Identifying the role of reactive oxygen species (ROSs) in *Fusarium solani* spores inactivation

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**Abstract**

The inactivation mechanism of photocatalytic disinfectants on bacteria is well known. In contrast, the potential inactivation of fungal spores by visible-light induced photocatalysis has been recognized, but the inactivation mechanism is poorly understood. We hypothesize that photocatalytically generated reactive oxygen species (ROSs) are directly involved in this mechanism. To test this hypothesis, we identified the roles of ROSs in the inactivation of *Fusarium solani* spores. As the photocatalysts, we doped TiO₂ with 3 typical dopants, forming Ag/TiO₂, N/TiO₂ and Er³⁺:YAlO₃/TiO₂. The Ag/TiO₂ photocatalysis was dominated by H₂O₂, with the longest lifetime among the investigated ROSs. Ag/TiO₂ photocatalysis yielded almost 100 % inactivation efficiency and preserved the cell-wall shape of the spores, thus minimizing the biomolecule leakage. Er³⁺:YAlO₃/TiO₂ was dominated by h⁺ ROSs, yielding an inactivation efficiency of 91 %; however, the severe leakage released large numbers of molecular bio-products. Severe damage to the cell walls by the h⁺ species was confirmed in micrograph observations. Subsequent to cell wall breakage, the Er³⁺:YAlO₃/TiO₂ nanoparticles entered the spore cells and directly oxidized the intracellular material. The N/TiO₂ photocatalysis, with •O₂⁻ dominated ROSs, delivered intermediate performance. In conclusion, photocatalysts that generate H₂O₂-dominated ROSs are most preferred for spore inactivation.

**Keywords:** *F. solani*, Visible light, Photocatalysis, Inactivation, Soluble microbial products, Spore

**Introduction**

According to the Food and Agriculture Organization of the United Nations, agriculture is the largest consumer of fresh water (Polo-López et al. 2014). Therefore, the reuse of wastewater for agriculture irrigation has received much attention in recent years. However, wastewater contains various pathogens that must be removed before the irrigation. Among these pathogens are theophytopathogenic fungi such as *Fusarium*, *Pythium*, *Phytophthora* and *Olpidium* species. The *Fusarium* genus, which is widely distributed in water and soil systems, causes decay of roots, stems and flowers. *Fusarium* spores, which develop into *Fusarium* fungal cells, are very difficult to inactivate owing to their thick cell walls and strong environmental resistance (Polo-López et al. 2010).

One of the most promising methods for disinfecting *Fusarium* spores is photocatalytic inactivation (Fernández-Ibáñez et al. 2009). The photocatalytic inactivation should preferably be mediated by visible light, because UV light comprises only 5 % of the solar light (Zuo et al. 2012). Moreover, the photocatalytic performances of *Fusarium* spore disinfection are affected by the properties of the photocatalysts, such as the adsorption capability of the nanoparticles on the spores (Polo-López et al. 2010), and the morphology (nanotubes, nanoplates, nanorods or nanospheres) (Turki et al. 2013) and components (Fernández-Ibáñez et al. 2015) of the photocatalysts.

In essence, the inactivation capability of a photocatalyst depends on the reactive oxygen species (ROSs) it can generate. As photocatalysts adsorb irradiation with
energies equal to or greater than their band gap energies, they generate \( e^-/h^+ \) pairs (Hou et al. 2012). In aqueous environments, ROSs are released through the chemical reaction of photogenerated species on TiO\(_2\) surfaces (Thabet et al. 2013). The released ROSs, which include \( e^-\), \( h^+\), \( \cdot\text{OH}\), \( \text{H}_2\text{O}_2\), and \( \cdot\text{O}_2^-\), then disinfect the fungal spores (Xia et al. 2013). The significant role of ROSs in photocatalytic bacterial disinfection is well recognized (Foster et al. 2011). The inactivation efficiency against Escherichia coli is linearly related to the steady-state \( \cdot\text{OH} \) concentration, suggesting that \( \cdot\text{OH} \) is the predominant inactivation species in this organism (Cho et al. 2005). This conclusion was disputed by Kikuchi et al. (1997), who separated E. coli suspension from a TiO\(_2\) thin film through hydrophilic polytetrafluoroethylene membranes. They found that neither the half-life nor the half diffusion length of \( \cdot\text{OH} \) was sufficient to traverse the membrane and inhibit the E. coli cells. Therefore, they concluded that the major bactericidal species was \( \text{H}_2\text{O}_2\) rather than \( \cdot\text{OH}\). ROSs can also attack the cell walls, causing leakage of intracellular macromolecules such as proteins and nucleic acids from the cells (Rahmanto et al. 2005). The leaking biomolecules can lower the efficiency of the treatment and adversely affect the effluent quality, seriously compromising the health of the receiving waters (Xie et al. 2012). Consequently, when applying a photocatalytic disinfection, we must also monitor the subsequent increment in soluble microbial products (SMPs).

The effects of ROSs on the disinfection efficiency and SMP release are well known in bacterial disinfection, but are poorly understood in fungal spore disinfection. In visible light photocatalysis, modifying the TiO\(_2\) surface with different dopants will alter the generated ROSs (Chong et al. 2014). The diverse TiO\(_2\) crystal structure admits a variety of dopants (Shah et al. 2002), inducing different spore-inactivation mechanisms. Among the versatile dopants trialed in recent studies, the most effective were the metallic element Ag (Lee et al. 2005), the nonmetal element N (Nakamura et al. 2004) and the upconversion luminescence agent \( \text{Er}^{3+}\):YAlO\(_3\) (Zhou et al. 2015). Under visible light, the silver atoms in Ag/TiO\(_2\) play a co-catalytic role by injecting plasmon-induced electrons into the photocatalyst. Thus, TiO\(_2\) generates high \( e^-/h^+ \) pair separation under visible light (Lee et al. 2005). In contrast, the nitrogen-doped TiO\(_2\) can respond to visible light because the N atoms decrease the band energy gap (Lu et al. 2014). In \( \text{Er}^{3+}\):YAlO\(_3\)/TiO\(_2\), the photocatalytic material assembles with the upconversion luminescence agents \( \text{Er}^{3+}\):YAlO\(_3\) (Wang et al. 2010), transforming the visible light to UV light and thus satisfying the requirement for anatase TiO\(_2\) photocatalysis (Dong et al. 2015).

In summary, photocatalytic inactivation of fungal spores is worthy of consideration, but the activation mechanism remains to be elucidated. In this work, we prepared three kinds of photocatalysts; a metal-doped photocatalyst (Ag/TiO\(_2\)), a nonmetal-doped photocatalyst (N/TiO\(_2\)) and an upconversion luminescence agent-doped photocatalyst (\( \text{Er}^{3+}\):YAlO\(_3\)/TiO\(_2\)), which were expected to generate different ROSs. We investigated the ability of the three photocatalysts to inactivate Fusarium solani (F. solani) spores, and the subsequently retained inactivation by-products. By analyzing the dominant ROSs released by the photocatalysts, we identified the preliminary mechanisms of photocatalytic spore inactivation, and highlighted the need for appropriate photocatalysts selection in future.

**Materials and methods**

**Catalyst preparation**

Nano-sized Ag/TiO\(_2\) particles were prepared by a sol–gel process as described in Lee et al. (2005). The nitrogen-doped photocatalysts were prepared by the calcinations method, using urea as the nitrogen source (Kontos et al. 2008). The \( \text{Er}^{3+}\):YAlO\(_3\)/TiO\(_2\) was prepared by a sol–gel method described in Dong et al. (2015).

**Fungal strain, cultivation and enumeration**

**Fusarium solani** was purchased from Beina Chuan-glan Biotechnology Institute. (Beijing, China, No. BNCC144579). Colonies of F. solani were transferred to sporulation agar medium containing potassium chloride and kept at 25 °C for 15 days (Fernández-Ibáñez et al. 2009). The spores were washed from the medium using sterilized distilled water. The obtained mixed suspension was centrifuged at 300×g for 10 min and washed three times with sterilized distilled water. The concentration of the suspension was determined by direct count in a counting chamber (Turki et al. 2013). The initial experimental concentration was approximately \(10^4\) CFU/mL. The fungal spore concentration during photocatalysis was determined by the pour plate technique (i.e., by spreading 100 µL of the sample in the plate, and counting the resulting colonies) (Polo-López et al. 2014). All samples and treatments were prepared in triplicate and the plates were incubated at 28 °C for 2 days in the dark before counting (Polo-López et al. 2014).

**Photocatalytic inactivation**

The experiments were performed in 27.5-mm × 95-mm (diameter × height) sealed glass bottles with a working volume of 40 mL. The light source was a 300-W xenon lamp with a 420-nm cutoff and an intensity of ~100 mW/cm\(^2\). The light beam was horizontally projected on the side wall of the bottle. In a typical inactivation test, the bottles containing magnetic stirrers were pre-sterilized before each batch.
The $F.\ solani$ spores (initial concentration ~ $10^4$ CFU/mL) and photocatalyst powder (1 g/L) were then added to the sterilized bottles. All experiments were performed in triplicate at room temperature (~20 °C).

The scavenging species and their concentrations in the scavenging experiments were as follows: 0.5 mmol/L sodium oxalate, 0.5 mmol/L isopropanol, 0.05 mmol/L Cr(VI), 0.1 mmol/L Fe(II)-EDTA, and 2 mmol/L TEMPO. By quenching the specific reactive species with individual scavengers, we can specify the reactive species’ contributions in the different photocatalytic systems: Cr(VI) for $e^-$, isopropanol for •OH, sodium oxalate for $h^+$, Fe(II) for $H_2O_2$, and TEMPOL for $O_2^-$ (Xia et al. 2013).

**Analytical methods**

**X-ray diffraction (XRD) analysis**

Powder XRD patterns were acquired by a Bruker D8 Advanced X-ray diffractometer using Cu Kα radiation ($\lambda = 0.15418$ nm) at a scanning rate of 2°/min. The 2θ range was 10°–90°.

**Optical microscope**

Drop samples were collected from the reaction solution at 0 and 4 h. The samples were observed under an optical microscope (CKX41, Olympus).

**Transmission electron microscopy (TEM)**

Samples (10 mL) were collected from the reaction solutions at 0 and 4 h, centrifuged and washed three times with 0.1 M phosphate buffer (PBS, pH = 7.2). Cell pellets of the samples were prepared by pre-fixing in 2.5 % glutaraldehyde at 4 °C for 12 h, washing three times with PBS, then pre-fixing in 1 % osmium tetroxide at 4 °C for 3 h. The cell pellets were dehydrated through a series of ethanol with graded concentration and embedded in Spurr solution at 70 °C for polymerization. The polymerized samples were sectioned into ultrathin slices (70 nm) using an ultramicrotome (Leica, Reichert Ultracuts, Wien, Austria), and stained with uranyl acetate and lead citrate. Finally, the sections were observed in a JEM1230 transmission electron microscope (JEOL Ltd., Tokyo, Japan).

**Three-dimensional fluorescence spectra (EEM) measurements**

The reaction solution (10 mL) was sampled from the three photocatalyst preparations at 0, 1 and 7 h, then filtered through a 0.22-μm membrane to remove the fungal cells. EEM spectroscopy measurements were conducted using a fluorescence spectrometer (F-7000, Hitachi, Japan) at a scan rate of 2000 nm/min and an excitation/emission slit bandwidth of 5 nm. The scanning field was set to 220–600 nm for the emission spectra and 220–450 nm for the excitation spectra.

**Molecular weight (MW) analysis**

The molecular weight of the aqueous phase was analyzed by gel filtration chromatography (GFC, Shimadzu, Japan), which performs high performance liquid chromatography (LC-10A, Shimadzu, Japan) with a differential refractive index (RID-10A, Shimadzu, Japan) detector. As the standard, we used glucan, which covers a molecular weight range of 200–1500,000 Da. The column temperature was controlled at 40 °C. The mobile phase was deionized doubly distilled water with a flow rate of 0.6 mL/min, and the hydraulic detention time of the column was 30 min.

**Results**

**Characterization of the prepared photocatalysts**

Figure 1 shows the XRD spectra of the prepared N/TiO$_2$, Er$^{3+}$:YAlO$_3$/TiO$_2$ and Ag/TiO$_2$ photocatalysts. The peaks in the XRD spectra of the three photocatalysts are generally sharp, with small full-width-at-half maximums. Therefore, the formation of the crystals was basically complete, and the photocatalysts were receptive to the photocatalytic reaction. The doping mechanisms of these nanoparticles were described above.

The three photocatalysts presented different characteristics as they were doped with different materials. The phase structure of the prepared Ag/TiO$_2$ was pure anatase TiO$_2$. The N/TiO$_2$ nanoparticles exhibited a phase structure of mixed anatase and rutile with mass fractions of ~97 and 3 %, respectively (computed by the Spurr–Myers equation; Spurr and Myers 1957). Er$^{3+}$:YAlO$_3$/TiO$_2$ presented two crystal forms; the visible light up-conversion components Er$^{3+}$:YAlO$_3$ and anatase, indicating that Er$^{3+}$:YAlO$_3$ was successively doped in the anatase TiO$_2$ (Dong et al. 2015).

**Inactivation of $F.\ solani$ spore by the prepared photocatalysts**

Figure 2 compares the $F.\ solani$ spore counts during photocatalysis inactivation with the three prepared photocatalysts under visible light irradiation. All of the photocatalysts efficiently inactivated the spores. Over a 4-h period, N/TiO$_2$ and Er$^{3+}$:YAlO$_3$/TiO$_2$ (at dosages of 1 g nanoparticles/L) achieved inactivation efficiencies of 78 and 87 %, respectively. During the following 3 h, the removal rates of living cells continuously increased, reaching 91 and 94.3 %, respectively. Notably, the Ag/TiO$_2$ nanoparticles inactivated 99.5 % of the $F.\ solani$ cells within 1 h of irradiation, and nearly all cells were inactivated within 4 h. Obviously, Ag/TiO$_2$ demonstrated higher fungal infection capability than the other photocatalysts. In comparison, none of the control treatments—visible light photolysis alone (no catalysts), dark adsorption (no irradiation) and the blank control (neither...
catalysts nor irradiation)—noticeably inactivated the \textit{F. solani} spores (data not shown).

Micro-observation of the inactivated spores
To better understand the inactivation mechanism, the outer shape and inner-microstructures of \textit{F. solani} before and after photocatalysis were examined under an optical microscope and TEM, respectively. As shown in Fig. 3, the active \textit{F. solani} spore cells were sickle-shaped, with approximate lengths of 10 µm and cell-wall thicknesses of 0.3 µm. Regular cell walls, membranes, nuclei and mitochondria-like components were clearly visible inside the cells.

All of the inactivation protocols shrunk the cells, deformed their shapes, and generated large quantities of cell debris. The photocatalyst nanoparticles were obviously adsorbed on the cell surfaces, causing initial physical damage to the cells (Caballero et al. 2009). The Ag/TiO\textsubscript{2} photocatalysis, which performed most efficiently among the three treatments, exhibited the highest number of photocatalysts enclosing the spores. Such direct contact suggests direct oxidation of the cell components and high killing efficiency against the microorganisms (Rahmanto et al. 2005), and is especially significant for \textit{F. solani} spores with their relatively thick cell walls (Thabet et al. 2014). Interestingly, the Er\textsuperscript{3+}:YAlO\textsubscript{3}/TiO\textsubscript{2} protocol performed less efficiently than Ag/TiO\textsubscript{2}, but caused much greater spore damage and produced the most cell debris among the protocols. These various consequences were related to the different ROSs characteristics of the photocatalysts.

The TEM results revealed microscopic changes in the spore cells (Fig. 3). After 4 h photocatalysis by all three protocols, the cells were disrupted to various degrees, showing damage features such as plasmolysis and ghosting of the intracellular vacuoles. Most of the intracellular components became unclear, indicating their decay. The Ag/TiO\textsubscript{2} protocol best preserved the cell wall structure, but cytoplasm leaking was observed. The N/TiO\textsubscript{2} protocol partially oxidized the cell wall, releasing the spore cell contents; further photocatalytic oxidization should completely kill the spores. No nanoparticles were observed in the spore cells subjected to these two protocols. In contrast, the Er\textsuperscript{3+}:YAlO\textsubscript{3}/TiO\textsubscript{2} photocatalysis introduced some nanoparticles into the inactivated spores (indicated by the red arrow). In these spore cells, the cytoplasm was seriously disrupted and even partially disappeared. The Er\textsuperscript{3+}:YAlO\textsubscript{3}/TiO\textsubscript{2} treatment yielded the thinnest cell walls among the three protocols, suggesting the strongest attacking capability on the spore cell wall, despite its weaker inactivation capability than Ag/TiO\textsubscript{2} (see Fig. 2).

Biomolecules leakage and degradation during inactivation
The EEM spectrum provides clues into the subsequent SMP release during the photocatalytic inactivation. Figure 4 shows the main SMP constituents in the spore cells prior to inactivation. We observe tyrosine/tryptophan amino acids (in region I), soluble microbial byproduct-like materials (in region VI) and humic acid-like organics (in region V). As evidenced by the gradual weakening of their peaks, all of these SMP constituents were significantly reduced by the Ag/TiO\textsubscript{2} and N/TiO\textsubscript{2} photocatalysts. Again, the Ag/TiO\textsubscript{2} photocatalysis demonstrated much higher removal efficiency for the generated SMPs than the other protocols. The tyrosine/tryptophan amino acid and soluble microbial byproduct-like compounds were almost completely removed, and the humic acid-like compounds were dramatically decreased. It appears that the Ag/TiO\textsubscript{2} and N/TiO\textsubscript{2} treatments simultaneously
Fig. 3  Optical microscope images (left column) and TEM (right column) of the active F. solani, and photocatalytically treated F. solani with Ag/TiO₂, N/TiO₂ and Er³⁺:YAlO₃/TiO₂, respectively, after 4 h visible light irradiation. The red arrow pointed the Er³⁺:YAlO₃/TiO₂ photocatalysis which entered the spores.
degraded the leaked cell contents (confirmed by the TEM results) while inactivating the *F. solani* cells. In the EEM spectra of the Er3+:YAlO3/TiO2 protocol, the peaks of the tyrosine/tryptophan proteins and soluble microbial byproduct-like compounds were red shifted and enhanced after 1 h, indicating that additional molecules of these species had formed during the inactivation. Moreover, these peaks were only slightly weaker after 7 h treatment, confirming that the new compounds were retained.

The above discussion of the SMP components was supported by the size exclusion chromatography and high performance liquid chromatography (SEC-HPLC) results (see Fig. 5). During 1 h inactivation, the molecular weights (MWs) of the SMPs decreased from 400–1500 kDa to 100–450 kDa in the Ag/TiO2 treatment and to 340–1200 kDa in the N/TiO2 treatment. Ag/TiO2 destroyed the initial cellular macromolecules more extensively than N/TiO2 and ultimately degraded them to much smaller and presumably less harmful compounds (Ni et al. 2010). After 7 h inactivation, intermediates with MWs as small as 10–70 kDa were detected in the Ag/TiO2 and N/TiO2 inactivation protocols, and the intensities of heavier intermediates had significantly decreased. In contrast, the Er3+:YAlO3/TiO2 protocol slightly increased the MW distribution of the SMPs, from its initial 400–1500 kDa to 600–1600 kDa after 1 h. The increase is attributable to the large MWs of the leaked intercellular material. The intensities of the accumulated SMPs in this MW range increased after 7 h, indicating their harmful and photocatalytically non-degradable characteristics. These high-weight SMPs (400–1600 kDa) are potentially harmful and persistent in the environment (Jarusutthirak and Amy 2007).

**Discussion**

In this work, *F. solani* spores were inactivated by three prepared photocatalysts, and different inactivation efficiencies, cell damage mechanisms and subsequent SMP leakage levels were observed. The Ag/TiO2 can kill the spores while maintaining the integrity of their cell walls and simultaneously degrading the SMPs leaked throughout the inactivation. The N/TiO2 nanoparticles ruptured the cell walls but similarly degraded the leaked SMPs. However, the Er3+:YAlO3/TiO2 nanoparticles entered the spore cells and significantly oxidized...
the intercellular contents, which likely explains the large molecular weights of the released SMPs. These differences among the inactivation behaviors were determined by the ROS species generated by the photocatalysts under visible light irradiation (Sun et al. 2014). The photogenerated ROSs, including $h^+$, $\cdot$OH, H$_2$O$_2$, and $\cdot$O$_2^-$, are all responsible for bacterial inactivation and play different roles in various photocatalytic systems (Hou et al. 2012).

As shown in Fig. 6, the Ag/TiO$_2$ photocatalysis system was dominated by H$_2$O$_2$ and assisted by $\cdot$OH. In the N/TiO$_2$ system, $h^+$ and $\cdot$O$_2^-$ played the important roles, with $\cdot$O$_2^-$ being the most determining species. The Er$^{3+}$:YAlO$_3$/TiO$_2$ inactivation system was dominated by $h^+$. These three ROSs have different average life-spans ($4 \times 10^{-9}$ and $2 \times 10^{-10}$ s for $\cdot$OH and $\cdot$O$_2^-$, respectively, and even shorter for $h^+$) (Xia et al. 2013). Conversely, H$_2$O$_2$ is relatively stable with a half-life of several days in water (Xia et al. 2013). Moreover, in the following generation sequence of ROSs (Chatterjee and Dasgupta 2005), ROSs produced in the earlier steps possess higher oxidizing potential.

$$\text{TiO}_2 + h\nu \rightarrow e^- + h^+$$
$$h^+ + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+$$
$$h^+ + \text{OH}^- \rightarrow \cdot\text{OH}$$
$$\text{O}_2 + e^- \rightarrow \cdot\text{O}_2^-$$
$$\cdot\text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2\cdot$$
$$2 \text{HO}_2\cdot \rightarrow \text{O}_2 + \text{H}_2\text{O}_2$$
$$\text{H}_2\text{O}_2 + \cdot\text{O}_2^- \rightarrow \cdot\text{OH} + \text{OH}^- + \text{O}_2$$

Thus, the oxidizing potentials of the dominant ROSs generated in this work increased in the order $h^+ > \cdot$O$_2^- >$ H$_2$O$_2$.

Accordingly, H$_2$O$_2$ has the longest span life but the weakest oxidation capability among the three ROSs.
This species, which dominated the Ag/TiO₂ photocatalysis, diffused into the cells without seriously damaging their cell structures. Consequently, the H₂O₂ molecules permeated the cell membranes, damaging the spores’ interiors without excessively leaking their cell contents (as confirmed by the EEM and SEC results). However, the dominant ROS in Er³⁺:YAlO₃/TiO₂ photocatalysis was h⁺, with the strongest oxidative potential but shortest life-span among the three ROSs. This species was generally produced on the surface of the catalyst and directly attacked the cell wall. The Er³⁺:YAlO₃/TiO₂ nanoparticles then entered the cells through the broken cell wall, causing abundant leakage of the intracellular components and subsequent pollution of the bulk water quality. The N/TiO₂ photocatalysis was dominated by •O₂⁻, with a life-span and oxidation capability between those of H₂O₂ and h⁺; consequently, the anodization performance of this photocatalysis was intermediate between Ag/TiO₂ and Er³⁺:YAlO₃/TiO₂. In summary, the H₂O₂-dominated Ag/TiO₂ photocatalysis delivered outstanding performance in both inactivation efficiency and SMP-leakage control.

Abbreviations
ROSs: reactive oxygen species; F. solani: Fusarium solani; SMPs: soluble microbial products; XRD: X-ray diffraction; TEM: transmission electron microscopy; EEM: three-dimensional fluorescence spectra; MW: molecular weight; SEC: size exclusion chromatography and; HPLC: high performance liquid chromatography.

Authors’ contributions
YD and SD designed the experiments. YD and DM conducted the experiments. YD, HX, ZJ analyzed data. YD wrote the paper with help from DZ. All authors read and approved the final manuscript.

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Competing interests
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Ethical approval and consent to participate
This article does not contain any studies with human participants or animals performed by any of the authors.

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