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Detoxification of Phytotoxic Compounds by TiO_2 Photocatalysis in a Recycling Hydroponic Cultivation System of Asparagus

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TiO_2 photocatalytic decomposition and detoxification of phytotoxic compounds released by the roots of asparagus (*Asparagus officinalis* L.) were investigated from the viewpoint of conservation-oriented cultivation. The phytotoxically active fraction was extracted either from dried asparagus roots or from the recycled nutrient solution of an asparagus hydroponic cultivation system. We found that the phytotoxic activity gradually decreased in the fraction with TiO_2 powder under irradiation with ultraviolet (UV) light at an intensity of 1.0 mW/cm^2. The growth of asparagus plants under actual cultivation conditions was also investigated by comparing asparagus grown in a hydroponic system where recycled waste nutrient solution was photocatalytically treated with solar light and a system with untreated recycled waste nutrient solution. The results showed, as measured by growth indices such as stem length and stem thickness, that asparagus growth in the photocatalytically treated system was superior to the untreated one. Furthermore, the yield of asparagus spears was 1.6-fold greater in the photocatalytically treated system, demonstrating the detoxification effect on the phytotoxic compounds and also the killing effect on pathogenic microorganisms.

KEYWORDS: TiO_2 photocatalysis; detoxification; phytotoxic compound; 3,4-dihydroxyphenyl acetic acid (3,4-DPAA)

INTRODUCTION

Hydroponic agriculture is increasing due to its advantages such as ease of controlling crop growth, low chance of infection by soil pathogens, and reduced risk of replant failures (*1, 2*). The current standard cultivation practice in hydroponics is to grow the plant roots in an inorganic medium such as rock wool and to add a nutrient solution containing NO_3^-, PO_4^{3-}, K^+, and other nutrients. The plants absorb the nutrients, using them for photosynthesis. However, the plants are generally supplied with more nutrient solution than they use in photosynthesis, and 10−30% of the supplied solution is not absorbed by the plant roots and is instead released into the environment as a waste product. Because of its high concentration of NO_3^- and PO_4^{3-}, the waste nutrient solution contributes to the eutrophication of soils and groundwater. Eutrophication is one of the major environmental pollution issues associated with agricultural production sites. Therefore, a recycling hydroponic cultivation system where the waste nutrient solution is recycled rather than emitted into the environment is desirable from the viewpoint of conservation-oriented agriculture.

In addition to man-made pollutants, plants release a variety of organic chemicals into the environment as well. For example, plants release phytotoxic chemicals into the soil where they accumulate and inhibit the growth and germination of other plants (*3–5*). Autotoxicity is a form of phytotoxicity that inhibits other individuals of the same species. Therefore, autotoxicity causes serious problems at agricultural production sites such as growth inhibition, yield declines, and replant failures (*5–7*). Asparagus, in particular, has been reported to release strong autotoxic compounds, which have been studied in detail (*8–16*). For example, asparagusic acid (1,2-dithiolane-4-carboxylic acid) (*8*), methylenedioxy cinnamic acid (MDCA) (*14*), caffeic acid (*15*), and 3,4-dihydroxyphenyl acetic acid (3,4-DPAA) (*12, 14*) have been isolated and characterized. Therefore, if the waste nutrient solution from hydroponic asparagus cultivation is recycled and reused in the system, these toxic compounds could inhibit the growth of the asparagus crop.

It is well-known that TiO_2 acts as a photocatalyst (*17–20*). When TiO_2 absorbs ultraviolet (UV) light with a wavelength

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shorter than its band gap (approximately 380 nm), it exhibits a strong oxidation effect, oxidizing organic compounds that adsorb to its surface and decomposing them into CO_2. This powerful oxidization effect has been tested for its efficacy in eliminating environmental pollutants, mainly from the atmosphere and water (*21–27*). The toxic compounds released by plants should also be decomposed and detoxified through a TiO_2 photocatalytic reaction under solar light, thereby making it possible to grow crops that release autotoxic compounds in a recycling hydroponic culture system.

Thus, in this study, we investigated whether plants that produce autotoxic compounds can be grown under a conservation-oriented cultivation system by allowing the recycling of the nutrient solution through TiO_2 photocatalytic treatment. First, the photocatalytic decomposition of the phytotoxic fraction extracted from asparagus roots will be described, followed by a description of the photodecomposition of the phytotoxic fraction found in the waste nutrient solution of an actual hydroponic asparagus cultivation system. Finally, we will present the results of a comparative evaluation of asparagus growth in a system where the waste nutrient solution was treated with TiO_2 photocatalysts before being recycled vs a system where untreated waste nutrient solution was recycled.

MATERIALS AND METHODS

Isolation of Phytotoxic Fraction from Asparagus Root. The phytotoxic fraction was extracted from asparagus (*Asparagus officinalis* L.) roots as previously described (*14*). Briefly, fresh asparagus roots were dried in an incubator at 65 °C and then pulverized in a mixer. Deionized water was added to the powdered roots, and this suspension was stirred overnight at 4 °C. Acetone (4:1 v/v acetone−sample) was added to the supernatant to precipitate the proteins and lipids, and this suspension was once again stirred overnight at 4 °C. The precipitate was then filtered, and the supernatant was concentrated to a quarter of its original volume using a rotary evaporator. Chloroform equal in volume to the concentrate was added, and the chloroform-soluble fraction was isolated and dried in a rotary evaporator. The dried sample was then dissolved in methanol, and the methanol-soluble fraction was refined using octadecyl (C18) column (200 mm × 18 mm) chromatography and eluted with a step gradient of acetonitrile (100%) to methanol (100%) at 25% intermediate steps.

Phytotoxic Activity Test. The phytotoxic activity was tested by the conventional method previously described using lettuce seed (*Lactuca sativa* L., Calmar MR) (*5, 14*). Briefly, 4 mL of each fraction was poured over filter paper (Advantec no. 2) in Petri dishes (9 cm in diameter). After the solvent (methanol, acetonitrile, etc.) in each fraction was completely evaporated from the filter, 4 mL of deionized water was added. Twenty-five lettuce seeds were sown in each dish, and each fraction was tested on two dishes. The dishes were incubated in the dark for 48 h at room temperature. Control tests using deionized water and pure solvent instead of the fraction were conducted for each assay. After 48 h, lettuce seed germination rates for both the sample and the control dishes were calculated, and the radicle lengths were measured. The indices for evaluating phytotoxic activity were germination rates and the ratios of radicle lengths between test samples and controls.

TiO_2 Photocatalytic Treatment of the Phytotoxic Fraction from Asparagus Roots. Photocatalytic treatment with TiO_2 of the phytotoxically active fraction extracted from asparagus roots was conducted as follows. After 10 mL of the active fraction remaining after column chromatography had been evaporated and dried in a rotary evaporator, it was dissolved in 90 mL of mixed solvent comprised of methanol (5 mL) and Milli-Q water (85 mL). The TiO_2 aqueous suspension, which was prepared by dispersing a commercially available TiO_2 powder (ST-31, Ishihara Sangyo Co.) in Milli-Q water by sonication, was then added at a concentration of 10 g/L. This suspension was irradiated with UV light at an intensity of ca. 1.0 mW/cm^2 from black light bulbs (Type FL15 BL-B, National) for 1, 2, and 4 days. The concentration of total organic carbon (TOC) was determined by a TOC analyzer (Shimadzu, TOC-5000A) after the TiO_2 powders had been filtered from the suspension. The phytotoxic activity of this filtrate was assayed using the method described above. In addition, the concentration of 3,4-DPAA, a common asparagus phytotoxin, in the same samples was measured using high-performance liquid chromatography (HPLC) (Shimadzu, Prominence).

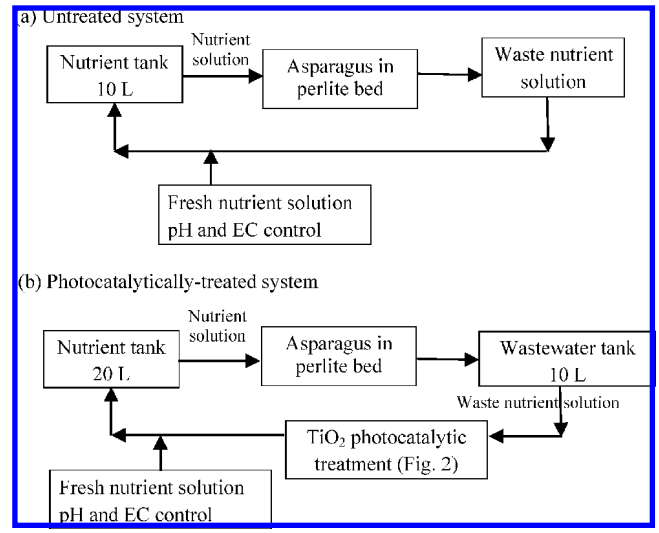

Figure 1. Schematic diagram for the (**a**) untreated system and (**b**) photocatalytically treated system in our recycling hydroponic asparagus cultivation system.

TiO_2 Photocatalytic Treatment of the Phytotoxic Fraction from Waste Nutrient Solution in a Recycling Hydroponic Asparagus Cultivation. Asparagus was grown in a glass greenhouse to ascertain the effect of photocatalytic treatment on phytotoxic compounds found in the waste nutrient solution of an actual hydroponic cultivation system. In February 2005, nine asparagus seedlings were transplanted in each bed [350 mm × 1000 mm × 170 (depth) mm] of the inorganic medium perlite and fed with a conventional nutrient solution containing NO_3^-, PO_4^{3-}, K^+, and other nutrients (Otsuka House I, II, Otsuka Kagaku Co.). The waste nutrient solution originated from the solution not absorbed by the asparagus. To obtain the phytotoxic fraction from the waste nutrient solution, the asparagus was grown for approximately 3 months with the recycled untreated nutrient solution through the hydroponic system so that the phytotoxic fraction would accumulate in the nutrient solution tank. Five liters from the tank was concentrated to 100 mL in a rotary evaporator at 60 °C. To remove the majority of salt components from the concentrate, it was refined using the above-mentioned C18 column chromatography and eluted with acetonitrile (100%). After the acetonitrile was evaporated and the remaining fraction was dissolved in 90 mL of Milli-Q water, photocatalytic treatment of the fraction was conducted. After UV irradiation for 1, 2, and 4 days, the TOC of the sample was measured, and its phytotoxic activity was assayed.

Effect of TiO_2 Photocatalytic Treatment on Recycling Hydroponic Cultivation System of Asparagus. To study the effectiveness of photocatalytic treatment under actual cultivation conditions and natural sunlight, asparagus in two hydroponic cultivation systems was observed over a 20 month period after transplantation of the seedlings. In the untreated system (**Figure 1a**), waste nutrient solution without photocatalytic treatment was recycled through the system, and in the photocatalytically treated system (**Figure 1b**), the waste nutrient solution received photocatalytic treatment before being recycled back through the system. In both systems, the nutrient solution was pumped from the nutrient solution tank through the perlite beds in which the asparagus was planted. In the untreated system, the waste nutrient solution was returned to the 10 L nutrient solution tank and reused. In contrast, in the photocatalytically treated system, the waste nutrient solution was temporarily stored in a wastewater tank and then treated photocatalytically in the presence of sunlight and TiO_2 for 2 days. Subsequently, the treated solution was returned to the 20 L nutrient solution tank for reuse. Fresh nutrient solution was added to both systems as needed,

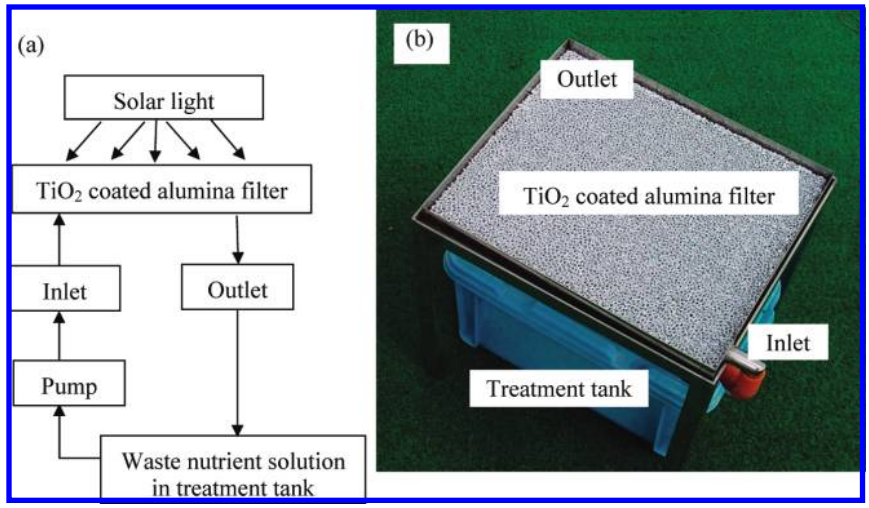

Figure 2. (**a**) Overview of the TiO_2 photocatalytic treatment method used in the recycling hydroponic culture system. (**b**) Photograph of the TiO_2-coated alumina filter (250 mm × 300 mm × 20 mm) showing the inlet and outlet lines and location of the treatment tank.

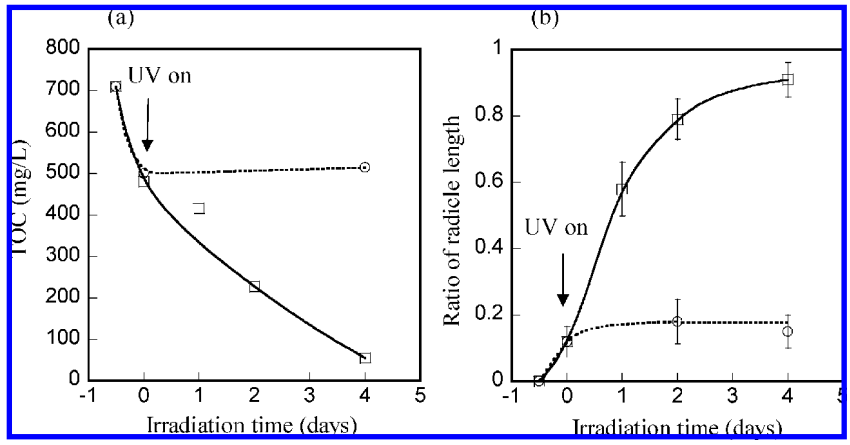

Figure 3. Changes over time in (**a**) TOC concentration and (**b**) lettuce radicle length ratio for the phytotoxically active fraction from asparagus roots with TiO_2 suspension as compared to controls. The suspension was incubated in the dark (○) or irradiated with UV light (□). Error bars: Standard deviations of two replicate evaluations in the phytotoxic activity test.

and the pH and electrical conductivity (EC) in the nutrient solution tanks were maintained at pH 7.2 and EC = 2.0, respectively. Photocatalytic treatment of the waste nutrient solution was conducted by cycling the waste nutrient solution through a porous alumina filter (250 mm × 300 mm × 20 mm, Seiwa Kogyo, Japan) coated with TiO_2 nanoparticles under solar light (**Figure 2**). The irradiated area by sunlight of the material coated with TiO_2 was 21% of cultivation bed area, to capture a large amount of solar light for the treatment of the waste nutrient solution.

To observe the asparagus growth in the two systems, the tallest stem length, thickest stem diameter, and total number of stems from an asparagus seedling were measured, and the average for the nine seedlings in each bed was calculated and compared between the photocatalytically treated and untreated systems. Asparagus spears were harvested once they reached a height of 250 mm in the second year after transplantation of the seedlings. The spears were cut to a uniform 250 mm in length if they were greater than 250 mm and weighed to determine the total yield.

RESULTS AND DISCUSSION

TiO_2 Photocatalytic Effect on Phytotoxic Compounds Obtained from Asparagus Roots. The phytotoxic fraction was extracted and isolated from asparagus roots, refined using column chromatography, and eluted with acetonitrile (100%). This fraction completely inhibited lettuce seed germination, showing strong phytotoxic activity. The fraction was then subjected to either TiO_2 photocatalytic treatment or incubation with TiO_2 in the dark. **Figure 3a** shows the time-dependent change of TOC concentration for each treatment. The TOC concentration initially decreased by 30% before leveling off when incubated in the dark. This decline was caused by the adsorption of organic compounds on the TiO_2 surface. In contrast, when the fraction was irradiated with UV light, the TOC decreased with increasing irradiation time. The TOC concentration after 4 days of UV irradiation was more than 90% lower than the initial concentration. This demonstrates that the organic constituents of the active fraction are oxidized to CO_2 by the TiO_2 photocatalytic reaction.

Parallel to this experiment, we also assayed the phytotoxic activity of the same samples for which we measured TOC concentrations. As shown in **Figure 3b**, the lettuce seed radicle length was only 20% as long as the control for the fraction incubated with TiO_2 in the dark. However, when compared to the UV irradiation treatment, the growth of the radicle improved with longer irradiation times, with the radicle length reaching 90% of the control after 4 days of UV irradiation. The results shown in **Figure 3a**,**b** suggest that the phytotoxic constituents of asparagus roots are decomposed by the photocatalytic reaction and that their toxic activity can also be essentially abolished.

Several phytotoxic compounds have been isolated and identified from asparagus roots, including the common compound, 3,4-DPAA (*8, 12, 14, 15*). In our study, the presence of 3,4-

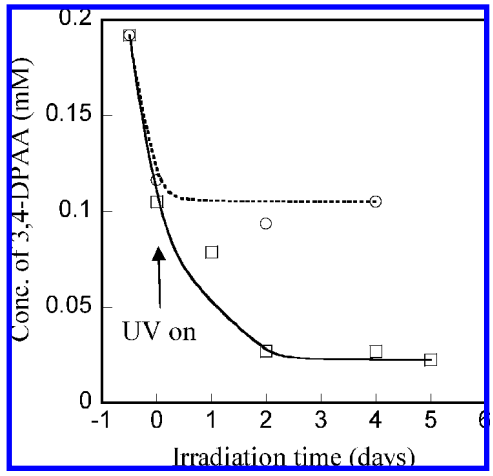

Figure 4. Changes in 3,4-DPAA concentration in the phytotoxically active fraction from asparagus root with TiO_2 suspension incubated in the dark (○) or exposed to UV irradiation (□). These were the identical samples as measured in **Figure 3**.

DPAA in the phytotoxically active fraction obtained from asparagus roots was shown through HPLC analysis. Concentrations of 3,4-DPAA during photocatalysis were measured for the same samples as shown in **Figure 3**. When incubated in the dark, the 3,4-DPAA concentrations initially declined by nearly 40−45% due to adsorption of the compound on the TiO_2 surface, but there were no subsequent changes in concentration (**Figure 4**). In contrast, the 3,4-DPAA concentrations dramatically dropped to 85% of the initial concentration after 2 days of UV irradiation. This decline was more rapid than the decrease in TOC concentrations, which we attribute to the following. While the TOC concentrations did not show a decline until the organic compounds had been decomposed completely into CO_2, in this experiment, the 3,4-DPAA levels would decline as soon as 3,4-DPAA was oxidized into other compounds, without its complete oxidization into CO_2. The decomposition of different types of organic compounds by photocatalytic reactions is known to occur with little discrimination and essentially all organic compounds will ultimately be decomposed. Thus, from **Figure 4**, it can be interpreted that phytotoxic compounds other than 3,4-DPAA in the phytotoxically active fraction are similarly decomposed. This decomposition of phytotoxic compounds through photocatalytic reactions is posited to account for the improved growth of the lettuce radicle in the TiO_2 photocatalytically treated root extracts.

TiO_2 Photocatalytic Effect on Phytotoxic Compounds in Waste Nutrient Solution from Hydroponic Cultivation of Asparagus. To ascertain whether phytotoxic compounds found in actual waste nutrient solution from hydroponic asparagus cultivation can be decomposed and detoxified by photocatalytic reactions, asparagus was cultivated hydroponically with recycled untreated waste nutrient solution. The fraction from the nutrient solution tank that had been concentrated by 50 times completely inhibited lettuce seed germination, showing that phytotoxic compounds are indeed released into waste nutrient solution during actual hydroponic asparagus cultivation. When this concentrated fraction was treated photocatalytically, the TOC initially decreased when incubated in the dark due to adsorption on the TiO_2 surface, followed by no further changes over time, whereas under constant UV irradiation, the TOC continued to decline over time (**Figure 5a**). In addition, while in the non-UV-exposed condition the length of the lettuce radicle was only around 15% that of the control, after 4 days of UV irradiation, the radicle length was 80% that of the control (**Figure 5b**). The presence of 3,4-DPAA was also confirmed in the concentrated fraction. When subjected to the same photocatalytic treatment, the 3,4-DPAA concentrations of dark-incubated samples initially decreased only through adsorption on the TiO_2 surface, while with UV irradiation the concentrations continued to decline with increasing irradiation time (data not shown). These results mirrored those from the photocatalytic treatment conducted on the active fraction obtained from asparagus roots (**Figures 2** and **3**). Taken together, these findings suggest that the phytotoxic compounds released in waste nutrient solution under actual hydroponic asparagus cultivation are also decomposed and detoxified by TiO_2 photocatalytic reaction.

Effect of Photocatalytic Treatment on Recycling Hydroponic Cultivation System. To study the effect of the photocatalytic treatment in a recycling hydroponic cultivation system, the growth of asparagus in photocatalytically treated and untreated systems was observed (**Figure 1a**,**b**). After 12 months of cultivation under recycling hydroponic conditions, the growth of the asparagus fed from the photocatalytically treated system (**Figure 6a**) was superior to the untreated system (**Figure 6b**). When examined for changes in stem length during the first year after transplantation, the difference between the two systems became apparent around the 90th day (**Figure 7**). Ultimately, the stem length of the asparagus in photocatalytically treated system was about 1.3-fold longer

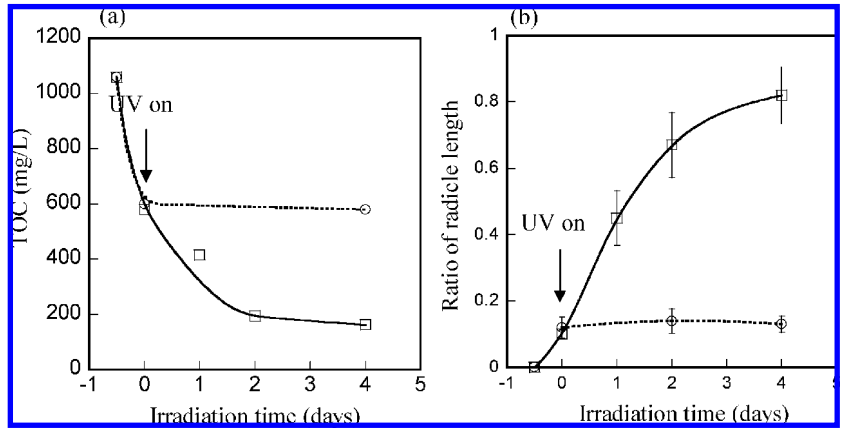

Figure 5. Changes over time in (**a**) TOC concentration and (**b**) lettuce radicle length ratio for the phytotoxically active fraction obtained from actual cultivation wastewater with TiO_2 suspension. The suspension was incubated in the dark (○) or irradiated with UV light (□). Error bars: Standard deviations of two replicate evaluations in the phytotoxic activity test.

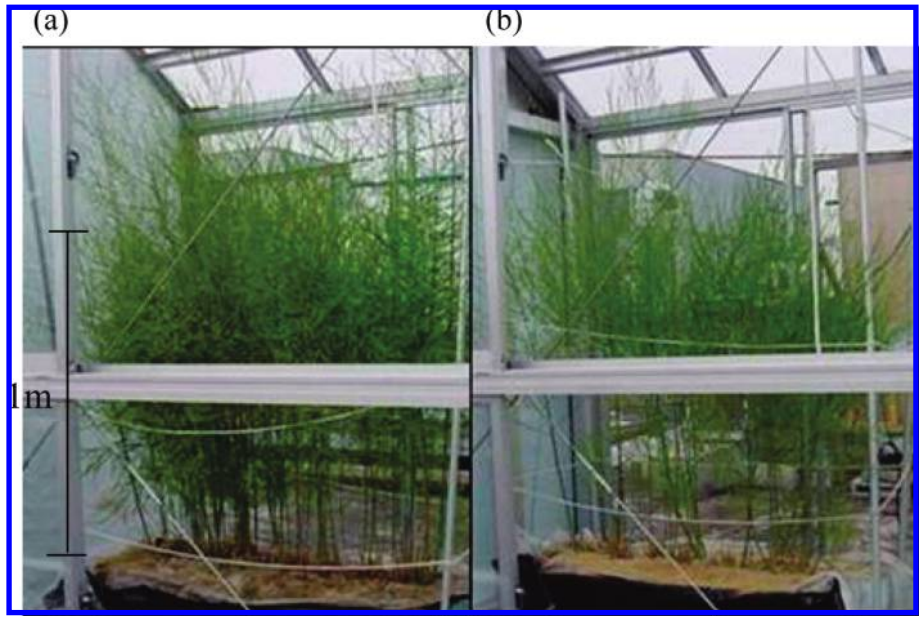

Figure 6. Photographs of the asparagus plants grown in either (**a**) the photocatalytically treated or (**b**) the untreated recycling hydroponic culture system after the 12th month of cultivation.

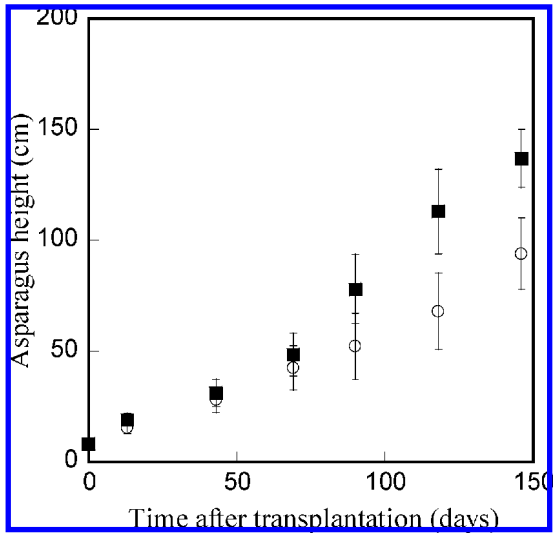

Figure 7. Comparison of asparagus height over time after transplantation in either the photocatalytically treated system (■) or the untreated system (○) of the recycling hydroponic cultivation. Error bars: Standard deviations of height measurements from nine seedlings.

Table 1. Asparagus Growth and Yield in the Photocatalytically Treated vs the Untreated System of the Recycling Hydroponic Cultivation

	photocatalytically treated system	untreated system
diameter of stem (mm)[a]	5.1 ± 1.3	3.0 ± 0.8
no. of stems from a seedling[a]	60 ± 17	38 ± 15
asparagus spear yield (g)[b]	3211	1966

[a] Measurements were made on the 146th day after transplantation. [b] The asparagus were harvested in the second year of cultivation.

than the stems in the untreated system. **Table 1** shows for both systems the maximum stem diameter and the total number of stems from one seedling on the 146th day after transplantation as well as the asparagus spear yield over a 9 month period between the 12th and 20th month after plantation. For growth indices, the photocatalytically treated system outperformed the untreated system, highlighted by a 1.6-fold increase in asparagus spear yield. The measurements of asparagus growth revealed that TiO_2 photocatalytic treatment under solar light removes hindrances to growth, which is thought to be due to the decomposition and detoxification of phytotoxic compounds. In contrast, these phytotoxins accumulated in the nutrient solution tank of the untreated system and inhibited asparagus growth. These findings also suggest that by incorporating photocatalytic treatment into recycling hydroponic culture systems, even crops that release autotoxins, such as asparagus, can be grown without the risks of yield declines or replant failures and help lower the environmental impact.

The inorganic medium perlite was used in the hydroponic cultivation system for this study, but from the viewpoint of conservation-oriented agriculture, an organic medium that can be easily returned to the environment such as rice hulls or coconut husks is more desirable. In a recycling hydroponic system, however, phytotoxic compounds released by the rice hulls or coconut husks do in fact inhibit plant growth (*28, 29*). It is hypothesized that TiO_2 photocatalytic treatment could also decompose and detoxify the phytotoxins released by organic media [such as momilactone from the rice hulls (*28, 29*)]. We are currently studying this issue.

It has been reported that replant failures and yield declines in asparagus are not due to phytotoxic compounds alone but occur synergistically with root and crown rots caused by the fungal pathogens from *Fusarium oxysporum* f.sp. asparagi, *F. moniliforme*, or *F. proliferatum* (*30–34*). Because of its antimicrobial effect, TiO_2 photocatalysis may be able to destroy these pathogens as well (*35, 36*). This study suggests that TiO_2 photocatalytic treatment under sunlight may be able to eliminate the problems of growth impediments to crops by phytotoxic compounds and pathogens and to help increase the yield of plant biomass, in addition to lowering the environmental impact of hydroponic agriculture.

The application of TiO_2 photocatalysis for the treatment of water has been studied for more than a quarter of a century. However, the treatment capacity by photocatalysis is limited by the amount of UV light present in the light source. For example, if sunlight is used as the UV source, only a small volume of water can be treated

due to the low amount of UV energy present in sunlight. This can be overcome by using an artificial light source, such as a Xe−Hg lamp, but the treatment costs become prohibitive. These factors have prevented TiO_2 photocatalysis from being used in practical applications to treat water. However, the results from this study showed that wastewater from agricultural production can be effectively treated with TiO_2 photocatalysis using solar light. It was achieved by capturing solar light using a large irradiated area of porous photocatalytic material in a shallow reaction tank. This study suggests that a water treatment system with a large catalyst area using only solar light can be applied for the treatment of wastewater and also be extended to environmental treatment applications in the cleanup of contaminated air and soil.

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