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Fabrication of transition metal-doped-ZnO photocatalyst and its photocatalytic degradation properties on formaldehyde

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Nano-ZnO/transition metal composites (NZTC) were prepared via sol-gel method where transition metal (Cu^{2+}, Ag^{+}, Co^{2+} and Ni^{2+}) and $ZnSO_4$ were used as the substrate. NZTC was characterized using scanning electronic microscope (SEM), ultraviolet-visible spectrophotometer (UV), fluorescence spectrophotometer (XRF), infrared spectrometer (IR), and so on. The photocatalytic degradation behaviors of nano-ZnO and NZTC for formaldehyde in gas and solution were investigated. The results indicated that nano-ZnO and NZTC could achieve the degradation of formaldehyde by photocatalytic process, and the degradation rates were up to 43.75% and 67.2% in gas and solution, respectively, thus thereby leading to good application prospects in the degradation of organic compounds.

Keywords: Formaldehyde, ZnO, NZTC, Photo catalytic degradation.

INTRODUCTION

Formaldehyde is recognized as a very strong carcinogen by the World Health Organization (WHO) because of long-term and irreversible harm to the human body. Due to the application of indoor decoration and preservatives, formaldehyde mainly exists in the air and water, and the release of formaldehyde is a slow and long-term process, which could last for 3–15 years, and seriously affects the safety of people's living environment and poses a great threat to people's health[1–3]. Usually, the concentration of indoor formaldehyde is reduced by ventilation, activated carbon adsorption, and photocatalytic oxidation degradation. Among them, photocatalytic oxidation technology has the advantages of being pollution-free and sustainable, which is an ideal method to remove indoor formaldehyde gas[4–5].

Zinc oxide (ZnO) is an n-type semiconductor oxide with special photoelectric properties, good photoelectric and piezoelectric properties, natural environmental protection, and good thermal stability. In recent years, nano ZnO as a new functional photocatalyst has been used in antibacterial, deodorization, air purification, water purification, pollution prevention, and so on[6–7]. However, the larger band gap and higher electron--hole recombination probability limit the photocatalytic efficiency of ZnO[8].

The methods of metal doping and nonmetal doping have been studied to improve the photocatalytic activity of ZnO[8–10]. ZnO by doping N, S and other nonmetals elements is beneficial to form a nonmental element-Zn-O bond in ZnO crystal, which wides the response range of ZnO to visible light, and increases the lattice constant, thereby resulting in more oxygen vacancies in ZnO and improving the photocatalytic activity and reaction rate constant of ZnO[9–10]. Additionally, Ga^{+}, $Au^{+,}$ and other metals doped ZnO can enhance the response range of ZnO to visible light, and have the perfect photocatalytic degradation effect[11].

In this paper, nano ZnO was modified by doping metal ions, and the modified photocatalyst was detected by using formaldehyde gas and dissolving in liquid. The photocatalytic activity of modified ZnO was discussed, so as to improve the photocatalytic effect. The particle size, spectral absorption, thermal stability, and structure of NZTC were tested by nano laser particle size analyzer, UV visible spectrophotometer, fluorescence spectrophotometer, infrared spectrometer, and thermogravimetric analyzer.

EXPERIMENTAL

Chemicals

Zinc sulphate ($ZnSO_4$), cupric sulfate ($CuSO_4$), silver nitrate ($AgNO_3$), cobalt sulfate ($CoSO_4$), nickel sulfate ($NiSO_4$), and potassium biphthalate ($KHC_8H_4O_4$) were purchased from Tianjin Kaitong Chemicals (Tianjin, China). All the reagents used in this work are of analytical grade.

Preparation of ZnO and NZTC

Nano-ZnO was readily prepared by sol-gel method, the typical synthesis procedure was as follows: 3 mmol of $ZnSO_4$ was dissolved in 20 mL of deionized water, and 6 mmol of $KHC_8H_4O_4$ was sequentially added in above solution. Subsequently, the mixture solution was transferred into an autoclave of 25 mL and heated in an oven at 120 °C for 6 h, and then cooled to room temperature. The obtained sample was washed with ethanol 3 times and dried in the oven, followed by being calcined in a muffle furnace at 400 °C for 2 h. Similarly, ZnO/Ag, ZnO/Co, ZnO/Ni, and ZnO/Cu composites were also fabricated via the same procedure.

Characterization and photocatalytic activity evaluation of nano-ZnO and NZTC

A transmission electron microscope (TEM, JEM-2010, JEOL Company, Japan) was performed at an accelerating voltage of 200 kV to observe the dispersion behavior of nano-ZnO and NZTC. A scanning electronic microscope (SEM, JSM 5600LV, Japanese Electronics, Japan) was employed at an accelerating voltage of 30 kV to examine the microstructure of nano-ZnO and NZTC. Prior to SEM observation, the surfaces of the specimens were spray-coated with gold. The X-ray diffraction (XRD) patterns of the as-prepared nano-ZnO and NZTC were obtained with a D/max 2550 V X-ray diffractometer (Philips, Holland; Cu K_α radiation, λ = 1.54178 Å). The ultraviolet-visible light (UV-vis) absorbance spectra of na-

no-ZnO and NZTC were measured over the wavelength range of 200~800 nm with a Cary 100 spectrophotometer. A fluorescence spectrometer (F-2700, Hitachi Company, Japan) was utilized to evaluate the fluorescent performances of ZnO, ZnO/Cu, ZnO/Ag, ZnO/Co, and ZnO/Ni in the wavelength range of 220~730 nm.

The photocatalytic activities of nano-ZnO and NZTC were evaluated by monitoring the decomposition of formaldehyde under the irradiation of simulated sunlight and natural sunlight where the operation conditions were as follows: simulated sunlight was got by using Xe lamp of 500 W (CHF-XM500, Perfect light) with electric current of 20 A and the distance of 30 cm between the breaker and the lamp holder, and those under nature sunlight was that the mixture solution of pollutants and photocatalyst was set in the outside platform. With formaldehyde as a representative, 0.05 g of the photocatalyst and 50 mL of formaldehyde solution (100 mg/L; solvent: water) were added into a 100-mL breaker. The resultant solution was magnetically stirred for 1 h to achieve adsorption saturation before illumination, followed by exposure to simulated or natural sunlight at room temperature (controlled with a constant-temperature circulating pump) for 0.5 h. Upon completion of irradiation, the aqueous solution (about 2 mL) in the reactor was transferred to a 10-mL test tube and centrifuged for about 30 min.

RESULTS AND DISCUSSION

Characterization

It can be seen from Fig. 1 that the characteristic peak of ZnO appears in the wave number range of 400 600 cm^{-1}, while none of the other four ZnO-modified catalysts has any characteristic peak of ZnO in this wave number range, which indicates that after doping metal ions, the red shift occurs, the light response range of ZnO is widened, and the photocatalytic efficiency of modified ZnO is also greatly improved after improving the utilization of light[12].

In Fig. 2, the absorbance of nano ZnO decreases sharply after the wavelength of 400 nm, which shows that the curve in the figure is relatively "steep", while the absorption of the catalyst doped with metal ions in the infrared visible light region is significantly enhanced,

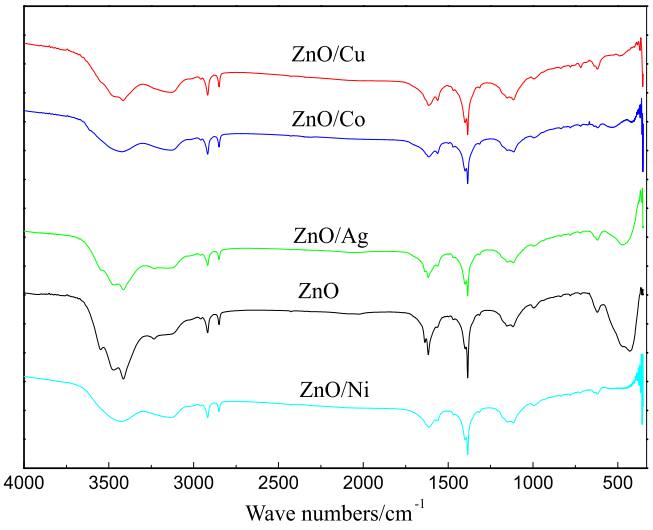

Figure 1. FTIR spectrum of ZnO and its composite

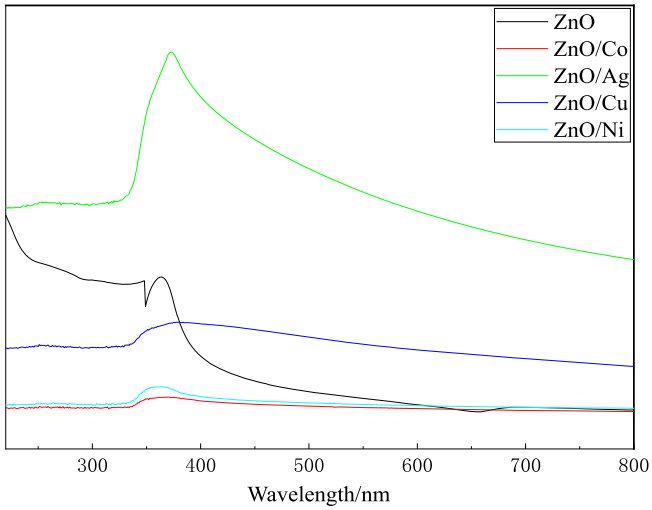

Figure 2. UV-vis spectrum of ZnO and its composite

indicating that the incorporation of metal ions in the nano ZnO will lead to the broadening of its available visible light range, which leads to the increase of photocatalytic efficiency of the catalyst[13].

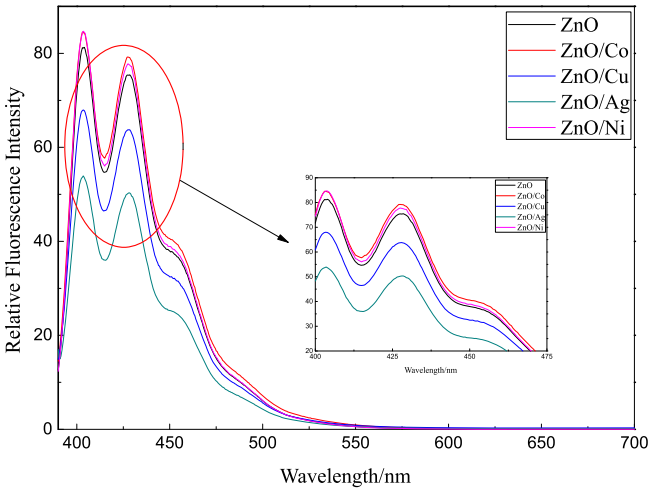

Figure 3. Fluorescence spectrum of nano-ZnO and NZTC

The emission light intensity of nano ZnO in Fig. 3 is the smallest, which indicates that there are fewer electrons excited by ZnO and the available light range is relatively narrow. The catalyst doped with metal ions has a wide range of light utilization, more electrons can be excited in the light, the probability of loading increases, and the response range of light increases[14].

The photocatalytic degradation properties of nano-ZnO and NZTC on formaldehyde

The measurement principle of a portable pump gas detector is to absorb the gas to decompose to determine the concentration of formaldehyde gas. The test of the formaldehyde concentration in water is carried out via the sodium sulfite method.

The photocatalysis results of different catalysts are shown in Fig. 4. Under the conditions of the same amount of catalyst, the same light intensity and the same catalytic time, the photocatalytic degradation efficiency of ZnO, ZnO/Cu, ZnO/Ag, ZnO/Co and ZnO/Ni towards to gas formaldehyde are 33.33%, 30.77%, 38.46%, 30.77%, and 25.00%, respectively. Therefore, as compared with the five catalysts, ZnO/Ag has the best photocatalytic degradation

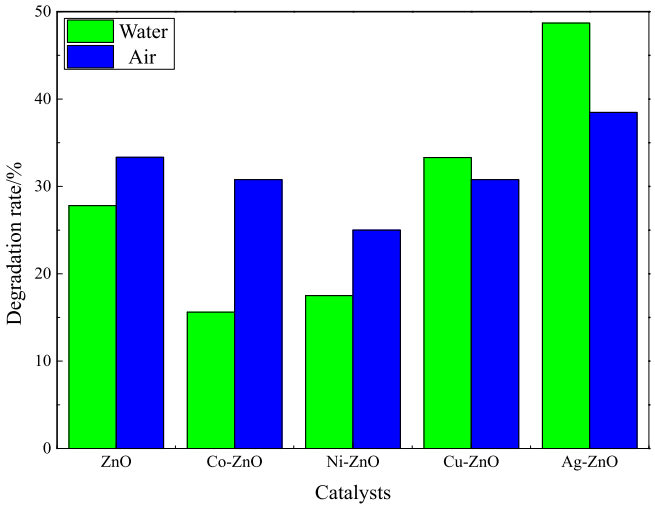

Figure 4. The photocatalytic degradation of formaldehyde in water and air

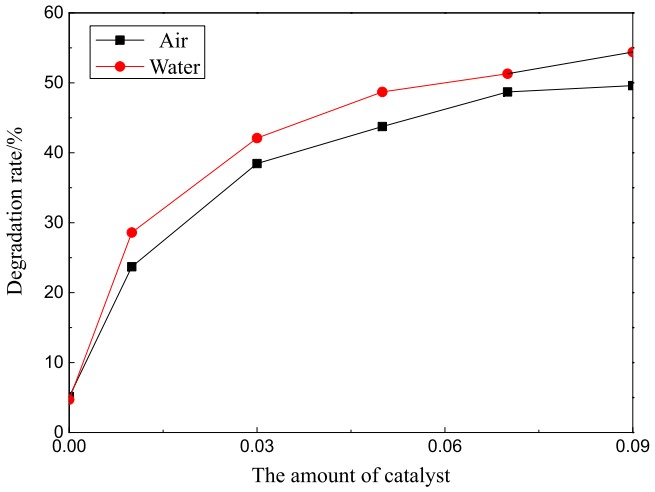

Figure 5. The effect of the amount of photocatalyst on degradation rate of formaldehyde

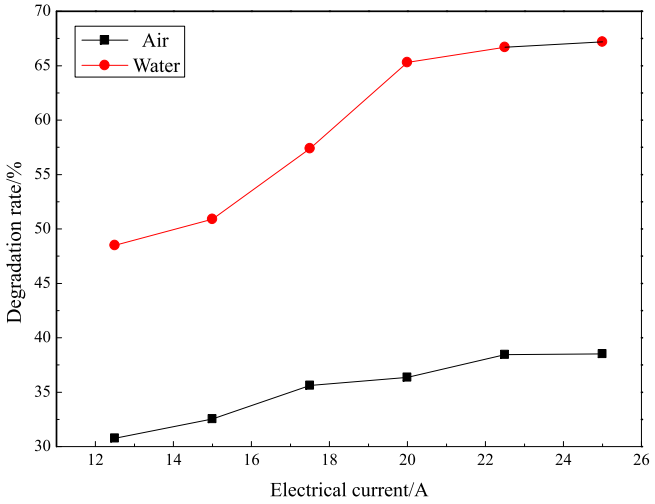

Figure 6. The effect of strength of illumination on degradation rate of formaldehyde

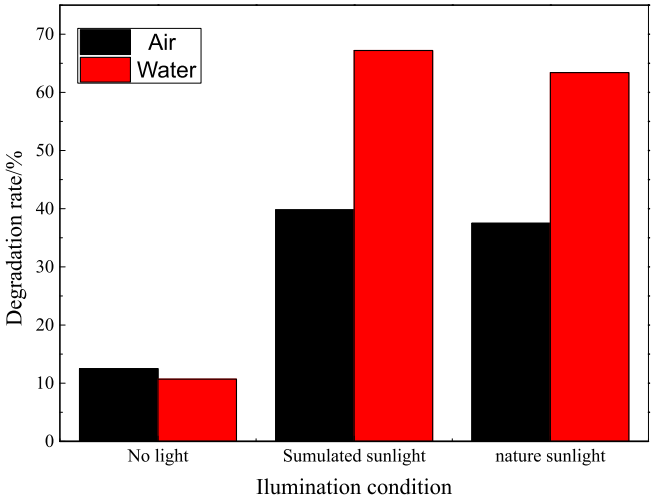

Figure 7. The effect of illumination environment on degradation rate of formaldehyde

effect[15]. In addition, the photocatalytic degradation rate of formaldehyde in water

The results of the photocatalytic experiment with different amounts of ZnO/Ag catalyst are shown in Fig. 5. When the amount of ZnO/Ag is 0.03 g, 0.06 g, and 0.09 g, the catalytic efficiency is 38.46%, 43.75%, and 43.75%, respectively. It can be seen that when other conditions are constant, the photocatalytic efficiency can be increased by increasing the amount of catalyst. However, there is an upper limit for the increase of photocatalytic efficiency When the amount of catalyst was 0.06 g, the photocatalytic efficiency was increased. When the amount of catalyst was increased to 0.09 g, the photocatalytic efficiency did not increase compared with that of 0.06 g, indicating that when the amount of catalyst was 0.06 g, the photocatalytic limit of ZnO/Ag reached 43.75%. Even if the amount of catalyst was increased, the photocatalytic efficiency would not increase[16–18].

The photocatalytic results of ZnO/Ag catalyst are shown in Fig. 6. The photocatalytic efficiency is 30.77%, 38.46% and 36.36%, respectively, under different light intensities (I: 12.5A, 15A, 17.5A, 20 A, 22.5A, and 25A); when the light intensity increases from I = 12.5A to 25A, the photocatalytic efficiency increases, but continues to increase the light intensity, the photocatalytic efficiency decreases. The results show that there is an optimal light intensity in the photocatalytic experiment, and the best light intensity in this group of experiments is the light intensity corresponding to I = 22.5 A. Additionally, the photocatalytic degradation of the formaldehyde in water shows the same trend.

It can be seen from Fig. 7 that when the photocatalytic time is 2 h, the photocatalytic efficiency of ZnO/Ag under simulated light irradiation is 38.46%, and that of ZnO/Ag under actual light irradiation is 36.67%. It shows that under certain other conditions, the photocatalytic effect of actual light is not as good as that of simulated light. Under the condition of no light, the adsorption rate of ZnO/Ag is 25.00%. The decrease of formaldehyde concentration under the condition of no light indicates that not all formaldehyde gases are degraded by the catalyst, but some gases are adsorbed on the surface of the catalyst, and some of the adsorbed gases are released, which will cause the experimental phenomenon of formaldehyde concentration rising[19].

To explore whether the used catalyst can be reused, the photocatalytic results are shown in Fig. 8. The photocatalytic efficiency of the used ZnO/Ag catalyst after 5 times were 35.64% and 48.93 to gas formaldehyde and in water, and that of the new ZnO/Ag catalyst under the

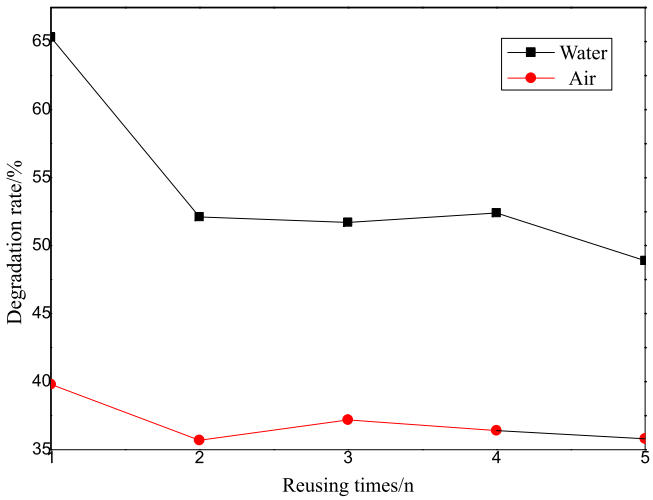

Figure 8. The reusing properties of photocatalyst

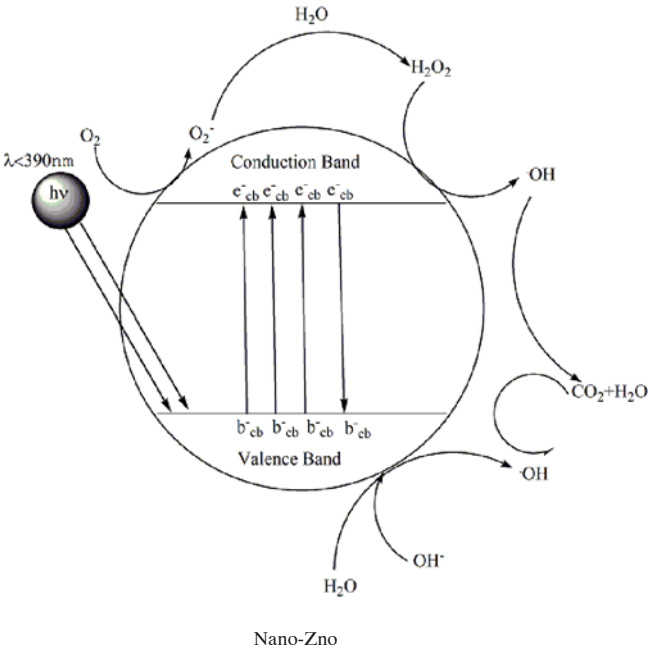

Figure 9. The photocatalytic degradation mechanism

same conditions were 39.78% and 65.46%, respectively, which indicates that the used catalyst can still be reused, but the catalytic efficiency will be reduced[20].

The mechanism of photocatalytic decomposition of formaldehyde

According to the energy band theory, there is an energy band structure in the crystal of semiconductor materials. The energy band is discontinuous, which is generally composed of a high-energy conduction band and a low-energy valence band. The band gap is the region between the conduction band and the valence band, and its size is called the band gap width (EG). Different semiconductor materials have different bandgap, and their corresponding optical absorption threshold (λg) is different[8, 11, 21–22].

When a semiconductor photocatalyst is excited by light with energy≥e_g, the valence band electrons are excited to the conduction band, and holes are generated in the valence band, and electrons are generated in the conduction band to form a hole electron pair with reactivity. Due to the effect of the external electric field, electrons, and holes separate and migrate to different positions on the surface of photocatalyst particles, and the materials attached to the surface of the photocatalyst are reduced or oxidized[23].

$$\text{Semiconductor} + h\nu \rightarrow e^-_{CB} + h^+_{VB} \quad (1\text{–}2)$$

$$h^+_{VB} + H_2O \rightarrow H^+ + {}^*OH \quad (1\text{–}3)$$

$$h^+_{VB} + OH^- \rightarrow {}^*OH \quad (1\text{–}4)$$

$$e^-_{CB} + O_2 \rightarrow O_2^- + H^+ \rightarrow HO^*_2 \quad (1\text{–}5)$$

$$HO^*_2 + O_2^- + H^+ \rightarrow H_2O_2 + O_2 \quad (1\text{–}6)$$

$$HO^*_2 + e^-_{CB} \rightarrow OH^- + {}^*OH \quad (1\text{–}7)$$

$$e^-_{CB} + h^+_{VB} \rightarrow \text{Semiconductor} + \text{Energy} \quad (1\text{–}8)$$

The hydroxyl radicals formed by the interaction of holes and water can oxidize most organic compounds because of their strong oxidation. It should also be noted that the disproportionation reaction, that is, electrons are transferred from the conduction band to the reactants, and form peroxide anions and protonated forms with oxygen molecules in the solution, so as to generate hydrogen peroxide, and hydroxyl radicals are also produced due to the continuous interaction between hydrogen peroxide and electrons. The strong oxidation ability of holes and hydroxyl radicals can degrade organic matter to produce carbon dioxide, water and mineralized substances (Fig. 9). A series of reactions occurred in this process are as follows (formula 1–2 ~ 1–8)[24–25].

CONCLUSION

Based on a single-factor experiment, the photocatalytic degradation efficiency of five kinds of nanocatalysts such as ZnO, ZnO/Cu, ZnO/Ag, ZnO/Co and ZnO/Ni was studied by the method of controlled variables. The following conclusions were obtained: (1) the photocatalytic efficiency of different catalysts for formaldehyde gas was different, among which ZnO/Ag had the best photocatalytic effect, and ZnO/Ni had the worst photocatalytic effect. (2) under other conditions, the photocatalytic efficiency of ZnO/Ni was the worst. The photocatalytic efficiency can be increased by increasing the amount of catalyst, but there is an upper limit for the increase of photocatalytic efficiency. (3) within a certain range of light intensity, increasing the intensity of light can increase the photocatalytic efficiency; if the light intensity continues to increase beyond this range, the photocatalytic efficiency will decrease. (4) the photocatalytic effect of actual light is not as good as that of simulated light. (5) The used catalyst can still be reused, but the catalytic efficiency will be reduced. (6) in the photocatalytic process, formaldehyde gas is not all degraded by the catalyst, but a part of the gas is adsorbed on the surface of the catalyst, resulting in the concentration change of formaldehyde gas.

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