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Non-UV germicidal activity of fresh TiO$_2$ and Ag/TiO$_2$

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Abstract

Fresh TiO$_2$ was found to possess a strong germicidal activity even without UV irradiation. Live Yeast (Saccharomyces cerevisiae) cells in contact with fresh TiO$_2$ were found deformed and dead after 15 min contact. The cause of germicidal activity was discussed from the observed cell deformation, lysis and increased absorption at 1680 cm$^{-1}$ in FT-IR spectra of the affected cells, which proved the oxidizing effect of fresh TiO$_2$ to cells. The deformation caused by the stretching of cell wall and pressure built-up inside the cell, led to cell burst and release of intracellular materials. The degree of cell deformation was found positively related with the wetting property of TiO$_2$. Cells are negatively charged, for Gram-negative cell (thinner cell wall), a higher germicidal effect was observed than Gram-positive cells. The germicidal effect of TiO$_2$ gradually decreased after exposure to air at room temperature, as the wetting property decreased. This kind of germicidal activity was more effective compared to other germicidal process such as UVA/TiO$_2$ or Ag$^+$. This shed light on designing new germicidal material either maintained by visible light irradiation, or by oxidation effect generated by reactive oxygen species.

Key words: germicidal activity; titanium dioxide; non-UV

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Introduction

Nowadays, new germicidal materials and mechanisms were studied for disinfection purposes, especially those non-UV based germicidal materials. Germicidal mechanisms studies are important for designing new and better germicidal material for disinfecting solid surface and air purification filters.

The confirmed mechanisms of germicidal activities include: oxidative destruction of cell wall (e.g., chlorine, ozone, peroxide, radical), inhibition of reproduction through DNA structural change (e.g., UV irradiation, reactive oxygen species are also generated), inhibition of respiration by inactivation of enzymes (chloramines, chlorine dioxide), and interfered metabolisms (Ag, Cu by combining with thiol groups), dehydration and denaturing proteins (70% ethanol) (Morato et al., 2003).

Disinfection by UV and TiO$_2$ (Armon et al., 2004, Cho et al., 2004) is caused by the radical (OH) peroxidation of the cell wall (Nadtochenko et al., 2004), and the change of DNA material through the absorption of UVC by its components. Many disinfection apparatus work in this way (Yu et al., 2003; Christensen et al., 2003; Jacoby et al., 1998; Ibanez et al., 2003), but UV increases equipment size and energy consumption. Therefore, reactors without UV for VOC removal and disinfection of bioaerosol has been studied, e.g., in HKUST.

Indoor air purifiers for both bioaerosol and VOCs removal (Hester and Harrison, 1995) perform by filtration, electrolysis, adsorption and/or photocatalytic oxidation (PCO) (Mills and Hunte, 1997; Zhao and Yang, 2003). PCO can degrade cell debris (Ibrahim and De Lasa, 2002; Choi et al., 2001; Maira et al., 2000) and VOC. Pure or doped metal oxide semiconductors (e.g., TiO$_2$, SiO$_2$-TiO$_2$) are often used as photo-catalysts in PCO.

A strange disinfecting phenomenon has been reported in our previous study (Liu et al., 2007), that fresh pure TiO$_2$ and metal-doped TiO$_2$ possessed non-UV germicidal effect, that was more effective than UVA and TiO$_2$. This strong germicidal activity appeared to be related to the wetting property. The high degree of germicidal activity detected within shorter contact time indicates the presence of a fast acting germicidal mechanism. Therefore, further investigation was carried out and discussed in this article, including the observation of cell deformation and FT-IR spectral change of cells. The importance of specifying catalyst storage time and condition in accurately describing germicidal tests and the results were highlighted.

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1 Materials and methods

1.1 Microorganisms

Yeast (Saccharomyces cerevisiae) cells were cultured overnight with a modified malt extract on an agar plate at 30°C. E. coli and Pseudomonas putida were grown on LB media overnight at the same incubator. The cells were swabbed off the plate and re-suspended in 0.8% saline. The cells suspension concentration was about 10^6 CFU/mL (optical density at 0.6). Usually, 10–15 μL cell suspension was loaded onto a TiO2 coated Al plate (1.8 cm × 1.8 cm), for a specified contact time. The cells were then stained for 15 min before using epifluorescent microscopy to observe their viability changes.

1.2 TiO2 coating

The aluminum plate (1.8 cm × 8 cm) was used as substrate. Prior to coating, all the substrates were ultrasonically cleaned in deionized and distilled (DDI) water and acetone, respectively, with several cycles to remove the surface contamination and dried in oven.

TiO2 coated plates (No. 1, 2, 3, 4) were prepared via sol-gel method through spin-coating onto cleaned Al plate, and calcinations to 450°C, then cooling in the oven to room temperature. A 1-mol/L of titanium isopropoxide (ACROS) and isopropanol solution (BDH) was slowly added to DDI water under vigorous stirring. The resulting solution was stirring for 1 h to ensure complete hydrolysis of titanium isopropoxide. A desired amount of nitric acid (1.0 mol/L, H^+ / Ti4+ = 0.4) was then added to peptize. The temperature was increased gradually to 70°C and then maintained for 2 h to evaporate the isopropanol. Subsequently, it was kept stirring at room temperature until the formation of a clear TiO2 sol (0.28 mol/L). When preparing Ag/TiO2, appropriate amount of AgNO3 (0.05 mol/L) solution was then dropped into the above TiO2 sol to obtain a desired metal loading (0.5 wt.%). A coating paste could be prepared by adding 5 wt.% of polyethylene glycol (PEG) with an average molecular weight of 400 g/mol (ACROS) into the above TiO2 sol and followed drying step in an oven at 65°C.

Crystalline TiO2 is basically of anatase type. Freshly prepared samples (No. 1, 2, 3) was tested immediately. No. 4 plate was stored in air for 3 h, and then used for UVA irradiation germicidal test (30 cm away from two 6 W black light lamps). Ag/TiO2 prepared by the same way under the same conditions was used for non-UV germicidal activity tests and UVA irradiation germicidal tests (14 cm away from two 6 W black light UVA lamps). UVC (254 nm, 15 W, 2 lamps, 10 cm away) was used for reactivating catalyst germicidal activity and improving wetting property, it is regarded as a way of regenerating non-UV germicidal activity.

Control tests on an inert surface (Al plate) were also carried out. To compare the cell morphology, Yeast cells were loaded to a clean glass slide and sprayed with an ethanol solution to affect cell (40% concentration as indicated). After evaporating ethanol, the cells were stained and microscopic analysis was undertaken.

1.3 Germicidal test of Ag+ solution

Solution with Ag+ was prepared by dissolving silver from a solid source material using distilled water to avoid introduction of any anions, such as nitrate or sulfate. The Ag+ concentration measured by ICP-AES (Perkin Elmer, USA) was 530 μg/L. A 40-mL of the solution was loaded to clean Al plate, dried in Biosafety cabinet by airflow, then cell suspension was loaded for germicidal activity measurement and cell morphology was observed using epifluorescent microscopy (Olympus BX, Japan).

1.4 Staining for germicidal activity measurement

BacLight bacteria viability kit 13152 from Invitrogen (USA), was used to measure the viability level of cells on the surface of catalyst. It consists of dyes mixture (Syto 9 and propidium iodide). The ratio of the dyes and staining condition were optimized according to the product manual. A full description of the staining method is given elsewhere (Liu et al., 2007).

1.5 Fluorescent microscopy analysis

Images were obtained using a digital camera and a CCD detector (Olympus, BX, Japan). About 20–30 microscopy pictures were taken and cell counts of different colors were averaged for calculating the viability level. Viability changes of cells before and after contact with catalyst were compared to determine the germicidal activity. Germicidal activity (%) = 100% × (initial viability – final viability)/initial viability.

1.6 FT-IR microscopy analysis

Perkin-Elmer I-series FT-IR microscope (USA) was used to obtain a spectrum of Yeast cells on blank Al plate and on a clean and fresh TiO2 coated plate. The loaded cell suspension was dried using the airflow in the bio-safety cabinet, then put on microscopy stage. Mapping was performed in reflection mode.

2 Results and discussion

2.1 Germicidal activity of fresh TiO2

The germicidal effect of pure TiO2 plates was measured at different contact time. The result presented in Table 1 shows that the percentage of killed cells (red or red and yellow) was very high after 15 min contact and 15 min staining. It gradually increased with extension of the contact time. The percentage of viable cells (green) gradually decreased. The percentage of yellow cells remained constant. Yellow cells are considered damaged, and have been subjected to germicidal effect. They may be cultured after a long incubation period (48 to 72 h). They are included with red cells in the germicidal activity calculation.

Fresh TiO2 plate has strong germicidal activity for Yeast cells (60% completely killing) and other bacteria cells. Its germicidal activity takes place in relatively short time
(15 min). Extending contact time 30 min did not change the cell viability or dead cell percentage (56%–58%). But when the contact time was 40 min, the germicidal activity increased to 98%, dead cell percentage increased to 68%.

The result of germicidal activity for No. 4 plate is also listed in Table 1 for comparison. The plate had been through 3 h storage in air, loaded with cell and irradiated with UVA (6 W × 2, 30 cm away) for 30 min. The cells viability was not greatly affected under this condition (only 13% cells were affected). The bad dispersion and poor contact of cells with the catalyst surface (bad wetting property) was presumably the main contributing factor for this result.

### 2.2 Germicidal activity of Ag/TiO₂ or UVA plus Ag/TiO₂

The results of germicidal activity of both fresh plate and relatively fresh plate coated with Ag/TiO₂ are listed in Table 2. For measuring the effect of Ag/TiO₂ without leaching of Ag, loaded cell suspension was blown-dry with compressed air. A high percentage (82.5% red) of non-viable cells was obtained, comparing with that on freshly UV activated Ag/TiO₂ (ca. 60% red). The measured distribution of stained cells according to their color after 20 min on freshly UV activated Ag/TiO₂ was (10.4 ± 5.6)% green, (7.0 ± 3.7)% yellow, (82.5 ± 6.1)% red. Ag doping introduced extra germicidal activity, therefore, the fresh Ag/TiO₂ has higher germicidal activity than fresh TiO₂ and stored Ag/TiO₂. This phenomenon was owing to the formation of reactive oxidizing species (He et al., 2004; Chen et al., 2007). The state of Ag should be mainly in its oxides form (Ag₂O), with very few Ag₃ existed (from thermal decomposition of Ag₂O), as there is no reduction treatment applied (Liu et al., 2006; Kubacka et al., 2008). For stored 0.5 wt.% Ag on TiO₂ (sealed in small petri-dish), total germicidal activity reached about 90% after 30 min. Cells distribution according to stained color was: 10.2% green (viable), 65.4% yellow, 24.4% red. The storage also caused a decrease in total killing, due to the gradual decrease of wetting property of TiO₂.

To check the effect of air and water on Ag/TiO₂ germicidal property during the storage, one fresh plate of Ag/TiO₂ was kept dry in air, another one was immersed in water and wet when being lifted out of water 20 min later. Cells were loaded immediately to both plates at the same time. Although there is dissolution of Ag, the immersed Ag/TiO₂ plate showed higher germicidal activity (82.5% red cells). While the dry Ag/TiO₂ plate has lost much of its germicidal activity, a 24.4% red cell, is similar to the germicidal effect of possibly dissolved Ag ions. The germicidal activity was somehow kept by the immersion in water. The reason may be that water fends off something, which caused the decrease of wetting property and germicidal property of TiO₂ in air.

A UV related reactivation mechanism of cells may be responsible for the low germicidal activity in using UVA. Soekmen et al. (2001) had reported that Ag/TiO₂ and UVC irradiation has lower bacteria germicidal activity than Ag/TiO₂ without irradiation. Recently, the same author had reported a lower germicidal activity for parasite A. castellani too when using Ag/TiO₂/UVC than using UVC alone (Soekmen et al., 2008).

Another reason accounting for the germicidal results in this study is the small volume of loaded cell suspensions to the plates. To simulate the contact of bioaerosol in air with catalyst, the loaded cell suspension volume was very small to allow good contact of cells with catalyst coatings, and this resulted in a high germicidal activity. During UVA irradiation tests, only ROS that comes in contact with the microbe can affect cell viability. The germicidal activity

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### Table 1 Germicidal effect of fresh TiO₂ without UV and after 3 h storage with UVA

| Plate                  | Wetting (15 µL) | Viable cells | Green cells (%) | Yellow cells (%) | Red cell (%) |
|------------------------|----------------|--------------|-----------------|-----------------|--------------|
| Without UV (fresh from oven) | Very good (80%–90% wet) | 15 | 12.2 ± 3.8 | 28.9 ± 4.6 | 87.8 |
|                        | Moderate (ca. 25% wet) | 30 | 12.5 ± 4.3 | 31.2 ± 3.5 | 87.5 |
|                        | Bad             | 40 | 1.9 ± 2.6  | 29.2 ± 2.5  | 97.1 |

### Table 2 Comparison of germicidal activity of Ag/TiO₂

| Condition                        | Contact time (min) | Viable cells | Affected cells |
|----------------------------------|--------------------|--------------|----------------|
| Immersed, washed                 | 15                 | 12.5 ± 9.1   | 5 ± 5.3, 82.5 ± 13.3 |
| Not immersed                     | 15                 | 95.1         | 0, 4.01         |
| Air dried, reused                 | 20                 | 10.4 ± 5.6   | 7.0 ± 3.7, 82.5 ± 6.1 |
| Only Ag                          | 30                 | 5.2–6.4      | 71.0–80.0, 15.0–23.0 |
| Stored relatively fresh           | 15                 | 10.2         | 65.4, 24.4      |
| With UVA irradiation              | 20                 | 52.6         | 47.4           |

* UVC cleaned and activated; b 14 cm away from the two 6 W black lamps.
relies on either direct contact of cells with the catalyst (dispersion and contact, also deformation as shown in Section 2.3.1), or Ag ion, hydroxyl radical or (Ti$^{3+}$ or O$_2^-$) ROS generated by UV excitations (Kubacka et al., 2008; Yan et al., 2005).

2.3 Cell deformations during germicidal tests

2.3.1 Cell deformation on fresh TiO$_2$

From microscopy observations, it is found that Yeast cells on fresh TiO$_2$ were deformed. Cells looked like kidney pea, basically with elongation at two ends and bending towards one side of the cell. The dead cells looked longer and larger, and some have red smear around. Intermediate compromised cell showed a nucleus which has moved towards the side of the cell wall away from the bending. Normal cells have a nucleus which appears free moving inside the cell. Some dead (red) cells looked like shuttle fish that had just released its inky fluids. The average size of normal cell is about 4–5 μm in diameter. The cause of cell deformation may arise from charge interaction between negatively charged Yeast and positively charged TiO$_2$ (around defect sites with more Ti$^{3+}$ and especially good wetting property of the catalyst surface). It makes the hydrophilic cell wall touch the surface more, lose its round shape and flattened up. The cell thus looks like a half-ball instead of a round ball with increasing contact area shape and flattened up. The cell thus looks like a half-ball form. Actually, cell volume could not be reduced, its diameter. The volume would equal to 85% of its original diameter of half-ball shaped cell will be 1.15 times the diameter of original round balled cell, the volume inside the half ball is only 77% of its original round volume, thereby the cell may burst.

Use a cylindrical form to depict the deformed cell, and assume the cell diameter reduced 1/3, the cell would be stretched to a length of 1.16 times its diameter without increasing its original surface, but with 89% of its original volume, the build-up pressure inside the cell is less than the case of a half sphere model. Suppose that a cylindrical form plus two half balls at the two ends of the cells were formed, the stretched middle part would have a length of 0.83 time its diameter, then total cell length is 1.83 times of its diameter. The volume would equal to 85% of its original sphere form. Actually, cell volume could not be reduced, therefore the cell wall becomes thinner and stretched; the weakest point will break when it cannot hold.

Larger cell can bear lower pressure rise than smaller cell. Under the same degree deformation, larger cell may burst more easily than smaller cell if the cell wall thickness is the same. Therefore, from the picture of stained cells, the burst cells looked larger, smeared a larger area than the smaller cells (Fig. 1). Small cells and rod or cocci bacteria cells may be less affected under this deformation based germicidal activity.

This explains the nature of relationship between wetting property and the germicidal activity. The higher the wetting property, the higher the degree of deformation, thus the higher the germicidal activity. This process takes place very quickly as the wetting process is fast (Nadtochenko et al., 2004; Wang et al., 1998). The killing was almost instant, promoted by the oxidative nature of the defect sites and the attraction of negatively charged cell to the catalyst.

From the microscopy picture in Fig. 1b, it is seen that some cells looked like shuttle fish, just released its inky liquid. The dead cells may have a length of 10 μm, and some still green or yellow cells have a patch of red stain nearby. This indicated that the cells had released part of its cellular content which is rich in DNA that binds with PI and appears red. Other part of the cell was still intact, because the oxidation may need more time to take effect.

2.3.2 Morphology of cell by Ag$^+$ on Al plate and UVA irradiated cell on Ag/TiO$_2$

Deformation was not observed for cells affected by Ag$^+$ on Al plate as shown in Fig. 2. Ag$^+$ may render many cells stained yellow or red. The staining showed 95% cells were affected by Ag ions. Distribution of stained cells according to coloration after 30 min contact with Ag ions on Al surface was 5.2%–6.4% viable, 71%–80% yellow, and 15%–23% red. Ag affected cells were not as round, nor as big as the cells affected by ethanol, in form and size (image not shown).

Low intensity UVA did not affect the cell viability obviously. The cells appeared normal in size and shape. With UVA intensity increased (shortened distance from plate/cell to black light), the cell viability decreased, and cells appeared to have more fragmented nucleus (image not shown).

2.4 Oxidation of cells confirmed by FT-IR spectra

Rincon and Pulgarin (2004) found that after illuminating TiO$_2$ and cells, cell count continues to decrease in the dark after illumination was stopped. The so-called post irradiation effect is possibly related with sites of O vacancy (Ti$^{3+}$), the cause of the super-hydrophilicity of the catalyst surface. It is regarded as the cause of cell oxidation in this study, as O$_2$ may dissociate or as adatom on TiO$_2$ surface vacancy (Wu et al., 2003). It can dissociate water in the hydration layer of cell wall and cause proton release and re-orientation of water molecules (Morra, 2001).

The dead cells seem settled or accumulated on the cracks of lower areas on the coated plate (image not shown). The green cells are on relative flat and high area. This coincides with the defects sites from catalyst preparation. The FT-IR result (Fig. 3) confirmed the oxidation effect to the Yeast cells.

FT-IR spectra of cells affected by TiO$_2$ have a higher absorption at 1680 cm$^{-1}$ than cells dried on AL plate. The final viability level of cell loaded to TiO$_2$ plate after 75 min was 5.86% (green), and cell percentage according to stained coloration was: ca. 40% yellow, 52% red. The initial loaded cell viability was 99.5%. In cells FT-IR spectra, increased C==O absorption in the cell/catalyst surface was obvious, by oxidation of Ti$^{3+}$ related oxidative active species, either by the vacancy(hole) itself or by the -OH radical formed by the dissociation of water with Ti$^{3+}$. The relative ratio of peak intensity of 1680 cm$^{-1}$/3400
Fig. 1  Epi-fluorescent microscopy picture of Yeast cells after contact with fresh TiO$_2$ surface (100×, image dimensions 90 μm ×120 μm)

Fig. 2  Morphology of normal stained cell, disinfected by Ag$^+$. Image dimensions 90 μm ×120 μm.

cm$^{-1}$ was 0.74 for the initial viable cells, was 1.125 for the TiO$_2$ affected cells.

2.5 Surface interaction of Gram positive (+) and negative (-) cell with TiO$_2$

Wang et al. (1998) reported that the amphiphilic property or hydrophilic property of the fresh TiO$_2$ arise from the Ti$^{3+}$ on the surface, which caused the dissociation of water molecules, forming small alternating hydrophobic and hydrophilic areas (about 30–80 nm in length), under AFM the hydrophilic area and hydrophobic area were distinctly white or gray. Cell membrane was hydrophilic, once in touch with the surface, it was attracted by the hydrophilic area and rejected by the hydrophobic area. The forces arising from the center of 4 adjacent areas caused the elongation and distortion of cell. The touching tip area of the round cell with the catalyst may be times of 200 nm × 200 nm, which may include many small alternating hydrophilic area and hydrophobic area.

That can explain why the germicidal activity is related with the wetting property of the surface and why germicidal activities to G(+) and G(-) strains are different. To cells with different mechanic strength, size and structure, the germicidal activity will be different. e.g., Yeast (G+) strain (thick cell membrane ) is less affected than G(-) strain (thinner cell membrane ) Pseudomonas (G-). Bacillus (G+) is less affected than Pseudomonas (G-) putida.

Testing with UVC activated TiO$_2$, the stained cell distribution according to coloration for P. putida (contact 15 min) was 2.5% green, 5.5% yellow and 93% red. Cells initial viability was 95% (green), at the same time the percentage for Yeast cells distribution was (28.0 ± 13)% green, (21.0 ± 7.6)% yellow, and (51.0 ± 11.3)% red (Table 3).

The germicidal activity lost during storage may be recovered by UVC irradiation, but can not be regenerated by heating to 100°C. Once absorbed, oxygen moves very fast on TiO$_2$ (Schaub et al., 2003) and facilitate diffusion of oxygen vacancy.

As Ag on Al$_2$O$_3$ was found to activate oxygen, causing
a potentially very strong oxidation effect to cells (Yan et al., 2005), Ag doped TiO$_2$ kills bacteria via both oxidation and deformation mechanisms.

### 3 Conclusions

The fast acting germicidal activity of fresh TiO$_2$ was studied and discussed based on the observation of cell deformation and FT-IR analysis. Oxygen vacancy was concluded as the cause of cell deformation and interaction between cell and TiO$_2$ coated surface. The degree of cell deformation was found positively related with the wetting property of TiO$_2$. For Gram-negative cell (thinner cell wall), a higher germicidal effect was observed than Gram-positive cells. The germicidal effect of TiO$_2$ gradually decreases after exposure to air in room temperature, as the wetting property decreases. This germicidal activity was more effective compared to other germicidal process such as UVA/TiO$_2$ or Ag$^+$. 

The results from this study are helpful for designing new germicidal material based on interaction and oxidation mechanisms. Thus a doping modified TiO$_2$ material with its wetting property maintained by visible light illumination may also have a lasting germicidal activity.

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