Treatment of formaldehyde by corona plasma cooperated with photo-catalysis

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Abstract. Formaldehyde, as a main indoor pollutant, is a serious hazard for human health. Here the experimental results of dielectric discharge, together with photo-catalysis to treat formaldehyde, were presented. The modified photocatalyst was loaded onto the electrode surface for degradation of formaldehyde in an artificially enclosed room. The effect of catalyst quantity, inlet rate, temperature, humidity and other process variables were examined in order to explore the relative purification factors of plasma cooperated with photo-catalysis. It is found that formaldehyde degradation efficiency is proportional to photo-catalyst quantity, and reciprocal to gas inlet rate and humidity. Experimental results confirm that plasma discharge combined with photo-catalysis can significantly improve the treatment efficiency of formaldehyde compared to a single plasma discharge. This research may form a basis for practical development of an efficient, low-power-cost, and relatively comprehensive indoor pollutant purification system.

1. Introduction

Indoor air pollution problems gain an increasing concern. Formaldehyde, as a main indoor pollutant, possesses serious hazards for human health [1]. However, most previous studies focus on benzene and its derivatives such as total volatile organic compounds (TVOC), comparing with less researches on formaldehyde removal. Previous studies have confirmed that the corona discharge plasma accelerating with photo-catalytic effect could degrade TVOC [2]. In order to provide the reference for understanding the mechanism of coordination, this study attempts to combine gas discharge with photo-catalysis, namely, using low temperature plasma, instead of simply ultra-violet light, during gas discharge process as the driving force for photo-catalytic materials, and further explores the influencing factors of synergistic purification and the relative impact mechanism.

Existing mainstream toward plasma discharge cooperating with photo-catalytic purification has accepted that the co-purification process mainly relied on the following three ways [2, 3]. Firstly, organic gases are to be excited, ionized, dissociated, etc. after the bombardment treatment by high energy electron, which leads to the chemical bond rupture and undermines the organic gases; Secondly, a large number of free radicals and ozone with strong oxidization abilities were produced by gas discharge to oxidize organic gases into CO₂, CO, and H₂O; Thirdly, when ultraviolet light produced by gas discharge irradiates nano photo-catalyst, the surface of the photo-catalyst will produce electron-
hole pairs, which react with O₂ or H₂O absorbed on the catalyst surface. The reaction will generate OH radicals which can oxidize the organic gases.

2. Experiment setup
The reactor used in the experiment for plasma corona discharge cooperating with photo-catalytic reaction is shown in figure 1. The reactor consists of one stainless steel rod (diameter of 22.5 mm) and one ceramic dielectric (inner diameter of 24.5 mm, outer diameter 31.5 mm). The ceramic tube wrap around with an aluminium foil of 83 mm length. Stainless steel aluminium foil as the induced pole, were energized with 5 ~ 10 kV AC voltage, and photo-catalyst TiO₂ thin film were deposited on the outer surface of the rod electrode and inner surface of the ceramic tube.

![Figure 1. Reactor structure (1-discharge electrode high voltage input, 2-air inlet, 3-air gate, 4-induced electrode aluminium foil, 5-TiO₂ thin film, 6-thermal slug, 7-ground connection).](image)

The photo-catalyst TiO₂ powder, which is characterized by high urging efficiency and stable non-toxic, is a well-recognized and efficient environment-friendly material [4, 5]. In order to improve its catalytic efficiency, a small amount of transition metal ions is doped in the mixture. Firstly, the precursor of iron and other transition metal are dissolved in isopropanol, and we mix tetrabutyl titanate and isopropanol with concentrated nitric acid by stirring; then mixture forms a white precipitated after aging 12 h at room temperature. By electrophoretic deposition technique we load the catalyst on the electrode, which is heated at 450 °C for 2 h. After detected by X-ray diffraction analysis equipment, the XRD spectrum of catalyst samples is shown in figure 2. We also obtain the spectra of catalyst samples by energy dispersive spectrometer, which is shown in figure 3.

![Figure 2. The spectra of catalyst by X-ray. The two main peaks could be introduced catalyst samples' particle size of 9.39 nm and 10.04 nm.](image)
Figure 3. The spectra of catalyst by energy dispersive spectrometer. Due to the glass vector of the electron microscope, Si element also could be detected.

3. Result and discussion

Experimental results confirm that the plasma discharge combining with photo-catalytic treatment has a degradation effect (figure 4) on formaldehyde, and which can significantly improve the treatment efficiency compared to a single plasma discharge. The degradation eventually tends to saturation since the oxidation reactions is high-energy process and the formaldehyde molecule is reversible, plus radicals’ transient existence and the ozone saturated concentration, which resulted in an oxidation equilibrium; Ultimate product H₂O would increase the humidity of air, so that the corona onset voltage increases, and the final concentration of formaldehyde gas is no longer reducing.

Figure 4. Comparison of formaldehyde concentration after different treatment. (Curve 1, 2, 3 reflect conditions of un-treatment, simply-discharge treatment and cooperate treatment, respectively).

Figure 5. Dependence of formaldehyde degradation efficiency on catalyst quantity. (Curve 1 and 2 respectively reflect TiO₂ thin film with single layer and bi-layer).

The detailed influence of loading quantity of catalyst on purifying effect is shown in figure 5. We can see from the figure 5, at the very beginning of the experiment, purifying efficiencies with different catalyst quantity almost show no difference; however, with the ongoing reaction, the purification efficiency of the bi-layer membrane is greater than the monolayer. It may be because electric field energy levels is relatively low on the initial discharge stage, and the TiO₂ catalyst has not all fully
activated, which leads to little impact on the treatment of formaldehyde. When the electric field energy level rises enough to fully activate the photo-catalyst and prompts the organic degradation process, the electron-hole pairs possess a great reactivity. The oxidative ability of hydroxyl radical is higher than that of ozone, so the photo-catalyst will play a dominant role during latter reaction. Therefore, more amount of catalyst generates more electron-hole pairs, and thereby the degradation efficiency of the bi-layer membrane is greater than the monolayer.

Figure 6. Dependence of formaldehyde degradation efficiency on gas inlet rate. (Curve 1, 2, 3 reflect respectively inlet rate at 1000 mL min⁻¹, 800 mL min⁻¹ and 600 mL min⁻¹).

Figure 7. Dependence of formaldehyde degradation efficiency on ambient humidity. (Curve 1 and 2 reflect relative humidity of about 30% and 72% (sunny and rainy), respectively).

The intake rate reflects the length of gas molecules’ residence time in the reactor, under the condition that electric field length is constant. When changing the rate of intake during experiment, we can see the purifying effect of intake rate in figure 6. Greater inlet rate, the more transient airflow stays in the reactor, and lower probability of collision between the gas molecules and free electrons are, which eventually results in the decrease of the probability of gas molecules’ dissociation and ionization, and thus the removal rate will drop.

The relationship between humidity and co-purifying efficiency is showed in figure 7. From one aspect, during the degradation process water vapour and reactants compete for absorption on the catalysts’ water active centre, thus the reaction rate is influenced by absorption competition. Once the humidity increases, the amount of pollutants adsorbed is reduced, so is reaction rate. From another aspect, electrons would be changed into anion when meeting water vapour. Due to anion’s low moving rate and small ionization ability, the effective number of electrons involved in the avalanche is thus reduced. Reduction of effective electron indirectly leads to plasma energy falling, hence results in the drop of purifying rate.

Previous experiments demonstrate almost no relationship between ambient temperature and formaldehyde purifying effect. On the one hand, the final decision on the collaborative purification efficiency is the direct reaction of the hole and pollutant gases. The reaction is a key step in the photo-catalytic reaction, which requires low apparent activation energy. When the temperature varies, the apparent activation change is smaller, and the reaction rate varies smaller responding to temperature, so is the temperature dependence of nano-TiO₂. On the other hand, the average field strength in the discharge space exceed 50 kV cm⁻¹, and the temperature in the reactor is proportional to electric field strength and reaction time length. The surface temperature of the reactor rose to 60 °C, which is 2~4 times than that of the external environment, so the influence of ambient temperature compared to the
temperature of the reactor can be negligible. Considering two factors above, there is almost no ambient temperature influence during the experiment for co-purification efficiency.

4. Conclusion

The project loads modified photo-catalyst on the electrode surface, and builds an artificial enclosed room to treat formaldehyde, we concentrate that the plasma discharge cooperating with photo catalytic truly has degradation effect on formaldehyde. It is found that the formaldehyde degradation efficiency is proportional to photo-catalyst quantity, and reciprocal to gas inlet rate and humidity. Experimental results confirm that the plasma discharge combining with photo-catalysis can significantly improve treatment efficiency compared to a single plasma discharge. We hope our research will provide the basis for understanding the mechanism of coordination and a viable direction for a multi-purpose, high efficiency, low consuming dealing system for indoor pollutants.

Acknowledgments

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