RESEARCH ARTICLE

Atmospheric formaldehyde degradation efficiency of modified bismuth vanadate-based photocatalytic materials in the context of green finance

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In recent years, the rapid development of green finance has significantly impacted environmental protection, particularly in the development of sustainable materials for air purification. Formaldehyde, a common indoor air pollutant, is carcinogenic and highly irritating, and its widespread presence and difficulty in effective removal make it a persistent challenge. Current photocatalytic materials such as $BiVO_4$ have shown potential in formaldehyde degradation, but their overall efficiency is limited due to issues like rapid charge recombination. To investigate the preparation of bismuth vanadate-based photocatalytic material Ag/AgBr/$BiVO_4$ and its application in atmospheric formaldehyde degradation in the context of green finance, this study synthesized $BiVO_4$ and Ag/AgBr/$BiVO_4$ photocatalysts using hydrothermal method to determine the optimal ratio of Ag/AgBr/$BiVO_4$ photocatalysts and the optimal parameters for formaldehyde degradation using one-factor controlled experiments. The atmospheric formaldehyde degradation efficiencies of $BiVO_4$ were compared with those of Ag/AgBr/$BiVO_4$ in the optimal parameter conditions. The optimum parameters for preparing Ag/AgBr/$BiVO_4$ photocatalyst were determined by precise control of hydrothermal synthesis conditions as hydrothermal reaction temperature of 170℃, reaction time of 4 hours, and the proportion of silver nitrate of 30%. The optimization of these conditions significantly improved the photocatalytic performance of the material, showing excellent light absorption over a wide wavelength range of 200 – 800 nm. Compared with the unmodified $BiVO_4$, the modified Ag/AgBr/$BiVO_4$ significantly improved the photocatalytic degradation efficiency of formaldehyde with the formaldehyde degradation rate reaching 92.3% under the optimal conditions, which was significantly higher than the 78.4% of $BiVO_4$. Closely combined with the concept of green finance, the research innovatively developed the modified bismuth vanadate based photocatalyst Ag/AgBr/$BiVO_4$, which significantly improved the efficiency of formaldehyde degradation by optimizing the preparation parameters, provided a new direction for the research and development of photocatalytic materials, promoted sustainable development, and was in line with the goal of green finance to pursue both environmental and economic benefits.

Keywords: green finance; bismuth vanadate; photocatalyst; formaldehyde; air pollution.

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Introduction

Bismuth vanadate ($BiVO_4$) has attracted much attention in the field of organic pollutant degradation due to its good stability, non-toxicity, and excellent photocatalytic activity in the visible light response range [1]. However, the fast charge carrier complexation rate of $BiVO_4$ leads to its unsatisfactory photocatalytic efficiency [2]. To overcome this limitation, researchers have used different strategies to improve its performance including doping,

loading, and composite methods. Silver-based (Ag/AgBr) materials are believed to significantly improve the photocatalytic performance of $BiVO_4$ due to their good visible light responsiveness and electron transport properties [3].

Formaldehyde is a common volatile organic compound, primarily originating from building materials, furniture, chemicals, cigarette smoke, and byproducts of industrial processes [4]. Prolonged exposure to low concentrations of formaldehyde can lead to chronic respiratory diseases, eye and skin irritation, while high concentrations of formaldehyde are closely associated with an increased risk of leukemia and nasopharyngeal cancer [5]. According to reports from the World Health Organization (WHO) and the U.S. Environmental Protection Agency (EPA), formaldehyde is widely present in indoor air worldwide with concentrations often exceeding safe limits in poorly ventilated environments [6]. Therefore, it is of great practical significance to study and develop effective formaldehyde removal methods. Under the promotion of the concept of green finance, it is more important to develop low-cost, high-efficiency, and no secondary pollution environmental treatment materials. The direct use of $Ag/AgBr/BiVO_4$ photocatalysts in the treatment of gaseous organic pollutants poses a number of challenges. For example, if the photocatalyst is dispersed in the air, it may cause secondary pollution. In addition, problems such as difficulty in recovering the photocatalyst due to its agglomeration, lower degradation efficiency, and increased cost may be encountered.

This study aimed to modify $BiVO_4$ to enhance its photocatalytic performance in formaldehyde-containing atmospheric air purification applications. Through Ag/AgBr loading, the composite was expected to exhibit superior photocatalytic performance and improve formaldehyde degradation efficiency. This study focused on the development of a novel modified bismuth vanadate based photocatalyst $Ag/AgBr/BiVO_4$, which could significantly improve its photocatalytic efficiency in atmospheric formaldehyde degradation by loading Ag/AgBr on $BiVO_4$. The study not only optimized the preparation parameters such as hydrothermal reaction temperature, time, and amount of silver nitrate, but also improved the material performance and effectively reduced the production cost. Further, this study was planned to evaluate how the indoor environmental factors affected the formaldehyde degradation ability of $Ag/AgBr/BiVO_4$ and to seek suitable host materials and methods. These innovations provided new ideas for the research and development of photocatalytic materials and would have important guiding significance for the development of environmentally friendly catalysts in the future. The results of this study not only promoted the progress of photocatalysis technology, but also provided a practical solution for dealing with indoor air pollution, which had wide application potential and scientific influence.

Materials and methods

Preparation of $Ag/AgBr/BiVO_4$ and $BiVO_4$ photocatalysts

The $BiVO_4$ was prepared by hydrothermal method, which provided a high-pressure and high-temperature environment to the growth and morphology control of $BiVO_4$ crystals. Different hydrothermal conditions including temperature, time, and pH value would affect the size, morphology, and crystallinity of the crystal, and then the photocatalytic performance. Briefly, 1.17 g of NH_4VO_3, 1.6 g of NaOH, and 40 mL of deionized water were mixed in a beaker and magnetically stirred for 30 min. The prepared solution was named as solution A. In addition, 4.85 g of $Bi(NO_3)$-$5H_2O$, 4.0 g of polyethylene-polypropylene polythene oxide (P123), 6.5 mL of 69% HNO_3, and 50 mL of deionized water were mixed in another beaker and then magnetically stirred for 30 min. The resulting solution was named solution B. P123 is a triblock copolymer and often used as a template agent or surfactant

to control pore structure and morphology in material synthesis. P123 can self-assemble to form micellar structures in aqueous solution, thus helping to control the size and morphology of crystals during hydrothermal synthesis. Solution A was then slowly added dropwise to solution B with continuous stirring throughout the process before the pH of the solution was adjusted to neutral using ammonia and stirring was continued for 1 hour. The resulting mixed solution was transferred to a high-pressure hydrothermal reactor and sealed, and then placed into a Boxun HHG-9080 electric constant temperature blast drying oven (Shanghai Boxun Medical Biological Instrument Co., Ltd., Shanghai, China) at 170°C for 16 hours before the high-pressure hydrothermal reactor was allowed to naturally cool down to room temperature. The precipitates were filtered and washed with deionized water and anhydrous ethanol several times and dried at 100℃ for 10 hours. The Ag/AgBr/$BiVO_4$ photocatalysts were prepared using the deposition-photoreduction method. Briefly, in a light-free environment, 0.0631 g of KBr was dissolved in 20 mL of deionized water, while 0.3 g of $BiVO_4$, 0.09 g of $AgNO_3$, and 20 mL of anhydrous ethanol were mixed and treated using Branson SB-5200D ultrasonic cleaner (Branson Ultrasonics, Danbury, Connecticut, USA) for 15 min. before adding KBr solution dropwise and stirring continuously. The mixed solution was continued to be magnetically stirred at room temperature for 4 h. An Osram 400 W halogen tungsten lamp (Osram GmbH, Munich, Germany) was used the light treatment of mixed solution for 30 min. The mixed solution was then filtered, and the precipitates were pumped and washed several times using deionized water and anhydrous ethanol, and finally dried at 60°C for 12 h.

Analysis of ratio optimization factors

The factors affecting the catalytic efficiency of Ag/AgBr/$BiVO_4$ photocatalysts were different in different preparation methods. In the production of photocatalysts by hydrothermal synthesis, both the temperature and the duration of the reaction affected the $BiVO_4$ crystals and morphology. Moreover, different adjustments of the hydrothermal temperature might play a decisive role in the crystal structure **[7**-9]. $BiVO_4$ showed different morphologies at different temperatures, and, with the prolongation of hydrothermal time, the $BiVO_4$ morphology would change from disorder to regular polyhedra [10, 11]. In the photocatalytic Ag/AgBr/$BiVO_4$ synthesis, the Ag/AgBr loading on the surface of $BiVO_4$ was controlled by adjusting the silver nitrate addition. The addition of silver nitrate amount had a significant effect on the photocatalytic performance [12-14]. A suitable proportion of silver nitrate could promote electron-hole separation, while a higher proportion of silver nitrate led to excessive Ag/AgBr accumulation on the surface of $BiVO_4$, which hindered the absorption of light. Three variables including hydrothermal temperature, reaction time, and the amount of silver nitrate added were chosen as the adjusting factors for the optimal ratios of the one-factor-controlled-variable method in the optimization experiment of the Ag/AgBr/$BiVO_4$ ratios. According to the previous research, the test ranges of the three variables could be determined as 90 - 190℃, 4 - 24 h, 10 - 35%, respectively. Therefore, the test values of each factor were set up in accordance with the equal gap approach as follows. The test values of hydrothermal temperature were 90, 110, 130, 150, 170, and 190°C, the test values of hydrothermal reaction time were 4, 8, 12, 16, 20, and 24h, the test values of silver nitrate dosage were 10, 15, 20, 25, 30, and 35%. All experiments were conducted in a home-made 0.010 m^3 environmental test chamber, which was a 600 × 150 × 150 mm^3 hollow metal rectangle with a round hole of 30 mm in diameter on each side for formaldehyde gas sampling and testing. There was a removable 600 × 300 mm^2 rectangle glass installed on the top of the test chamber for the photocatalyst to receive the light radiation from the halogen lamps.

Degradation of formaldehyde

The conditions during the degradation experiments of the same optimization factor were kept consistent with the air temperature

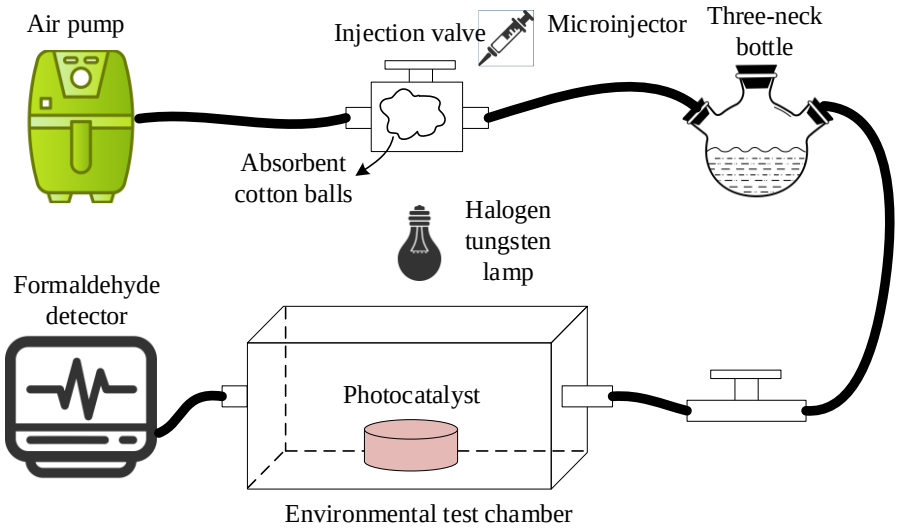

Figure 1. Scheme of the experimental setup for formaldehyde degradation using photocatalysts.

and humidity maintained within the ranges of 25 ± 0.25°C and 50 ± 0.5%, respectively. The optimal values were obtained by counting the formaldehyde degradation data under each factor and combined to determine the optimized preparation ratio solution. The prepared photocatalysts were analyzed using ultraviolet-visible reflectance spectroscopy and fluorescence spectroscopy. After obtaining the optimal Ag/AgBr/$BiVO_4$ ratio scheme, the formaldehyde degradation of Ag/AgBr/$BiVO_4$ and $BiVO_4$ was compared. Briefly, the catalytic material of the optimal solution was weighed and placed in a closed space environment irradiated by a 400 W tungsten halogen lamp with the distance between the light source and the surface of the material (subsequently referred as "light distance") set in accordance with the optimal solution. The initial formaldehyde concentration was set to simulate the degradation of formaldehyde by the catalysts in the atmospheric environment. The degradation experiment lasted for 180 min, during which the formaldehyde concentration in the confined space was measured using PPM500 formaldehyde detector (PPM Technology, Caernarfon, Gwynedd, UK). The experimental setup was shown in Figure 1, which mainly consisted of a formaldehyde detection apparatus, an environmental testing chamber, and a gas injection system. Formaldehyde in the air was added to the experimental setup through a Hamilton 7μL micro injector (Hamilton Company, Reno, Nevada, USA). After adding the photocatalyst sample, the formaldehyde solution was added to the adsorbed cotton ball using microinjector. The tungsten halide lamp was then turned on to start the experiment, and the changed data of formaldehyde concentration was recorded. The experiment was completed by turning off the tungsten halide lamp and recording the final formaldehyde concentration. To accurately test the formaldehyde degradation efficacy of photocatalysis, the experimental setup should have no adsorption of formaldehyde, good airtightness, uniform distribution of formaldehyde gas, and sufficient light source irradiation. The formaldehyde adsorption capacity and sealing of the chamber was evaluated in a blank test before official readings were taken, and the results were calibrated accordingly. The chamber was equipped with a small electric fan to evenly distribute formaldehyde gas. The glass partition of the chamber allowed a light transmittance of 80 - 90%, which ensured that the light of 380 -780 nm wavelength could penetrate. The relationship between the light intensity and the distance

between the tungsten halogen lamp and the photocatalyst was calculated below.

$$E = \left(I \cos \alpha \right) / R^2 \quad (1)$$

where *E* was the light intensity in *lx*. *I* was the luminous intensity of the point light source in cd. *R* was the distance from the point light source to the plane. *α* was the angle between the illuminated plane and the light. When other conditions remained unchanged, the light intensity in the test chamber could be effectively controlled by adjusting the distance between the tungsten halogen lamp and the photocatalyst.

Indoor formaldehyde degradation by Ag/AgBr/$BiVO_4$

Glass petri dishes were chosen as the host material. To optimize the dispersion of the photocatalyst and facilitate the recycling, temperature-controlled drying was adopted as the loading method of Ag/AgBr/$BiVO_4$ photocatalyst in this study. There are more factors affecting the degradation efficiency of formaldehyde in indoor air including the amount of photocatalyst, the starting concentration of formaldehyde, light conditions, air temperature, and humidity. Regarding the air temperature, the current general opinion is that it has less influence on the efficiency of photocatalysis. As for humidity, its main influence on the photocatalytic efficiency lies in affecting the generation of OH^-, and the content of water molecules is positively correlated with the number of OH^- ions. The higher the number of OH^- ions, which is a major strong oxidant, the higher the photocatalytic efficiency. When the content of water molecules in the air decreases, the number of OH^- decreases and the probability of electron-hole complexation increases, which reduces the photocatalytic efficiency. However, in the application environment of atmospheric formaldehyde treatment, the air temperature and humidity are often uncontrollable. Therefore, the air temperature of about 25°C and 50% air humidity were maintained in this study to simulate the atmospheric environment. The initial formaldehyde concentration, catalyst dosage, and light intensity were selected as experimental variables. According to available data, formaldehyde concentrations in the atmosphere where formaldehyde contamination existed were mostly in the range of 0.02 to 0.92 mg/m³. Therefore, 0.60, 0.80, and 1.00 mg/m^3 were selected as the initial concentrations of formaldehyde in this study. As the key factor of photocatalytic reaction, the amount of catalyst directly affects the photocatalytic degradation efficiency. Four different catalyst dosages of 0.20, 0.40, 0.60, and 0.80 g were selected for comparative analysis. Light is one of the key conditions of photocatalytic reaction. In this experiment, the light intensity was controlled by adjusting the vertical distance between the halogen lamp and the photocatalytic material to 30, 35, and 40 cm, respectively. During the experiment, the corresponding working time of air pump was set as 5, 8, and 12 seconds, respectively.

Results

Modified bismuth vanadate-based photocatalytic material

The UV-vis diffuse reflectance spectra of the two photocatalysts $BiVO_4$ and Ag/AgBr/$BiVO_4$ showed that $BiVO_4$ photocatalyst had a good light absorption performance in the ultraviolet region of 200 – 500 nm, but its absorption capacity was significantly weakened in the visible light region above 500 nm. In contrast, the Ag/AgBr modified $BiVO_4$ photocatalyst showed enhanced light absorption in the wide spectral range of 200 - 800 nm, and significantly improved light absorption in the visible region of 500 – 780 nm (Figure 2). This improvement was mainly due to the Ag/AgBr heterostructure and the surface plasmon resonance effect of silver elemental, which worked together on the surface of $BiVO_4$, effectively expanding the photo response range of the material, and making the modified photocatalyst more efficient in using visible light for photocatalytic degradation.

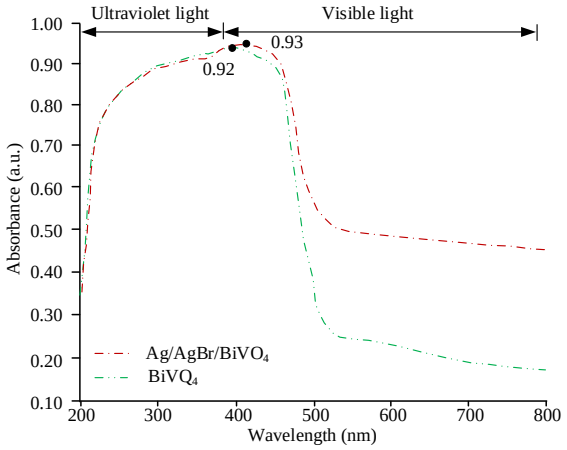

Figure 2. UV-vis diffuse reflectance spectra of two photocatalysts.

Both $BiVO_4$ and Ag/AgBr/$BiVO_4$ photocatalysts had fluorescence emission peaks at 550 nm wavelength, but the modified Ag/AgBr/$BiVO_4$ photocatalyst showed a lower fluorescence intensity (Figure 3). The introduction of Ag/AgBr not only changed the fluorescence characteristics of the photocatalyst, but also effectively reduced the photogenerated electron-hole pair recombination through the surface plasmon resonance effect and the formed heterojunction structure, which was crucial for improving the efficiency of the photocatalyst. The modification strategy of Ag/AgBr/$BiVO_4$ improved the absorption capacity to visible light and enhanced photocatalytic performance by reducing the electron-hole recombination rate.

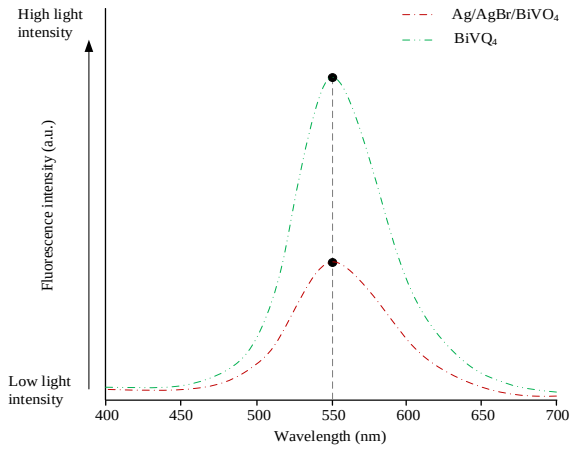

Figure 3. Fluorescence spectra of two photocatalysts.

The variation of atmospheric formaldehyde degradation rate of Ag/AgBr/$BiVO_4$ photocatalyst under different hydrothermal reaction temperature, reaction time, and silver nitrate dosage demonstrated that the formaldehyde degradation rate of Ag/AgBr/$BiVO_4$ was the highest when the hydrothermal reaction temperature, reaction time, and silver nitrate dosage were 170℃, 16 h, and 30%, respectively, which was the optimal ratio of Ag/AgBr/$BiVO_4$ photocatalyst (Figure 4).

Atmospheric formaldehyde degradation

The changes of formaldehyde concentration and degradation rate in the blank experiment showed that the formaldehyde concentration in the experimental space was only reduced from 0.980 to 0.933 mg/m^3 with the maximum formaldehyde degradation rate of 4.8% (Figure 5). After comparison of the photocatalysts degradation efficiency at the different initial formaldehyde concentrations, the results showed that Ag/AgBr/$BiVO_4$ photocatalyst reduction of formaldehyde concentration at the end of the experiment increased with the increase of the initial formaldehyde concentration, while the degradation rate also increased. The formaldehyde degradation rates were 40.8%, 58.3%, and 73.8% when the initial formaldehyde concentrations were 0.6 mg/m^3, 0.8 mg/m^3, and 1.0 mg/m^3, respectively (Figure 6). The comparison results of the degradation efficiency and degradation rate under the initial formaldehyde concentration of 1.0 mg/m^3 with different photocatalyst dosages demonstrated the decrease of formaldehyde concentration at the end moment of the experiment using Ag/AgBr/$BiVO_4$ photocatalyst with the elevation of the photocatalyst dosage. The formaldehyde degradation rates at the end of the experiment were 53.6%, 69.4%, 85.2%, and 88.9% for photocatalyst dosages of 0.20 g, 0.40 g, 0.60 g, and 0.80 g, respectively (Figure 7). The results of the degradation efficiency comparison under different light intensities were shown in Table 1, where the light distance was used to adjust the light intensity with the farther the light distance, the smaller the light intensity. The results

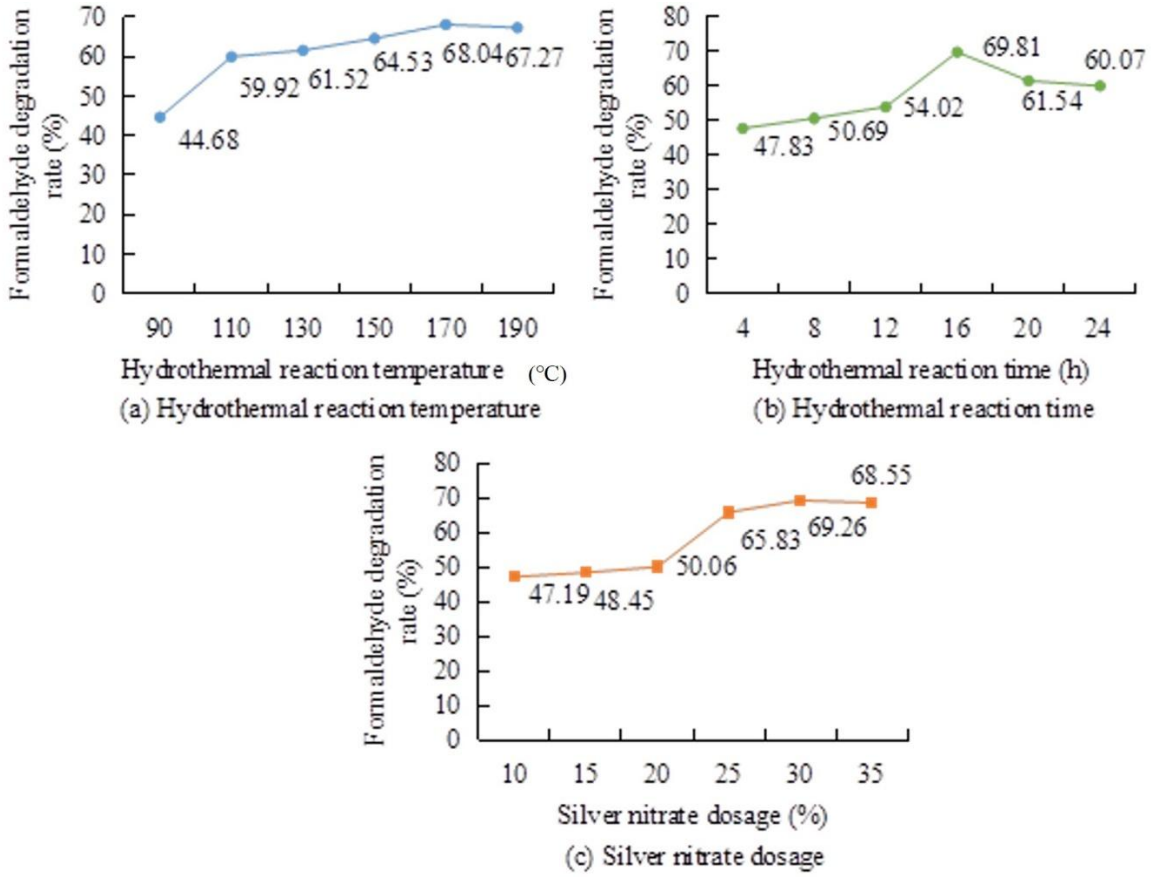

Figure 4. Changes in atmospheric formaldehyde degradation rate under different reaction conditions.

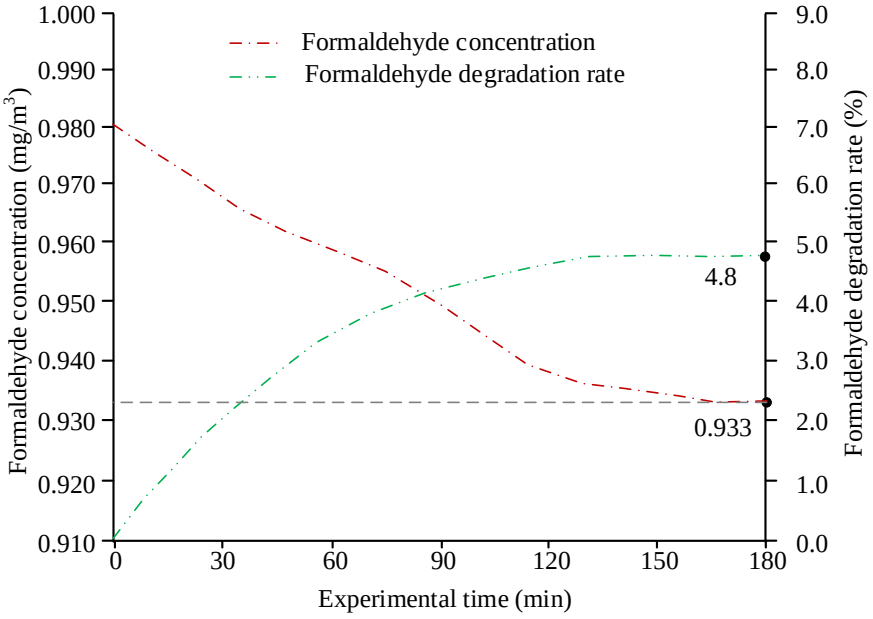

Figure 5. Comparison of formaldehyde concentration and degradation rate in blank.

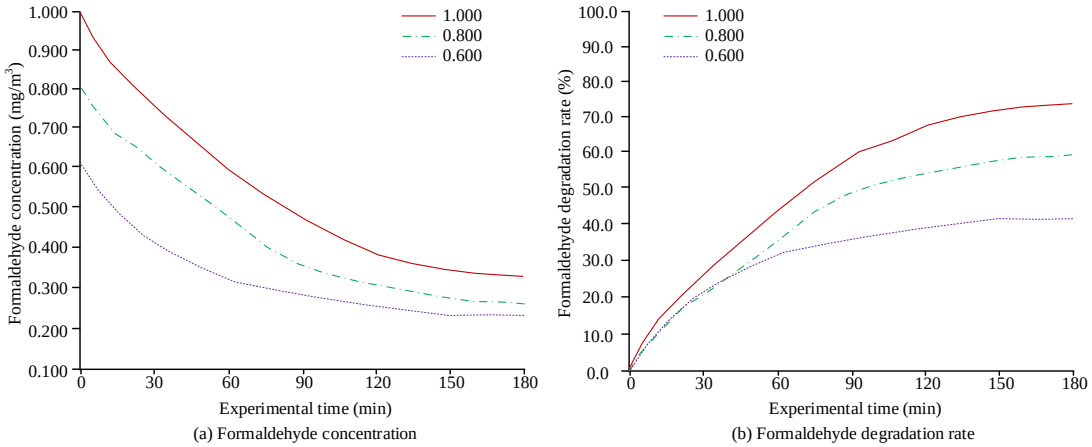

Figure 6. Comparison of formaldehyde degradation efficiency under different initial concentrations of formaldehyde.

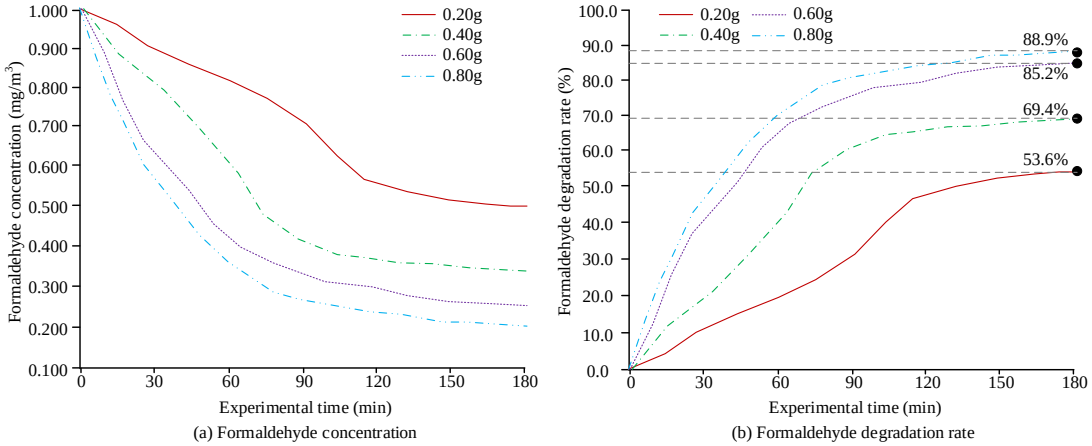

Figure 7. Comparison of formaldehyde degradation efficiency under different amounts of photocatalyst.

Table 1. Comparison of degradation efficiency under different light intensities.

Experimental time (min)	Optical distance (30 cm)		Optical distance (35 cm)		Optical distance (40 cm)	
	Concentration (mg/m³)	Degradation rate (%)	Concentration (mg/m³)	Degradation rate (%)	Concentration (mg/m³)	Degradation rate (%)
0	1.000	0	1.000	0	1.000	0
20	0.856	14.4	0.869	13.1	0.881	11.9
40	0.724	27.6	0.745	25.5	0.751	24.9
60	0.618	38.2	0.648	35.2	0.653	34.7
80	0.536	46.4	0.568	43.2	0.574	42.6
100	0.448	55.2	0.496	50.4	0.519	48.1
120	0.379	62.1	0.428	57.2	0.463	53.7
140	0.305	69.5	0.356	64.4	0.416	58.4
160	0.241	75.9	0.374	62.6	0.382	61.8
180	0.215	78.5	0.328	67.2	0.359	64.1

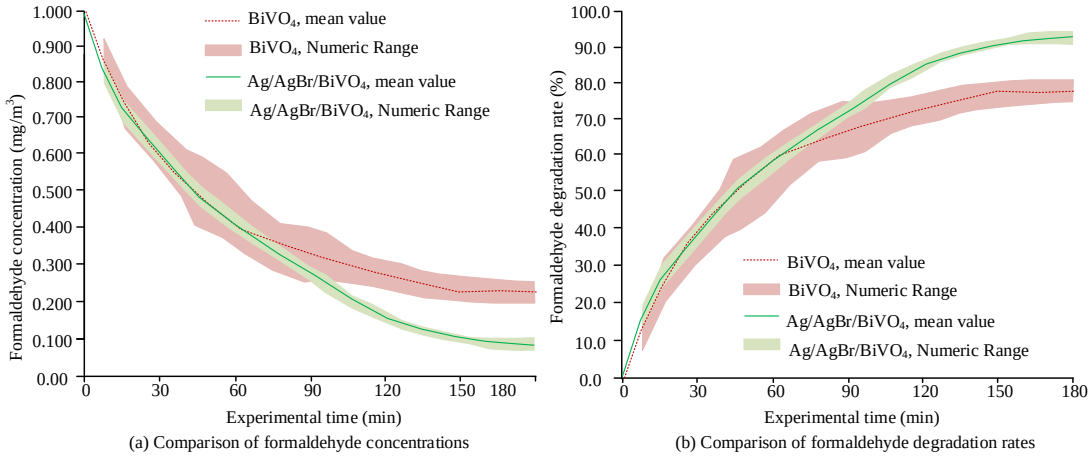

Figure 8. Comparison of stability and formaldehyde purification effect of two photocatalysts.

showed that, with the increase of light distance, the formaldehyde concentration at the end moment of the degradation experiment using Ag/AgBr/$BiVO_4$ photocatalyst increased and the degradation rate decreased. The formaldehyde degradation rate at the end of the experiment was 78.5%, 67.2%, and 64.1% when the light distance was 30 cm, 35 cm, and 40 cm, respectively. The formaldehyde degradation experiments of Ag/AgBr/$BiVO_4$ and $BiVO_4$ were then carried out according to the experimental conditions of the initial formaldehyde concentration of 1.0 mg/m^3, the photocatalyst dosage of 0.8 g, and the light distance of 30 cm. To verify the stability of the performance of the two catalysts, this experiment was repeated 10 times. The results showed that, at the end of the experiment, the Ag/AgBr/$BiVO_4$ photocatalyst reduced the formaldehyde concentration to 0.087 mg/m^3 on average, while the $BiVO_4$ photocatalyst reduced the formaldehyde concentration to 0.246 mg/m^3 on average (Figure 8a). The degradation rate of Ag/AgBr/$BiVO_4$ photocatalyst was 92.3% at the end of the experiment, which was significantly higher than 78.4% of $BiVO_4$ photocatalyst (Figure 8b). The standard deviations of real-time formaldehyde concentration data of Ag/AgBr/$BiVO_4$ and $BiVO_4$ were 0.042 mg/m^3 and 0.115 mg/m^3, respectively. The results demonstrated that the comprehensive performance of Ag/AgBr/$BiVO_4$ photocatalyst in formaldehyde degradation was better than $BiVO_4$.

Discussion

With the rapid development of industrialization and urbanization, air pollution has become increasingly severe with indoor formaldehyde pollution standing out as a significant threat to public health [15-17]. This study explored the degradation efficiency of formaldehyde in indoor air using modified bismuth vanadate (Ag/AgBr/$BiVO_4$) photocatalytic materials, and then compared it with unmodified $BiVO_4$ photocatalyst. The results on formaldehyde degradation efficiency demonstrated that, under the condition of an indoor formaldehyde concentration of 1.0 mg/m^3, the degradation efficiency of the Ag/AgBr/$BiVO_4$ photocatalyst reached a peak of 73.8%, which indicated that, at a specific formaldehyde concentration, the reaction kinetics between the photocatalyst and formaldehyde molecules achieved an optimal state. Further optimization of the catalyst dosage revealed that 0.80 g was the optimal amount with the degradation efficiency of formaldehyde increasing to 88.9%, suggesting that an appropriate amount of catalyst could maximize contact and degradation of formaldehyde molecules. To ensure the accuracy of the results, a series of experiments were conducted in a well-

designed and highly airtight environmental test chamber, where the chamber's absorption effect on formaldehyde was minimal. The results were consistent with the findings of Spencer *et al*. [18]. The optimization of light intensity showed that the optimal distance between the halogen tungsten lamp and the photocatalyst was 32 cm, resulting in a formaldehyde degradation rate of 74.33%. The positive correlation between light intensity and formaldehyde degradation efficiency further confirmed that light intensity played a key role in promoting the generation of electron-hole pairs in the photocatalyst, which was crucial for improving degradation efficiency [19, 20]. Further, the Ag/AgBr/$BiVO_4$ photocatalytic material consistently exhibited excellent catalytic performance, particularly in its stability during repeated use, indicating its potential for long-term application. Under the same experimental conditions, the formaldehyde degradation rate of Ag/AgBr/$BiVO_4$ exceeded 90%, while that of $BiVO_4$ was 84.7%, demonstrating the high efficiency of the modified material in formaldehyde degradation. This study suggested that Ag/AgBr/$BiVO_4$, as a modified photocatalyst, had significant advantages in improving formaldehyde degradation efficiency. These results demonstrated the enhanced light absorption, effective separation of electron-hole pairs, and high reaction kinetics under optimized conditions brought about by the material modification. The study successfully developed the Ag/AgBr/$BiVO_4$ photocatalytic material and proved its high efficiency and stability in photocatalytic formaldehyde degradation. This research not only provided a new and efficient solution for indoor air purification but also laid a solid foundation for future environmental improvement efforts, promoting the application and development of environmentally friendly materials within the context of green finance.

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