

## Article

# A Simple Preparation Method of Graphene and TiO<sub>2</sub> Loaded Activated Carbon Fiber and Its Application for Indoor Formaldehyde Degradation

Fang Liu <sup>1,2,\*</sup>, Xuezhi Gao <sup>1,2</sup> and Man Peng <sup>3</sup>

<sup>1</sup> Beijing Key Laboratory of Heating, Gas Supply, Ventilation and Air Conditioning, Beijing University of Civil Engineering and Architecture, Beijing 100044, China; gaouxuezh@stu.bucea.edu.cn

<sup>2</sup> Collaborative Innovation Center of Energy Conservation & Emission Reduction and Sustainable Urban-Rural Development in Beijing, Beijing University of Civil Engineering and Architecture, Beijing 102616, China

<sup>3</sup> S.Y. Technology, Engineering & Construction Co., Ltd., Wuhan 430200, China; pengman@sdic.com.cn

\* Correspondence: liufang@bucea.edu.cn

**Abstract:** Formaldehyde has a significant impact on human health. This study used a simple dipping method to load graphene-titanium dioxide (GR-TiO<sub>2</sub>) on activated carbon fibers (ACFs). The microstructure of GR-TiO<sub>2</sub>/ACF hybrid material was observed by SEM, combined with XRD and BET analysis. The result showed that the GR-TiO<sub>2</sub>/ACF hybrid material had a specific surface area of 893.08 m<sup>2</sup>/g and average pore size of 2.35 nm. The formaldehyde degradation efficiency of the prepared material was tested under different conditions, such as ultraviolet (UV) radiation, air supply volume, relative humidity, initial mass concentration. The results showed that the UV radiation intensity, airflow and the initial mass concentration were positively correlated with the formaldehyde removal rate, and the relative humidity was negatively correlated with the formaldehyde removal rate. The GR-TiO<sub>2</sub>/ACF hybrid material had a maximum formaldehyde removal rate of 85.54% within 120 min.

**Keywords:** indoor air; formaldehyde; TiO<sub>2</sub>/ACF; graphene; photocatalysis; purification technology



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## 1. Introduction

People spend most of their time indoors, and pollutants in indoor air are an important cause of human diseases [1–4]. As one of the main indoor pollutants, formaldehyde has the characteristics of wide sources, significant harm, and a long release period [5,6]. Formaldehyde mainly comes from interior decoration materials, furniture and coatings. Materials based on artificial boards and adhesives will release a large amount of free formaldehyde [5,7,8]. Short-term exposure to formaldehyde can cause human eye and nose irritation, respiratory discomfort, and even acute poisoning. Long-term indoor low-level exposure to formaldehyde can cause neurasthenia, including headaches, dizziness, sleep disturbance, memory loss, lung function damage and cancer [9,10].

As a kind of indoor air purification technology with a simple process and no secondary pollution, many studies have been carried out on photocatalysis [11]. It can oxidize formaldehyde and other VOCs into CO<sub>2</sub> and water in indoor environments. TiO<sub>2</sub> has strong oxidizing properties and good stability. Thus, it is currently one of the most widely studied and used photocatalysts [12,13].

In 1972, Japanese scientists Fujishima and Honda first discovered the phenomenon of titanium dioxide (TiO<sub>2</sub>) single crystal electrode decomposing water under the action of photocatalysis, laying the foundation for the study of TiO<sub>2</sub> photocatalysis [14,15]. When TiO<sub>2</sub> absorbs photons with energy greater than or equal to its bandgap, electrons (e<sup>−</sup>) in the valence band are excited and migrate to the conduction band, thereby generating holes (h<sup>+</sup>). Electrons and holes will react with the H<sub>2</sub>O attached to TiO<sub>2</sub> to generate strong

oxidizing hydroxyl radicals ( $\cdot\text{OH}$ ), which can oxidize most VOCs, including formaldehyde molecules, into  $\text{CO}_2$  and water. At the same time, due to the low cost and safe use of  $\text{TiO}_2$ , it is now often used to remove indoor formaldehyde. Compared with the degradation of acetaldehyde,  $\text{TiO}_2$  has a better effect on the degradation of formaldehyde, and at the same time,  $\text{TiO}_2$  has shown a higher adsorption capacity than traditional adsorbents [16].

However, the easy recombination of photogenerated electrons and holes reduces the photocatalytic efficiency. To enhance the photocatalytic activity of  $\text{TiO}_2$  and further improve the efficiency of formaldehyde purification, many studies have been carried out on the modification of  $\text{TiO}_2$ . The common modification methods of  $\text{TiO}_2$  mainly include photosensitization, semiconductor recombination, precious metal deposition and ion doping, carbon element modification, etc. [17,18].

Graphene (GR) is a carbon material composed of a single-layer graphite sheet with good electrical conductivity [19]. Graphene can promote the photoelectron transfer and transition in photocatalytic reactions, and effectively inhibit the recombination of photogenerated holes and electrons. Graphene materials can be used as dopants or photocatalyst carriers to synthesize composite materials with  $\text{TiO}_2$ , which can improve photocatalytic efficiency [20–23]. Reports have shown that the composites with graphene as dopant have a great effect on the degradation of formaldehyde [24,25].

Combining the photocatalytic method and physical adsorption method can significantly improve the removal effect of indoor air pollutants [26]. Adsorption has been proved to be good in the purification of indoor volatile organic compounds [27,28]. Xiao et al. proposed an in-situ thermally regenerated process based on granular activated carbon, which dramatically prolonged the sorbent's life span [27]. However, a packed bed of granular activated carbon usually exhibited significant pressure drop and poor purifying performance, as the slow molecular diffusion inside the adsorbents [29,30]. Activated carbon fiber (ACF) is cheap and stable. With a large specific surface area and rich microporous structure, ACF can provide more surface area for the photocatalyst to remove indoor pollution to improve the purification effect and is currently often used as a carrier for adsorption-photocatalytic composite materials [31–35].

It may be a good method to combine graphene,  $\text{TiO}_2$  and ACF to synthesize composites for indoor formaldehyde degradation. This combination can improve the adsorption and photocatalytic effect of the material on formaldehyde degradation [36]. Compared with the combination of materials with different dopants, GR- $\text{TiO}_2$ /ACF may have better advantages in removing formaldehyde [24,37]. In addition, due to different experimental parameter settings, the performance of materials under different light intensity, air supply volume, relative humidity and other conditions is also different [25,38]. Some studies have shown significant differences in the initial degradation effects of materials at low concentrations of formaldehyde [16,24]. Furthermore, many studies are carried out in relatively closed small experimental systems to study the purification performance of materials more rigorously. There are few studies in a large-volume indoor environment, which is somewhat different from the actual application of materials.

In this study, a simple preparation method was developed to synthesize a GR- $\text{TiO}_2$ /ACF hybrid material. An air circulation system was specially designed to carry the hybrid materials. Further, the formaldehyde degradation efficiency of the prepared material was tested in an environmental cabin similar to the actual room size.

## 2. Experimental

### 2.1. Chemicals and Materials

GR- $\text{TiO}_2$  dispersion was purchased from Hangzhou Jiupeng New Material Co., Ltd. (Hangzhou, China). in Zhejiang, using water as solvent. Formaldehyde gas was generated by evaporating liquid formalin (37–40% solution; Tianjin Damao Chemical Reagent Factory, Tianjin, China). Activated carbon fibers (ACF) (6 mm) were purchased from Jiangsu Maoheng Carbon Industry Technology Co., Ltd. (Yixing, China). and treated as follows before used: first placed in distilled water and washed for 30 min, then dried under  $100^\circ\text{C}$

for 2 h. The UV light bulbs (10 W, 253.7 nm, quartz glass) were purchased from Snow Wright Broadcasting Technology Co., Ltd. (Foshan, China). Light intensity of the UV light was measured by TES-1333 data logging solar power meter (TES Electrical Electronic Corp., Taiwan, China).

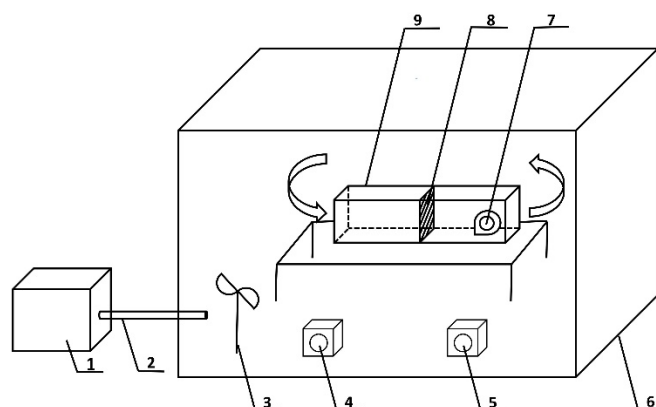
## 2.2. Synthesis and Characterization

In this study, we chose a simple dipping method to synthesize GR-TiO<sub>2</sub>/ACF composite materials. The steps were as follows: a proper amount of GR-TiO<sub>2</sub> dispersion was put into the tray, and the catalyst loading on the carrier was planned to be 50%. The treated ACF fiber (42 cm × 32 cm) was slowly immersed in the dispersion of GR-TiO<sub>2</sub> for 30 min, then dried at 120 °C for 2 h to constant weight. This dipping method has been used in some studies to synthesize materials [39–41]. Through the actual measurement and weighing of the material before and after loading, the actual loading ratio of the GR-TiO<sub>2</sub>/ACF hybrid material produced in this research was 43.6%.

The microscopic morphology and structural characteristics of the samples were carried out with SU8010 SEM. During the test, the acceleration voltage was set to 3 kV. The crystalline information of GR-TiO<sub>2</sub>/ACF hybrid material was measured by Ultima IV from Rigaku Corporation (Japan). The test range is 10°~80°, the scanning speed of the instrument is 10°/min, the X-ray working voltage is 40 kV, the working beam current is 40 mA, the divergence slit parameter (DivSlit) is 1°, the height limiting slit parameter (DivH.L.Slit) is 10 mm, and the anti-scatter slit parameter (SctSlit) is 8.0 mm. Specific surface area, pore volume and average pore diameter of the hybrid material were obtained from ASAP 2460 Accelerated Surface Area and Porosimetry System from Micromeritics Co. with nitrogen as the adsorption medium. During the test, the degassing temperature was 250 °C, and the degassing time was 3 h.

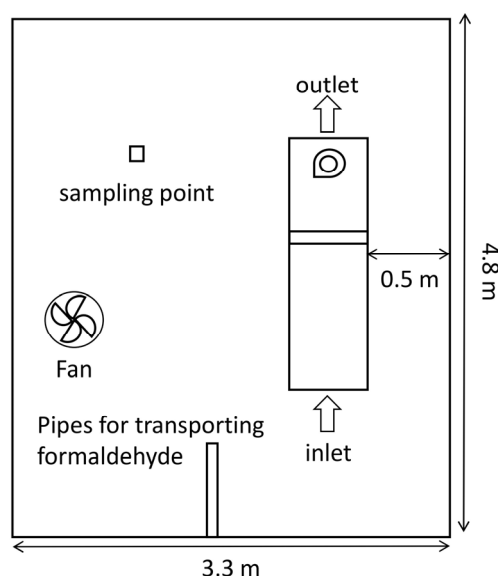
## 2.3. Experimental Methods

This study was conducted in an environmental chamber (4.8 m × 3.3 m × 3.3 m) to simulate a realistic indoor environment. The chamber was completely enclosed, and no fresh air entered. As shown in Figure 1, the experiment system is composed of an air circulation system, a formaldehyde generator, two air quality monitors, and a fan for assisting in the circulation of indoor air. Indoor temperature, humidity, and formaldehyde concentration were measured by two air quality monitors (JT2082, Beijing Century Construction Technology Co., Ltd., Beijing, China), with the precisions of 0.1 °C, 0.1%, and 0.001 mg/m<sup>3</sup>, respectively. The air quality monitors have built-in ZE08-CH<sub>2</sub>O sensor module, which measures the formaldehyde concentration by electrochemical method and are placed 1.1 m from the ground.

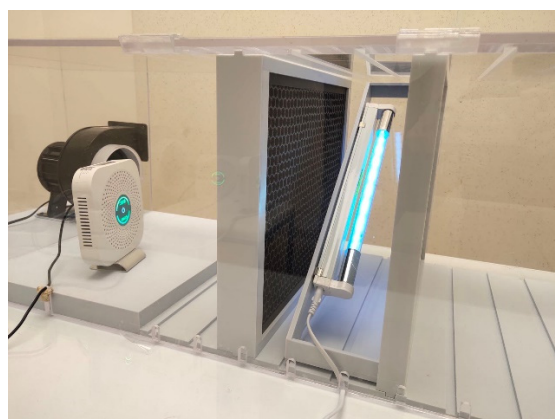


**Figure 1.** The layout of the test system (1—Formaldehyde generator; 2—Air pipe; 3—Fan; 4, 5—Air quality monitor; 6—Environment chamber; 7—Turbo blower; 8—Purification material; 9—Purification device).

The air circulation system consisted of an air purification channel and a turbo blower with adjustable wind speed. The main frame of the whole system was built by acrylic panels, including the supply and return air section, the purification section, the sampling section and the fan section. The cross-section size was 420 mm × 320 mm, and the air outlet size was 60 mm × 65 mm. The spatial arrangement of the test system is shown in Figure 2. A card slot was set inside the purification section to fix the purification module, and the purification material was also custom-framed and packaged by acrylic boards. The materials were placed inside the purification section and tightly connected with the device to prevent air leakage at the edge of the module from affecting the test results. Three ultraviolet lamps were installed on the purification frame for subsequent photocatalytic performance research. Figure 3 shows the purification section and fan section in the purification system.



**Figure 2.** The spatial arrangement of the test system.



**Figure 3.** Purification section and fan section.

The formaldehyde generator was placed outdoors. A quantitative amount of formaldehyde solution analytically pure was injected into the equipment through a micro-injector, and the temperature of the heating plate in the equipment was raised to 70–80 °C through electric heating. The air entered the constant temperature heating place through the air pump inlet tube. Under the action of the air pump inside the device, the rapidly evaporated formaldehyde gas was taken out, and the gaseous formaldehyde with a constant mass concentration was stably released through the equipment outlet tube into the environment chamber.

Besides, the environmental chamber is equipped with auxiliary humidity control equipment. The background concentration of formaldehyde and the airtightness of the chamber had been checked before this study. During the blank test period of 2 h, the background concentration of formaldehyde in the environment chamber was  $0.026 \pm 0.006 \text{ mg/m}^3$ , indicating that the background concentration of formaldehyde in the chamber was relatively low. In the airtightness experiment, the high concentration formaldehyde gas was used, and the concentration fluctuation range was  $1.851\text{--}1.825 \text{ mg/m}^3$ , which decreased by 1.39% after 2 h, proving the airtightness of the environment chamber well.

Before starting the experiment, the GR-TiO<sub>2</sub>/ACF hybrid material was fixed in the specially designed purification material frame and inserted into the card slot of the purification system. After that, the air circulation system is completely sealed, except for the air inlet and outlet. The outside of the purification device was wrapped with aluminum foil to reduce the influence of external light. The circulation fan and the air quality monitors were turned on to ensure that the indoor formaldehyde background concentration and the natural attenuation rate of formaldehyde meet the requirements. The quantitative formaldehyde solution was injected into the formaldehyde generator. After the formaldehyde concentration in the chamber reached the predetermined value and stabilized, the purification device and the ultraviolet lamp were turned on.

After the experiment started, the formaldehyde concentrations in the chamber were recorded by the air quality monitors, the total duration of this experiment was set as 120 min. The removal rate of formaldehyde was calculated as Equation (1):

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where  $\eta$  represents the removal rate of formaldehyde (%);  $C_0$  represents the initial formaldehyde concentration in the chamber ( $\text{mg/m}^3$ );  $C_t$  represents the formaldehyde concentration in the chamber at time  $t$  ( $\text{mg/m}^3$ ).

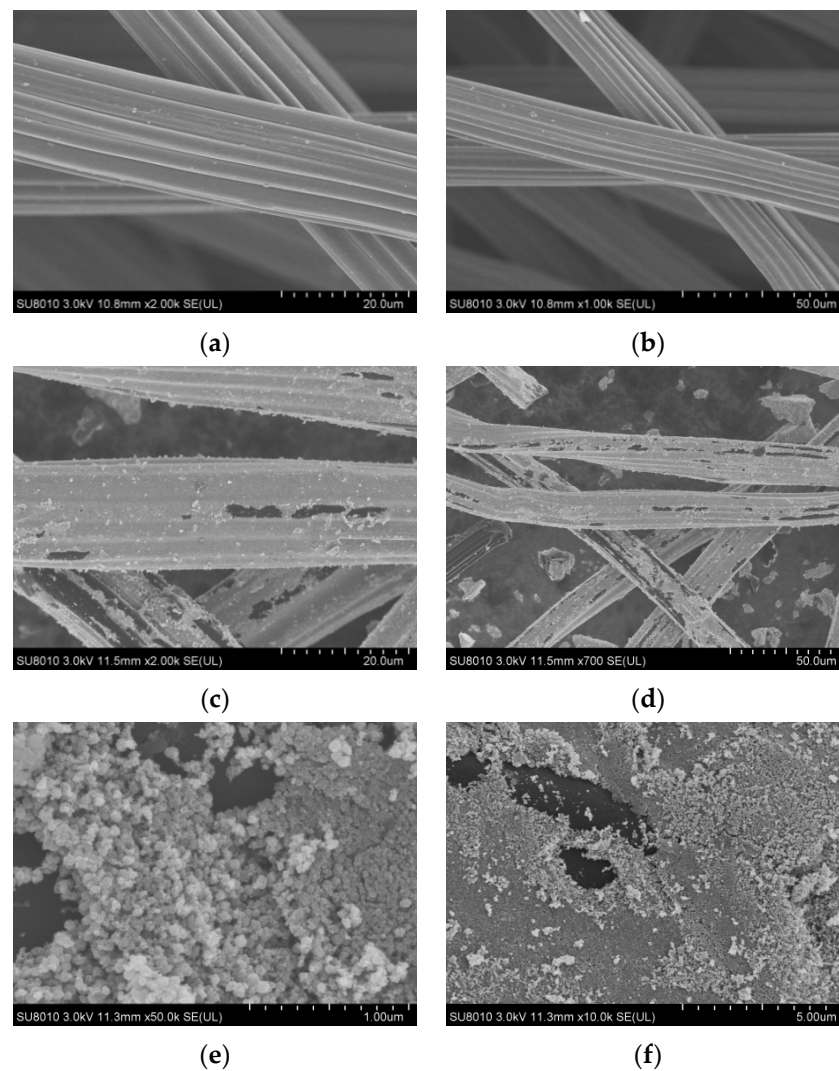
### 3. Results

#### 3.1. Characterization of the GR-TiO<sub>2</sub>/ACF Hybrid Materials

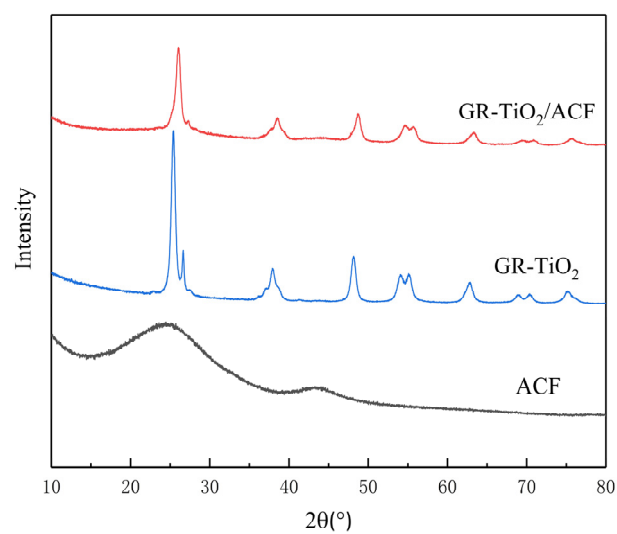
Figure 4 shows the SEM morphological characterization of the unmodified ACFs and GR-TiO<sub>2</sub>/ACF hybrid materials. It can be observed that the surface of the ACF fiber monofilament is wrapped by the GR-TiO<sub>2</sub> photocatalyst. A relatively uniform film is attached to the ACF surface, and its gully structure can be clearly observed, indicating that the load condition is good.

Figure 5 shows the XRD patterns of ACF, GR-TiO<sub>2</sub> and GR-TiO<sub>2</sub>/ACF hybrid materials. The TiO<sub>2</sub> powder shows sharper diffraction peaks than TiO<sub>2</sub>/ACFs, which is consistent to the fact that the TiO<sub>2</sub>/ACFs have lower TiO<sub>2</sub> content. It can be seen that the characteristic peaks of GR-TiO<sub>2</sub>/ACF hybrid materials and GR-TiO<sub>2</sub> were not significantly different, and the patterns were basically consistent. It shows that during the loading process of the hybrid material, the phase structure of the GR-TiO<sub>2</sub> photocatalyst was not destroyed, and the crystal form did not change significantly.

BET characterization of GR-TiO<sub>2</sub>/ACF hybrid material showed that the specific surface area of GR-TiO<sub>2</sub>/ACF was  $893.08 \text{ m}^2/\text{g}$ , and the pore volume was  $0.52 \text{ m}^3/\text{g}$ . The specific surface area of the YCS1300 ACF material used in the experiment was  $1300 \text{ m}^2/\text{g}$ , and the pore volume was  $0.91 \text{ cm}^3/\text{g}$ . Compared with the carrier ACF, the specific surface area of the loaded GR-TiO<sub>2</sub>/ACF material was reduced by 31.3%, and the pore volume was reduced by 41.76%. It shows that during the loading process of the hybrid material, GR-TiO<sub>2</sub> blocked the micropore structure of the ACF material to a certain extent.



**Figure 4.** SEM micrographs of the unmodified ACFs and GR-TiO<sub>2</sub>/ACFs photocatalyst: (a) original ACFs, 2000×; (b) original ACFs, 1000×; (c) GR-TiO<sub>2</sub>/ACFs, 2000×; (d) GR-TiO<sub>2</sub>/ACFs, 700×; (e) GR-TiO<sub>2</sub>/ACFs, 50,000×; (f) GR-TiO<sub>2</sub>/ACFs, 10,000×.

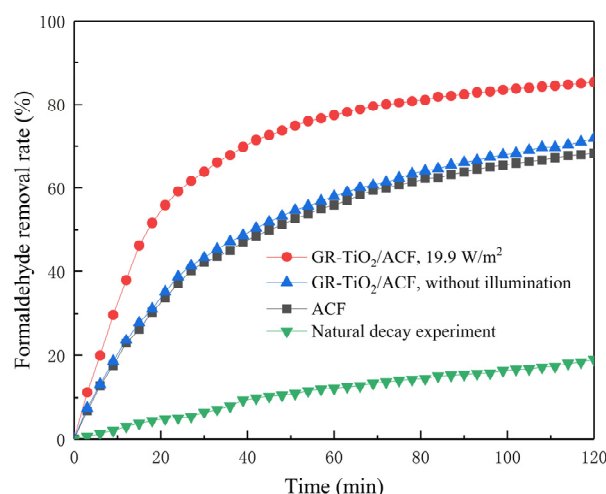


**Figure 5.** XRD patterns of ACF, GR-TiO<sub>2</sub> and GR-TiO<sub>2</sub>/ACF.

### 3.2. The Effect of Different Factors on the Degradation of Formaldehyde by GR-TiO<sub>2</sub>/ACF

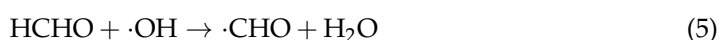
#### 3.2.1. Comparison of Formaldehyde Removal Rate before and after Activated Carbon Fiber Loading GR-TiO<sub>2</sub>

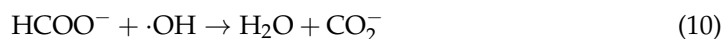
The initial mass concentration of formaldehyde (1.000 mg/m<sup>3</sup>, 1.038 mg/m<sup>3</sup>, 1.011 mg/m<sup>3</sup>) in the three testing groups differed by 3.8% between the maximum and the minimum values. Figure 6 shows the change in the formaldehyde removal rate of activated carbon fiber before and after loading GR-TiO<sub>2</sub> at an indoor temperature of 20 °C, air relative humidity of 27%, and an airflow rate of 183 m<sup>3</sup>/h. It can be seen from Figure 6 that the formaldehyde removal rate increased rapidly within 30 min after the purification device was turned on. ACF adsorbed 0.422 mg/m<sup>3</sup> of formaldehyde, and GR-TiO<sub>2</sub>/ACF adsorbed 0.439 mg/m<sup>3</sup> of formaldehyde. After 30 min, the formaldehyde purification rate gradually slowed down. At 60 min, it gradually flattened out. At 2 h, ACF adsorbed 0.683 mg/m<sup>3</sup> of formaldehyde, and GR-TiO<sub>2</sub>/ACF adsorbed 0.727 mg/m<sup>3</sup> of formaldehyde. It is clear that under the same working conditions, GR-TiO<sub>2</sub>/ACF hybrid material has a slightly higher formaldehyde adsorption effect than the unloaded ACF, indicating that under the test conditions, the formaldehyde adsorption capacity of the ACF loaded with GR-TiO<sub>2</sub> is hardly affected. Combined with relevant report [42], modified TiO<sub>2</sub> will not have a significant impact on the adsorption effect of ACF, and the simultaneous photocatalytic degradation of adsorbed formaldehyde can play an important role in the regeneration of ACF adsorption capacity.



**Figure 6.** Comparison of formaldehyde removal performance before and after ACF loading GR-TiO<sub>2</sub>.

The synergistic reaction mechanism of adsorption and photocatalysis of formaldehyde degradation by composite A is shown in Equations (2)–(11). The addition of graphene with good conductivity makes the GR-TiO<sub>2</sub>/ACF hybrid material more effective in electron transfer in photocatalytic reaction. In addition, the recombination of photogenerated holes and electrons is inhibited, which improves the effect of the material on formaldehyde degradation.

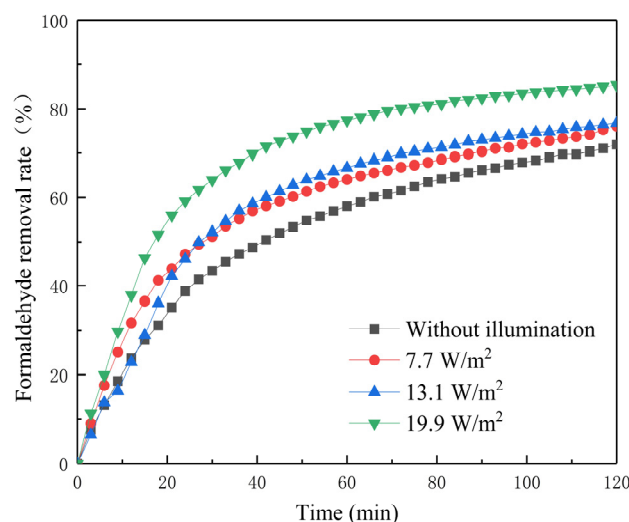




### 3.2.2. The Effect of Different Radiation Intensity

The number of UV lamps was adjusted to change the radiation intensity. The radiation intensity of the three UV lamps is 7.7 W/m<sup>2</sup>, 13.1 W/m<sup>2</sup>, and 19.9 W/m<sup>2</sup> when the three UV lamps are turned on sequentially. In this experiment, the four groups of formaldehyde initial mass concentrations (1.011 mg/m<sup>3</sup>, 1.025 mg/m<sup>3</sup>, 1.054 mg/m<sup>3</sup>, 1.038 mg/m<sup>3</sup>) differed by 4.1% between the maximum and minimum values.

Figure 7 shows the effect of the system temperature at 20 °C, air relative humidity of 27%, and an airflow rate of 183 m<sup>3</sup>/h on the formaldehyde purification performance of GR-TiO<sub>2</sub>/ACF hybrid material. It can be seen from Figure 7 that within 25 min of the purification device being turned on, the formaldehyde removal rate under various radiation intensity conditions increased rapidly. Among them, the GR-TiO<sub>2</sub>/ACF under no-light conditions had the worst formaldehyde degradation effect. The formaldehyde adsorption capacity was 0.392 mg/m<sup>3</sup> at 25 min. The removal rate of formaldehyde is 38.77%, and the hybrid material only adsorbs formaldehyde. The two sets of working conditions with an irradiance of 7.7 W/m<sup>2</sup> and 13.1 W/m<sup>2</sup> have similar degradation effects on formaldehyde within 120 min, and the purification efficiency is 76.58% and 76.85%. When the irradiance is 19.9 W/m<sup>2</sup>, GR-TiO<sub>2</sub>/ACF has the best formaldehyde degradation effect, and the formaldehyde adsorption capacity is 0.614 mg/m<sup>3</sup> at 25 min and the formaldehyde removal rate is 59.15%. It can be seen that within the scope of this test, with the increase of radiation intensity, the removal rate of formaldehyde by GR-TiO<sub>2</sub>/ACF gradually increases. Under the same working conditions, the efficiency of purifying formaldehyde under different radiation intensities is as follows: 19.9 W/m<sup>2</sup> > 13.1 W/m<sup>2</sup> > 7.7 W/m<sup>2</sup> > 0 W/m<sup>2</sup>.



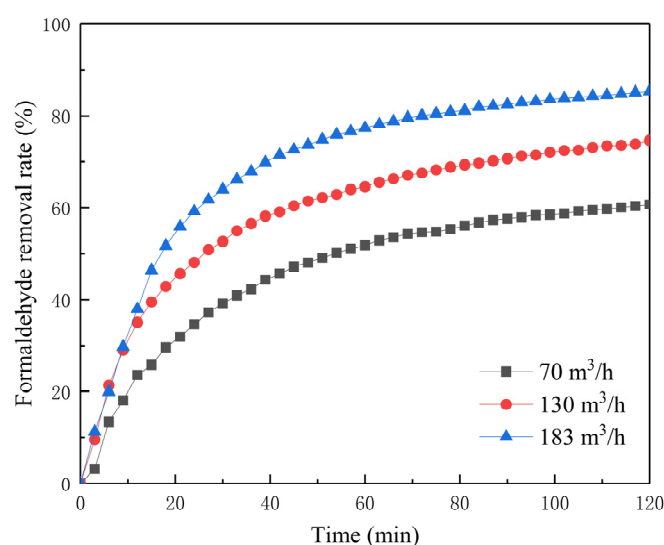
**Figure 7.** Comparison of formaldehyde removal performance under different radiation intensity.

Compared with other modified TiO<sub>2</sub> materials, this material has shown good photocatalytic performance. The greater the radiation energy absorbed by GR-TiO<sub>2</sub> photocatalyst, the more photons it receives, which excites and generates more photo-generated holes with strong oxidation and photogenerated electrons with strong re-duction, and correspondingly produces more hydroxyl radicals (·OH) and other active substances [43,44]. At 120 min, there is a 13.4% difference between the removal rate of formaldehyde under no-light conditions and under 19.9 W/m<sup>2</sup>, indicating that the adsorption of ACF plays a significant role in the purification of formaldehyde at this time.

### 3.2.3. The Effect of Air Supply Volume

In this experiment, the air supply of the purification device was adjusted by the turbo blower. During the experiment, all the ultraviolet lamps on the purification module were turned on. The initial concentrations of three groups of formaldehyde were (1.054 mg/m<sup>3</sup>, 1.022 mg/m<sup>3</sup>, 1.038 mg/m<sup>3</sup>), and the difference between the maximum and minimum values was 3%.

Figure 8 shows the influence of different airflow rates on the adsorption and degradation of formaldehyde by the GR-TiO<sub>2</sub>/ACF hybrid material under the indoor temperature of 20 °C, air relative humidity of 27% and irradiance of 19.9 W/m<sup>2</sup>, and the setting of airflow rate in the chamber were 70 m<sup>3</sup>/h, 130 m<sup>3</sup>/h, and 183 m<sup>3</sup>/h.

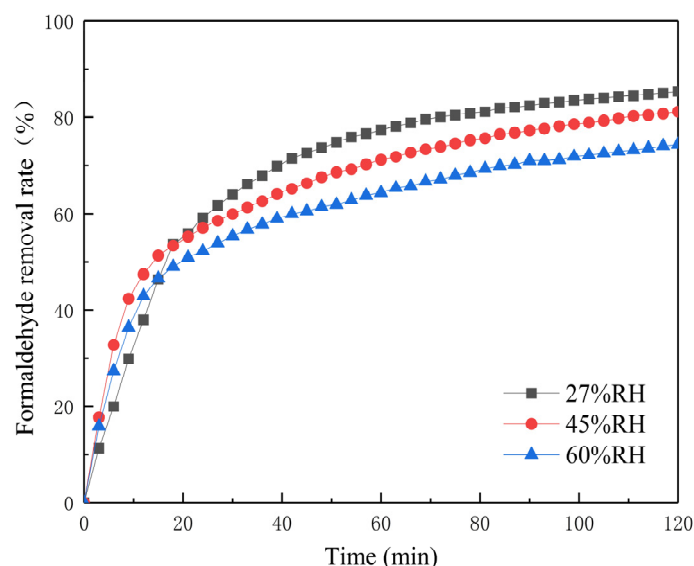


**Figure 8.** Comparison of formaldehyde removal performance under different air volume.

It can be seen from Figure 8 that within 20 min of the purification device being turned on, the removal rate of formaldehyde under different air supply rates increased rapidly. After 20 min, the rate of formaldehyde purification began to slow down. After 40 min, the removal rate of formaldehyde gradually became flat. When the air supply rate was 70 m<sup>3</sup>/h, GR-TiO<sub>2</sub>/ACF had the worst formaldehyde degradation effect, the formaldehyde adsorption capacity was 0.365 mg/m<sup>3</sup> at 25 min, and the formaldehyde removal rate was 34.63%. It is because the gas flow rate is too low, the gas flow speed cannot overcome the mass transfer resistance between substances, and the surface of the hybrid material cannot absorb more formaldehyde molecules. At the same time, because the amount of clean air provided by the purification device was relatively small, the indoor formaldehyde concentration was still high. When the air supply rate was 183 m<sup>3</sup>/h, GR-TiO<sub>2</sub>/ACF had the best formaldehyde degradation effect. The formaldehyde adsorption capacity was 0.614 mg/m<sup>3</sup> at 25 min, and the formaldehyde removal rate was 59.15%. The performance of purifying formaldehyde efficiency under different air supply volumes was: 183 m<sup>3</sup>/h > 130 m<sup>3</sup>/h > 70 m<sup>3</sup>/h. Within the scope of this test, the formaldehyde removal rate is positively correlated with the air supply volume. The larger the air supply volume, the higher the formaldehyde removal rate of the GR-TiO<sub>2</sub>/ACF hybrid material. This is because with the increase in air supply, the mixing rate of formaldehyde molecules with indoor clean air is increased, and at the same time, more oxygen molecules are provided for the photocatalytic process, which inhibits the recombination of electron-hole pairs, thereby increasing the formaldehyde purification efficiency. However, some studies have pointed out that excessive airflow will reduce the residence time of pollutants on the ACF and thus reduce the efficiency [45]. The formaldehyde degradation efficiency of the GR-TiO<sub>2</sub>/ACF hybrid material under a larger airflow will also bring an improvement.

### 3.2.4. The Effect of Relative Humidity

The relative humidity in the chamber is adjusted to 27%, 45% and 60% through a humidity regulator. In this experiment, the difference between the maximum and minimum values of the three groups of formaldehyde initial mass concentrations (1.008 mg/m<sup>3</sup>, 1.024 mg/m<sup>3</sup>, 1.038 mg/m<sup>3</sup>) was 2.9%. Figure 9 shows the effect of different relative humidity on the adsorption and degradation of formaldehyde by the GR-TiO<sub>2</sub>/ACF at the conditions of 20 °C, airflow of 183 m<sup>3</sup>/h, and UV irradiation of 19.9 W/m<sup>2</sup>.



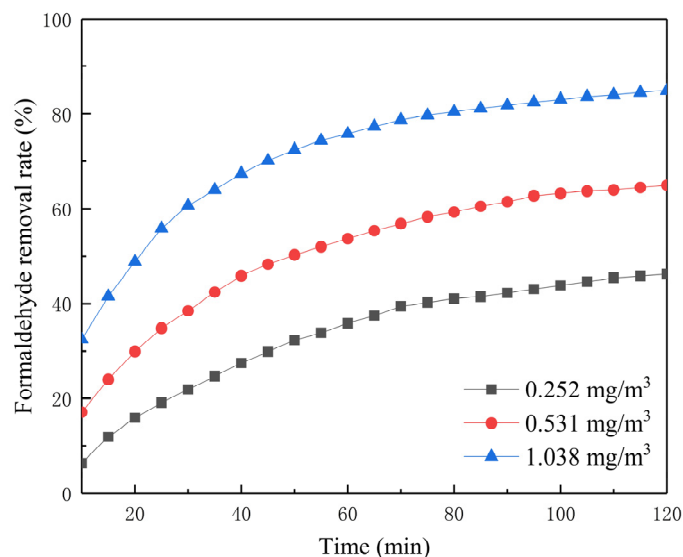
**Figure 9.** Comparison of formaldehyde removal performance under different relative humidity.

It can be seen from Figure 9 that when the relative humidity of the air was 60%, the GR-TiO<sub>2</sub>/ACF hybrid material had the worst formaldehyde degradation effect. The formaldehyde adsorption capacity was 0.659 mg/m<sup>3</sup> at 120 min, and the formaldehyde removal rate was 74.41%. When the relative humidity of the air was 27%, the formaldehyde degradation effect was the best. The formaldehyde adsorption capacity is 0.803 mg/m<sup>3</sup> at 120 min, and the formaldehyde removal rate was 84.87%. From the final test results, it can be seen that under the test conditions, the removal rate of formaldehyde increases with the relative humidity increases and decreases, and the efficiency of the material to purify formaldehyde under different relative humidity was: 27% > 45% > 60%. As the relative humidity increases, more water molecules compete with formaldehyde gas molecules for the adsorption sites on the surface of the ACF in the indoor environment, which agrees with results reported by Mo et al. [46]. The unexpected competition will affect the generation of hydroxyl radicals and other active substances, resulting in the inefficient adsorption-photocatalytic reaction, thereby reducing the formaldehyde removal rate.

In the first 20 min of the test, the formaldehyde removal rate was the highest when the relative humidity was 45%. This phenomenon may be because the competition between water molecules and the adsorption-photocatalytic reaction was not very serious at the beginning of the test, and there was a certain amount of water molecules in the air. It can provide ·OH for the photocatalytic reaction, thereby improving the efficiency of formaldehyde purification in a short time [45,47]. However, although the increase of relative humidity will reduce the adsorption effect of ACF, it can greatly increase the photocatalysis and further improve the purification effect of the material. The purification ability of the material is affected by both adsorption and photocatalysis according to the results reported by Bi et al. [48].

### 3.2.5. The Effect of Initial Mass Concentrations of Formaldehyde

The initial mass concentration of formaldehyde can be changed by adjusting the amount of formaldehyde solution injected into the formaldehyde generator. Figure 10 shows the effects of different initial mass concentrations ( $0.25 \text{ mg/m}^3$ ,  $0.5 \text{ mg/m}^3$ ,  $1.0 \text{ mg/m}^3$ ) on the adsorption and degradation of formaldehyde by the GR-TiO<sub>2</sub>/ACF hybrid material. ( $130 \text{ m}^3/\text{h}$ ,  $19.9 \text{ W/m}^2$ ,  $20^\circ\text{C}$ ,  $26\%\text{RH}$ ).



**Figure 10.** Comparison of formaldehyde removal performance under different initial mass concentrations.

It can be seen from Figure 10 that at low initial mass concentrations, the removal rate of formaldehyde was lower, and the growth rate was relatively gentle. Under high initial concentration, the formaldehyde purification rate increased rapidly in the first 30 min, and gradually became flat after 30 min. The removal rate of formaldehyde at high initial mass concentration was significantly higher than that at low initial mass concentration because there were more sparse free molecules in formaldehyde gas molecules at low concentrations GR-TiO<sub>2</sub>/ACF hybrid material captures formaldehyde. As the concentration increased, the formaldehyde gas molecules passing through the purification material increased significantly, increasing the probability that the material could capture formaldehyde molecules. More formaldehyde molecules are adsorbed and then photocatalyzed, so that the removal rate of formaldehyde was improved.

## 4. Conclusions

In this work, we successfully synthesized the GR-TiO<sub>2</sub>/ACF hybrid material by a simple dipping-coating method. The structure and morphology of the synthesized materials were characterized by means of XRD, SEM and BET. The characterization results of the materials. The characterization results of the hybrid material show that GR-TiO<sub>2</sub> will block the micropore structure of ACFs to a certain extent during the loading process. The formaldehyde degradation performance of the hybrid materials under different conditions was tested. The irradiance, air supply and initial mass concentration were positively correlated with the removal rate of formaldehyde by the GR-TiO<sub>2</sub>/ACF hybrid material. The relative humidity was negatively related to the removal rate of formaldehyde by GR-TiO<sub>2</sub>/ACF hybrid material. The GR-TiO<sub>2</sub>/ACF hybrid material had a high formaldehyde purification efficiency in the environment chamber within 20 min. The formaldehyde removal rate at 120 min was up to 85.54% under the best combination of conditions in this experiment ( $19.9 \text{ W/m}^2$ ,  $183 \text{ m}^3/\text{h}$ ,  $45\%\text{RH}$ ). It indicates that the GR-TiO<sub>2</sub>/ACF hybrid material had good adsorption-photocatalytic performances. Finally, the GR-TiO<sub>2</sub>/ACF hybrid material synthesized using dipping-coating method have shown promising formaldehyde degrada-

tion. In addition, the material's removal effect on other indoor pollutants and its properties under more conditions will be investigated.

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