Biological Visual Detection for Advanced Photocatalytic Oxidation toward Pesticide Detoxification

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ABSTRACT: Photocatalytic oxidation treatment is an emerging and fast developed eco-friendly, energy-saving, and efficient advanced oxidation technology for degrading hazardous pesticides. The conventional chemical detection to evaluate the effects for this process depends on the broken chemical structure, only giving residual content and product chemical composition. However, it misses direct visual detection on the toxicity and the quantitative analysis of pesticide detoxification. Here, we develop a novel strategy to combine photocatalytic oxidation with a zebrafish biological model to provide a direct visual detection on the environmental detoxification. The mortality or deformity of zebrafish embryos (ZEs) acts as an indicator. Over the irradiation duration threshold, the mortality of ZEs decreases to 23.3% for pure chlorothalonil (CTL-P) after photocatalytic oxidation treatment for 1 h, and the deformity reduces to 13.3% for commercial CTL (CTL-C) after 30 min and to 3.33% for tetramethylthiuram disulphide (TMTD) after 20 min. The toxicity of CTL-C and TMTD could be completely removed by photocatalytic oxidation treatment and causes no damage to the ZE developmental morphology. Chemical analyses demonstrate the degradation of CTL into inorganic compounds and TMTD into small organic molecules. Among these highlighted heterogeneous photocatalysts (g-$\text{C}_3\text{N}_4$, BiVO$_4$, Ag$_3$PO$_4$, and P25), g-$\text{C}_3\text{N}_4$ exhibits the highest photocatalytic detoxification for CTL-P, CTL-C, and TMTD.

1. INTRODUCTION

Chlorothalonil (2,4,5,6-tetrachloro-1,3-benzenedicarbo-nitrile, CTL), a broad-spectrum organochlorine pesticide, is extensively used in agriculture, horticulture, and other applications as a protectant, bactericide, and mildewcide. However, it is known as an acute and chronic toxic carcinogen and teratogen according to World Health Organization classification of hazards. In China, the production of CTL reaches 8.0 × 10$^6$ kg/year, whereas in the United States, it is approximately 5.0 × 10$^6$ kg/year and growing year by year. The half-life of CTL ranges from several days to 1 year in soil and 8 to 220 days under different concentrations in water and seasonal conditions. Upon degradation, it produces a series of metabolites such as 2,4,5-trichloroisophthalonitrile, 2,5,6-trichloro-4-methoxyisophthalonitrile, 4-hydroxychlorothalonil, 1-carbamoyl-3-cyano-4-hydroxy-2,5,6-trichlorobenzene, and 1,3-dicarbamoyl-2,4,5,6-tetrachlorobenzene. It is considered that the displacement of chlorine into the hydroxyl group (−OH) and the oxidation/hydration of the cyano group (−CN) produce 4-hydroxychlorothalonil, which is more stable and more toxic than its parent compound.

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Thiram (tetramethylthiuram disulfide, TMTD), a dimethyl dithiocarbamate compound, is widely used as a pesticide in crop protection. It is also used as an animal repellent to protect ornamental plants and fruit trees from animal foraging. In the rubber industry, TMTD is used as a vulcanizing agent and an accelerator for rubber. It is also used in cosmetics and biomedical fields. It can be slightly soluble in water and strongly adsorb on soil particles with a certain durability. The acidity of the soil has a great influence on the degradation of TMTD. TMTD can be completely decomposed within 14–15 weeks at pH 7, and at pH 3.5, it takes 4–5 weeks. The final decomposition products in soil are copper dimethylthiocarbamate, dimethylamine, and carbon disulfide. Under acidic condition, TMTD can be degraded completely in water through photolysis. Simultaneously, the formation of CS₂ causes toxicity in liver and damages skin, eyes, and respiratory tract, although CS₂ is not carcinogenic. TMTD is highly toxic to fishes. Therefore, it is of great importance to develop eco-friendly and efficient methods to eliminate these hazardous pesticide residues.

Several methods, such as microbial degradation, photocatalysis, photolysis, Fenton reaction, ultrasonic irradiation, and hydrolysis, have been developed and evaluated.3,8 Bahmann and Kaneco et al. utilized the traditional P25 to degrade pesticides and detect the products by liquid chromatograms (liquid chromatography/mass spectrometry, LC/MS).8,14 The TiO₂−PVA polymer composite was used as a photocatalyst to degrade thiram, which was completely eliminated within 150 min under visible light.15 ZnO and Ag₃PO₄ were used as photocatalysts to degrade TMTD, and 0.01 g L⁻¹ of Ag₃PO₄ within 2 h under sunlight irradiation.16 Moreover, over 90.0% of fungicide o-phenyl phenolate were decomposed by 1.6 g L⁻¹ of Ag₃PO₄ within 2 h under sunlight.17 Wu et al. found a biological photocatalytic cooperative treatment with pseudomonas and TiO₂ for CTL removal, eliminating over 90% of CTL after 7 days.6 Fe³⁺/H₂O₂ has been shown to remove 71.7% of CTL (2 mg L⁻¹) within 60 min in a Fenton reaction.18 Ozonation,19 FeGAC/H₂O₂20 and TiO₂/H₂O₂21 are effective advanced oxidation techniques in the mineralization of CTL into CO₂, H₂O, and NH₃.22,23 Singh et al. controlled the release of TMTD by synthesizing supramolecular beads containing a certain proportion of kaolin and bentonite, which can be used for the safe handling of thiram.24 Additionally, Jiang et al. summarized many kinds of microbes with functions of degrading various pesticides.25 Stenotrophomonas acidaminiphila BJ1, epigallocatechin gallate, Bacillus subtilis WB800, and procyanidolic oligomers were also applied to reduce CTL residues.3,10,26,27

Presently, as one of the most convenient vertebrate developmental biology models, zebrafish (Danio rerio) shows great advantages in detecting environmental and pathological toxicity.28,29 Zebrafish is a small tropical fish with the following characteristics: (1) large amount of spawning throughout a year, (2) early embryonic development and incubation time being approximately 2–3 days, (3) transparent embryo body making it easy to be observed directly under a microscope, and (4) a common method to identify the genes and the genome project.1,2,30,31

Zhu et al. used the zebrafish to examine the developmental toxicity of metal oxide nanoparticles released into the aquatic environment. The toxicological effects of nanoscale ZnO, TiO₂, and Al₂O₃ aqueous suspensions on zebrafish embryos (ZEs) and larvae were compared, and the developmental toxicity of the bulk counterparts was also considered. The results are as follows: ZnO is the most toxic substance in ZEs and larvae.32 Bai et al. demonstrated that nano-ZnO killed ZEs (50 and 100 mg L⁻¹), retarded the embryo hatching (1–25 mg L⁻¹), reduced the body length of larvae, and caused tail malformation after the 96 hpf exposure. Comparative experiments showed that nano-ZnO at high concentrations of 10–100 mg L⁻¹ led to a more severe inhibition of embryonic development than the corresponding concentrations of Zn²⁺ (>3.63 mg L⁻¹), suggesting that dissolved Zn species only partially contributed to the toxicity of nano-ZnO.33 In contrast to visual toxicity detection by zebrafish, and the conventional chemical detection to evaluate the effects for the degradation process depends on the chemical structure broken of pesticides. It can only detect the residual content and chemical composition of products after pesticide degradation. However, it misses a direct visual detection on the toxicity of the photocatalyst and the extent of detoxification for pesticides, especially the degree of biological response and damage to directly show the toxicity to the organism.

Here, we develop a novel strategy to combine photocatalytic oxidation with a zebrafish biological model to provide a direct visual detection on the environmental detoxification for different photocatalysts (g-C₃N₄, BiVO₄, Ag₃PO₄, and P25). The spine of zebrafish is normally straight, whereas low toxic pesticides malformed the embryo development, resulting in a curved spine, and high toxic pesticides directly cause the death of ZEs. The mortality and deformity of ZE can be visually identified by optical microscopy. Together with gas chromatography/MS (GC/MS) or high-performance liquid chromatography/MS (HPLC/MS), the residual concentrations and degradation products of pesticides were analyzed. The results show that over the irradiation duration threshold, the mortality of ZE decreased to 23.3% for pure CTL (CTL-P) after photocatalytic oxidation treatment for 1 h, and the deformity reduced to 13.3% for commercial CTL (CTL-C) after 30 min and to 3.33% for TMTD after 20 min. The toxicity of CTL-C and TMTD could be completely removed by photocatalytic oxidation treatment and causes no damage to the ZE developmental morphology. Chemical analyses demonstrate the degradation of CTL into inorganic compounds and TMTD into small organic molecules. Among these highlighted heterogeneous photocatalysts, g-C₃N₄ exhibits the highest photocatalytic oxidation activity for the detoxification of CTL-P, CTL-C, and TMTD.

2. RESULTS AND DISCUSSION

2.1. Direct Zebrafish Visual Detection on Environmental Toxicity of Pesticides. Scheme 1 gives a straightforward illustration depicting the idea of combining photocatalytic oxidation treatment with the zebrafish biological model to provide a direct visual detection on the environmental detoxification. In principle, the highly active oxygen-containing radicals could oxidize the pesticides into CO₂ and soluble salts during the photocatalytic oxidation process. The spine of zebrafish is normally straight, whereas low toxic pesticides malformed the embryo development, resulting in a curved spine. Highly toxic pesticides directly cause the death of ZEs. The mortality and deformity of the ZE can be visually identified.
The environmental toxicity of CTL and TMTD was first investigated using zebrafish as a biological model. The lethal process of CTL-P (0.01 mg mL\(^{-1}\)) on ZEs occurs within 28 hpf, where they all have died without hatching, indicating the high toxicity of CTL-P to the organism. The biological response and visual indicators are the malformation of the ZE tail end, the damage of the outer membrane causing the cells or yolk sac to overflow, and the black dead cells (Figure 1).

After exposure to 0.01 mg mL\(^{-1}\) of CTL-P for 16 hpf, we directly observed a corroded outer membrane, leading to the overflow of cells or yolk sac. In contrast, we observed the developmental tail and head in the control embryos (Figure 1c). Further extending the postfertilization to 28 hpf, we also observed that CTL-P faded these embryonic cells until the color disappeared into black, denoting the final death of ZE cells, whereas the control grew into a baby zebra fish.

2.2. Quantitative Evaluation on the Photocatalytic Detoxification for CTL-P Using Mortality Rate versus Conventional GC/MS Analysis. Observing the ZE death as a biological visual indicator for the toxicity of CTL-P, we make a quantitative evaluation on the detoxification of photocatalytic oxidation treatments for CTL-P by comparing the mortality rate (%). To accurately present the statistic results, 20 well-developed ZEs and 8 experimental groups including one control were set up, and three parallel experiments were carried out for each pesticide concentration, numbered deaths after ZE exposure to pesticides for 72 h, and averaged for SPSS analysis, where P was considered to be statistically significant for P value < 0.05 and marked as “*” for unobvious differences for P ≥ 0.05. The ZE mortality rate was 11.67% in the control group (solution only contains dimethyl sulfoxide (DMSO)), while it reached higher than 91.6% after exposure to 0.01 mg mL\(^{-1}\) of CTL-P (Figure 2a). Regarding different photocatalysts, a one-way ANOVA with a post-hoc Dunn’s test as independent variables was conducted. The photocatalytic detoxification kinetics were evaluated every 10 min by irradiating for 1 h. The CTL-P dispersion was taken from the photocatalytic system, followed by centrifugation, and then mixed with the ZE culture fluid for visual detection. After the addition of g-C\(_3\)N\(_4\) and UV–vis light irradiation, the mortality rate still remains high above 90.0% in the early 30 min. Prolonging the irradiation time to 40 min, it decreases to almost 70.0%. When the irradiation is prolonged more, the mortality rate becomes less, reducing to 23.3% after 60 min illumination (Figure 2b).

Similar detoxification kinetics occur for g-C\(_3\)N\(_4\), BiVO\(_4\), P25, and Ag\(_3\)PO\(_4\): the mortality rate remains high in the early stage of photocatalytic oxidation treatment (Figure 2c–e). After an irradiation duration threshold (40 min), the mortality rate reduces fast, indicating a concentration limit for the toxicity of CTL-P. Below this toxicity concentration limit through photocatalytic oxidation treatment, the mortality rate will obviously decrease until complete detoxification under irradiation. Because of the distinct dispersion attribute in solution (Table S1) and optical absorption capability in the UV–vis spectrum, the photocatalysts exhibit different detoxification effects, with a mortality rate of 48.3% for Ag\(_3\)PO\(_4\), 53.3% for BiVO\(_4\), and 83.3% for P25 under the same irradiation conditions (Figure 2f).

The conventional GC/MS analysis was also used to probe the concentration change and degradation production of the CTL-P solution after photocatalytic oxidation treatment for 1 h with an intention to verify the conclusions from biological visual detection. Figure 3 shows a retention time of CTL at 8.66 min and the corresponding MS data. The response value of CTL-P is approximately 3.61 × 10\(^8\), which corresponds to the S.40 × 10\(^6\) peak area and a strong abundance CTL ratio of about 4.51 × 10\(^7\) at 265.8 m/z (mass-to-charge ratio). In comparison, the abundance ratio gives a 16.89 times reduction after irradiation solely under UV–vis (Xe lamp) light. A 1119.11 times reduction was further observed after photocatalytic oxidation treatment by g-C\(_3\)N\(_4\) under UV–vis light irradiation, indicating the effective decomposition of CTL-P (Figure 3b). The degradation products of CTL after photocatalytic oxidation treatment are inorganic compounds (m/z of 44.1). For different photocatalysts, the abundance ratio gives an order of g-C\(_3\)N\(_4\) > Ag\(_3\)PO\(_4\) > BiVO\(_4\) > P25 according to the lowering extent with 738.13 times for Ag\(_3\)PO\(_4\), 255.71 times for BiVO\(_4\), and 111.91 times for P25 (Figure S3b–d). Obviously, the conventional GC/MS gives an assessment result for different photocatalysts after photocatalytic oxidation treatment, which is completely similar to the one by the visual ZE death. In addition, the significance of
biological visual detection is the more efficiently and conveniently evaluation on the detoxification effects and identify the detoxification capability for various photocatalysts as well.

2.3. Quantitative Evaluation on the Photocatalytic Detoxification for CTL-C and TMTD Using Deformity Rate versus Conventional GC/MS and HPLC/MS Analyses. To further demonstrate the wide applicability of zebrafish as a direct visual detection for photocatalytic detoxification, we examined another two available commercial CTL (CTL-C) and TMTD pesticides. Figure 4 shows the representative process of ZE from an initial normal state to the embryonic spine deformity and finally to the larva fish curved spine after exposure to CTL-C for 52 hpf. The observing ZE growth to larva fish indicates the low toxicity of CTL-C in comparison to that of CTL-P. However, CTL-C and TMTD still lead to the teratogenesis of the zebrafish with a curved spine, indicating that the toxicity is strongly dependent on the kind and concentration of the hazardous pesticides.

For the evaluation of photocatalytic detoxification for CTL-C, observing malformed zebrafish with a curved spine and tail as the biological visual indicators for the toxicity of CTL-C, we make a quantitative assessment on the photocatalytic detoxification for CTL-C by comparing the deformity rate (%). Similarly, the malformed zebrafish deformity rate is less than 10% in the control group, while it is almost 100% after exposure to 6.25 μg mL⁻¹ of CTL-C (Figure 5a). The photocatalytic detoxification kinetics for g-C₃N₄ indicate that the deformity rate still remains high (nearly 100.0%) in the early 20 min. Prolonging the irradiation time to 30 min, it begins to descend to 13.33%. When the irradiation is prolonged more, the deformity rate becomes less, which reduces to 0 after 60 min (Figure 5b). The irradiation duration threshold for decreasing the deformity rate depends on the photocatalysts, with 20 min for g-C₃N₄, 30 min for Ag₃PO₄, and 50 min for BiVO₄ and P25. The photocatalytic detoxification effects for these highlighted photocatalysts give a deformity rate of 0 for g-C₃N₄ and Ag₃PO₄, 11.67% for BiVO₄, and 30.0% for P25 under the same irradiation for 60 min (Figure 5c–f). More visual lines of evidence are shown by the cartilage staining, where the straight spine is recovered after exposure to CTL-C detoxification by g-C₃N₄ in comparison with the curved spine after exposure to CTL-C (Figure 7a–c).

For TMTD, the malformed zebrafish deformity rate is less than 10% in the control group, while it is almost 100% after exposure to 0.121 mg mL⁻¹ of TMTD (Figure 6a). The photocatalytic detoxification kinetics for g-C₃N₄ indicate that the deformity rate still remains high (nearly 100.0%) in the early 10 min. Prolonging the irradiation time to 20 min, it begins to descend to 3.33%. When the irradiation is prolonged more, it reduces to 0 after 60 min (Figure 6b). The irradiation duration threshold for decreasing the deformity rate is 10 min for g-C₃N₄, 30 min for Ag₃PO₄, and 50 min for BiVO₄ and P25. The photocatalytic detoxification effects for these
highlighted photocatalysts give a deformity rate of 0 for g-C₃N₄ and Ag₃PO₄, 18.33% for BiVO₄, and 45.0% for P₂₅ under the same irradiation for 60 min (Figure 6c). For more clear comparison of the photocatalytic detoxification, we present the typical zebrafish morphology (76 hpf) exposure to TMTD after photocatalytic oxidation treatment for 20 min. For g-C₃N₄, the morphology of zebrafish exhibits no difference compared to the control (Figure 7d–f). However, the zebrafishes with the curved spine were observed for Ag₃PO₄, BiVO₄, and P₂₅. This result indicates that the toxicity of TMTD could be completely removed by photocatalytic oxidation treatment and causes no damage to the developmental morphology of ZEs (Figure 8a–e).

As mentioned above, conventional GC/MS analysis was also used to examine the residual concentration after photocatalytic oxidation treatment for 1 h. CTL-C solution was pretreated by diluting 100 times before the GC/MS test. The results show the retention time of CTL at 8.66 min and the actual concentration of CTL-C of 6.25 μg mL⁻¹. After 60 min irradiation, the concentration of CTL-C changes to 0.98 μg mL⁻¹ for g-C₃N₄, 1.04 μg mL⁻¹ for Ag₃PO₄, 1.59 μg mL⁻¹ for BiVO₄, 2.27 μg mL⁻¹ for P₂₅, and 4.39 μg mL⁻¹ without a photocatalyst (Figure S4 and Table S2). The C/C₀ plot also clearly presents the contribution from different photocatalysts to degrade CTL-C. Because of the different boiling point of

Figure 3. Conventional GC/MS analysis on CTL-P. (a) GC spectrum with a retention time of 8.66 min for CTL-P (0.01 mg mL⁻¹) and corresponding m/z in MS. (b) GC spectrum with a retention time of 8.66 min for CTL-P after photocatalytic oxidation treatment for 60 min by g-C₃N₄ and corresponding m/z in MS, where the red circle represents the peak retention time of CTL.

Figure 4. Representative images of lifetime of the ZE (4–52 hpf) exposure to CTL-C (6.25 μg mL⁻¹) (a–c). Control embryos: (d–f).
TMTD, HPLC/MS was utilized to separate and detect TMTD. Similarly, the TMTD solution was pretreated by diluting 100 times for the measurement. The initial actual concentration is 121.12 μg mL⁻¹ and changes to 0.01 μg mL⁻¹ for g-C₃N₄, 0.03 μg mL⁻¹ for Ag₃PO₄, 0.71 μg mL⁻¹ for BiVO₄, 12.98 μg mL⁻¹ for P₂₅, and 39.22 μg mL⁻¹ without a photocatalyst (Table S2). The C/Cₒ plot gives the photocatalyst activity for degrading TMTD. These results provide strong lines of evidence to support the fact that the toxicity depends on the pesticide concentration, and the detoxification effect appears only over this concentration threshold. In this perspective, it is a big advantage of biological visual detection over the conventional chemical analysis with the complicated pretreatment process to indicate the toxicity intensity and evaluate the detoxification efficiency.

3. CONCLUSIONS

In summary, we develop a biological visual detection with ZEs to evaluate pesticide detoxification during photocatalytic oxidation treatment. The mortality and deformity of ZEs act as quantitative indicators for analyzing the photocatalytic detoxification. Over the irradiation duration threshold, the mortality and deformity rate reduce fast, and the toxicity of pesticides can be completely removed by photocatalytic oxidation treatment. Compared to the conventional chemical analysis, it provides more efficient and convenient evaluation techniques for the photocatalytic detoxification toward hazardous pesticides.

4. EXPERIMENTAL SECTION

4.1. Materials and Reagents. All reagents were of analytical grade and used as received. Sodium phosphate dibasic anhydrous (Na₂HPO₄, 99.0%) and urea (99.0%) were provided by Sinopharm Chemical Reagent Co. Ltd. CTL-P (98.0%), CTL-C (75%), TMTD (97%), DMSO, titanium dioxide (P₂₅, 99.0%), bismuth vanadium oxide (BiVO₄, 99.0%), and silver nitrate (AgNO₃, 99.8%) were purchased from Sinopharm Chemical Reagent Co. Ltd.

4.2. Preparation of g-C₃N₄ and Ag₃PO₄. Urea (20 g) was ground into powder and dried at 80 °C. The powder was then heated at 550 °C for 1 h to obtain a yellow powder, which was then rinsed with nitric acid and deionized water, filtered, and dried to obtain g-C₃N₄. Ag₃PO₄ was synthesized by an ultrasonic method.¹⁴ AgNO₃ (0.20 g) and 0.42 g of Na₂HPO₄...
were dissolved into 100 mL of deionized water, assisted by an ultrasonic treatment for 15 min, centrifuged, and then dried at 80 °C in a vacuum oven.

4.3. Experiment Methods. CTL-P (0.01 mg mL\(^{-1}\)) in DMSO solution was first prepared. In a typical photocatalytic oxidation experiment, 10 mg of powder photocatalyst was dispersed in 20 mL of 0.01 mg mL\(^{-1}\) CTL-P solution by sonication. The suspension was irradiated by a 300 W Xe lamp under magnetic stirring. CTL-P dispersion (1 mL) was taken out at every 10 min from the reaction systems, followed by centrifugation at 15 000 rpm for 10 min. The supernatant was exposed to ZEs as described below. After 60 min, both CTL-C and CTL-P centrifuged after photocatalytic oxidation treatment was detected by GC/MS and HPLC/MS for TMTD (0.121 mg mL\(^{-1}\)).

4.4. Zebraﬁsh Experiment. The zebraﬁsh (D. rerio, AB strain) was reared at 28.5 °C at a light/dark ratio of 14 h:10 h with a ratio of 2 males to 1 female and fed with general ﬁsh food. Embryos were collected on the next day, and only well-developed embryos were selected under a microscope. After 4 h of post-fertilization (4 hpf), about 20 well-developed embryos in 3 cm Petri dishes with 5 mL of culture ﬂuid were treated with 5 μL of either CTL-C (0.00625 mg mL\(^{-1}\)) and CTL-P (0.01 mg mL\(^{-1}\)) or TMTD (0.121 mg mL\(^{-1}\)), mixed, and cultured in a 28.5 °C incubator until observation. The morphological observation was performed under the microscope. Eight experimental groups including one control group were set up, and three parallel experiments were carried out for each exposure concentration and averaged for analysis.

In order to stain the cartilage, ZEs were ﬁrst stained in 4% paraformaldehyde solution for no more than 24 h and washed twice with phosphate-buffered solution for 1 h. The embryos were stained with Alican blue 8 GR at room temperature for 6
h and then washed once with 95, 90, 80, 70, 50, and 20% ethanol and distilled water for 1 h each time. Next, after adding 1.5 mg mL$^{-1}$ protease K for 30–60 min, the embryos were dipped in 0.5% KOH for 1 h and then washed with distilled water. Finally, the embryos were fixed in 10–20% glycerol, observed, and photographed.

4.5. Determination of Embryo Mortality and Deformity. Early-stage embryos were visually opaque and coagulated. End-stage embryos without heartbeat and ceasing development were assumed to be dead. The control group exhibited the normal development morphology with a straight spine, whereas malformed zebrafish exhibited a curved spine and tail.

Mortality rate (%) = \( \frac{\text{number of deaths}}{\text{total number of embryos}} \times 100\% \)

Deformity rate (%) = \( \frac{\text{number of deformities}}{\text{total number of embryos}} \times 100\% \)

4.6. Characterization. The phase structures of the prepared samples were determined by X-ray diffraction (XRD) on a SmartLab 9 kW (Rigaku, Cu Ka, \( \lambda = 1.5406 \) Å). Optical properties were determined by a UV–vis diffuse reflectance spectrophotometer (Agilent Cary 300) with BaSO$_4$ as a reference. The morphological observations of embryos were conducted via a MDG41 optical microscope. Agilent 7000D GC/MS was used to acquire gas chromatograms and mass spectra of CTL. Agilent 1260/6420 HPLC/MS was used to acquire liquid chromatograms and mass spectra of TMTD.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02289.

XRD, UV–vis diffuse reflectance spectroscopy spectra, zeta potential, GC/MS analysis, thermogravimetric analysis curves, content of hazardous pesticides after photocatalytic oxidation treatment, and lifetime of ZEs at natural conditions (PDF)

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