Ultraviolet-Photocatalytic Combined Catalytic Degradation of Formaldehyde

Xuege Sun[1], Xiaoyu Cui[2], Mingda Sun[3], Wei Cui[4,*]

[1]Shanghai No.4 High School, Shanghai, China
[2]Changzhou Xinbei Experimental Middle School, Changzhou, China
[3]Shanghai Doesun Energy Technology Co., Ltd; Shanghai, China
[4]Shanghai Yue Rong Science and Technology Development Co., Ltd, Shanghai, China

*Corresponding author. Email: cuiwei_hit@163.com

Abstract. The hazards of formaldehyde is a highly concerned issue in environmental management. Efficient, clean, and convenient methods for formaldehyde treatment still need to be developed, among which photocatalytic method is a promising approach. This study designed an experimental apparatus using TiO_2 photocatalyst and ultraviolet irradiation to improve its catalytic effect. The 5% TiO_2 -containg water solution was spraied on transparent SiO_2 glass. Nano Al_2O_3 was added in the solution to enhance catalyst effect. The contant of Al_2O_3 was 0%, 1%, 2%, and 3%. The distribution morphology of photocatalyst on glass surface was observed using scanning electron microscope, and the relationship between its structure and properties was studied. Experiments have shown that UV irradiation or TiO_2 photocatalyst can both reduce the concentration of formaldehyde, yet the effect is relatively poor. Combined action of UV-TiO_2 photocatalyst show better efficiency of formaldehyde decomposition. Adding Al_2O_3 as an enhancement can effectively improve the decomposition rate of formaldehyde, which may be because the addition of Al_2O_3 particles can increase the contact area between TiO_2 photocatalyst and air. However, excessive Al_2O_3 particles can actually reduce the rate of formaldehyde decomposition. The optimal content of nano Al_2O_3 is 2%, and its formaldehyde degradation coefficient in 60 minutes reaches 32%, which is much higher than the case without alumina.

Keywords: Formaldehyde, Photocatalyst, Ultraviolet Radiation, Pollution control

1 Introduction

Formaldehyde is a colorless, water-soluble liquid with strong volatility and a pungent odor. Formaldehyde is a toxic gas that can seriously harm human health. It has a strong irritant effect on the mucous membranes of the eyes, nose, and throat, and can cause allergic dermatitis and asthma in severe cases. The main sources of formaldehyde in daily life are indoor decoration materials and furniture, such as floor glue, plywood, latex paint, synthetic fibers, etc., especially artificial boards[1~3].

W. He et al. (eds.), *Proceedings of the 2024 10th International Conference on Advances in Energy Resources and Environment Engineering (ICAESEE 2024)*, Atlantis Highlights in Engineering 36,
https://doi.org/10.2991/978-94-6463-708-3_53

The commonly used methods for formaldehyde removal are adsorption, such as using activated carbon adsorption, and catalytic degradation, such as titanium dioxide photocatalysis and manganese dioxide catalysis. The treatment method of photocatalytic oxidation is to treat formaldehyde by converting it into carbon dioxide through the principle of temperature programmed desorption (TPD), electron spin resonance (ESR), and spin capture electron spin resonance (ST-ESR). During the photocatalytic oxidation of formaldehyde, oxygen adsorbed on the catalyst surface in the air is reduced to · O-2 by photo generated electrons, and trace amounts of water are oxidized to · OH. Formaldehyde is oxidized to the endpoint product carbon dioxide through the intermediate product formic acid.

The currently common photocatalyst is TiO_2, and some mature products can spray nano TiO2 into indoor spaces to stimulate its activity using ultraviolet light in sunlight. But indoor ultraviolet radiation is very weak, so the formaldehyde degradation effect that can be generated is limited. Moreover, the photocatalyst attached to the surface of furniture is easily covered by dust or erased during the cleaning process. In response to these issues, this study proposes using ultraviolet light to enhance the effect of TiO_2 photocatalyst, and increasing the contact area between photocatalyst and air by adding Al_2O_3 particles, thereby improving the degradation of formaldehyde.

2 Materials and Experiments

The materials used in this study are commercially available nano TiO_2 photocatalyst suspension(5%), nano Al2O3 particle powder, quartz glass flakes, and formaldehyde standard solution (100mg/L).he equipment used includes: sealed organizer, power supply, computer case fan, pipette, cotton pieces, pipettes, UV lamp (7W), plastic bracket, spraier, cardboard box, MEF-500 formaldehyde detector (with data recording and storage functions), etc. The experimental process is shown in Figure 1.

In the first step, the UV lamp was placed on top of the steel bracket and the fan on the side of the steel bracket. The quartz glass piece was placed on a small plastic bracket under the UV lamp. All the equipment and materials are palced in a sealed box, so as to prevent leakage of the formaldehyde.In the experiment, TiO_2 dispersions with Al_2O_3 contents of 0%, 1%, 2%, and 3% were first prepared and sprayed onto quartz glass. They were then dried in air so as to form a thin film on the glass. In the experiment, 0.5ml of formaldehyde standard solution was taken from the solution using a pipette, dropped onto a cotton pad, and placed near a fan. Close the sealed box lid and apply experimental conditions, as shown in Table 1. The formaldehyde detector was used to record changes in formaldehyde, and select data every 5 minutes for analysis. Each group lasts for 60 minutes. Scanning electron microscopy (SEM) was used to observe the film formation state of catalysts with different alumina contents on the surface of quartz glass. Before the SEM observation, the sample was sprayed with gold (ion sputtering) to form a nano thin gold film on the surface for observation, without affecting the morphology of the sample itself.

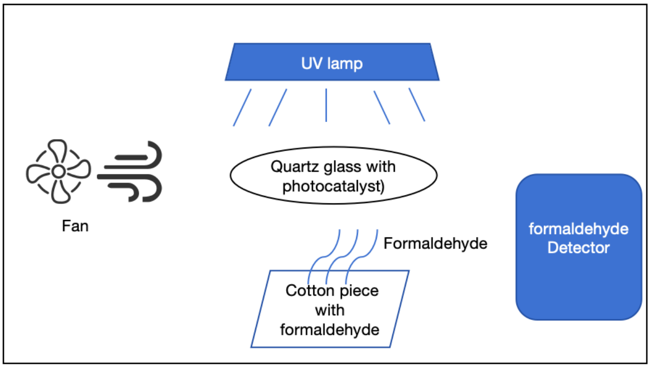


Fig. 1. Schematics of the experiment

Table 1. Expeirmental parameters and groups

Group No.	Containing photocatalyst	Al_2O_3 content in photocatalyst	UV-lamp	Remarks
#1	No	-	-	Control group
#2	-	3%	-	Control group
#3	-	-	Yes	Control group
#4	Yes	0%	Yes	Experiment group
#5	Yes	1%	Yes	Experiment group
#6	Yes	2%	Yes	Experiment group
#7	Yes	3%	Yes	Experiment group

3 Results and Discussion

3.1 Degradation of Formaldehyde In the Control Groups

The data and graphs of the degradation of formaldehyde in the control groups is shown in the Figure 2 and Table 2. The formaldehyde concentration in the control group first increases and enters a relatively stable peak after 20 minutes, because the volatilization of formaldehyde solution requires a certain process. After the formaldehyde concentration reached its peak, all three control groups entered a holding phase, during which the formaldehyde concentration slightly decreased.

Due to slight differences in the experimental process between groups, directly comparing the absolute value of formaldehyde concentration may not fully accurately reflect the changes in formaldehyde concentration. Therefore, this study defines the formaldehyde degradation coefficient to represent the decomposition of formaldehyde as follows:

$$\gamma = 1 - (\text{final formaldehyde concentration}/\text{peak formaldehyde concentration})$$

In the control groups, γ_1=0.03, γ_2=0.03, γ_3=0.05. It can be seen that the degradation of formaldehyde by pure ultraviolet radiation or TiO_2 photocatalyst in dark environments is very weak and can be ignored.

Table 2. Data of formaldehyde degradationin the control groups

Time(min)	1#	2#	3#
5	0.45	0.48	0.52
10	0.59	0.61	0.55
15	0.63	0.6	0.59
20	0.62	0.59	0.61
25	0.62	0.6	0.6
30	0.63	0.6	0.6
35	0.61	0.59	0.58
40	0.6	0.6	0.58
45	0.6	0.58	0.57
50	0.59	0.59	0.56
55	0.59	0.57	0.56
60	0.58	0.57	0.55

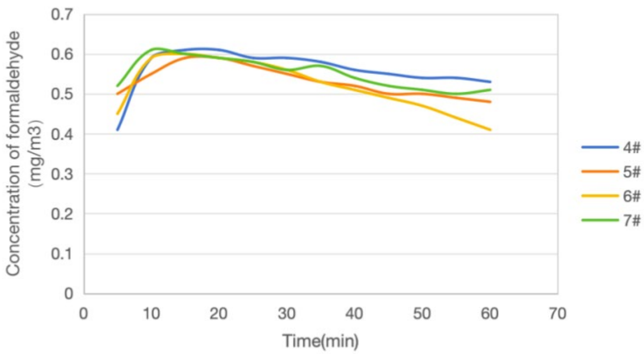


Fig. 2. Degradation of formaldehyde in the control groups

3.2 Degradation of Formaldehyde in the Experiment Groups

The data and graphs of the degradation of formaldehyde in the experiment groups is shown in the Figure 3 and Table 3. The formaldehyde degradation coefficients of the experimental group are, γ_4=0.15，γ_5=0.19，γ_6=0.32，γ_7=0.16。 The formaldehyde degradation coefficients of groups 4 #, 5 #, 6 #, and 7 # were significantly higher than those of the control group, indicating that the combination of ultraviolet radiation and catalyst can significantly improve the efficiency of formaldehyde degradation, greatly exceeding the individual effects of ultraviolet radiation or catalyst.

Comparing the data of 4 #, 5 #, 6 #, and 7 #, it can be seen that as the Al_2O_3 content in the catalyst solution increases, the formaldehyde degradation coefficient first increases and then decreases, reaching its peak when the alumina content reaches 2%. This may be because the increase of alumina particles can improve the surface roughness of the catalyst membrane, thereby enhancing the catalytic effect. However, when the alumina content is too high, the surface state deteriorates and the catalytic efficiency decreases. This hypothesis will be further verified in the next section by observing the surface film state of the glass sheet using an electron microscope.

Table 3. Data of formaldehyde degradationin the experiment groups

Time(min)	4#	5#	6#	7#
5	0.41	0.5	0.45	0.52
10	0.59	0.55	0.59	0.61
15	0.61	0.59	0.6	0.6
20	0.61	0.59	0.59	0.59
25	0.59	0.57	0.58	0.58
30	0.59	0.55	0.56	0.56
35	0.58	0.53	0.53	0.57
40	0.56	0.52	0.51	0.54
45	0.55	0.5	0.49	0.52
50	0.54	0.5	0.47	0.51
55	0.54	0.49	0.44	0.5
60	0.53	0.48	0.41	0.51

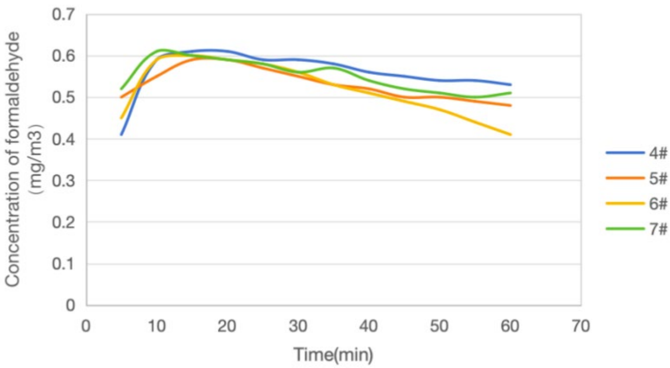


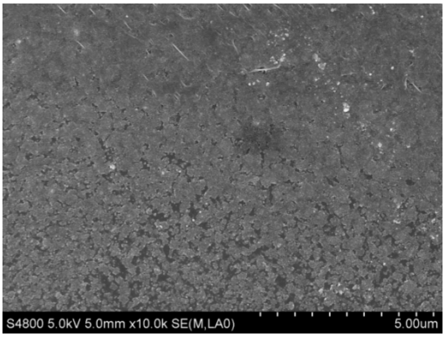
Fig. 3. Degradation of formaldehyde in the control groups

3.3 Investigation of Microstructure of the Photocatalyst Film

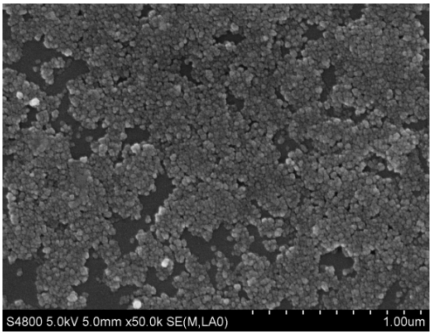
The microstructure of the photocatalyst film is shown in the figure 4. With the increase of Al_2O_3 particles, coarsening particles gradually appear in the catalyst coating on the surface of quartz glass. The Al_2O_3 particle content in Group 4 is 0%, and the catalyst film formed is composed of agglomerated small-sized TiO_2 with a thin thickness, which is spread flat on quartz glass. The Al2O3 particle content in Group 5 is 1%, and the catalyst film formed is composed of agglomerated small-sized TiO_2 and larger Al_2O_3 particles, with increased thickness and surface area. The Al_2O_3 particle content in Group 6 is 2%, and the catalyst film formed is composed of agglomerated small-sized TiO_2 and larger Al_2O_3 particle aggregates, with an increased thickness and many gaps inside. The Al_2O_3 particle content in Group 7 is 3%, and a large number of Al_2O_3 particles appear in the formed catalyst film. These particles agglomerate together, greatly increasing the thickness of the catalyst layer. Although it may further increase the surface area, these agglomerated Al_2O_3 particles may hinder the interaction between ultraviolet radiation and the active ingredient TiO_2, thereby reducing the catalytic effect.

Overall, an increase in the content of Al_2O_3 particles may increase the area of the catalyst membrane, thereby improving catalytic efficiency; On the other hand, it may be due to the lack of catalytic activity of Al_2O_3 particles themselves, and excessive content of Al_2O_3 particles may hinder ultraviolet radiation, so the catalytic efficiency will not continue to improve with the increase of Al_2O_3 particles.

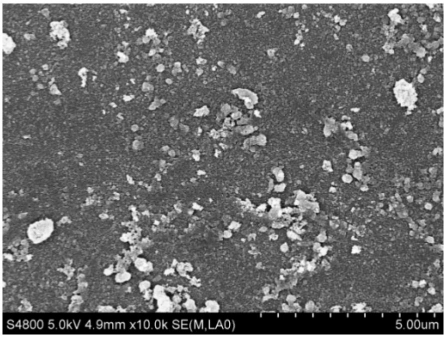
Further comparison was made between the results of this study and those of other researchers. Lu et. Al. Used BiOX-Red Mud/Granulated Blast Furnace Slag Geopolymer Microspheres to achieve photocatalytic degradation of formaldehyde, and found that Loading BiOX (X=Cl, Br, I) photocatalyst on the surface of geopolymer microspheres for photocatalytic degradation of formaldehyde, which can adsorb 85.71% formaldehyde gas within 60 minutes[4]. This show a very goode effect of BiOX, however the materials can hard be reused. Qiu et. Al found that TiO2/C/CaCO3 heterojunction photocatalyst can enchance hotocatalytic degradation efficiency of formaldehyde[5]. Yan also found that BiOI-Carbon sphere core–shell nanostructures composite photocatalyst can improve photocatalytic performance[6]. Nhan et. al. also found that carbon nanodots/TiO2 composite can enhance photocatalytic oxidation of VOCs[7]. All these measures show that combined efforts can be explored to improve the photocatalytic performance. The addition of Al_2O_3, which is emploied in this study can lower the cost as alumina can be easily obtained, comparing to these materials in the previous studies. Thus, a very practical and affordable measure to degrate formaldehyde is authenticated here.



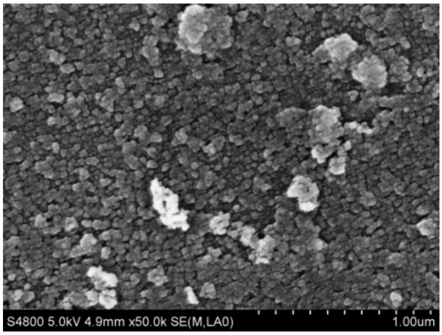
(a) 4#-10000x



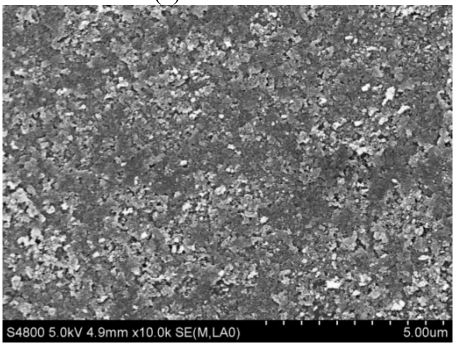
(b) 4#-50000x



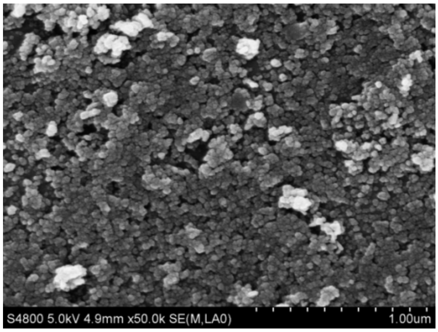
(c) 5#-10000x



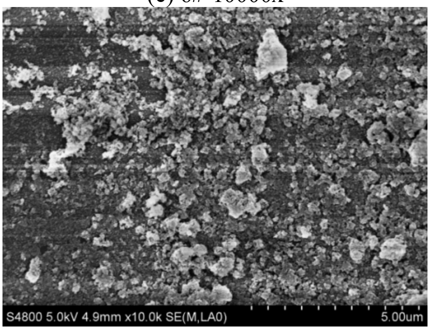
(d) 5#-50000x



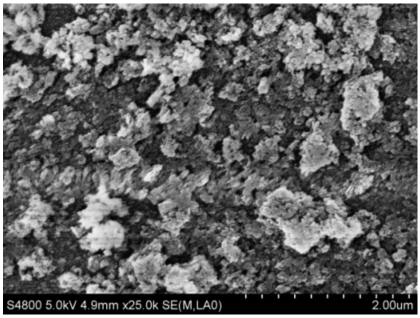
(e) 6#-10000x



(f) 6#-50000x



(g) 7#-10000x



(h) 7#-50000x

Fig. 4. SEM image of the surface of SiO_2 plates

4 Conclusions

This study established a closed formaldehyde degradation experimental device and investigated the enhancement effect of nano Al_2O_3 as a photocatalyst carrier under the conditions of 0%, 1%, 2%, and 3% content on the catalytic effect. The distribution morphology of photocatalyst on glass surface was observed using optical microscope and electron microscope, and the relationship between its structure and properties was studied. The conclusions drawn from the study are as follows:

(1) Under separate UV irradiation or TiO_2 photocatalyst, the concentration of formaldehyde can be reduced, but the effect is relatively poor. Under the combined action of UV-TiO_2 photocatalyst, the efficiency of formaldehyde decomposition is higher.

(2) Adding Al_2O_3 as a photocatalyst carrier can effectively improve the decomposition rate of formaldehyde, which may be because the addition of Al_2O_3 particles can increase the contact area between TiO_2 photocatalyst and air. However, excessive Al_2O_3 particles can actually reduce the rate of formaldehyde decomposition.

(3) The optimal content of nano Al_2O_3 is 2%, and its formaldehyde degradation coefficient in 60 minutes reaches 32%, which is much higher than the case without alumina.

References

1. Mondal I, Groves M, Driver E M, et al. Carcinogenic formaldehyde in U.S. residential buildings: Mass inventories, human health impacts, and associated healthcare costs[J].Science of the Total Environment, 2024, 944. DOI:10.1016/j.scitotenv.2024.173640.
2. Ufelle A C, Asfaw H, Lee A G ,et al.Health Effects and Factors Affecting Formaldehyde Exposure Among Students in a Cadaver Laboratory[J].Journal of environmental health, 2022(6):84.
3. Letellier N , Gutierrez L A , Pilorget C ,et al.Association Between Occupational Exposure to Formaldehyde and Cognitive Impairment[J].Neurology. 2022(6): 98. DOI:10.1212/WNL.0000000000013146.
4. [Lu P , Zhang N , Wang Y ,et al.Synthesis of BiOX-Red Mud/Granulated Blast Furnace Slag Geopolymer Microspheres for Photocatalytic Degradation of Formaldehyde[J].Materials (1996-1944), 2024, 17(7).DOI:10.3390/ma17071585.
5. A S Q , B W W , A J Y ,et al.Enhanced photocatalytic degradation efficiency of formaldehyde by in-situ fabricated TiO 2 /C/CaCO 3 heterojunction photocatalyst from mussel shell extract[J].Journal of Solid State Chemistry, 2022.DOI:10.1016/j.jssc.2022.123110.
6. Yan G , He R , Cao X ,et al.Study on photocatalytic degradation of formaldehyde and rhodamine by BiOI@Carbon sphere core–shell nanostructures composite photocatalyst[J].Inorganic Chemistry Communications, 2024, 164. DOI:10.1016/j.inoche.2024.112410.
7. Nhan N V H , Tu L N Q , Loc B T ,et al.Microwave-assisted Synthesis of Carbon Nanodots/TiO2 Composite with Enhanced Photocatalytic Oxidation of VOCs in a Continuous Flow Reaction[J].Topics in Catalysis, 2024, 67(9-12).DOI:10.1007/s11244-023-01889-2.