

TiO₂ photocatalytic antifungal technique for crops diseases control

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Abstract: TiO₂ and 1%Ce³⁺-TiO₂ prepared by hydrothermal method were characterized by means of XRD and UV-visible diffusive reflectance spectra(DRS). The results of DRS analysis indicated that the 1%Ce³⁺-TiO₂ catalyst had significant optical absorption in the visible region between 400–450 nm because electrons could be excited from the valence band of TiO₂ or cerium oxides to Ce 4f level. To investigate the photocatalytic activity of different catalysts for crop fungal disease control, a series of Quine tests were carried out for cucumber powdery mildew and litchi downy blight control in home-made photocatalytic reactor. The results showed that TiO₂ photocatalysis technique should be effective to inhibit the growth of fungal diseases to some extent and P-25 had a higher activity for antifungal control than home-made TiO₂ catalysts. TiO₂-A prepared with Ti(SO₄)₂ is more active to control antifungal disease than TiO₂-B prepared with TiOSO₄ as precursor because the crystalline of TiO₂-A was higher than that of TiO₂-B. The antifungal index litchi downy blight control was greatly enhanced by doping 1% cerium ion. The antifungal index of 1.0%Ce³⁺-TiO₂ was (47.0 ± 4.7)%, (82.2 ± 3.5)%, (100 ± 0.0)% under indoor weaker light, solar light and black light, respectively. The results of field experiments showed that the antifungal index of 1.0%Ce³⁺-TiO₂ was more than that of P-25. The antifungal index of 1.0%Ce³⁺-TiO₂ was (81.7 ± 6.5)%, (67.5 ± 4.7)%, (38.6 ± 1.9)% for litchi downy blight, maize southern leaf spot, and rice blast, respectively. It was concluded that TiO₂ photocatalysis technique should be an effective way for litchi fungal disease control in practice.

Keywords: titanium dioxide; photocatalytic; fungal disease; solar light; litchi downy blight

Introduction

Numerous studies have utilized a strong oxidizing powder of TiO₂ photocatalysts to degrade aqueous or gaseous toxic organic pollutants for water purification, wastewater treatment and air pollution control (Fujishima *et al.*, 2001; Kamat, 1993; Hoffmann *et al.*, 1995; Yu *et al.*, 2001, 2003). TiO₂ photocatalytic process can generate strong oxidative holes (R⁺) in the valence band and with hydroxyl radical (·OH) by the oxidation of water. TiO₂ photocatalysts have also extensively been applied to kill or inactivate microorganisms including bacteria, viruses, cancer cells, fungal spores, and protozoan (Kim *et al.*, 2003; Lonnen *et al.*, 2005; Rincón and Pulgarin, 2005; Sunada *et al.*, 2003; Wolfrum *et al.*, 2002). Fungal is a very special kind of microorganism. Many crop diseases should be attributable to pathogenic fungi. Although some literature reported the antifungal effect of TiO₂ photocatalysis (Hur *et al.*, 2005; Lonnen *et al.*, 2005; Rincón and Pulgarin, 2005; Seven *et al.*, 2004), to our best knowledge, there is not any journal literature except for Chinese patent 200410077615 concerning TiO₂ photocatalysis for crop fungi disease control (Li and Liu, 2004). It is noticeable that more than 300 thousand ton pesticides have been used for agricultural disease control. The usage of antibacterial pesticides and antifungal pesticides is about 30%–40% of the total usage of pesticides, most of which consists of organic

pollutants. Therefore, chemical antibacterial pesticides and antifungal pesticides are very harmful to animals and human being, and easily polluted food chains. Then the food safety has been increasingly serious and its public concerns have been caused extensively.

Because TiO₂ photocatalysts have strong antibacterial and antifungal abilities and photocatalytic anti-disease is friendly to the environment and animals, it is reasonable to be believed that solar-irradiated TiO₂ photocatalysis can be applied to crops fungal disease control. However, pure TiO₂ can only be excited by UV light with a wavelength of less than 387 nm. It had been extensively reported that doping/implanting/depositing with a group of transitional metal ions (Yu *et al.*, 2002; Umebayashi *et al.*, 2002) with *d* electronic configuration into TiO₂ lattice could result in extension of their wavelength response into the visible light region. Alternatively, TiO₂-based photocatalysts would have visible light activity by doping with lanthanide ions/oxides with 4f^{*n*} electron configuration (Ikeda *et al.*, 2001; Xie and Yuan, 2004). It has been proven that TiO₂ is an ideal host matrix with strong optical absorption and efficient energy transfer to lanthanide ions, and is stable to environmental conditions. The ground states of most lanthanide ions lie below the valence band of metal oxides including TiO₂ (Jia *et al.*, 2002). Among the lanthanide oxides, ceria has been paid great attention to its catalytic properties due to two features: (1) the redox couple Ce³⁺/Ce⁴⁺ with the ability of ceria to shift

between CeO_2 and Ce_2O_3 under oxidizing and reducing conditions; and (2) the easy formation of labile oxygen vacancies (OV) with the relatively high mobility of bulk oxygen species (Jia *et al.*, 2002). Furthermore, the different electronic structures of the Ce^{3+} with $4f^{15}d^0$ and the Ce^{4+} with $4f^05d^0$ would lead to different optical properties and dissimilar catalytic properties for CeO_2 , $\text{CeO}_x\text{-TiO}_2$, and also $\text{Ce}^{3+}\text{-TiO}_2$ (Coronado *et al.*, 2002).

In present paper, TiO_2 catalysts were prepared by the hydrothermal method. The fungal disease includes cucumber powdery mildew (*Enysiphe cichoracearum de candolle*) and litchi downy blight (*Peronophythora litchic* Chen ex Ko *et al.*). The aim of this study was to investigate (1) the antifungal effects of TiO_2 photocatalysts on crop fungal disease control including litchi (*L. chinensis* Sonn.), cucumber (*Cucumis sativus* L.), and rice (*Oryza Sativa* L. var) in dish experiments and in the field experiments; (2) the enhanced effect of ceria doped TiO_2 for litchi downy blight antifungal effect.

1 Experimental section

1.1 Preparation of TiO_2 catalysts

TiO_2 and 1% $\text{Ce}^{3+}\text{-TiO}_2$ catalysts using $\text{Ti}(\text{SO}_4)_2$ as a titanium precursor were prepared by a hydrothermal method (Andersson *et al.*, 2002) at moderate temperature with the following procedure: $\text{Ti}(\text{SO}_4)_2$ was first mixed with 80 ml distilled water or 80 ml 6 mmol/L $\text{Ce}(\text{NO}_3)_3$ solution respectively to prepare a mixture with the concentration of 0.6 mol/L $\text{Ti}(\text{SO}_4)_2$; then the mixture was stirred for 10 min and aged in a PTFE-lined autoclave at 393 K for 12 h; after quenching the autoclave in the cold water, the precipitated powder was collected, washed with distilled water for 5 times to remove sulfate ion and nitrate ion, filtered, and finally dried at 378 K for 24 h. These TiO_2 samples were named $\text{TiO}_2\text{-A}$, 1% $\text{Ce}^{3+}\text{-TiO}_2$, respectively.

Another TiO_2 catalyst using TiOSO_4 as a precursor was prepared by a hydrothermal method (Andersson *et al.*, 2002) with the following procedure: TiOSO_4 chemical was mixed with distilled water to prepare a mixture with a concentration of 0.6 mol/L; then the mixture was stirred for 10 min and aged at 393 K for 12 h in a PTFE-lined autoclave; after quenching the autoclave in the cold water, the precipitated powder was collected, washed with distilled water for 5 times, filtered, and finally dried at 378 K for 24 h. This TiO_2 sample was named $\text{TiO}_2\text{-B}$.

Other 2 kinds of TiO_2 including P-25 from Degussa (Germany) and pure TiO_2 from Titan Kogyo Co. Japan named as $\text{TiO}_2\text{-D}$ with the specific surface area of 61 m^2/g and 32 nm particle size were selected to compare their photocatalytic activity for antifungi control.

1.2 Characterization of catalysts

To determine the crystal phase composition of the TiO_2 catalysts, X-ray diffraction (XRD) measurement was carried out at room temperature using a Rigaku D/MAX-III A diffractometer with CuK_α radiation ($\lambda = 0.15418$ nm). The accelerating voltage of 35 kV and emission current of 30 mA were applied. The specific surface area was measured by the Brunauer-Emmett-Teller (BET) method, in which the N_2 adsorption at 77 K was applied and a Carlo Erba Sorptometer was used. To study the light absorption of the catalysts, the diffuse reflectance spectra (DRS) of the catalyst samples in the wavelength range of 200–800 nm were obtained using a UV-visible scanning spectrophotometer (Shimadzu UV-2101 PC, Japan), while BaSO_4 was used as a reference.

1.3 Photocatalytic experiment for fungi control

The fungi including cucumber powdery mildew (*Enysiphe cichoracearum de candolle*) and litchi downy blight (*Peronophythora litchic* Chen ex Ko *et al.*) were collected from the cucumber field and litchi (*L. chinensis* sonn.) field. After separated and purified for three times, fungi were stocked and cultured at $25 \pm 1^\circ\text{C}$.

The home-made photocatalytic reactor was used to investigate the activity of catalysts for inhibition effects. The $1 \times 0.5 \times 0.6$ m^3 photocatalytic reactor consisted of four 20-W black light lamps and reaction bed. The black light lamps were set up above the reaction bed with 30 cm distance. The reaction bed had an effective area of 0.32 m^2 . The relative humidity of laboratory was $(70 \pm 5)\%$, while the room temperature was $25 \pm 1^\circ\text{C}$. The light intensity was measured by a model UV-A meter (from Photoelectric Instrument Factory of Beijing Normal University, China) in the wavelength range of 320–400 nm.

Three sets of experiments were designed under indoor weaker light, solar light and black light lamp irradiation, respectively. For indoor weaker light set, the dishes placed in the laboratory opposite to window for 7 d at room temperature with the average light intensity of 0.6 ± 0.3 $\mu\text{W}/\text{cm}^2$ at daylight. For solar light set, the dishes placed outdoor for 7 d from 8:00 to 12:00 and 15:00 to 18:00 at daylight at outdoor temperature with the average light intensity of 0.8 ± 0.2 mW/cm^2 at daylight. For black light set, the dishes placed in the home-made photocatalytic reactor and were illuminated with for 7 d with the light intensity of 2.01 ± 0.05 mW/cm^2 by black light lamps. The lamps were kept turning on from 8:00 to 18:00 at daylight.

The DPA culture media was prepared as following procedures: firstly, mixing up 200 g potato, 10–20 g glucose or sucrose, 17–20 g agar, and 1000 ml tap water; secondly heating until being melted; thirdly, 20 ml 0.4% TiO_2 suspension solution was added into the DPA culture media; finally sterilizing.

The anti-fungi experiment was done according to Quine test. The mycelium in culture media was cut into round cakes with diameter 1.0 cm, and then inoculated onto the PDA culture media. Every petri dish was inoculated one cake of the mycelium with culture media and cultured under different irradiation condition. For control test, no mycelium was inoculated onto the PDA culture. Every treatment and control was replicated three times. The mycelium of pathogenic fungi was overspread in the petri dish of bland culture media after 7 d. The diameter of the pathogenic fungi colony in each petri dish was determined twice at the crossed place of the colony, and the average diameter of each colony was calculated. The index for fungi disease control(*E*) was calculated. $E = [(X1-1.0)/(X2-1.0)] \times 100\%$. *X*1 is the diameter of the fungi for TiO₂ treatment, and *X*2 is the diameter of the fungi for blank treatment.

1.4 Photocatalytic field experiment for fungi disease control

The TiO₂ suspension was prepared as following procedures: 4.0 g P-25 or 1% Ce³⁺- TiO₂ and 50 ml distilled water, and then diluted in 100 times. Litchi(*L. chinensis* Sonn.), maize (*Zea Mays* L.), and rice(*Oryza Sativa* L. var) were selected. Distilled water was used for the blank experiments. And every experiment was done in triplicates at least. The TiO₂ suspensions were sprayed one time once two weeks. The field experiment was done in 2002 May—July and lasted 6 weeks. The index for fungi disease control (*E*) was

calculated as $E = M1/M$. *M*1 is the amounts of disease samples, and *M* is the amount of all samples.

2 Results and discussion

2.1 Crystal structure of catalysts

The XRD photographs of TiO₂ and 1%Ce³⁺-TiO₂ catalysts are presented in Fig.1, where TiO₂-A, TiO₂-B, TiO₂-D, and 1% Ce³⁺-TiO₂ prepared with Ti(SO₄)₂ or TiOSO₄ as precursor had an anatase structure while P-25 had the mixture structure of anatase and rutile. The crystalline of TiO₂-A, TiO₂-B, and 1% Ce³⁺-TiO₂ was much lower than that of TiO₂-D. The crystal size of these catalysts determined by the Scherrer equation and the specific surface area by means of BET are listed in Table 1. These results indicated that TiO₂-A, TiO₂-B, and 1%Ce³⁺-TiO₂ had higher specific surface area and smaller crystal size than TiO₂-D and P-25.

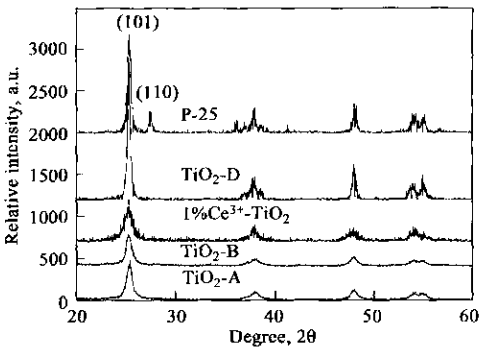


Fig.1 XRD photographs of all the catalysts

Table 1 Crystal structure, crystal size and the specific surface area of catalysts

Catalyst	TiO ₂ -A	TiO ₂ -B	P-25	TiO ₂ -D	1.0%Ce ³⁺ - TiO ₂
Crystal structure	Anatase	Anatase	Anatase	Anatase/Rutile	Anatase
Crystal size, nm	18.8	21.0	32	32	15.2
Specific surface area, m ² /g	158.9	154.9	61.0	50.0	179.8

2.2 UV-vis diffusive reflectance spectra

To investigate the optical absorption properties of catalysts, the DRS of TiO₂-A and 1% Ce³⁺- TiO₂ catalysts in the range of 250—750 nm were examined and shown in Fig.2. The DRS results demonstrated pure TiO₂ had no absorption in the visible region(>400 nm) and 1% Ce³⁺- TiO₂ had significant absorption between 400—450 nm. In addition, the optical absorption in the UV region was almost unchanged. In fact, the enhanced absorption in the visible region for the Ce³⁺-doped Y₂O₃, Lu₂O₃, ZrO₂ or La₂O₃ had been reported and the onset of the predominant Ce³⁺ absorption was found at about 460 nm (Orera *et al.*, 1994). CeO₂ is an *n*-type semiconductor with a band gap of about 3.2 eV (Elidrissi *et al.*, 2000). Therefore, the absorption at 400—450 nm by the Ce³⁺- TiO₂ catalysts could not be attributed to CeO₂ but Ce₂O₃. In contrast to the closed shell Ce⁴⁺ ion (4f⁰), Ce³⁺ ion possesses a single optically-active electron with the

ground-state configuration in the 4f¹ orbital. Within this configuration, there are only two electronic levels, an excited state of ²F_{7/2} and a ground state of ²F_{5/2}. The 4f-4f transitions attributed to Ce³⁺ may only be observed in the infrared spectral region. However, Ce³⁺ has the first state configuration 5d¹ that is rather close in energy. The electronic dipole transitions 4f¹ ↔ 5d¹ may occur in either UV or visible region. Based on the valence band of Ce³⁺-TiO₂, it is proposed that electron-hole pairs could be generated in both types of catalysts: Ce³⁺-TiO₂ and Ce₂O₃ in two approaches, including (1) electron can be excited from the valence band of Ce³⁺-TiO₂ into Ce 4f level when the energy of photon is more than(E_{C_{4f}} - E_v), and (2) electron can be excited from the ground state of Ce₂O₃ into Ce 4f level. Therefore, the red-shift of absorption edge for Ce³⁺- TiO₂ was expressed in the following Eq. (1) and (2). It should be indicated that the Ce 4f levels might play a crucial role in generating electron-hole

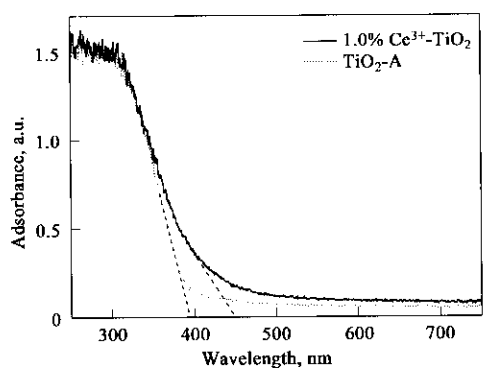
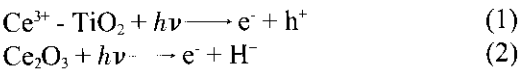


Fig.2 UV-visible diffusive reflectance spectra of TiO₂-A and 1% Ce³⁺-TiO₂ powders

pairs under visible light illumination.



2.3 Photocatalytic experiment for fungi control

To investigate the photocatalytic activity of home-made catalysts for crop fungal disease control, 2 sets of Quine tests were carried out for cucumber powdery mildew and litchi downy blight control in home-made photocatalytic reactor under black light lamp and the tests lasted 7 d. The results are listed in Table 2. The results showed that TiO₂ photocatalysis technique should be effective to inhibit the growth of 2 kinds of fungal diseases to some extent. Obviously, P-25 had the highest activity for fungal disease control. The antifungal index for litchi downy blight control by using all catalysts was more than that for cucumber powdery mildew control. TiO₂-A prepared with Ti(SO₄)₂ is more active to control fungal disease than TiO₂-B prepared with TiOSO₄ as precursor because the crystalline of TiO₂-A was higher than that of TiO₂-B.

Table 2 The antifungal index (%) for litchi downy blight and cucumber powdery mildew control

Catalyst	TiO ₂ -A	TiO ₂ -B	TiO ₂ -D	P-25
Cucumber powdery mildew	16.5±3.7	12.5±1.8	20.0±0.9	62.2±4.7
Litchi downy blight	55.8±3.6	45.8±1.8	57.8±1.8	64.2±3.6

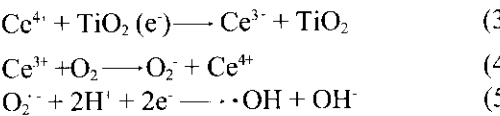
In order to enhance the effect of TiO₂-A on fungal disease control, 1% Ce³⁺-TiO₂ catalyst was prepared by doping Ce³⁺ ion. And three sets of tests were carried out to investigate the enhanced effect of 1% Ce³⁺ ion doping on the antifungal index with the average light intensity of 2.01±0.05 mW/cm², 0.8±0.2 mW/cm², and 0.6±0.3 μW/cm² under black light, solar light at daytime and indoor weaker light at daytime, respectively. The antifungal index is listed in Table 3. The antifungal index under solar light irradiation was up to 100% and more than that under black lamp light. And the antifungal index by using

1.0% Ce³⁺-TiO₂ was much more than that by TiO₂-A under any condition. It is noticeable that 1.0% Ce³⁺-TiO₂ should be effective to control litchi downy blight under weaker light with less than 1 μW/cm². In Guangdong Province, litchi downy blight happens in the end of May to in the beginning of July every year. We had tested the light intensity in the litchi tree for 100 times in 2002. The average light intensity in the litchi tree was 1.15±0.38 μW/cm² in cloudy or rainy days and 7.85±0.66 μW/cm² in sunny days. Therefore, it implies that TiO₂ photocatalysis technique for litchi downy blight control should not be limited by weather conditions.

Table 3 Effect of 1% Ce³⁺ doping on the antifungal index (%) for litchi downy blight control

Catalyst	TiO ₂ -A	1.0%Ce ³⁺ -TiO ₂
Indoor weaker light	23.7±3.6	47.0±4.7
Black lamp light	56.4±3.3	82.2±3.5
Solar light	57.3±6.9	100±0.0

Our previous work has proven that there is the more efficient separation of electron-hole pairs in Ce³⁺-doped TiO₂ than that in pure TiO₂ (Li *et al.*, 2005). For Ce³⁺-TiO₂, Ce 4f level plays an important role in interfacial charge transfer and elimination of electron-hole recombination. Lanthanide ions could act as an effective electron scavenger to trap the CB electrons of TiO₂. Lanthanide ions, acting as Lewis acid, apparently were superior to the oxygen molecule (O₂) in the capability of trapping CB electrons. The electrons trapped in Ce⁴⁺/Ce³⁺ site was subsequently transferred to the surrounding adsorbed O₂. The presence of Ce⁴⁺ on TiO₂ surface may promote the following processes expressed by Eq.(3) and (4). The formation of ·OH might be proposed as Eq.(5) and photogenerated electron was transferred efficiently. For Ce³⁺-TiO₂, the formation of labile oxygen vacancies and particularly the relatively high mobility of bulk oxygen species have been reported, which ceria had a high oxygen transport and storage capacity. Hence, the excited electrons might be more easily transferred to O₂ on the surface of Ce³⁺-TiO₂ catalysts. This should be the reason why Ce³⁺-TiO₂ was more effective to control Litchi downy blight than pure TiO₂.



2.4 Photocatalytic fungi disease control in the field

To investigate the effect of TiO₂ photocatalysis technique for fungal disease control in practice, three kinds of crops including litchi (*L. chinensis* Sonn.), maize (*Zea Mays* L.), and rice (*Oryza Sativa* L.var)

were selected to do the field experiments. The solar light intensity was recorded for 3 times every day at 8:00, 12:00 and 18:00 during filed experiments. The average intensity was 0.96 ± 0.26 mW/cm². The results of the antifungal index for rice blast, maize southern leaf spot and litchi downy blight control are listed in Table 4. The antifungal index followed the order as litchi downy blight > maize southern leaf spot > rice blast. Obviously, 1.0% Ce³⁺-TiO₂ was more effective than P-25. However, the antifungal index for litchi downy blight by using chemical pesticide metalaxyl was 100%. Therefore, it is necessary to enhance the antifungal index of TiO₂ photocatalysis technique in order to promote its application in practice.

Table 4 The antifungal index for photocatalytic fungi disease control in the field(%)

Catalyst	P-25	1.0%Ce ³⁺ -TiO ₂
Rice blast (<i>Pyricularia grisea</i> Saccardo)	30.1 ± 2.2	38.6 ± 1.9
Maize southern leaf spot (<i>Sienocarpella macrospora</i>)	58.3 ± 3.4	67.5 ± 4.7
Litchi downy blight (<i>Peronophythora litchic</i> Chen ex Ko <i>et al.</i>)	69.2 ± 4.8	81.7 ± 6.5

3 Conclusions

A series of Quine tests were carried out to investigate the effect of TiO₂ photocatalyst on cucumber powdery mildew and litchi downy blight control. The results showed that TiO₂ photocatalysis technique should be effective to inhibit the growth of fungal diseases to some extent and P-25 had a higher activity for antifungal control than home-made TiO₂ catalysts. TiO₂-A prepared with Ti(SO₄)₂ is more active to control antifungal disease than TiO₂-B prepared with TiOSO₄ as precursor. The antifungal index for litchi downy blight control was greatly enhanced by doping 1% cerium ion. The antifungal index of 1.0% Ce³⁺-TiO₂ was (47.0 ± 4.7)%, (82.2 ± 3.5)%, (100 ± 0.0)% under indoor weaker light, solar light and black light, respectively. The results of field experiments showed that the antifungal index of 1.0% Ce³⁺-TiO₂ was more than that of P-25. The antifungal index of 1.0% Ce³⁺-TiO₂ was (81.7 ± 6.5)%, (67.5 ± 4.7)%, (38.6 ± 1.9)% for litchi downy blight, maize southern leaf spot, and rice blast, respectively. It was concluded that TiO₂ photocatalysis technique should be an effective way for litchi fungal disease control in practice.

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