, was approximately 10-20 mg/L. In Class III wastewater obtained from primary treatment, the dye concentration was approximately 5 mg/L or so [2].

As depicted in Fig.S2b, after 60 minutes of light exposure, the concentration of RhB solution increased from 5 mg/L to 40 mg/L, and the removal rate of RhB by CPK-TiO<sub>2</sub>-10 decreased from 100% to 59.3%. This observation indicates that the higher the concentration of RhB dye solution, the lower the photocatalytic efficiency. Several factors contribute to this phenomenon. Firstly, as the concentration of RhB dye solution increases, the demand for active species also rises. However, the quantity and rate of active species generated by introducing the same amount of CPK-TiO<sub>2</sub>-10 remain constant, leading to a decrease in the degradation rate. Secondly, the escalating concentration of RhB dye solution induces a masking effect on light, affecting light transmission and diminishing its utilization, thereby reducing the degradation rate.

### **3.3 Impact of initial pH of RhB solution on photocatalytic performance**

The RhB solution had an initial concentration of 10 mg/L, with a volume of 100 mL, and the CPK-TiO<sub>2</sub>-10 dosage was 50mg/100mL. After dark adsorption at 25 °C for 30 minutes, the reaction system underwent a 60-minute irradiation with a 300 W mercury lamp as a light source. The effects of different initial pH values (2.0, 4.9, 7.0, and 10.0) on the removal rate of RhB were then investigated. The pH of the RhB solution was adjusted using HNO<sub>3</sub> and NaOH solutions, and no further adjustments were made during the reaction.

As depicted in Fig.S2c, the removal rate of RhB displayed an initial increasing and then decreasing trend as the initial pH of the reaction system increased from 2.0 to 10.0. Specifically, the sequence of removal rates was pH 4.9 > pH 7.0 > pH 2.0 > pH 10.0, with the optimum pH identified as 4.9 (unmediated original pH). After 60 minutes, the removal rate of RhB reached 100%, while

the removal rates of RhB were 88.8%, 93.4%, and 82.6% at pH 2.0, 7.0, and 10.0, respectively. The primary reason for this variation is the increased  $H^+$  concentration on the surface of CPK-TiO<sub>2</sub>-10 at low pH, leading to a heightened positive charge that hinders the adsorption of RhB cationic dyes by CPK-TiO<sub>2</sub>-10, thereby slowing down the photocatalytic degradation reaction. Conversely, at higher pH levels, the replacement of H with Na in the hydroxyl on the surface of CPK-TiO<sub>2</sub>-10 generates -ONa, reducing the number of hydroxyl groups on the particle surface and diminishing the photocatalytic degradation efficiency. Consequently, the optimal pH for the photocatalytic degradation of RhB by CPK-TiO<sub>2</sub>-10 is determined to be the initial pH of 4.9.

### **3.4 Impact of Salt effect on photocatalytic performance**

Printing and dyeing wastewater carries a certain amount of inorganic salts. Consequently, exploring the impact of the salt effect on the degradation of RhB is of great practical significance. The RhB solution had an initial concentration of 10 mg/L and a volume of 100 mL, and the CPK-TiO<sub>2</sub>-10 dosage was 50mg/ 100mL. After dark adsorption at 25°C for 30 minutes, the reaction system underwent a 60-minute irradiation with a 300 W mercury lamp. The investigation focused on the impact of the salt effect on the removal rate of RhB produced by NaCl. The concentrations of NaCl were: 0 mmol/L, 15 mmol/L, 30 mmol/L, 45 mmol/L.

As evident from Fig. S2d, the introduction of NaCl in the reaction system exhibited an inhibitory effect on the photocatalytic degradation of RhB by CPK-TiO<sub>2</sub>-10. The degradation rate of RhB experienced a reduction ranging from 30% to 50% when the added NaCl concentrations fell within the range of 15-45 mmol/L.

According to reports, cations present in inorganic salts influence the compounding of electron-hole pairs, whereas anions can be adsorbed on the surface of holes, impacting the photocatalytic process. Therefore, Na<sup>+</sup> and Cl<sup>-</sup> produced by NaCl ionization in the reaction system can affect the CPK-TiO<sub>2</sub> photocatalytic effect.

## References

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- 2 P. Ke, Wuhan University of Science and Technology.2022.