

Photosensitizing Effects of Nanometer TiO₂ on Chlorothalonil Photodegradation in Aqueous Solution and on the Surface of Pepper

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ABSTRACT: The present study examined the effects of anatase nanometer TiO₂ on photochemical degradation of chlorothalonil in aqueous solution and on the plant surface. Results showed that nanometer TiO₂ exhibited a strong photosensitizing effect on the degradation of chlorothalonil both in aqueous solution and on the surface of green pepper. The photosensitization rate was the highest in the sunlight compared to illumination under high-pressure mercury and UV lamps. Use of distinct hydroxyl radical scavengers indicated that nanometer TiO₂ acted by producing hydroxyl radicals with strong oxidizing capacity. Notably, nanometer TiO₂ facilitated complete photodegradation of chlorothalonil with no detectable accumulation of the intermediate chlorothalonil-4-hydroxy. Nanometer TiO₂ was also active on the surface of green pepper under natural sunlight both inside and outside of plastic greenhouse. These results together suggest that nanometer TiO₂ can be used as a photosensitizer to accelerate degradation of the pesticides under greenhouse conditions.

KEYWORDS: chlorothalonil, photochemical degradation, nanometer TiO₂, aqueous solution, pepper

■ INTRODUCTION

Chlorothalonil (2,4,5,6-tetrachloro-1,3-dicyanobenzene) is a highly effective, broad spectrum fungicide with a potent bactericidal effect. Chlorothalonil is widely used in the prevention and control of crop diseases in vegetables, fruit trees, wheat, and beans as well as in pepper cultivation.^{1,2} Chlorothalonil is described in the database PPDB as a solid compound with a melting point of 252 °C and low water solubility and volatility. It is resistant to hydrolysis at pH 4 and 7, but hydrolyses slowly at pH 9. The octanol–water partition coefficient of chlorothalonil is log Pow 2.9 (pH 7, 20 °C), and its Henry's law constant is 2.5×10^{-2} Pa m³ mol⁻¹ (25 °C). Chlorothalonil sprayed on the surface of crop leaves is slowly degraded mainly through photodegradation and biodegradation with an estimated half-life of 5.3 days.³ However, chlorothalonil is used mostly as a fungicide in plastic greenhouse production of vegetables in recent years and the degradation rate of chlorothalonil is comparatively slower in plastic greenhouses than in open fields.⁴ The slow degradation in the environment and the transport and toxicity of chlorothalonil are of concern, especially in aquatic systems, because it is highly toxic to fish and invertebrates with acute toxicity levels of 10–80 µg/L.⁵ For example, chlorothalonil was found to be one of the most frequent pollutants in inland lakes and sediment in Ontario, Canada.⁶ In addition, chlorothalonil was detected in 97% of ambient air samples collected during 2002–2004 in the Prince Edward Island, Canada.⁷ Therefore, it is necessary to develop innovative approaches to prevent environmental contamination of chlorothalonil from agricultural applications.

Photosensitizers refer to a class of molecules that transfer energy to the reactants via proton absorption in photochemical reactions, thereby promoting the degradation of the reactants by oxidation. A compound is defined as an active photosensitizer if it can be activated by illumination, exists at a level in

the reaction system to absorb a sufficient amount of photons, and can transfer its energy to the reactant. Photosensitizers include aromatic ketones that initiate radical polymerization by extracting the hydrogen atom and benzoin derivatives and acyl phosphine oxides that act by direct photofragmentation.⁸ Common photosensitizers include inorganic compounds, metal ions, natural organic matters, surfactants, and some pigments. In 1976, Carey⁹ first employed nanometer titanium dioxide (TiO₂) to degrade organic pollutants in water. Thereafter, photocatalytic oxidation by nanometer TiO₂ has attracted substantial attention as a water pollution control technology.^{10,11} Currently, nanometer TiO₂ has become one of the popular photocatalysts because of its low cost, nontoxicity, antilight corrosion, high catalytic activity, strong oxidation ability, and good stability.^{12–14} Nanometer TiO₂ occurs in three different crystal structures, i.e., anatase, rutile, and brookite, of which anatase TiO₂ is widely used as a photocatalyst.¹⁵ By comparison, the bandgap of anatase TiO₂ is 3.2 eV, greater than that of rutile TiO₂, so that the former has stronger reducing capacity than the latter. In addition, anatase TiO₂ has stronger capacity to adsorb reactive hydroxyl radicals than rutile TiO₂. Previously, Penuela et al.¹⁶ studied the photodegradation of chlorothalonil in the sunlight and under a xenon lamp and found that the half-life of chlorothalonil in deionized water was significantly shortened with the addition of TiO₂. However, it is unknown if nanometer TiO₂ is also active on chlorothalonil photodegradation at the surface of plants or on the 4-hydroxy derivate of chlorothalonil, a toxic intermediate of chlorothalonil photodegradation.

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The present study aimed to examine the effects of anatase nanometer TiO₂ on photochemical degradation of chlorothalonil in aqueous solution and on the surface of green pepper with or without plastic cover. High-pressure mercury lamp, ultraviolet (UV) lamp, and sunlight were used as the light sources. The study also determined if chlorothalonil-4-hydroxy accumulated following chlorothalonil photodegradation mediated by nanometer TiO₂. Chlorothalonil is used frequently for disease control in greenhouse production of peppers. This project was part of a research program in the Provincial Key Lab to develop cost effective and environmentally safe approaches for accelerating degradation of chlorothalonil without requiring an additional postharvest treatment.

MATERIALS AND METHODS

Chemicals and Reagents. The following chemicals and reagents were used in the study: chlorothalonil (99.1% purity, J&K Chemical Ltd., Shanghai, China), chlorothalonil-4-hydroxy (99% purity, J&K Chemical Ltd., Shanghai, China), *N,N*-dimethyl-*p*-nitrosoaniline ((PNDA), 98% purity, J&K Chemical Ltd., Shanghai, China), acetonitrile (analytical grade), acetonitrile (high performance liquid chromatography (HPLC) grade), methanol (HPLC grade), sodium chloride (analytical grade), and nanometer TiO₂ (anatase, <5 nm particle size, and 99.9% purity).

Analytical Instruments. Agilent 1200 HPLC (variable wavelength detector), American Agilent high-pressure mercury lamp (150W), UV lamp (20W), rotary quartz water-cooled photodegradation instrument, illuminometer (JD-3), constant temperature shaking incubator (SHAC type), ultrasonic cleaner (KQ3200E), Aquapro ultrapurified water machine, and UV spectrophotometer (UV-1800).

Experimental Procedures. The standard stock solution of chlorothalonil (1.0 g/L) was prepared and diluted to the desired working solutions with acetonitrile as the solvent. To determine the effect of nanometer TiO₂ on chlorothalonil photodegradation in aqueous solution, chlorothalonil standard stock solution was transferred into 100 mL flasks, and nanometer TiO₂ was added at a weight to weight ratio of 1:5, 1:10, 1:50, or 1:100. The mixture was diluted with double-distilled water and subjected to ultrasonic solubilization. The reaction solution (10 mL) of chlorothalonil and nanometer TiO₂ was transferred to a quartz cuvette with stopper and placed under different light sources for photodegradation experiments. The light intensity was 7000–8000 lx for the high-pressure mercury lamp, 230 lx for the UV lamp, or 80000–100000 lx for direct sunlight (N 31° 52', E 117° 17'). The distance of the quartz tube from the light source was 15 cm, and the temperature of the reaction system was set at 25 ± 1 °C except for the sunlight treatment in which temperature varied between 25–30 °C. Use of a rotary water bath was necessary to maintain the temperature for the mercury lamp illumination, and the quartz tube was tilted in a 30° angle with the ground to face the sun directly. A control experiment for dark treatment was conducted by wrapping the flasks in aluminum foil under the same conditions. The samples were taken at different time points, and each treatment was repeated twice.

To determine the effects of nanometer TiO₂ on chlorothalonil photodegradation on the surface of plants, fresh green chili pepper was cut as 2 × 3 cm² flakes (the thickness of chili pepper flake is approximately 3 mm). Chlorothalonil (2.5 mg/kg) was added to the surface of pepper flakes, followed by addition of nanometer TiO₂ at a weight to weight ratio of 1:1, 1:5, 1:10, or 1:20. The pepper flakes were placed in a fume hood in darkness to allow evaporation of the solvent in chlorothalonil working solution before they were fixed on a cardboard for treatment under various types of light as described above. The distance of the pepper flakes from the light source, the temperature of illumination system, the light intensity, and the conditions for a control treatment in darkness were the same as the treatments in aqueous solution. The sunlight treatment was conducted both outside (90000–100000 lx) and inside (60000–70000 lx) an

agricultural greenhouse covered with plastic film, with the temperature around 25–30 °C. Each treatment was repeated twice.

Detection of Free Hydroxyl Radicals. PNDA has the maximum absorption at 440 nm, and its adsorption decreases when combined with hydroxyl groups. The reduction of PNDA thus reflects the amount of ·OH it captures. In the present study, PNDA was used as the ·OH scavenger for indicating the changes in the amount of ·OH generated by nanometer TiO₂ in aqueous solutions under the high-pressure mercury lamp. PNDA standard stock solution was transferred to a 100 mL flask, and nanometer TiO₂ was added at a ratio of 1:1 and 1:2 (conc/conc, 5 mg/L PNDA). The mixture solution of PNDA and nanometer TiO₂ was diluted with double-distilled water and subjected to ultrasonic solubilization. PNDA control group was prepared without adding nanometer TiO₂. The reaction solution (10 mL) was transferred to quartz tubes with stoppers and placed under a high-pressure mercury lamp for illumination treatment. Samples were taken at different time points for measuring the absorbance at 440 nm using a UV spectrophotometer. The results were used for calculating the residual concentration of PNDA at each time point in order to reflect the changes in the amount of ·OH.

Sample Extraction and Clean-Up. Photodegradation solution samples (1 mL) were transferred to a 5 mL test tube with a stopper, followed by the addition of 2 mL of acetonitrile and 0.1 g of sodium chloride. After 5 min of oscillation, 1 mL of the supernatant was taken from the mixture and filtered through 0.22 μm membrane for further analysis. The pepper flake samples were placed in 50 mL centrifuge tubes, and 20 mL of acetonitrile and 0.2 g of sodium chloride were added. The mixture was oscillated on a constant-temperature shaking incubator for 1 h, followed by ultrasonic vibration for 20 min. Then, the mixture was centrifuged at 3800 rpm for 5 min, and the supernatant was filtered through 0.22 μm membrane for the subsequent analysis.

The following parameters were used for the detection of chlorothalonil by an Agilent 1200 HPLC and Agilent HC-C18 column (4.6 mm × 250 mm, 5 μm), 236 nm detection wavelength in variable-wavelength UV detector, acetonitrile/water mobile phase (80:20 v/v), flow rate of 1.0 mL/min, column temperature of 30 °C, autosampling, and injection volume of 10 μL. The LOD for chlorothalonil was 0.01 mg/L. The LOQ for chlorothalonil in water and pepper was 0.02 and 0.2 mg/kg, respectively. When the concentration of chlorothalonil in the aqueous solution samples was 0.02–1.0 mg/kg, the recovery was 92.79–96.16% (coefficient of variation 2.79–5.5%), and when the concentration of chlorothalonil applied to the pepper samples was 0.2–2.0 mg/kg, the recovery was 89.13–96.44% (coefficient of variation 2.43–4.96%).

The instrumental parameters for the detection of chlorothalonil-4-hydroxy using Agilent 1200 HPLC included the following: Agilent HC-C18 column (4.6 mm × 250 mm, 5 μm), 248 nm detection wavelength in variable-wavelength UV detector, acetonitrile/0.5% phosphoric acid mobile phase (60:40 v/v), flow rate of 1.0 mL/min, column temperature of 30 °C, autosampling, and injection volume of 20 μL. The LOD and LOQ for chlorothalonil-4-hydroxy in water was 0.01 and 0.02 mg/L, respectively. When the concentration of chlorothalonil-4-hydroxy added to the aqueous solution was 0.02–0.2 mg/kg, the recovery was 91.6–96.34% (coefficient of variation 3.97–5.78%).

Calculation Methods. Photodegradation rate was calculated using the following equation:

$$\begin{aligned} \text{photodegradation rate(\%)} &= \left(\frac{\text{residual concentration of chlorothalonil in dark control} - \text{residual concentration of chlorothalonil in light treatment}}{\text{residual concentration of chlorothalonil in dark control}} \right) \\ &\times 100 \end{aligned}$$

Photodegradation half-life was calculated using the following equation: photodegradation half-life ($T_{1/2}$) = ln 2/ k . The constant of photodegradation rate (k) was calculated from the following

Table 1. Effects of Nanometer TiO₂ on Photodegradation of Chlorothalonil in Water Solution under Different Light Sources Illumination^a

light sources	dose-ratio (chlorothalonil/nanometer TiO ₂)	kinetic equations			half-life T _{1/2} (h)
		C _t = C ₀ e ^{-kt}	rate constant k/h ⁻¹	R ²	
high-pressure mercury lamp	1:0	C _t = 1.103e ^{-0.4693t}	0.4693	0.9601	1.48a
	1:5	C _t = 1.1814e ^{-0.6225t}	0.6225	0.9055	1.11b
	1:10	C _t = 1.1506e ^{-1.0449t}	1.0449	0.9725	0.66c
	1:50	C _t = 1.2258e ^{-0.7883t}	0.7883	0.9139	0.88d
	1:100	C _t = 1.1322e ^{-0.6363t}	0.6363	0.9618	1.09b
ultraviolet lamp	1:0	C _t = 1.2754e ^{-0.8874t}	0.8874	0.8928	0.78a
	1:5	C _t = 1.307e ^{-0.9145t}	0.9145	0.917	0.75a
	1:10	C _t = 1.34e ^{-1.2908t}	1.2908	0.9639	0.53b
	1:50	C _t = 1.3116e ^{-1.1181t}	1.1181	0.9667	0.62c
	1:100	C _t = 1.2478e ^{-1.063t}	1.063	0.9785	0.65c
sunlight	1:0	C _t = 1.036e ^{-0.3836t}	0.3836	0.9763	1.80a
	1:5	C _t = 0.8812e ^{-1.0824t}	1.0824	0.9808	0.64b
	1:10	C _t = 0.63e ^{-1.4229t}	1.4229	0.9147	0.49c
	1:50	C _t = 0.4328e ^{-1.6408t}	1.6408	0.7924	0.42c
	1:100	C _t = 0.5186e ^{-2.2293t}	2.2293	0.8121	0.31d

^aNote: different letter means significant difference at 0.05 level ($P < 0.05$).

equation: $C_t = C_0 \cdot e^{-kt}$, where C_0 was the residual concentration at time zero and C_t was the residual concentration at time t of light treatment.

Photosensitization rate was calculated using the following formula:

$$\begin{aligned} & \text{photosensitization rate}(\%) \\ &= \left(\frac{\text{reaction rate of chlorothalonil with nanometer titania} - \text{reaction rate of chlorothalonil without nanometer titania}}{\text{reaction rate of chlorothalonil without nanometer titania}} \right) \\ & \times 100 \end{aligned}$$

RESULTS AND DISCUSSION

Photosensitizing Effect and Associated Mechanism of Nanometer TiO₂ on Chlorothalonil Degradation in Aqueous Solution. Table 1 shows that the degradation rate of chlorothalonil induced by the three different light sources occurred in the following order: UV lamp > high-pressure mercury lamp > sunlight (Table 1). The maximum absorption wavelength of chlorothalonil solution was found to be 233 nm by a UV spectrophotometric scan (Figure 1). The shortwave emission spectra of the high-pressure mercury and UV lamps could be adsorbed by chlorothalonil to facilitate its photodegradation. By contrast, the sunlight mainly consists of visible light with less short-wave emission spectra so that sunlight adsorption by chlorothalonil may not occur readily.¹⁷ Nanometer TiO₂ exhibited a clear photosensitizing effect on chlorothalonil photodegradation in aqueous solution; however, the sensitization efficiency differed significantly under the three light sources in the following order: sunlight > high-pressure mercury lamp > UV lamp (Figure 2). It is known that the photosensitizing effect of nanometer TiO₂ is induced by light sources of wavelength shorter than 387.8 nm.^{18,19} The UV and high-pressure mercury lamps used in this study had their main emission spectra at 254 and 365 nm, respectively. The significantly broader and continuous spectrum of sunlight may be more conducive to light adsorption by nanometer TiO₂, which explain why sunlight has a higher photosensitization efficiency than mercury and UV lamps. Moreover, the sunlight

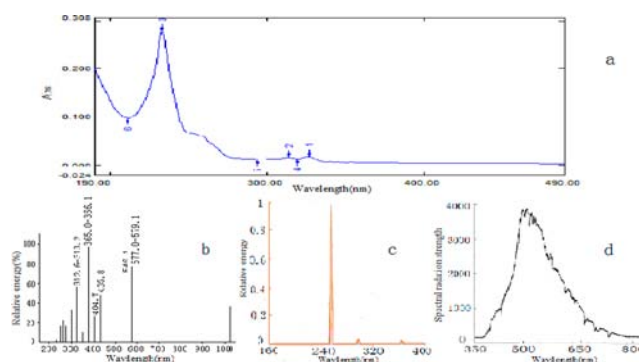


Figure 1. The UV absorption spectra of chlorothalonil in water solution and spectra distribution of three kinds of light sources. (a) The UV absorption spectra of chlorothalonil (1 mg/L) in water solution; (b) The spectra distribution of high-pressure mercury lamp; (c) The spectra distribution of ultraviolet lamp; (d) The spectra distribution of sunlight.

used in this study has the highest intensity, which may also contribute to its enhanced photosensitization efficiency.

The photodegradation and photosensitization rates of chlorothalonil were found to be positively correlated with the concentrations of nanometer TiO₂ at lower dose ranges. The photosensitization rate of chlorothalonil reached the highest under high-pressure mercury (122.65%) and UV (45.46%) lamps when the ratio of chlorothalonil: nanometer TiO₂ was 1:10 (Figure 2). However, whereas higher nanometer TiO₂ content was inhibitory to photosensitization under mercury and UV lamps, the photosensitization rate of chlorothalonil continued to increase with increasing concentrations of nanometer TiO₂ (Figure 2).

Nanometer TiO₂ photocatalyst eventually mineralizes refractory organic pollutants in water to produce CO₂ and H₂O.²⁰ The mechanism of the photocatalytic reaction^{18,19} involves the full valence band and an empty conduction band in the electronic structure of nanometer TiO₂. When illuminated by light of wavelength shorter than 387.8 nm, the electrons of

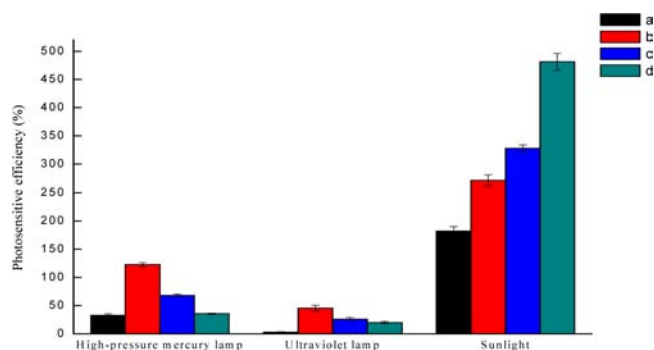


Figure 2. Effects of nanometer TiO_2 on photodegradation of chlorothalonil in aqueous solution under different light sources illumination. (a) The photosensitive efficiency in A treatment (chlorothalonil:nanometer $\text{TiO}_2 = 1:5$). (b) The photosensitive efficiency in B treatment (chlorothalonil:nanometer $\text{TiO}_2 = 1:10$). (c) The photosensitive efficiency in C treatment (chlorothalonil:nanometer $\text{TiO}_2 = 1:50$). (d) The photosensitive efficiency in D treatment (chlorothalonil:nanometer $\text{TiO}_2 = 1:100$). Vertical bars represent the standard errors of the means.

anatase nanometer TiO_2 could be excited into the conduction band from the valence band to form a corresponding hole in the valence band and generate the electron–hole pair. The hole has a greater reactivity and is the main component to carry the light quantum. It generally reacts with the surface-adsorbed H_2O or OH^- to form surface hydroxyl groups with strong oxidability and can directly decompose organic matters. The electrons generally react with the surface-adsorbed oxygen molecules. The resulting reactive oxygen molecules not only participate in the reduction reactions but also serve as an alternative source of surface hydroxyl groups. Sclafani et al.²¹ had proved the presence of $\cdot\text{OH}$ by determining the optical conductivity of TiO_2 .

PNDA was used next as the $\cdot\text{OH}$ scavenger to determine the production and role of $\cdot\text{OH}$ on nanometer TiO_2 -sensitized photodegradation of chlorothalonil. The concentration of residual PNDA significantly decreased under illumination of a high-pressure mercury lamp compared to that in the dark control. The steady-state concentration of hydroxyl radicals in natural water is 1.5×10^{-18} to 5×10^{-16} mol/L.²² In the present study, the photolysis solution was prepared with ultrapure water. After 60 min irradiation, the concentration of $\cdot\text{OH}$ in ultrapure water was 2.4% of that in photolysis solution containing 5 mg/L nanometer TiO_2 . This indicated that $\cdot\text{OH}$ was generated in the aqueous solution and the production of $\cdot\text{OH}$ by 10 mg/L nanometer TiO_2 was higher than that of 5 mg/L nanometer TiO_2 (Figure 3). The production of $\cdot\text{OH}$ was consistent with the observed photodegradation rate of chlorothalonil shown in Table 1, suggesting that enhanced $\cdot\text{OH}$ production induced by nanometer TiO_2 accelerated chlorothalonil photodegradation. *tert*-Butanol is also a hydroxyl radical scavenger. Addition of *tert*-butanol was found to reduce the rate of photocatalytic degradation of chlorothalonil mediated by nanometer TiO_2 (Table 2). This further indicates that nanometer TiO_2 plays a role in photocatalytic degradation of chlorothalonil via the action of hydroxyl radicals. These results together indicated that nanometer TiO_2 under light treatments generated hydroxyl radicals in aqueous solution with strong oxidizing capacity, which played a key role in the nanometer TiO_2 -mediated photolysis of chlorothalonil.

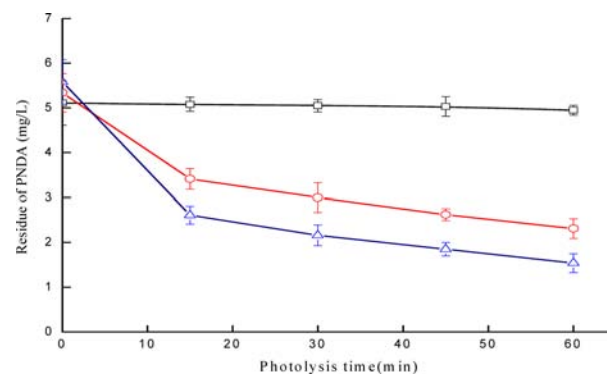


Figure 3. Effects of nanometer TiO_2 on the residue of PNDA. (□) The residue of PNDA in control group (CK). (○) The residue of PNDA in A treatment (PNDA:nanometer $\text{TiO}_2 = 1:1$). (△) The residue of PNDA in B treatment (PNDA:nanometer $\text{TiO}_2 = 1:2$). Vertical bars represent the standard errors of the means.

Effect of Nanometer TiO_2 on the Major Metabolite of Chlorothalonil Photodegradation in Aqueous Solution.

The water-soluble polar substance, chlorothalonil-4-hydroxy, is the major metabolite of chlorothalonil degradation. Compared to chlorothalonil, chlorothalonil-4-hydroxy has been reported to have greater stability and persistency than chlorothalonil in natural water. The reported 96 h and 28 day LC_{50} of chlorothalonil-4-hydroxy for rainbow trout *Oncorhynchus mykiss* were 9200 and 3200 $\mu\text{g/L}$, respectively, and the toxicity values were about 161 and 63 times higher than the corresponding values determined for chlorothalonil in the same set of experiments.²³ Under the illumination of a high-pressure mercury lamp, chlorothalonil produced chlorothalonil-4-hydroxy derivatives through photodegradation, and the production of chlorothalonil-4-hydroxy continuously increased with further degradation of chlorothalonil. However, when nanometer TiO_2 was added to the chlorothalonil solution at 5 or 10 mg/L, chlorothalonil-4-hydroxy was not detectable in the resulting photodegradation solution (Figure 4). It is likely that the $\cdot\text{OH}$ generated by nanometer TiO_2 in the light is characterized with a strong oxidability, whereas the reactive hydroxyl groups have 402.8 MJ/mol reaction energy, which is higher than that of various types of chemical bonds in organic compounds such as C–C (607 kJ/mol), C–H (338.32 kJ/mol), and C–N (754.3 kJ/mol). Therefore, addition of nanometer TiO_2 may facilitate complete degradation of chlorothalonil to generate nontoxic products such as CO_2 and H_2O without the accumulation of chlorothalonil-4-hydroxy. These results together indicate that application of nanometer TiO_2 under light treatments induces production of hydroxyl radicals in aqueous solution that subsequently facilitate the photolysis of chlorothalonil. Notably, photodegradation of chlorothalonil mediated by nanometer TiO_2 is not associated with the accumulation of chlorothalonil-4-hydroxy, an intermediate with higher toxicity, at a level higher than 0.01 mg/L (minimum limit of detection 0.01 mg/L). This finding further indicates the food and environmental safety of nanometer TiO_2 as a photocatalyst for chlorothalonil removal.

Photosensitizing Effect of Nanometer TiO_2 on Chlorothalonil Degradation on the Surface of Pepper.

Unlike chlorothalonil photodegradation in aqueous solution (Table 1), the photodegradation rate of chlorothalonil on the surface of pepper was higher in sunlight than in UV light (Table 3). However, nanometer TiO_2 showed photosensitizing effects

Table 2. Inhibitory Effects of *tert*-Butyl Alcohol on Photodegradation of Chlorothalonil Catalyzed by Nanometer TiO₂ in Water Solution^a

dose ratio (PNDA/nanometer TiO ₂ /TBA)	residue of PNDA(mg/L)	decrement of PNDA(mg/L)	clearance rate of ·OH (%)	dose ratio (chlorothalonil/Nanometer TiO ₂ /TBA)	residue of chlorothalonil (mg/L)	degradation rate of chlorothalonil (%)
1:0:0	4.82			1:0:0	0.564	45.2 ± 3.2
1:0:2	4.85			1:0:1	0.565	43.9 ± 2.9
1:1:0	2.47	2.42		1:5:0	0.45	57.6 ± 4.4
1:1:0.2	2.54	2.24	7.4 ± 0.6	1:5:1	0.461	56.0 ± 4.8
1:1:1	2.73	2.05	15.3 ± 1.2	1:5:5	0.499	51.6 ± 5.1
1:1:2	2.98	1.83	24.4 ± 2.6	1:5:10	0.525	50.8 ± 3.2

^aNote: The initial concentration of PNDA was 5 mg/L. The initial concentration of chlorothalonil was 1 mg/L. The light intensity of the high-pressure mercury lamp was 5200 lx, and the illumination time was 1.5 h. Data are expressed as the mean ± SE of triplicate assays.

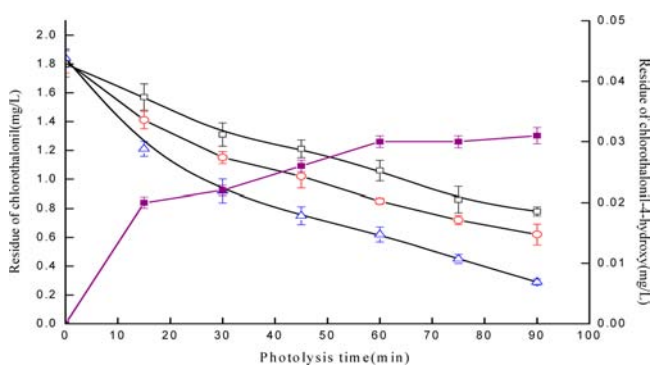


Figure 4. Effects of nanometer TiO₂ on the photolysis product of chlorothalonil under high-pressure mercury lamp illumination. (□) The residue of chlorothalonil in control group (CK). (○) The residue of chlorothalonil in A treatment (chlorothalonil:nanometer TiO₂ = 1:5). (△) The residue of chlorothalonil in B treatment (chlorothalonil:nanometer TiO₂ = 1:10). (■) The residue of chlorothalonil-4-hydroxy producing by the control group (CK). Vertical bars represent the standard errors of the means.

on chlorothalonil photodegradation on the surface of pepper in both sunlight and UV light. Sunlight treatments were more effective in the induction of photosensitization than UV light as

was found in aqueous solution (Figures 2 and 5). By comparison, nanometer TiO₂ was less effective in causing

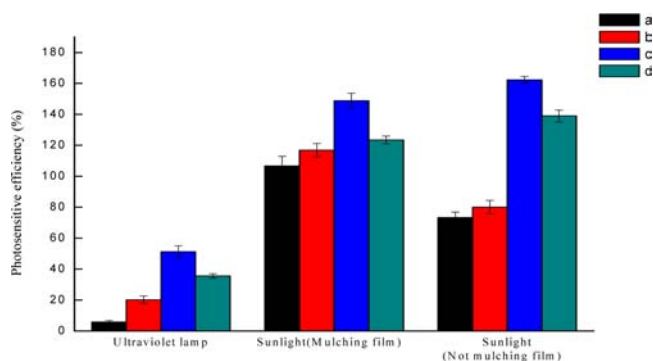


Figure 5. Effects of nanometer TiO₂ on photodegradation of chlorothalonil on pepper under different light sources illumination. (a) The photosensitive efficiency in A treatment (chlorothalonil:nanometer TiO₂ = 1:1). (b) The photosensitive efficiency in B treatment (chlorothalonil:nanometer TiO₂ = 1:5). (c) The photosensitive efficiency in C treatment (chlorothalonil:nanometer TiO₂ = 1:10). (d) The photosensitive efficiency in D treatment (chlorothalonil:nanometer TiO₂ = 1:20). Vertical bars represent the standard errors of the means.

Table 3. Effects of Nanometer TiO₂ on Photodegradation of Chlorothalonil on Pepper under Different Light Sources Illumination^a

light sources	dose ratio (chlorothalonil/nanometer TiO ₂)	kinetic equations			half-life T _{1/2} (h)
		C _t = C ₀ e ^{-kt}	rate constant k/h ⁻¹	R ²	
ultraviolet lamp	1:0	C _t = 2.249e ^{-0.2375t}	0.2375	0.9718	2.92a
	1:1	C _t = 2.194e ^{-0.2513t}	0.2513	0.9482	2.76a
	1:5	C _t = 2.103e ^{-0.2855t}	0.2855	0.8884	2.45b
	1:10	C _t = 2.123e ^{-0.3592t}	0.3592	0.9763	1.93c
	1:20	C _t = 1.838e ^{-0.3218t}	0.3218	0.8628	2.15c
sunlight (mulching film)	1:0	C _t = 2.159e ^{-0.2214t}	0.2214	0.983	3.13a
	1:1	C _t = 2.181e ^{-0.4575t}	0.4575	0.9797	1.51b
	1:5	C _t = 2.23e ^{-0.4801t}	0.4801	0.9714	1.44b
	1:10	C _t = 2.158e ^{-0.5509t}	0.5509	0.9928	1.26c
	1:20	C _t = 2.132e ^{-0.4947t}	0.4947	0.9973	1.4b
sunlight (not mulching film)	1:0	C _t = 2.215e ^{-0.28t}	0.28	0.9836	2.48a
	1:1	C _t = 2.119e ^{-0.4853t}	0.4853	0.9651	1.43b
	1:5	C _t = 2.201e ^{-0.504t}	0.504	0.9408	1.38b
	1:10	C _t = 2.217e ^{-0.7344t}	0.7344	0.9934	0.94c
	1:20	C _t = 2.214e ^{-0.6692t}	0.6692	0.9986	1.04c

^aNote: Different letter means significant difference at 0.05 level ($P < 0.05$).

photodegradation of chlorothalonil on the surface of pepper than in aqueous solution. The difference could be caused by the special distribution of nanometer TiO₂ and chlorothalonil on the pepper surface and by penetration of some chlorothalonil into the cuticle of pepper. Consistently, application of an increasing amount of nanometer TiO₂ led to gradually increased photodegradation and photosensitization rates of chlorothalonil. When chlorothalonil and nanometer TiO₂ were added at a ratio of 1:10, the photosensitization rate of chlorothalonil was 51.24% under UV light and 162.29% under sunlight.

When covered with plastic film, the photodegradation rate of chlorothalonil on the surface of pepper was lower than that without the plastic film cover as expected (Table 3). Partial blockage of sunlight by the thin film and thereby reduction in its light intensity could result in the reduced photodegradation. In addition, Niu et al.⁴ demonstrated that the photodegradation rate of chlorothalonil could decrease with an increased thickness of the cover film. Notably, results presented in Table 3 and Figure 5 showed that nanometer TiO₂ exhibited strong photosensitizing effect on the degradation of chlorothalonil on the surface of pepper covered by the plastic film.

Reducing pesticide residues in greenhouse vegetables is critical to food and environmental safety. The results presented from this study show that nanometer TiO₂ can be used as a photosensitizer to accelerate the degradation of pesticides on pepper under greenhouse conditions. It is likely that the findings of this study may provide guidance to the use of nanometer TiO₂ as a photosensitizer of chlorothalonil in the control of other crop diseases both in the greenhouse and in open field.

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Notes

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