



# Article Three-Dimensional Porous ZnO-Supported Carbon Fiber Aerogel with Synergistic Effects of Adsorption and Photocatalysis for Organics Removal

Wubo Wan<sup>1</sup>, Yu Li<sup>1</sup>, Shiwei Bai<sup>1</sup>, Xiaoyan Yang<sup>2,\*</sup>, Mingming Chi<sup>3</sup>, Yaqin Shi<sup>1</sup>, Changhua Liu<sup>3</sup> and Peng Zhang<sup>3,\*</sup>

- <sup>1</sup> Yazhou Bay Innovation Institute, Hainan Tropical Ocean University, Sanya 572022, China; wanwubo@163.com (W.W.); m19814788056@163.com (Y.L.); baisvv4827@163.com (S.B.); shiyaqincelia@163.com (Y.S.)
- <sup>2</sup> Engineering Research Center for Optoelectronic Functional Materials of Henan Province, School of Chemistry and Chemical Engineering, Shangqiu Normal University, Shangqiu 476000, China
- <sup>3</sup> State Key Laboratory of Separation Membranes and Membrane Processes, School of Environmental Science and Engineering, Tiangong University, Tianjin 300387, China; chimingchem@163.com (M.C.); liuchanghua2022@163.com (C.L.)
- \* Correspondence: yxysmall@126.com (X.Y.); pengzhang@tiangong.edu.cn (P.Z.)

Abstract: A three-dimensional (3D) ZnO-supported carbon fiber aerogel (ZnO/CFA) was successfully prepared by using natural cotton with hydrophilicity as the precursor. The facile synthetic strategy includes two steps: Zn<sup>2+</sup> exchange on the surface of cotton and thermal treatment at high temperatures. Particularly, the calcination temperature was found to greatly affect the content, dispersity, and size of supported ZnO nanoparticles, and the product obtained at 600 °C (ZnO/CFA-600) exhibited both high ZnO loading and well-dispersed ZnO nanoparticles. Therefore, ZnO/CFA-600 has superior photocatalytic activity for tetracycline (TC) degradation under UV light irradiation compared with others. Additionally, the unique 3D crosslinking network inside the ZnO/CFA generates an open channel for the rapid migration and diffusion of reactants and products. In a dynamical water-treated system, the 3D porous ZnO/CFA-600 continuously works for TC removal without any separation operation and maintains high synergistic performance of adsorption and photocatalysis for at least 8 h. Consequently, the 3D porous ZnO/CFA product, with its large adsorbability and high photoactivity, shows a lot of industrial potential in wastewater treatments.

Keywords: carbon aerogel; cotton; adsorption; photocatalysis; ZnO

# 1. Introduction

Organic antibiotics are the main pollution sources in pharmaceutical industrial wastewater, which have high toxicity and structural stability and are hardly eliminated by themselves under natural conditions. Although many methods have been developed to treat antibiotic pollution, photocatalysis is believed to be a more green and sustainable technology due to its high efficiency, cheapness, and lack of secondary pollution [1,2]. Under the irradiation of incident light, many semiconductor materials, such as  $TiO_2$  [3,4], ZnO [5], CeVO<sub>4</sub> [6,7], and ZnIn<sub>2</sub>S<sub>4</sub> [8–10], are found to be excited to catalyze the decomposition of organic molecules. For existing photocatalysts, their handling capacity for organics is still too low to be applied in practical wastewater treatments. On the other hand, physisorption features a large organics treatment capacity and a high rate while having noncontinuous operation and the possible generation of secondary pollution [11]. Therefore, it will be exciting to integrate the good adsorbability into photocatalysts with high photoactivity, which will be expected to be an ideal candidate for industrial wastewater purification.

After being hybridized with photocatalysts, carbon materials would transfer their photoinduced electrons to improve the photocatalytic activity of photocatalysts; thus, they



Citation: Wan, W.; Li, Y.; Bai, S.; Yang, X.; Chi, M.; Shi, Y.; Liu, C.; Zhang, P. Three-Dimensional Porous ZnO-Supported Carbon Fiber Aerogel with Synergistic Effects of Adsorption and Photocatalysis for Organics Removal. *Sustainability* 2023, *15*, 13088. https://doi.org/ 10.3390/su151713088

Academic Editor: Cinzia Buratti

Received: 17 July 2023 Revised: 12 August 2023 Accepted: 23 August 2023 Published: 30 August 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). are regarded as good cocatalysts [12]. Meanwhile, the large surface area, porous structure, and hydrophobicity endow carbon materials with a high adsorption capacity and rate for organic contaminants or heavy metal ions [13–17]. Therefore, hybridizing semiconductors with carbon materials seems to be an intelligent strategy to simultaneously enhance the photoactivity and adsorption capacity of photocatalysts such as C/Fe<sub>2</sub>O<sub>3</sub> microflowers [18], Ag@Ag<sub>2</sub>S@C nanocables [19], and C/TiO<sub>2</sub> microspheres [20]. However, owing to being powder samples, those existing carbon-based materials generally have a complicated regeneration process, a low recovery ratio, and high operational costs.

In the last decade, three-dimensional (3D) graphene or C<sub>3</sub>N<sub>4</sub> aerogel materials have been widely developed as the matrix to anchor semiconductor particles, fabricating many 3D carbon-based photocatalysts, such as  $TiO_2/graphene$  [21],  $Ag_3PO_4/graphene$  [22],  $g-C_3N_4$ /graphene hydrogel [23], and polyaniline/ $C_3N_4$  [24]. Compared with powder catalysts, these 3D monolithic carbon-based materials provide many advantages for photocatalytic applications, including the following: (a) A porous carbon matrix increases the adsorbability of 3D photocatalysts for organic pollution to greatly enhance their organics removal efficiency; (b) As a good electron reservoir, a carbon matrix can facilitate the separation of photogenerated carriers via rapidly trapping photoinduced electrons, thus improving the photocatalytic activity [25–27]; (c) More importantly, the unique 3D architecture guarantees the free flow of reaction solutions inside the materials, thus facilitating the rapid diffusion of reactants and products. As a result, these 3D graphene-based and  $C_3N_4$ -based photocatalysts can be freely separated from the reaction solution and exhibit good photocatalytic performance for the removal of various pollutants [28–31]. However, the preparation of graphene and  $C_3N_4$  usually involves the use of a strong acid (for graphene) or toxic organics (for  $C_3N_4$ ) and a time-consuming and complex synthetic route, which significantly limit their economy and large-scale production. Therefore, it is highly desirable to explore a simple, facile, and inexpensive strategy for synthesizing 3D porous carbon-based materials with high adsorbability and photoactivity for the removal of organic pollutants. On the other hand, necessary efforts still need to be devoted to exploring the relationship between the adsorbability and catalytic activity of 3D porous carbon-based photocatalysts.

Herein, we utilize abundant oxygen-containing groups on the surface of cotton to capture  $Zn^{2+}$  in solution [32–34]. Subsequently, high-temperature calcination carbonizes the cotton into a 3D porous carbon fiber aerogel while transforming adsorbed  $Zn^{2+}$  into well-dispersed and nanosized ZnO particles. The adsorption capacity of a 3D fibrous ZnO/C aerogel for tetracycline (TC) removal and its photodegraded performance under UV light irradiation were both investigated in detail.

#### 2. Experimental

#### 2.1. Preparation of Photocatalysts

All reagents used in this work were of analytical grade, while cotton fibers were adopted from Taihang Medical Materials Co., Xingtai, China. Typically, 0.5 g of cotton was totally impregnated in 50 mL of a  $Zn(Ac)_2$  solution (0.1 mol/L) and statically left at room temperature for 24 h. After the  $Zn^{2+}$  adsorption process, the resultant  $Zn^{2+}$  cotton was dried at 80 °C overnight and sealed in a tube furnace, which was then heated at predetermined temperatures for 2 h with an acceleration of 5 °C/min. According to the calcination temperatures of 500 °C, 600 °C, 700 °C, and 800 °C, the corresponding 3D fibrous aerogel products were denoted as ZnO/CFA-500, ZnO/CFA-600, ZnO/CFA-700, and ZnO/CFA-800, respectively.

For comparison, 0.5 g of cotton was soaked in 50 mL of deionized water and carbonized at 600 °C using a standard thermal treatment procedure to yield the carbon fiber aerogel denoted as CFA-600.

#### 2.2. Characterization

The morphology and size of various photocatalysts were observed by a scanning electron microscope (SEM; Hitachi S4800, Tokyo, Japan) and a transmission electron microscope (TEM; Hitachi S-7650, Tokyo, Japan), where 150 individual particles were measured to obtain the size distribution of ZnO nanoparticles in the ZnO/CFA-600. The crystal structure was analyzed by X-ray diffraction with a Cu K $\alpha$  radiation source (XRD; Bruker D8 Advance A25, Billerica, MA, USA) and high-resolution transmission electron microscopy (HRTEM; JEOL JEM-2100F, Japan). The distribution of Zn, O, and C in the ZnO/CFA-600 was observed by energy dispersive spectrometry (EDS; Hitachi S4800, Japan). Fourier transform-infrared (FTIR) spectra were measured on a Thermo Fisher (Waltham, MA, USA) FTIR-650 spectrometer (USA) to explore the carbon structure. Estimations of the carbon content in ZnO/CMF-t aerogels were conducted using a thermogravimetric (TG; Shimadu, DTG-60, Kyoto, Japan) analysis in air, where they were heated from 50 °C to 800 °C at a heating rate of 10 °C/min. Specific surface areas and pore structures could be fitted by the N<sub>2</sub> adsorption–desorption isotherms measured at -196 °C using a Micromeritics ASAP 2020 (Norcross, GA, USA). Before the analysis, various ZnO/CFA-t products were degassed at 250 °C for 5 h.

To investigate the photoelectronic properties of ZnO/CFA-t products, a standard three-electrode system was built in a 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution, which was utilized to measure both their photocurrent response and electrochemical impedance spectroscopy (EIS). Particularly, all photoelectrochemical experiments were performed on an electrochemical workstation (CHI 760E; Chenhua Instruments Co., Shanghai, China), while a platinum wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. To obtain working electrodes, the sample slurry was first prepared by ultrasonically dispersing 4 mg of ZnO/CFA-t powder in 2 mL of ethanol, which was then dipped onto an indium–tin oxide (ITO) glass with a groove (1 × 1 cm). After drying at 80 °C overnight, the sample-ITO glass was heated at 200 °C for 8 h in N<sub>2</sub>, forming the working electrode. Photocurrent response curves were recorded at a constant potential of 0.27 V, while the EIS was measured at 0.0 V with a 5 mV sinusoidal AC perturbation.

# 2.3. Adsorption and Photocatalytic Experiments

# 2.3.1. Static Adsorption

A static adsorption experiment for tetracycline (TC) was carried out in the dark as follows: 15 mg of sample powder was added to 40 mL of a TC aqueous solution (20 mg/L) and magnetically stirred at room temperature. About 3.5 mL of solution was taken out at an interval of 10 min and centrifuged to correct the filtrate, which was tested by a UV-vis spectrophotometer (Thermo Evolution 300). The adsorption capacities of various samples were calculated according to Equation (1):

$$Q_e = (C_0 - C_e) \times V/M \tag{1}$$

where  $Q_e$  (mg/g) is the equilibrium adsorption quantity for TC,  $C_0$  and  $C_e$  (mg/L) are the initial and equilibrium TC absorbance at 375 nm, V (mL) is the volume of TC solution, and M (mg) is the sample mass.

#### 2.3.2. Static Photocatalysis

A total of 15 mg of sample powder was dispersed into 40 mL of a TC aqueous solution (20 mg/L) and magnetically stirred for 30 min in the dark, establishing the adsorption/desorption equilibrium. A high-pressure Hg lamp with 500 W was then turned on to illuminate the reaction mixture. At intervals of 15 min, 3.5 mL of mixture was taken out and immediately centrifuged to remove the residual solid, while the filtrate was analyzed using a UV-vis spectrometer (Thermo Evolution 300). The adsorption and photocatalysis processes of different ZnO/CFA-t products were evaluated by  $C/C_0$ , where  $C_0$  and C referred to the initial and intermediate TC absorbance at 375 nm. The intermediate products of TC

were analyzed by high-performance liquid chromatography–tandem mass spectrometry (HPLCMS; Waters Xevo TQ-S, Waters, Milford, MA, USA).

After the photocatalytic reaction, the used ZnO/CFA-600 was recovered, fully washed with water several times, and dried at 80 °C. To investigate the photostability, the collected ZnO/CMF-600 sample was repeatedly applied for the photodegradation of TC under the catalytic procedure.

#### 2.3.3. Synergy of Adsorption and Photocatalysis in a Flow System

A total of 0.1 g of the 3D ZnO/CFA-600 photocatalyst was loaded into a quartz tube and kept at a loading height of 5 cm. A dynamic water-treated device was set up by vertically fixing the reactor beside the Hg lamp, and the inlet and outlet of the reactor were connected with a peristaltic pump and effluent pool, respectively. When the reaction was beginning, the initial TC solution (5 mg/L) was continuously pumped into the quartz reactor from the top, while the Hg lamp was turned on to provide the UV light. During the dynamic reaction, the treated water was analyzed via a UV-vis spectrophotometer (Thermo Evolution 300) at an interval of 30 min.

#### 3. Results and Discussions

#### 3.1. Morphology and Structure of ZnO/CFA

After the high-temperature treatment, the carbonized product exhibited a monolithic appearance with a fluffy structure and an ultralight weight. As shown in Figure 1a, about 80 mg of this product could stabilize on a Setaria glauca but not crush its capillary structure. For the microscopic morphology, the ZnO/CFA-600 is observed to be composed of spiral fibers with diameters of  $5-10 \mu m$  (Figure 1b). Those micro-sized spiral fibers connect with each other to simultaneously form the three-dimensional (3D) network and interspace. As a result, the resultant product calcined in this work displays an ultralight and fluffy appearance, which would be defined as a 3D carbon fiber aerogel. Meanwhile, the carbonization temperature of 500–800 °C is demonstrated to have an ignored effect on the structure and morphology of corresponding products, resulting from the fact that similar crosslinked fibers could be seen in ZnO/CFA-500, ZnO/CFA-700, and ZnO/CFA-800 (Figure 1d–f).

To figure out the effect of absorbed  $Zn^{2+}$  ions, a contrast sample was also prepared by soaking cotton in deionized water and obtaining a carbon fiber aerogel denoted as CFA-600. In comparison to ZnO/CFA-600, an identical morphology and size of the fibers were generally found in CFA-600 (Figure 1g), suggesting that the absorbed  $Zn^{2+}$  ions barely change the carbonization process of cotton fibers. Nonetheless, the magnifying SEM image of the CFA-600 (Figure 1h) exhibits a smooth surface, which is very different from the ZnO/CFA-600's coarse one (Figure 1c). Obviously, the overadsorption of  $Zn^{2+}$  ions will form large-sized ZnO particles in the high-temperature process to deposit onto the surface of carbon fibers. Additionally, the EDS elemental mapping (Figure 1i) reveals the even distributions of Zn, C, and O. It is concluded that the thermally formed ZnO particles are uniformly supported on the carbon matrix, benefiting from the in situ synthetic method designed in this work.

XRD is utilized to investigate the crystal compositions of various ZnO/CFA-t products, whose corresponding XRD patterns are shown in Figure 2a. A group of diffraction peaks can be clearly seen in the ZnO/CFA-500, ZnO/CFA-600, and ZnO/CFA-700, which are indexed to hexagonal ZnO (JCPDS No. 89-1397) [5]. Particularly, the peak intensity of the ZnO/CFA-600 is higher than that of the ZnO/CFA-500, resulting from the fact that the elevating thermal temperature strengthens the crystallinity of ZnO. However, all XRD peaks are found to be remarkably weakened when the calcination temperature exceeds 700 °C. This result is attributed to the continuous loss of ZnO particles on the carbon matrix with the increasing thermal treatment temperature. As for the ZnO/CFA-800, no diffraction

peak is found in its XRD pattern, indicating that the ZnO content almost vanishes from the ZnO/CFA sample. Under high-temperature conditions, ZnO will react with C as follows:

$$ZnO + C = Zn(g) + CO(g)$$

where the yielded Zn gas is swept away with the carrier gas [35]. Therefore, ZnO loading in the ZnO/CFA product is verified to continually decrease from 600 to 800 °C in the atmosphere of  $N_2$ .



**Figure 1.** (a) Photograph of ZnO/CFA-600 on a Setaria glauca; SEM images of (b,c) ZnO/CFA-600, (d) ZnO/CFA-500, (e) ZnO/CFA-700, (f) ZnO/CFA-800, and (g,h) CFA-600; (i) EDS elemental mapping of ZnO/CFA-600.



Figure 2. (a) XRD patterns and (b) TG analysis in air of various ZnO/CFA-t products.

A TG analysis in air was carried out to confirm the C and ZnO contents of various 3D ZnO/CFA-t products, and the corresponding results are shown in Figure 2b. A rapid weight loss at 400–600 °C could be observed in four TG curves due to the thermodynamic combustion of carbon fibers. When the temperature exceeds 650 °C, the TG curve stays constant until 800 °C, resulting from the fact that the residual ZnO can stably exist in the air. It is concluded that the ZnO loading in the ZnO/CFA samples increases with the calcination temperature below 700 °C and inversely decreases in the range of 700–800 °C. This trend matches well with the XRD analysis above and further certifies the thermal loss of supported ZnO. As shown in Figure 2b and Table 1, only 6.5% of ZnO is calculated to remain in the ZnO/CFA-800, while the ZnO loading of the ZnO/CFA-600 reaches ca. 34.5%.

**Table 1.** ZnO contents, BET surface areas, rate constants, and adsorption capacities of various ZnO/CFA-t products.

Sample	ZnO Content (wt %) <sup>a</sup>	BET Surface Area (m <sup>2</sup> /g)	Rate Constant (k, mol <sup>-1</sup> min <sup>-1</sup> ) <sup>b</sup>	Saturated Adsorption Capacity ( <i>Qe</i> , mg/g)
ZnO/CFA-500	25.2	297.6	$1.54 imes10^{-4}$	3.53
ZnO/CFA-600	34.5	259.9	$2.33 imes10^{-4}$	5.87
ZnO/CFA-700	28.1	357.7	$2.16 imes10^{-4}$	16.46
ZnO/CFA-800	6.5	500.4	$0.62  imes 10^{-4}$	20.09

<sup>a</sup> ZnO content is calculated by TG. <sup>b</sup> The reaction rate constant is obtained by photocatalytic degradation of TC (20 mg/L) over 15 mg of photocatalyst under UV-light irradiation.

The detailed structural variation of four 3D ZnO/CFA-t products was explored by their TEM images. In Figure 3a, many tiny particles are hazily seen on the ZnO/CFA-500, suggesting the preliminary formation of ZnO crystals. When the calcination temperature was increased to 600 °C, the initial ZnO particles grew to nanoscale and were evenly anchored on the carbon fibers, as shown in the TEM image of the ZnO/CFA-600 (Figure 3b). The statistical result (Figure 3c) shows that these ZnO particles have a uniform size in the narrow range of 16–56 nm. The corresponding HRTEM image (Figure 3d) reveals a distinct lattice fringe with a distance of 0.26 nm, attributed to ZnO (002). This result indicates the good crystallinity of ZnO in the ZnO/CFA-600, which is consistent with the XRD analysis above. However, the excessive temperature will destroy the high dispersity and uniformity of supported ZnO nanoparticles, as witnessed on the TEM image of the ZnO/CFA-700 (Figure 3e). Meanwhile, some nanosized pores are also formed on the carbon matrix due to the high-temperature etch of ZnO, as confirmed by the XRD and TG analyses above. When the calcination temperature reaches as high as 800 °C, the deep etch of ZnO produces a large number of pores on the surface of the ZnO/CFA-800 (Figure 3f), while no ZnO particle is clearly seen.



**Figure 3.** TEM images of (**a**) ZnO/CFA-500, (**b**) ZnO/CFA-600, (**e**) ZnO/CFA-700, and (**f**) ZnO/CFA-800; (**c**) Size distribution of ZnO particles in ZnO/CFA-600; (**d**) HRTEM image of ZnO/CFA-600.

The N<sub>2</sub> adsorption–desorption isotherms of four ZnO/CFA-t samples were also measured to investigate the effect of high-temperature calcination on their pore structures and specific surface areas. As shown in Figure 4a, both the high N<sub>2</sub> adsorption quantity at a relative pressure of 0–0.1 and the clear hysteresis loop at a relative pressure of 0.4–0.9 are included in the four isotherms. Obviously, all ZnO/CFA products involved in this work have abundant micropores and mesopores. This porous structure will accelerate substance migration during the reaction process. Compared with the other three samples, the ZnO/CFA-800 shows both a higher N<sub>2</sub> adsorption at a low relative pressure and a larger loop area, indicating that the ZnO etch greatly enlarges the micropore volume and mesopore volume of the carbon matrix. This pore structural variation of the four ZnO/CFA-t composites could be intuitively confirmed by their pore size distributions, as shown in Figure 4b. Moreover, the high-temperature etch of the ZnO nanoparticles also increases the BET surface area of the 3D ZnO/CFA-500, ZnO/CFA-600, ZnO/CFA-700, and ZnO/CFA-800, respectively.



Figure 4. (a)  $N_2$  adsorption-desorption isotherms and (b) pore size distributions of various ZnO/CFA-t products.

In the present study, tetracycline (TC) was chosen to evaluate the adsorption capacity and photocatalytic activity of the as-obtained ZnO/CFA-t products. As shown in Figure 5a, both the CFA-600 and four ZnO/CFA photocatalysts are found to exhibit a rapid adsorption capacity for TC, all of which could reach saturated adsorption within 10 min. From the adsorption isotherms (Figure 5b), it is illustrated that the adsorption capacity of CFA-600 is improved after hybridization with ZnO nanoparticles. As for the 3D ZnO/CFA samples, their saturated adsorption capacities (*Qe*) gradually increase with the calcination temperature, resulting from the high-temperature etch of ZnO and the enlargement of surface area. As summarized in Table 1, the *Qe* of the CFA-600, ZnO/CFA-500, ZnO/CFA-600, ZnO/CFA-700, and ZnO/CFA-800 was calculated to be 1.56, 3.53, 5.87, 16.46, and 20.09 mg/g, respectively.



**Figure 5.** (a) Time-dependent adsorption curves of CFA-600 and ZnO/CFA-t products for TC and (b) their corresponding adsorption isotherms.

The photocatalytic activities of various ZnO/CFA-t composites were investigated for the degradation of TC under UV light irradiation. As shown in Figure 6a, it is clearly seen that the intrinsic absorbance peak of TC at 357 nm red-shifts to 363 nm upon the addition of ZnO/CFA-600 due to the coordination of TC molecules and Zn<sup>2+</sup>. When the photoreaction begins, this feature peak of TC progressively decreases with UV-light-irradiated time, suggesting that ZnO/CFA-600 has good photocatalytic activity. To expediently compare the photocatalytic activity, the  $C/C_0$  variations of various ZnO/CFA-t samples are calculated and directly represented by their photodegradation processes, as shown in Figure 6b. A blank experiment with no catalyst proves that TC molecules cannot be degraded by themselves, and carbon fibers barely have a photocatalytic performance owing to no obvious declining  $C/C_0$  plot with CFA-600. After supporting ZnO nanoparticles, the 3D ZnO/CFA-t products show dramatically improved photodecomposing activity for TC under the illumination of UV light. Particularly, ZnO/CFA-600 and ZnO/CFA-700 possess the highest removal efficiency for TC, both of which can remove ca. 70% of TC. According to the following second-order reaction kinetic equation:

$$\nu = -\mathrm{d}C/\mathrm{d}t = k_1 C^2 \tag{2}$$

$$1/C = k_2 t + b \tag{3}$$

$$C_0/C = C_0 \times k_2 t + C_0 b = kt + m$$
(4)

The kinetic plots of four ZnO/CFA-t photocatalysts could be fitted and show a clear linear relationship between  $C_0/C$  and time (Figure 6c). It is concluded that all photocatalytic processes are second-order reactions, and the corresponding rate constants are summarized in Table 1. Therefore, ZnO/CFA-600 ( $k = 2.33 \times 10^{-4} \text{ mol}^{-1}\text{min}^{-1}$ ) has higher photocatalytic

(



activity than ZnO/CFA-700 ( $k = 2.16 \times 10^{-4} \text{ mol}^{-1}\text{min}^{-1}$ ), whereas the adsorption capacity of ZnO/CFA-700 (Qe = 16.46 mg/g) is superior to ZnO/CFA-600 (Qe = 5.87 mg/g).

**Figure 6.** (a) Time-dependent absorbance of TC solution with ZnO/CFA-600 under UV light irradiation; (b) Photocatalytic degradation of TC with no catalyst, CFA-600, and various ZnO/CFA-t products, and (c) their corresponding kinetic plots; (d) Cycling performance of ZnO/CFA-600 for photodegradation of TC.

A normalized reaction rate (*h*) is defined to compare the photocatalytic activity of the ZnO/CNF-t aerogel with other photocatalysts reported for TC degradation. In terms of the photocatalytic data, *h* of the ZnO/CNF-600 is estimated to be 0.025 g·g<sup>-1</sup>·h<sup>-1</sup> by Equation (5) as follows:

$$h = m_{org} / m_{cat} \cdot t \tag{5}$$

where  $m_{org}$  and  $m_{cat}$  refer to the mass of degraded TC and reacted catalyst. As summarized in Table 2, ZnO/CNF-600 could be determined to have superior photocatalytic performance compared to many recently developed materials.

Table 2. Normalized reaction rates of various reported photocatalysts for TC degradation.

Photocatalyst	$g \cdot g^{-1} \cdot h^{-1}$	Reference
ZnO/CFA-600	0.025	This work
Bi <sub>2</sub> O <sub>3</sub> /CF	0.0032	[19]
ZnO/ZnS/C microsphere	0.006	[36]
Bi <sub>2</sub> O <sub>3</sub> @CeO <sub>2</sub> microsphere	0.006	[37]
Bi <sub>2</sub> O <sub>2</sub> CO <sub>3</sub> microsphere	0.013	[38]
ZnO/ZnS erythrocyte	0.0032	[39]

Furthermore, possible photodegraded products are analyzed by HPLC-MS spectrometry, as shown in Figure 7. Besides the TC molecule with a m/z of 445, several strong peaks at 365, 297, and 279 come from some intermediate organics with small molecular weights, the possible structural formulas of which are also shown in Figure 7. Although the TC pollution is not completely mineralized, its stable structure could be destroyed by photocatalysis to greatly decrease its toxicity.



Figure 7. HPLC-MS spectrum of TC solutions with a reaction time of 90 min.

After the photocatalytic reaction, the ZnO/CFA-600 is recovered, washed, and used for the next cycle to investigate its repeatability and catalytic stability. As shown in Figure 6d, ZnO/CFA-600 generally maintains an identical removal efficiency for TC in four runs, including adsorption capacity and photocatalytic activity. It is determined that the 3D ZnO/CFA-600 photocatalyst has good light resistance and structural stability, which would be expected as an ideal potential catalyst applied for industrial water treatment.

## 3.3. Synergy of Adsorption and Photocatalysis of ZnO/CFA in a Dynamic System

Due to its good adsorption capacity and photocatalytic activity, ZnO/CFA-600 was chosen to measure its synergistic removal performance for organic pollutants in a flowing system. Particularly, the 3D open-framework architecture ensures the free flow of solution inside the ZnO/CFA-600, which could continuously decompose organic molecules under UV light irradiation. Figure 8a shows the time-dependent  $C/C_0$  variation of a TC solution (5 mg/L) over the 3D ZnO/CFA-600 with different flow rates. At the initial stage of reactions, carbon fibers with good adsorbability make a fast drop in TC content in solution, which then slowly rises to reach a stable value. It should be noted that the synergistic TC removal ratio over the ZnO/CFA-600 photocatalyst gradually declines with the increasing flow rate. However, its removal efficiency for TC has the opposite trend, which is reckoned to increase from 1.25 mg/min to 4.0 mg/min, as shown in Figure 8b.



**Figure 8.** (a) Time-dependent removal ratio of TC over 3D ZnO/CFA-600 sample with different flow rates in a dynamic system, and (b) corresponding TC removal efficiency.

Furthermore, a contrast experiment without UV light was also performed to analyze the equilibrium adsorbability of the 3D ZnO/CFA-600 under a flow rate of 0.25 mL/min.

Therefore, in Figure 8a, the  $C/C_0$  drop between the blank and red plots mainly results from the good photocatalytic activity of ZnO/CFA-600 for TC degradation. It is indicated that the as-obtained 3D ZnO/CFA-600 product possesses high photocatalytic activity under flowing conditions, which plays an important role in the continuous removal of organic pollutants. On the other hand, the synergistic TC removal curves with different flow rates can be stably maintained for a long time, certifying the great photocatalytic stability of the 3D ZnO/CFA-600 photocatalyst.

# 3.4. Photocatalytic Mechanism of ZnO/CFA

To figure out the photoelectronic property of ZnO/CFA products, photocurrent measurements were performed for four UV-light-on/off cycles in a 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution, as shown in Figure 9a. ZnO/CFA-600 and ZnO/CFA-700 exhibit higher photocurrent densities in comparison to the other two photocatalysts during UV light irradiation. In terms of the XRD and TG results, it is certified that the ZnO/CFA-600 and ZnO/CFA-700 both have high ZnO loading and good ZnO crystallinity, thus explaining their superior photo-to-electron transfer efficiency. However, the photocurrent density of the ZnO/CFA-700 is slightly higher than that of the ZnO/CFA-600, resulting from the fact that highly graphitized carbon fibers will be produced at 700 °C or above, which is more favorable to the fast transfer of surface electrons. Consequently, the graphitized structure of carbon fibers will be important to effectively separate the photogenerated electron/hole pairs, further enhancing the photocatalytic performance of the ZnO/CFA aerogel.



**Figure 9.** (a) Photocurrent responses and (b) Nyquist plots of various ZnO/CFA-t electrodes in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution.

Similarly, Nyquist plots (Figure 9b) also revealed that ZnO/CFA-700 has a smaller arc radius compared with others, indicating that ZnO/CFA-700 is endowed with a rapid electron transfer rate and a high charge diffusion efficiency. Theoretically, ZnO/CFA-700 will have superior photocatalytic activity than ZnO/CFA-600 due to its better photoelectronic properties. However, more active cites (i.e., ZnO) in the ZnO/CFA-600 finally contribute the higher photoactivity for TC photodegradation, where the ZnO loadings of the ZnO/CFA-600 and ZnO/CFA-700 are 34.5% and 28.1%, respectively (Table 1).

Based on the experimental and analyzed results, the photocatalytic mechanism of the ZnO/CFA photocatalysts is explored in the present work. As shown in Scheme 1, under UV light irradiation, ZnO nanoparticles could be excited to allow for the separation of photogenerated electron/hole ( $e^-/h^+$ ) pairs. In an aqueous solution,  $e^-$  will react with dissolved O<sub>2</sub> to produce  $\cdot$ O<sub>2</sub>, while  $h^+$  combines with OH<sup>-</sup> to form  $\cdot$ OH radicals. As a result, those highly active species, i.e.,  $\cdot$ OH,  $\cdot$ O<sub>2</sub>, and  $h^+$ , could simultaneously decompose TC to yield small organic molecules [5]. In the ZnO/CFA photocatalyst, ZnO nanoparticles play the role of the real reactive center, and their loading and dispersion will greatly affect the overall photocatalytic performance.



**Scheme 1.** Photocatalytic mechanism of 3D ZnO/CFA sample for TC degradation under UV light irradiation.

Generally, the photogenerated  $h^+$  on ZnO will rapidly recombine with  $e^-$  within an extremely short time; thus, most of the  $h^+/e^-$  pairs fail to be utilized to degrade TC molecules. As for the ZnO/CFA composites, the 3D crosslinked framework of the carbon fiber aerogel guarantees the free mobility of reaction solutions as well as the fast migration of reactants. As the electron capturer, the carbon fibers are also proven to induce surface charge transport to prolong the lifetime of  $h^+/e^-$  pairs [15]. Therefore, the combined carbon fibers not only increase the adsorption of TC but also improve the photocatalytic performance of ZnO. The ZnO/CFA photocatalysts exhibit good synergistic effects of adsorption and photocatalysis and successfully maintain a long-term high efficiency for TC removal in flowing water treatment systems.

### 4. Conclusions

In summary, in order to in situ fabricate 3D fibrous ZnO/C aerogel materials, abundant oxygen-based groups in cotton are utilized to adsorb Zn<sup>2+</sup> ions, which are then thermally treated under high-temperature conditions. A systematic study reveals that calcination temperature plays an important role in the content, dispersity, and size of ZnO nanoparticles, as well as the specific surface area of the 3D ZnO/CFA products. Compared with others, ZnO/CFA-600 exhibits the highest removal efficiency for TC after physisorption for 30 min and photodegradation for 90 min. Benefiting from the carbon-fiber-crosslinked open framework, the 3D ZnO/CFA materials make the inside channel for mass transmission, which ensures that the ZnO/CFA catalyst could continuously work in the flowing water treatment system. As a result, ZnO/CFA-600 is confirmed to stably maintain the great synergistic performance of adsorption and photocatalysis for TC removal within at least 8h. Consequently, the cheap precursor, simple preparation route, and superior organics removal ability jointly make the 3D ZnO/CFA product a promising industrial material to be applied in future wastewater purification.

**Author Contributions:** W.W.: investigation, resources, writing—original draft, and funding acquisition; Y.L.: data curation, investigation, and formal analysis; S.B.: data curation and formal analysis; X.Y.: methodology, validation, and writing—original draft; M.C.: investigation and formal analysis; Y.S.: project administration and supervision; C.L.: validation and formal analysis; P.Z.: methodology, supervision, and writing—review and editing. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was partly supported by the Youth Project of Yazhou Bay Innovation Institute of Hainan Tropical Ocean University (No. 2022CXYQNXM01), the National Natural Science Foundation of China (No. 22068012), the Hainan Province Science and Technology Special Fund (No. ZDYF2022GXJS004, ZDYF2021GXJS028), and the China Postdoctoral Science Foundation (No. 2022M710988).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

**Data Availability Statement:** The research data can be provided upon request to the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

#### References

- 1. Weng, B.; Qi, M.-Y.; Han, C.; Tang, Z.-R.; Xu, Y.-J. Photocorrosion Inhibition of Semiconductor-Based Photocatalysts: Basic Principle, Current Development, and Future Perspective. *ACS Catal.* **2019**, *9*, 4642–4687. [CrossRef]
- Wang, S.; Liu, G.; Wang, L. Crystal Facet Engineering of Photoelectrodes for Photoelectrochemical Water Splitting. *Chem. Rev.* 2019, 119, 5192–5247. [CrossRef] [PubMed]
- 3. Ma, Y.; Wang, X.; Jia, Y.; Chen, X.; Han, H.; Li, C. Titanium Dioxide-Based Nanomaterials for Photocatalytic Fuel Generations. *Chem. Rev.* **2014**, *114*, 9987–10043. [CrossRef]
- 4. Kumaravel, V.; Mathew, S.; Bartlett, J.; Pillai, S.C. Photocatalytic Hydrogen Production Using Metal Doped TiO<sub>2</sub>: A Review of Recent Advances. *Appl. Catal. B Environ.* **2019**, 244, 1021–1064. [CrossRef]
- 5. Zhang, P.; Yang, X.; Jin, Z.; Gui, J.; Tan, R.; Qiu, J. Insight into the Impact of Surface Hydrothermal Carbon Layer on Photocatalytic Performance of ZnO Nanowire. *Appl. Catal. A Gen.* **2019**, *583*, 117145. [CrossRef]
- 6. Zhang, P.; Yang, X.; Du, S.; Yin, L.; Wang, J.; Liu, P.; Hou, W. Insight into the Crystal Facet Effect of {101} and {100} Facets of CeVO<sub>4</sub> in the Photochemical Property and Photocatalysis. *J. Phys. Chem. Lett.* **2022**, *13*, 10432–10438. [CrossRef]
- Lu, G.; Lun, Z.; Liang, H.; Wang, H.; Li, Z.; Ma, W. In Situ Fabrication of BiVO<sub>4</sub>-CeVO<sub>4</sub> Heterojunction for Excellent Visible Light Photocatalytic Degradation of Levofloxacin. J. Alloys Compd. 2019, 772, 122–131. [CrossRef]
- Liu, C.; Zhang, Q.; Zou, Z. Recent Advances in Designing ZnIn<sub>2</sub>S<sub>4</sub>-Based Heterostructured Photocatalysts for Hydrogen Evolution. J. Mater. Sci. Technol. 2023, 139, 167–188. [CrossRef]
- Liu, C.; Xiao, W.; Yu, G.; Wang, Q.; Hu, J.; Xu, C.; Du, X.; Xu, J.; Zhang, Q.; Zou, Z. Interfacial Engineering of Ti<sub>3</sub>C<sub>2</sub> Mxene/CdIn<sub>2</sub>S<sub>4</sub> Schottky Heterojunctions for Boosting Visible-Light H<sub>2</sub> Evolution and Cr(VI) Reduction. *J. Colloid Interface Sci.* 2023, 640, 851–863. [CrossRef] [PubMed]
- 10. Liu, C.; Zhang, Y.; Wu, J.; Dai, H.; Ma, C.; Zhang, Q.; Zou, Z. Ag-Pd Alloy Decorated ZnIn<sub>2</sub>S<sub>4</sub> Microspheres with Optimal Schottky Barrier Height for Boosting Visible-Light-Driven Hydrogen Evolution. *J. Mater. Sci. Technol.* **2022**, *114*, 81–89. [CrossRef]
- Yang, J.; Chen, D.; Zhu, Y.; Zhang, Y.; Zhu, Y. 3D-3D Porous Bi<sub>2</sub>WO<sub>6</sub>/Graphene Hydrogel Composite with Excellent Synergistic Effect of Adsorption-Enrichment and Photocatalytic Degradation. *Appl. Catal. B Environ.* 2017, 205, 228–237. [CrossRef]
- 12. Zhang, N.; Yang, M.Q.; Liu, S.; Sun, Y.; Xu, Y.J. Waltzing with the Versatile Platform of Graphene to Synthesize Composite Photocatalysts. *Chem. Rev.* **2015**, *115*, 10307–10377. [CrossRef] [PubMed]
- 13. Alatalo, S.-M.; Mäkilä, E.; Repo, E.; Heinonen, M.; Salonen, J.; Kukk, E.; Sillanpää, M.; Titirici, M.-M. Meso- and Microporous Soft Templated Hydrothermal Carbons for Dye Removal from Water. *Green Chem.* **2016**, *18*, 1137–1146. [CrossRef]
- Alatalo, S.-M.; Pileidis, F.; Mäkilä, E.; Sevilla, M.; Repo, E.; Salonen, J.; Sillanpää, M.; Titirici, M.-M. Versatile Cellulose-Based Carbon Aerogel for the Removal of Both Cationic and Anionic Metal Contaminants from Water. ACS Appl. Mater. Interfaces 2015, 7, 25875–25883. [CrossRef]
- 15. Zhang, P.; Yin, L.; Yang, X.; Wang, J.; Chi, M.; Qiu, J. Cotton-Derived 3D Carbon Fiber Aerogel to in Situ Support Bi<sub>2</sub>O<sub>3</sub> Nanoparticles as a Separation-Free Photocatalyst for Antibiotic Removal. *Carbon* **2023**, 201, 110–119. [CrossRef]
- Tian, X.; Zhu, H.; Meng, X.; Wang, J.; Zheng, C.; Xia, Y.; Xiong, Z. Amphiphilic Calcium Alginate Carbon Aerogels: Broad-Spectrum Adsorbents for Ionic and Solvent Dyes with Multiple Functions for Decolorized Oil–Water Separation. ACS Sustain. Chem. Eng. 2020, 8, 12755–12767. [CrossRef]
- 17. Zulfiqar, U.; Kostoglou, N.; Thomas, A.G.; Rebholz, C.; Matthews, A.; Lewis, D.J. Flexible Nanoporous Activated Carbon for Adsorption of Organics from Industrial Effluents. *Nanoscale* **2021**, *13*, 15311–15323. [CrossRef]
- Zhang, P.; Yang, X.; Zhao, Z.; Li, B.; Gui, J.; Liu, D.; Qiu, J. One-Step Synthesis of Flowerlike C/Fe<sub>2</sub>O<sub>3</sub> Nanosheet Assembly with Superior Adsorption Capacity and Visible Light Photocatalytic Performance for Dye Removal. *Carbon* 2017, *116*, 59–67. [CrossRef]
- 19. Wan, W.; Yang, X.; Du, M.; Shi, Y.; Wang, J.; Wang, L.; Chin, Y.; Liu, H.; Zhang, P. One-Dimensional Ternary Ag@Ag<sub>2</sub>S@C Nanocable with Plasmon-Enhanced Photocatalytic Performance. *Mol. Catal.* **2021**, *505*, 111531. [CrossRef]
- Li, B.; Zhao, Z.; Gao, F.; Wang, X.; Qiu, J. Mesoporous Microspheres Composed of Carbon-Coated TiO<sub>2</sub> Nanocrystals with Exposed {001} Facets for Improved Visible Light Photocatalytic Activity. *Appl. Catal. B Environ.* 2014, 147, 958–964. [CrossRef]
- 21. Li, Y.; Cui, W.; Liu, L.; Zong, R.; Yao, W.; Liang, Y.; Zhu, Y. Removal of Cr(VI) by 3D TiO<sub>2</sub>-Graphene Hydrogel Via Adsorption Enriched with Photocatalytic Reduction. *Appl. Catal. B Environ.* **2016**, *199*, 412–423. [CrossRef]
- 22. Mu, C.; Zhang, Y.; Cui, W.; Liang, Y.; Zhu, Y. Removal of Bisphenol a over a Separation Free 3d Ag<sub>3</sub>PO<sub>4</sub>-Graphene Hydrogel Via an Adsorption-Photocatalysis Synergy. *Appl. Catal. B Environ.* **2017**, *212*, 41–49. [CrossRef]

- Wang, X.; Liang, Y.; An, W.; Hu, J.; Zhu, Y.; Cui, W. Removal of Chromium (VI) by a Self-Regenerating and Metal Free G-C<sub>3</sub>N<sub>4</sub>/Graphene Hydrogel System Via the Synergy of Adsorption and Photo-Catalysis under Visible Light. *Appl. Catal. B Environ* 2017, 219, 53–62. [CrossRef]
- Jiang, W.; Liu, Y.; Wang, J.; Zhang, M.; Luo, W.; Zhu, Y. Separation-Free Polyaniline/TiO<sub>2</sub> 3D Hydrogel with High Photocatalytic Activity. *Adv. Mater. Interf.* 2016, 3, 1500502. [CrossRef]
- Liang, Q.; Ploychompoo, S.; Chen, J.; Zhou, T.; Luo, H. Simultaneous Cr(VI) Reduction and Bisphenol a Degradation by a 3D Z-Scheme Bi<sub>2</sub>S<sub>3</sub>-BiVO<sub>4</sub> Graphene Aerogel under Visible Light. *Chem. Eng. J.* 2020, 384, 123256. [CrossRef]
- Yang, J.; Miao, H.; Wei, Y.; Li, W.; Zhu, Y. p-p Interaction between Self-Assembled Perylene Diimide and 3D Graphene for Excellent Visible-Light Photocatalytic Activity. *Appl. Catal. B Environ.* 2019, 240, 225–233. [CrossRef]
- Zhang, J.; Yuan, W.; Xia, T.; Ao, C.; Zhao, J.; Huang, B.; Wang, Q.; Zhang, W.; Lu, C. A TiO<sub>2</sub> Coated Carbon Aerogel Derived from Bamboo Pulp Fibers for Enhanced Visible Light Photo-Catalytic Degradation of Methylene Blue. *Nanomaterials* 2021, *11*, 239. [CrossRef]
- Jiang, W.; Luo, W.; Zong, R.; Yao, W.; Li, Z.; Zhu, Y. Polyaniline/Carbon Nitride Nanosheets Composite Hydrogel: A Separation-Free and High-Efficient Photocatalyst with 3D Hierarchical Structure. *Small* 2016, 12, 4370–4378. [CrossRef]
- Dong, C.; Lu, J.; Qiu, B.; Shen, B.; Xing, M.; Zhang, J. Developing Stretchable and Graphene-Oxide-Based Hydrogel for the Removal of Organic Pollutants and Metal Ions. *Appl. Catal. B Environ.* 2018, 222, 146–156. [CrossRef]
- Fan, Y.; Ma, W.; Han, D.; Gan, S.; Dong, X.; Niu, L. Convenient Recycling of 3D AgX/Graphene Aerogels (X = Br, Cl) for Efficient Photocatalytic Degradation of Water Pollutants. *Adv. Mater.* 2015, 27, 3767–3773. [CrossRef]
- Qiu, B.; Xing, M.; Zhang, J. Mesoporous TiO<sub>2</sub> Nanocrystals Grown in Situ on Graphene Aerogels for High Photocatalysis and Lithium-Ion Batteries. J. Am. Chem. Soc. 2014, 136, 5852–5855. [CrossRef] [PubMed]
- 32. Zhang, P.; Zhao, Z.; Dyatkin, B.; Liu, C.; Qiu, J. In Situ Synthesis of Cotton-Derived Ni/C Catalysts with Controllable Structures and Enhanced Catalytic Performance. *Green Chem.* **2016**, *18*, 3594–3599. [CrossRef]
- Li, F.; Bhushan, B.; Pan, Y.; Zhao, X. Bioinspired Superoleophobic/Superhydrophilic Functionalized Cotton for Efficient Separation of Immiscible Oil-Water Mixtures and Oil-Water Emulsions. J. Colloid Interface Sci. 2019, 548, 123–130. [CrossRef] [PubMed]
- Liu, S.; Zhao, C.; Wang, Z.; Ding, H.; Deng, H.; Yang, G.; Li, J.; Zheng, H. Urea-Assisted One-Step Fabrication of a Novel Nitrogen-Doped Carbon Fiber Aerogel from Cotton as Metal-Free Catalyst in Peroxymonosulfate Activation for Efficient Degradation of Carbamazepine. *Chem. Eng. J.* 2020, 386, 124015. [CrossRef]
- 35. Li, Y.; Liu, Z.; Liu, H.; Peng, B. Clean Strengthening Reduction of Lead and Zinc from Smelting Waste Slag by Iron Oxide. *J. Clean Prod.* 2017, 143, 311–318. [CrossRef]
- 36. Zou, Z.; Yang, X.; Zhang, P.; Zhang, Y.; Yan, X.; Zhou, R.; Liu, D.; Xu, L.; Gui, J. Trace Carbon-Hybridized ZnS/ZnO Hollow Nanospheres with Multi-Enhanced Visible-Light Photocatalytic Performance. J. Alloys Compd. 2019, 775, 481–489. [CrossRef]
- Yang, X.; Zhang, Y.; Wang, Y.; Xin, C.; Zhang, P.; Liu, D.; Mamba, B.B.; Kefeni, K.K.; Kuvarega, A.T.; Gui, J. Hollow b-Bi<sub>2</sub>O<sub>3</sub>@CeO<sub>2</sub> Heterostructure Microsphere with Controllable Crystal Phase for Efficient Photocatalysis. *Chem. Eng. J.* 2020, 387, 124100. [CrossRef]
- Yang, X.; Wang, Y.; He, N.; Wan, W.; Zhang, F.; Zhai, B.; Zhang, P. One-Step Hydrothermal Synthesis of Hierarchical Nanosheet-Assembled Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> Microflowers with a {001} Dominant Facet and Their Superior Photocatalytic Performance. *Nanotechnology* 2020, 31, 375604. [CrossRef]
- 39. Zhang, Y.; Yang, X.; He, N.; Zhang, P.; Ding, Y.; Liu, D.; Zou, Z.; Gui, J. One-Step Hydrothermal Fabrication of Erythrocyte-Like ZnS/ZnO Composite with Superior Visible Light Photocatalytic Performance. *Mater. Lett.* **2018**, 228, 305–308. [CrossRef]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.