

NANO REVIEW

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The Application of Nano-TiO₂ Photo Semiconductors in Agriculture

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Abstract

Nanometer-sized titanium dioxide (TiO₂) is an environmentally friendly optical semiconductor material. It has wide application value in many fields due to its excellent structural, optical, and chemical properties. The photocatalytic process of nano-TiO₂ converts light energy into electrical or chemical energy under mild conditions. In recent years, the study and application of nano-TiO₂ in the agricultural sector has gradually attracted attention. The nano-TiO₂ applications of degrading pesticides, plant germination and growth, crop disease control, water purification, pesticide residue detection, etc. are good prospects. This review describes all of these applications and the research status and development, including the underlying principles, features, comprehensive applications, functional modification, and potential future directions, for TiO₂ in agriculture.

Keywords: Nano-TiO₂, Photo semiconductors, Agriculture, Pesticide

Review

Introduction and Background

To date, the photo semiconductor, titanium dioxide (TiO₂), has been proven to be the most effective and useful photocatalyst for both fundamental research and practical applications due to its high-efficiency, photochemical stability, nontoxic nature, and low cost [1–4]. Much research has been performed to explore the photocatalytic activity of TiO₂ photo semiconductors in their nano form [5–7]. The photocatalytic activity mechanism of nano-TiO₂ has been extensively studied in the literature [8–13], and the basic photocatalytic mechanism is shown in Fig. 1. Upon absorption of light energy larger than the band gap of TiO₂, electrons are excited from the valence band to the conduction band, which creates electron (e⁻)–hole (h⁺) pairs. These charge carriers can rapidly migrate to the surfaces of catalyst particles, where they are ultimately trapped and undergo redox chemistry with suitable substrates. Thus, the trapped hole can react with chemisorbed OH⁻ or H₂O to produce the OH· radicals. Oxygen, which is present in the

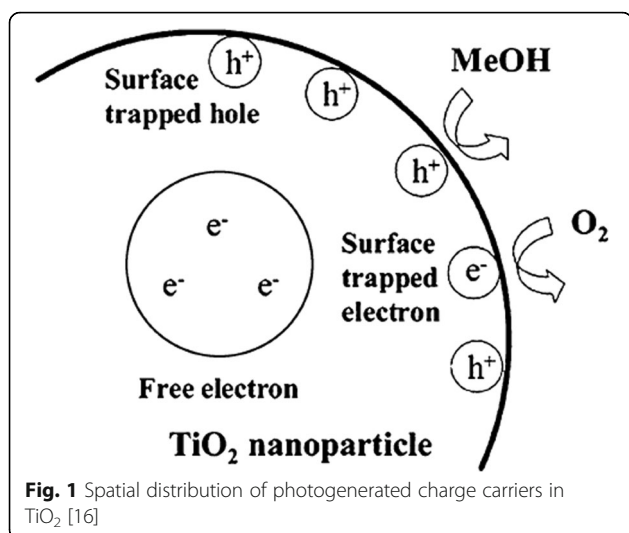
system, acts as an efficient electron scavenger. Additionally, any other oxidant, such as OH⁻, can trap electrons [14–16].

Nano-TiO₂ photo semiconductors have many applications in many fields including photocatalysis, agriculture, dye-sensitized solar cells, and biomedical devices [17]. However, in the agricultural field, the use of TiO₂ nanomaterials is relatively new and requires further exploration. The nano-TiO₂ photo semiconductor continues to attract attention of agricultural researchers because of its favorable physical/chemical properties, low cost, availability, and high stability. Thus, nano-TiO₂ photo semiconductors have many application possibilities in agriculture including degradation of pesticides, plant protection, and residue detection. However, one disadvantage of TiO₂ nanomaterials is that they are mostly active in the presence of UV light due to their large band gap of approximately 3.2 eV [18, 19]. The UV regime is only a small fraction of the Sun's energy (<10%) [20]. Therefore, this property limits the application of TiO₂ nanomaterials in agriculture, and the highly efficient use of TiO₂ nanomaterials is sometimes prevented. Thus, several approaches have been developed to alleviate this problem and to improve the photocatalytic activity of TiO₂ nanomaterials for a wide range of applications. One effective method for improving the performance of TiO₂ nanomaterials is to increase their optical activity by shifting the response onset from the UV to the visible region by

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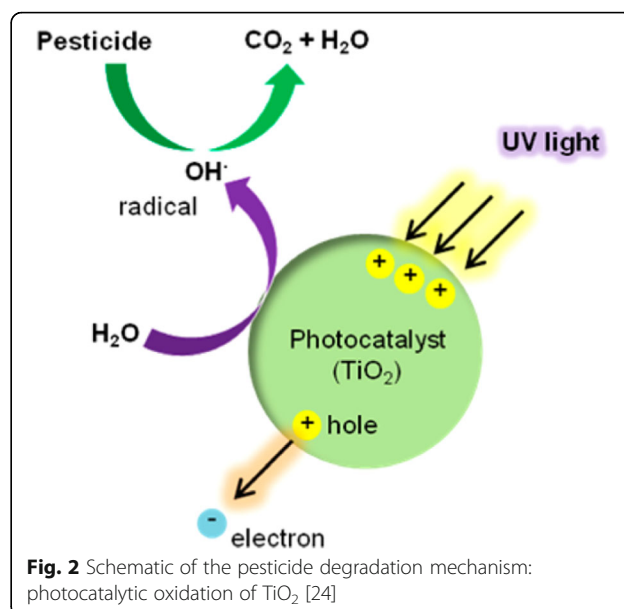
doping the TiO_2 nanomaterial with different metals or other elements [21].

This paper aims to review and summarize the recent applications and research on nano- TiO_2 photo semiconductors and their doping complexes in agriculture. The topics include pesticide degradation, plant germination and growth, crop disease control, water purification, and pesticide residue detection.

Application of TiO_2 Photo Semiconductors in Agriculture Pesticide Degradation

Pesticides are widely used in agriculture, although their excessive usage may create hazards to both humans and the environment. Repeated use of pesticides results in a frequent occurrence of residues in the environment and in biota. Most pesticide residues require effective treatment and further removal due to their toxicity, high chemical stability, and low biodegradability. Consequently, considerable efforts have been devoted to developing methods that can remove residual pesticides and destroy bio-recalcitrant organic contaminants [22]. Semiconductor photocatalysis is a promising approach to remedy the pesticide residue problem, and it has attracted significant attention [14, 23]. TiO_2 is the most investigated photo semiconductor. For the past decade, it has been widely studied as an efficient photocatalyst for pesticides [14].

In the photocatalytic oxidation process, pesticides are destroyed in the presence of TiO_2 photocatalysts and a UV light source. As illustrated in Fig. 2, when TiO_2 is irradiated with photons whose energy is equal to or greater than its band gap energy ($E_g = 3.2$ eV), electron-hole pairs are created. In an aqueous system, these holes react with H_2O or OH^- that are adsorbed on the semiconductor surface to produce OH^\cdot radicals, which are the strongest oxidants in this process [24–27]. These radicals react with pesticides that are adsorbed on the surface and decompose the



pesticides [20]. The pesticides are degraded into H_2O , CO_2 , and other biologically degradable and less toxic substances without secondary pollution. Rabindranathan reported that the TiO_2 photocatalyst is effective in degrading the phosphamidon insecticide [28]. Several factors (e.g., phosphamidon concentration, pH of the system, catalyst loading, and the presence of anions) influence the degradation rate [28]. Lhomme reported the photocatalytic degradation of chlorotoluron and cyproconazole pesticides on TiO_2 -coated media, and the process was found to be effective in degrading and mineralizing the pesticides [29]. Recent studies have found that the TiO_2 morphology plays a key role on the photocatalytic activity. As shown in Fig. 3, TiO_2 nanotube length has significant effect on the photocatalytic degradation of paraquat [30], and short tubes with a small internal diameter exhibit poor photocatalytic activity because pollutant diffusion is ineffective. The result shows that the optimal activity was found for 7- μm -long TiO_2 tubes, and tubes longer than 7 μm have thinner walls; thus, light is absorbed on a longer distance and pollutant has to diffuse further to reach the oxidizing species [30].

This TiO_2 photocatalytic degradation process of pesticides mainly relies on the in situ generation of highly reactive OH^\cdot radicals, which are capable of converting pesticides into relatively innocuous end products. However, the limitations for the wide application of TiO_2 semiconductors for pesticide photocatalytic degradation include the high rate of electron-hole recombination, wide band gap, and inefficient visible light harvesting catalysts [31, 32]. Minimization of the electron-hole recombination and efficient visible light excitation are the major issues that increase the photocatalytic efficiency for pesticide degradation. To overcome these problems, many modifications have been applied to TiO_2 nanomaterials such as doping with a metal coating,

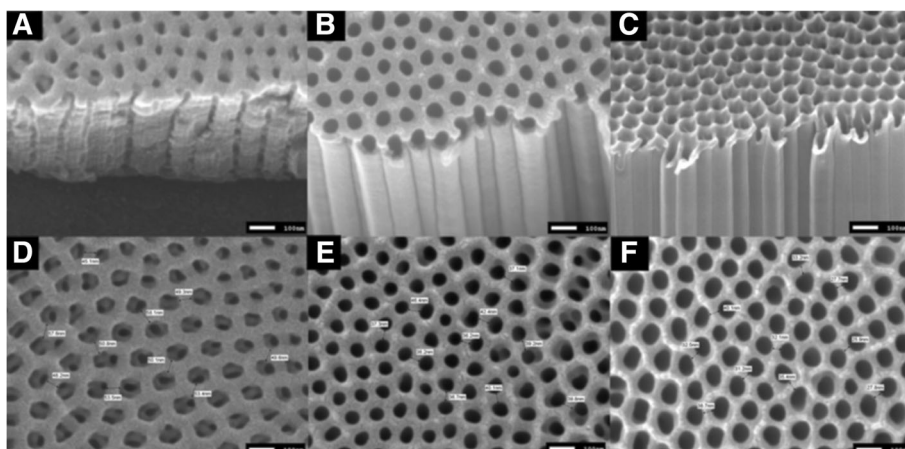


Fig. 3 SEM analysis—side and top view for various tube lengths: 1.5 μm (a, d), 7 μm (b, e), and 10 μm (c, f) [30]

surface sensitization, surface area increase or designing, and developing secondary mixed oxides [33, 34]. The modifications of TiO_2 nanomaterials with different special modifiers, such as Ag^+ , WO_3 , and W, have enhanced the pesticide photocatalytic degradation properties of the catalyst [35, 36]. An efficient charge separation can be obtained by coupling two semiconductor particles that have different energy levels [34, 37]. Figure 4 presents WO_3 doping as an example. WO_3 ($E_g = 2.8$ eV) can function as an electron accepting species in the presence of visible light, which is favorable for producing electron–hole pairs and for improving the pesticide photocatalytic degradation [34].

A substantial amount of research has been focused on modifying the TiO_2 photocatalyst for enhancing pesticide degradation [22]. Ramos-Delgado et al. reported the solar photocatalytic activity of TiO_2 , which was modified with WO_3 , for degrading the organophosphorus pesticide [34]. The TiO_2 semiconductor, which was loaded with 2% WO_3 , exhibited better solar photocatalytic behavior for degrading

the malathion pesticide compared with bare TiO_2 . This was attributed to the formation of smaller clusters and a higher surface area, which reduced the electron–hole recombination process and resulted in a better contact area between the catalyst particles and the pesticide. Thus, the photocatalytic reactivity and efficiency were improved [34]. Guan et al. reported a W/TiO_2 catalyst that was constructed for the photocatalytic degradation and mineralization of avermectin insecticide microcapsules. The catalyst had the highest photocatalytic activity with a 4.0 mol% W-doped amount due to the presence of electron-trapping centers (W^{6+}) in W-doped TiO_2 solid solutions. Guan et al. reported different types of TiO_2 -based photodegradable nano-imidacloprid insecticides [14]. Photocatalysts, including TiO_2 , sodium dodecyl sulfate (SDS)/ TiO_2 , Ag/TiO_2 , and $\text{SDS}/\text{Ag}/\text{TiO}_2$, were constructed for the photocatalytic degradation of the nano-imidacloprid insecticide. The photocatalytic activity of $\text{SDS}/\text{Ag}/\text{TiO}_2$ was the highest among all of the photocatalysts due to its large specific

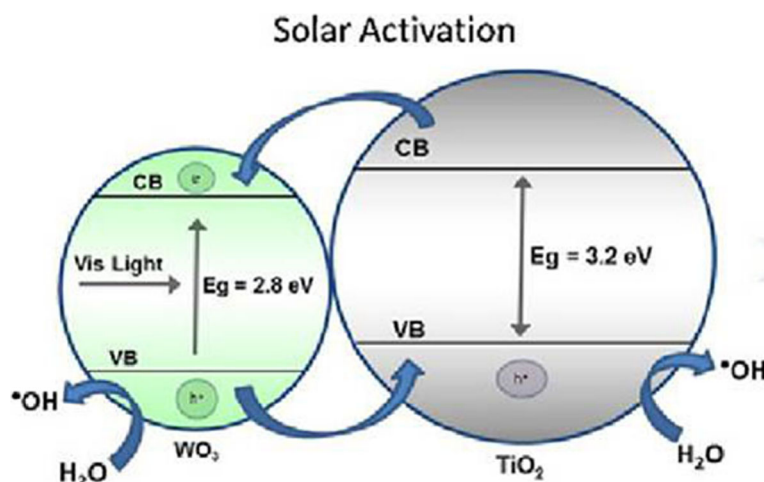


Fig. 4 Solar photocatalytic activity of TiO_2 modified with WO_3 for the organophosphorus pesticide degradation [34]

surface area compared with TiO_2 , which led to the fast adsorption of reactants and enrichment of the insecticide. Moreover, depositing silver in the SDS/Ag/TiO_2 photocatalyst significantly promotes the photocatalytic activity.

Plant Germination and Growth

In recent years, various researchers have studied the effects of nanomaterials on plant germination and growth to promote the use of nanomaterials for agricultural applications [38]. TiO_2 nanomaterials can induce active oxygen, including superoxide and hydroxide anions, in the photocatalytic process, which increases the seed stress resistance and water and oxygen intake. These are required for the fast germination of plants. Zheng et al. reported the effects of TiO_2 photocatalysts on the growth of spinach seeds. They demonstrated that the nano- TiO_2 -treated seeds that were produced from plants that had a higher dry weight, higher photosynthetic rate, and increased chlorophyll formation. This suggested that TiO_2 nanomaterials promoted the absorption of inorganic nutrients and increased the photosynthetic rate [39]. The research results of Song et al. showed that the effect on plant growth was more pronounced with TiO_2 nanoparticles than with bulk TiO_2 . TiO_2 nanoparticles stimulated plant growth at low concentrations but inhibited plant growth at high concentrations [40]. Yang showed that spinach leaves could be kept green using nano-anatase TiO_2 treatment due to N_2 fixation. Additionally, the fresh weight, dry weight, and the content of total nitrogen, NH_4^+ , chlorophyll, and protein in spinach were clearly increased [41]. As shown in Fig. 5, Raliya et al. reported the physiological effects of TiO_2 nanoparticles in mung bean. The results demonstrated a significant increase in plant growth for plants that were treated with TiO_2 nanoparticles. In the control, plants exposed to TiO_2 nanoparticles showed significant improvements in shoot length, root length, root area, and root nodules [42].

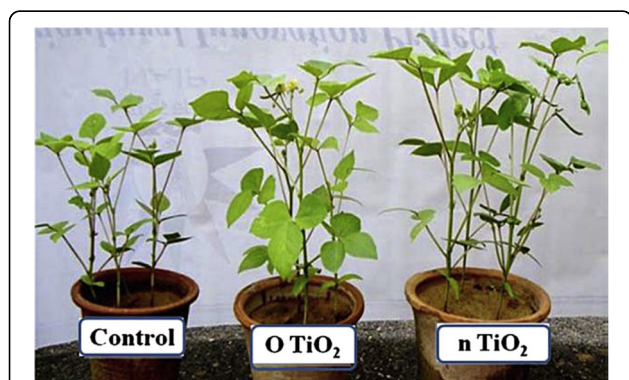


Fig. 5 Phenology of a mung bean plant under various treatments (control, O TiO_2 : ordinary titanium dioxide, n TiO_2 : nano titanium dioxide) [42]

Crop Disease Control

Conventional bactericidal methods that are used to protect plants against pathogens apply chemical pesticides to the irrigation water. However, this method of controlling plant diseases is hazardous both to humans and to the environment. Photochemical disinfection of plant pathogens using TiO_2 thin films offers an alternative method for preventing plant pathogens [43]. The TiO_2 photocatalyst technique has a potential for agricultural applications because it does not form dangerous compounds [44]. Under light, TiO_2 nanomaterials generate superoxide ion radicals and hydroxides. These active oxygen species are effective antimicrobial agents. In recent years, various researchers have studied the effect of nano- TiO_2 photo semiconductors in controlling crop diseases. However, UV accounts for only approximately 3% of the solar light spectrum. This limits the TiO_2 photocatalytic disinfection application under visible light irradiation [44]. Yao et al. reported that the TiO_2 thin film photocatalytic efficiency is improved under visible light by doping with a novel photosensitive dye. Thus, phytopathogenic bacteria in vegetable crops can be effectively inhibited by visible light irradiation. Cui et al. studied the bactericidal effect of nano- TiO_2 on cucumbers [45]. The nano- TiO_2 formed a successive, adhesive, and transparent film on the surface of the leaves. Further, the nano- TiO_2 -treated cucumber leaves had powerful bactericidal effects on plant pathogens due to the photocatalytic and photo biological effects of TiO_2 , which inhibited bacterial and fungal diseases.

Water Purification

In recent years, the growing concern about the problem of water decontamination from organic pollutants during agricultural production has led to research on methods that improve the efficiency and lower the consumption of chemical reagents [46]. Because photocatalysts use solar energy, the photocatalytic decomposition of organic pollutants in water is of particular interest and has received significant attention from scientists [47–50]. TiO_2 is the most popular semiconductor that is used in photocatalytic processes [47–50]. TiO_2 photo semiconductors that are a large size are stoichiometric and thus exhibit poor photocatalytic activity. However, nano- TiO_2 crystallites (typical size <50 nm) have the expected electronic properties for applications in photocatalysis because of their higher activity [51]. In this photocatalysis process, reactive species can be formed on the surface of a nano- TiO_2 photocatalyst that is exposed to UV radiation. The complete degradation and mineralization of a large variety of organic contaminants can be achieved in most cases [52, 53].

However, the main problem, which has limited the practical application of nano- TiO_2 photocatalysis for water purification, is either a relatively low process rate or a limited efficiency for the use of irradiated energy [1, 54, 55]. A possible approach to solve this problem is the exploitation

of low-cost radiation such as solar energy [56, 57]. However, the intensity of ultraviolet radiation in the solar spectrum is very limited. Therefore, the use of metals or metal oxide doping to extend the TiO_2 absorption to the visible range is currently a good option for solving the problem. This approach enhances the photocatalytic activity of TiO_2 and improves the utilization efficiency of the radiation energy [20, 58]. For instance, it was determined that the addition of fluoride to TiO_2 significantly enhances the degradation rate of phenol [22, 59]. The dominant parameters (e.g., dopant nature, dopant concentration, and thermal treatment) affect the material [60]. Vione reported that fluoride addition to TiO_2 enhanced the photocatalytic degradation of many organic compounds that were transforming via different pathways [46]. Bessekhouad reported that alkaline-doped TiO_2 at low concentrations could be a promising material to degrade organic pollutants. The best results were obtained for 5% Li-doped TiO_2 that was prepared using the impregnation technique [51]. Brezová et al. reported that the presence of metals, such as Li^+ , Zn^{2+} , Cd^{2+} , Pt^0 , Ce^{3+} , Mn^{2+} , Al^{3+} , and Fe^{3+} , could significantly change the photoactivity of TiO_2 that was prepared using the sol-gel technique [60]. In addition, the effect of doping TiO_2 with Li and Rb was studied by López et al., and the obtained materials were used to decompose 2,4-dinitroaniline [59].

Pesticide Residue Detection

Depending on their aqueous solubility, pesticides either remain in the soil or enter surface waters and ground waters. Pesticide degradation residues can remain in vegetables, animals, and water sources and can become more concentrated as they move up the food chain. There is an increasing interest in developing systems to sense, monitor, and remove pesticide residues because they are toxic even at trace levels.

Currently, pesticide detection methods typically use liquid or gas chromatography coupled with mass spectrometric detection (HPLC-MS and GC-MS) due to the sensitivity and reliability of these techniques. However, these approaches require meticulous sample preparation and highly qualified technicians [61]. Nanomaterial-based sensors can be used to detect pesticide residues. These nanosensors are alternatives to traditional methods due to their high sensitivity, low detection limits, high selectivity, fast response, and small size. Because of their simplicity, low cost, and ease of miniaturization, electrochemical and optical biosensors are widely used for detecting pesticides.

During recent decades, nano- TiO_2 photo semiconductors, which are efficient sorbents for enriching and detecting pesticides, have attracted significant attention in the photocatalytic and photoelectrochemical area due to their nontoxicity, hydrophilicity, availability, and stability against photocorrosion. Additionally, they have a suitable flat band

potential and are easily supported on various substrates [62–65].

TiO_2 was used as an efficient and selective sorbent to recognize the phosphorylation moiety based on a strong chelation with phospho-moieties. The affinity of TiO_2 towards the phosphoric group is favorable for fast enrichment and detection of free organophosphate pesticides [19]. However, the wide band gap of TiO_2 (~3.2 eV, anatase) allows it to absorb only the ultraviolet light (<387 nm). To extend its photo response to the visible region and to promote the photoelectric conversion efficiency, many modification methods have been applied (e.g., dye sensitization, metal ion/nonmetal atom doping, semiconductor coupling, and noble metal deposition) [19, 66]. Of the abovementioned methods, by considering the high electron mobility of nanocrystals and the possibility of shifting the optical band gap to the visible light region using organic materials, the organic-inorganic heterojunction can produce a robust photoelectrochemical sensor. Zhou reported that graphene-modified TiO_2 nanotube arrays exhibit an excellent enrichment efficiency for carbamate pesticides including metolcarb, carbaryl, isoprocarb, and diethofencarb. The detection limits of these carbamate pesticides range from 2.27 to 3.26 $\mu\text{g L}^{-1}$. The method could be used as a faster and easier alternative procedure for routine analysis of carbamate pesticides [67]. Li et al. developed two photoelectrochemical sensors to detect dichlofenthion and chlorpyrifos pesticides. The sensors were based on a TiO_2 photocatalyst coupled with electrochemical detection, which is a derivative of an electrochemical sensor and sensitized TiO_2 [68, 69].

Conclusions

Over the past decades, nano- TiO_2 has shown its potential for agricultural applications because of its high photocatalytic disinfection and photo biological effects coupled with its low price, nontoxicity, and stable performance. The continuous breakthroughs in the synthesis and modifications of TiO_2 nanomaterials have resulted in new properties and new agricultural applications including pesticide degradation, plant germination and growth, crop disease control, water purification, and pesticide residue detection with improved performance. The research demonstrates that nano- TiO_2 photo semiconductors are essential for degrading organic pollutants, preventing and controlling plant diseases with an antiviral or antibacterial function, and protecting the environment. These characteristics provide new approaches for solving environmental pollution and pesticide residue problems in agriculture.

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Authors' Contributions

YW collected and reviewed the data and drafted the manuscript. CS, XZ, and AW modified the first version of the draft and after revision. HC, ZZ, BC, and GL participated in discussions. YW and HC analyzed and interpreted the data. All authors read and approved the final manuscript.

Authors' Information

YW is an associate professor. HC, ZZ, and GL are professors. CS, XZ, and BC are assistant professors, and AW is a graduate student in the Institute of Environment and Sustainable Development in Agriculture, Chinese Academy of Agricultural Sciences.

Competing Interests

The authors declare that they have no competing interests.

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