Study on the Photocatalytic Degradation Rate of Indoor Formaldehyde with Nano-TiO₂ Coating

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Abstract. With the improvement of people's living standard, diverse home decoration has become popular. However, it results in indoor hazardous gas emission, especially formaldehyde, bringing harm to people’s health. To address this issue, one positive strategy is to remove the hazardous volatile organic compounds through environment friendly nanomaterials. Nano-TiO₂ is such a kind of semiconductor material, which can decompose the volatile pollutants via photocatalytic process. In this work, the removal of indoor volatile pollutants by applying home-made nano-TiO₂ was studied. The dependence of treatment efficiency of indoor formaldehyde on varying flow rate, coating times, humidity and temperature was systematically investigated. As a result, the highest purification efficiency was achieved when it was coated three times at the relative humidity of 50%. The faster the flow rate, the higher the air purification efficiency. Temperature is also an important factor affecting degradation efficiency, and the degradation has peaked at 22°C. This study demonstrates the effective removal of indoor volatile organic compounds via green nano-TiO₂ coating at low cost, and paves way for nanomaterials in applications of indoor environment improvement.

1. Introduction

People's living environment has been greatly improved since the 21st century. However, the survey also found that there are more and more symptoms of coughs, headaches, and other physical discomforts when people live in newly built buildings for a long time. In recent years, researchers have found that the amount of indoor air pollutants is more than twice that of outdoors, and the types are more complex. The main indoor pollutants include formaldehyde, benzene, xylene and other organic pollutants, and there come from natural gas, decoration materials, paint, etc [1-5]. These pollutants can irritate skin, cause respiratory diseases, high blood pressure, high cholesterol and other diseases, which are very harmful to human beings.

For different indoor pollutants [6], there are currently the following treatment technologies: (1)
Adsorption technology: such as activated carbon adsorption. This technology is particularly effective in treating low concentration CO and nitric oxide. The advantage is that when choose the porous physical properties of activated carbon to adsorb harmful gases in the room it has better treatment effects on some harmful gases, low technical requirements, and low price; its drawback is easy to reach saturation and needs to be replaced or desorbed in time. (2) Closed treatment technology: Closed treatment technology has obvious effects on improving the indoor environment where the release source has been identified. (3) Green plant purification technology: Planting green plants indoors, using the photosynthesis of plants and the mechanism of plants themselves, to absorb harmful gases in the room, so as to achieve the purpose of treating pollutants and purifying indoor air quality. (4) Titanium dioxide visible light photocatalytic purification technology. Nanomaterials photocatalysis is the most promising indoor air purification technology, but it cannot purify suspended matter and fine particles in the air. At the same time, the micropores of the catalyst are easy to be blocked by dust or particulate matter. The problems of semiconductor photocatalysis include low quantum efficiency (about 4%) and the recombination of photo-generated carriers. Building thermal ventilation and air conditioning makes photocatalysis difficult to compete with conventional environmental protection technology economically. At present, there are also some techniques that can improve the efficiency of photocatalytic purification, mainly including photosensitization, transition metal ion doping, semiconductor coupling, noble metal precipitation, electron capture and synergistic enhancement of external fields such as microwave, which is expected to improve the activity of visible photocatalytic purification of TiO₂.

Since Fujishima and Honda of Japan published their research work on TiO₂ as a photocatalyst in the 1970s, photocatalytic technology has developed extremely rapidly. The research in environmental science has made unexpected progress and the photocatalytic air purification technology has been paid more and more attention by researchers, which has become a hot spot in the research and development of various countries. At present, the newly developed air catalyst [8] does not require specific UV light exposure. Under the action of this catalyst, harmful gases will be decomposed into harmless substances such as H₂O and CO₂ in the air which will expand the application of photocatalytic purification technology. And the life of the catalyst is long.

In this paper, photocatalytic technology is applied to degrade indoor formaldehyde gas, which involves the development and utilization of solar energy and the sustainable development of environment. A type of home-made nano-TiO₂ with visible light response was prepared to be a suspension, forming coatings. Then the dependence of formaldehyde degradation efficiency on the flow rate, coating thickness, environment temperature and humidity were systematically investigated. The results demonstrate the home-made TiO₂ has excellent decomposition ability to hazardous volatile organic compounds, possessing great economic and social value.

2. Experiment

2.1. Preparation of catalyst film

A method of loading TiO₂ of porous carrier materials used in this experiment is sol-gel method. The butyl titanate [Ti (OC₄H₉)₄] alcohol solution is hydrolyzed, and a uniform and transparent yellow TiO₂ sol was obtained by magnetic stirring. Using the dipping method, the self-made pulling machine was used to form a uniform TiO₂ film on the honeycomb substrate structure, and then dried at 100°C for 10 minutes. Then, the dipping process was repeated to form a multilayer film. Finally, it was placed in a muffle furnace and fired at about 400°C for 2 hours to form a stable TiO₂ film.

The reagents required for this experiment (photocatalytic purification test of formaldehyde) and their manufacturers: formaldehyde solution, Tianjin Shengao Chemical Reagent Co., Ltd.; reagents for formaldehyde detection, Changchun Jida· Little Swan Instrument Co., Ltd. The main reagents and specifications required for photocatalyst preparation: absolute ethanol, specification AR, Tianjin Huadong Reagent Factory; butyl titanate, specification AR, Tianjin Damao Chemical Reagent Factory.
2.2. Experimental Details

2.2.1. Laboratory equipment. The test reaction equipment mainly included humidifier, blower, separate electric heating cup, and self-made adsorption column. The test parameters mainly contained temperature and humidity inspection instrument and formaldehyde tester. In addition, there were ultraviolet lamps and electronic balances.

Equipment required for photocatalyst preparation: electronic balance; digital display blast drying oven; magnetic heating stirrer; ultrapure water machine.

2.2.2. Experimental Setup. This test platform is mainly composed of three parts: formaldehyde generation system, data monitoring system and TiO\textsubscript{2} and its composite material catalytic degradation purification system.

(1) Formaldehyde generation system: Place 1 ml of formaldehyde solution in the formaldehyde generator, and at the same time put it in a big beaker with hot water which temperature is greater than 19 °C. To prevent rapid cooling of the hot water, take an insulation measures around the large beaker. The above integral device is placed in a self-made formaldehyde generator box. The water bath heating is used to promote the volatilization of formaldehyde in the solution into the air and to mix with the air, simultaneously the ultrasonic humidifier is connected with the formaldehyde generator box to maintain the air humidity in the formaldehyde generator box at a constant value to simulate the indoor air environment contaminated by formaldehyde. The air in the box is sent to the TiO\textsubscript{2} and its composite catalytic degradation purification system for photocatalytic purification by using a fan.

(2) TiO\textsubscript{2} and its composite material catalytic degradation purification system: put the photocatalyst into the self-made adsorption column, the air mixed with formaldehyde is sent into it by the fan, the gas passes through the photocatalyst, and the photocatalyst is irradiated with a purple light. And the irradiation intensity of purple lamp is controlled by the 5-speed regulator, that makes the formaldehyde react with the photocatalyst to be degraded and purified, and then could test the photocatalytic performance of the photocatalyst. The air flowing through the photocatalyst is sent into the formaldehyde absorber through a pipe, because there is still a small amount of formaldehyde to avoid indoor pollution.

(3) Data detection system: use a formaldehyde meter to measure the initial concentration of formaldehyde in the box and the concentration of formaldehyde after the air passes through the photocatalyst. The photocatalytic effect of photocatalyst was determined by comparing the concentration of formaldehyde in air before and after photocatalyst. The gas temperature and humidity in the reaction process are tested by precision temperature and humidity inspection instrument. Place a temperature probe at the outlet of the formaldehyde generating box and a humidity probe at the self-made adsorption column, respectively, to measure the gas temperature and humidity in real time to ensure that the reaction is carried out under the required test conditions.

2.2.3. Calculation of formaldehyde removal efficiency. The formula of standard method concentration of formaldehyde in the air:

\[ C = \frac{C_0}{V_0} \times 5 \]

Formula:

- \( C \)——Absorb the concentration of formaldehyde in the air, mg/m\textsuperscript{3};
- \( C_0 \)—— The concentration value displayed by the formaldehyde analyzer;
- \( V_0 \)—— Sampling volume of the formaldehyde analyzer under standard conditions, L;
- 5——The volume of absorption liquid, ml.

The formula for calculating the removal efficiency of formaldehyde:

\[ \eta = \left( \frac{C_1 - C_2}{C_1} \right) \times 100\% \]

Formula:
η——formaldehyde removal efficiency;

C1——The mass concentration of formaldehyde at the entrance of the adsorption column after calculation, mg/m³;

C2——The mass concentration of formaldehyde at the outlet of the adsorption column after calculation, mg/m³.

3. Results and discussion

3.1. The effect of flow rate on the photocatalytic degradation rate of formaldehyde

In order to explore the effect of photocatalysis on formaldehyde decomposition efficiency at different concentrations and flow rates, formaldehyde at different flow rates was introduced under the premise of high concentration (0.635 mg/m³) and low concentration (0.2125 mg/m³). The results are shown in Figure 1 and Figure 2, while other influencing factors remain the same.

Figure 1 shows the effect of flow velocity on the photocatalytic degradation efficiency of formaldehyde when the initial concentration of formaldehyde is 0.635 mg/m³. It can be seen that the flow velocity increases from 0.2 m³/min to 4.0 m³/min, the degradation rate of formaldehyde also rises from 53.5% to 71.7%, indicating the probability of formaldehyde molecules adsorbed by titanium dioxide is increasing. Figure 2 shows the effect of flow rate on the photocatalytic degradation efficiency of formaldehyde when the initial concentration of formaldehyde is 0.2125 mg/m³. The degradation rate of formaldehyde decreased from 69.8% to 66.1% m³/min, when the flow rate is reduced from 0.2 m³/min to 4.0 m³/min. This is because the initial concentration of formaldehyde is low, the concentration of formaldehyde transferred to the surface of titanium dioxide is small. The faster the flow rate, the shorter the residence time of formaldehyde on the surface of titanium dioxide, lowering the degradation rate of formaldehyde.

Conclusions are drawn from the experimental results that the concentration and flow rate of formaldehyde are both important factors affecting the photocatalytic purification of titanium dioxide. To improve the efficiency of formaldehyde purification, it is necessary to control the concentration of formaldehyde. Photocatalytic degradation of formaldehyde is a chemical equilibrium reaction, in which the left side of the reaction involves in formaldehyde, oxygen, water (oxygen and water in the light to provide energy under the action of the catalyst to generate OH⁻ ions and then react with formaldehyde), and the right side produces water, carbon dioxide.

When the temperature and light balance, the higher the concentration of the left component (e.g. formaldehyde), the faster the reaction is. Therefore, the higher the formaldehyde concentration, the
higher the removal rate of formaldehyde. However, when formaldehyde is higher than the amount of oxygen, the reaction to a certain extent (oxygen consumption, concentration is too low) cannot be carried out positively, then the removal rate will decrease.

3.2. The effect of coating times on the degradation of formaldehyde
To explore the effect of photocatalysis on the degradation efficiency of formaldehyde, this study also explored the effect of different coating times on the degradation rate of formaldehyde. The coating times were set to be 2, 3, 4, respectively. The experimental results are shown in Figure 3.

![Figure 3. The influence of coating times on the degradation of formaldehyde.](image)

The efficiency of formaldehyde purification corresponds to 10.8%, 15.2%, and 12.6%, as shown in Figure 3. The increase in titanium dioxide coating represents the growth of titanium dioxide quantity. With the increasing amount of titanium dioxide, the efficiency of formaldehyde purification does not fluctuate too much. When the number of films increases to 4 times, the efficiency of formaldehyde purification decreases. The reason for this is that formaldehyde can only be degraded when it enters the coating. When the number of layers is low, the amount of titanium dioxide is insufficient, which will affect its reflection efficiency. However, if the number of layers is too high, titanium dioxide will hinder the diffusion of formaldehyde, reducing the efficiency of formaldehyde purification. The optimum value of titanium dioxide coating load is 3 layers.

In the practical application of photocatalytic technology to treat formaldehyde, different strategies should be adopted based on the different concentration to achieve the purpose of high purification efficiency. To be more accurate, when moving into a new home, the initial indoor formaldehyde concentration is relatively high, the formaldehyde purification device can be used at high flow rate and high power. The coating of titanium dioxide is preferably 3 layers. When the formaldehyde concentration is high and the flow rate is also set to be great, it can maintain high efficiency to purify formaldehyde and reduce indoor formaldehyde concentration in a short time. After a period of time, if the concentration of formaldehyde is reduced but still exceeds the standard, it is necessary to reduce the flow rate so that the formaldehyde and the titanium dioxide coating are in full contact to achieve a good purification efficiency.

3.3. The effect of humidity on the photocatalytic degradation rate of formaldehyde
Before studying the influence of humidity on the photocatalytic degradation effect, the influence of humidity on the natural reduction of formaldehyde was first studied. The results are shown in Figure 4.

![Figure 4. The effect of humidity on the natural reduction of formaldehyde.](image)
The above results showed that in a closed environment, humidity has no obvious effect on the natural reduction of formaldehyde. Therefore, in the following study, it is safe to conclude that the effect of humidity on the degradation of formaldehyde is caused by photocatalysis.

When the temperature is kept at 25 °C but with a varying humidity of 30%, 55%, 60%, the corresponding purification efficiency is 68.2%, 71.3%, 68.8%, respectively, as displayed in Figure 5. The above results showed that with the increase in humidity and light exposure time, the efficiency of formaldehyde purification firstly increased and then decreased, indicating that the humidity has an optimal effect on the photocatalytic degradation effect, which is determined by the adsorption performance of the TiO$_2$ catalyst to water molecules. When the relative humidity of air is about 50%, the purification efficiency of formaldehyde reaches the highest value. If the humidity is greatly over 50% or less than 50%, the purification efficiency of formaldehyde will be reduced. The reason can be explained as that when the relative humidity increases to 50%, water molecules play a positive role in purifying formaldehyde by hindering the recombination of holes in nanomaterials to produce hydroxyl radicals and promote the process of formaldehyde purification. However, if the relative humidity continues to increase, excessive water molecules will form competitive adsorption with formaldehyde on the surface of titanium dioxide, resulting in a decrease in the efficiency of formaldehyde purification. Therefore, when dealing with indoor formaldehyde, the relative humidity of air should be about 50% to ensure the best purification efficiency.

3.4. The effect of temperature on the photocatalytic degradation rate of formaldehyde

Irrespective of mass transfer, the photocatalytic reaction experiments were carried out at different temperatures under the conditions of 0.817 cm/s velocity of flow, 10.81 g/m$^3$ humidity. The relationship between temperature and reaction rate is shown in Figure 6. It is observed that when the temperature reaches 22 °C, the reaction rate is the highest with the value of 1.228 mg/m$^3*min$. When the temperature is approaching 22 °C, the chemisorption is increasingly enhanced, and the free hydroxyl groups will also grow, facilitating the reaction and resulting in a nearly linear growth in reaction rate. If photocatalytic technology is applied to degrade formaldehyde in real life, the appropriate temperature $^{[12]}$ should be kept at around 22°C, so as to achieve the highest efficiency in the treatment of indoor polluted gas.

4. Conclusion

Taking formaldehyde as example, this paper studied the application of nano-TiO$_2$ photocatalytic oxidation in the treatment of indoor volatile pollutants. The focus was on the decomposition efficiency at varying flow rates, coating times, humidity, and temperatures on indoor formaldehyde treatment.
The results showed that the concentration and flow rate of formaldehyde are critical factors affecting the photocatalytic purification of titanium dioxide. In order to improve the efficiency of formaldehyde purification, the concentration of formaldehyde should be controlled. The results also revealed that the efficiency of formaldehyde degradation reached best performance when the concentration is 0.635 ppm, the flow rate of 4 m³/min, the coating number of 3, the room temperature of 22℃, and the relative humidity of 50%. The investigations in this work provide a directional guide for the removal of indoor hazardous volatile organic compounds by photocatalytic nanomaterials so as to improve indoor air quality.

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