POLITECNICO
MILANO 1863

DIPARTIMENTO DI
CHIMICA, MATERIALI E
INGEGNERIA CHIMICA
"GIULIO NATTA"

Milano, 01/03/2020

Alla cortese attenzione di:

NextMaterials Srl
Via Turati nr40
20121 - Milano

Photocatalytic activity of titanium dioxide against bacteria and viruses

Prof. Gabriele Candiani

Indagine multisponsor commissionata da:

- **NextMaterials srl**
- **Soliani EMC srl**
- **Pan Electron srl / Liteon**
- **Air Control srl**
- **Metalarredo srl**
- **Imoon srl**

POLITECNICO
MILANO 1863

Introduction

Increasing concern about pandemics of disease-causing bacteria and viruses (e.g., swine influenza H1N1 and severe acute respiratory syndrome coronavirus (SARS-CoV)) and overall airborne pollution have attracted worldwide attention and spurred the development of air purification technologies [1,2]. Environmental contamination is a complex and intriguing problem involving the presence of contaminants in the form of particles (i.e., dust and smoke), biological agents, such as bacteria, molds and viruses, and other gaseous contaminants such as CO, CO_2, NO_x, SO_x and volatile organic compounds (VOCs) [3].

Purification from contaminants can be achieved by means of disinfection or sterilization processes. In more detail, disinfection describes a process that eliminates many or all potentially pathogenic microorganisms, except bacterial spores, on inanimate objects. Instead, sterilization describes a process that destroys or eliminates all forms of microbial life and is carried out in health-care facilities by physical or chemical methods. Widely used air purification techniques for disinfection include the treatment with non-thermal plasma (NTP), thermal treatment, use of antimicrobial material-embedded filters, ultraviolet (UV) light, and photocatalysts [2–4]. In the NTP air-cleaning systems, energetic electrons excite, dissociate, and then ionize gas molecules, giving rise to chemically reactive species such as atomic oxygen, hydroxyl radicals, and ozone [4]. Such active species inactivate biotic and abiotic particles, eventually forming secondary pollutants (e.g., ozone, CO, or NOx) [5]. In thermal treatment, exposure to high temperature induces protein denaturation through disrupting the polypeptide structures, thus resulting in damage to microorganisms [6]. However, it may consume much power to apply thermal energy at high temperature [7]. Filtration systems, in which airborne biological particles are collected on the surface of a filter, are great options to overcome the limitations of the aforementioned techniques.

However, these antimicrobial material-embedded filters are generally effective in the short-term because of the accumulation of dust that progressively clogged them and cause a large pressure drop, so that they must be replaced regularly to prevent the possible re-introduction of airborne microorganisms into the environment all of a sudden [5].

Another approach to prevent the transmission of airborne-mediated disease relies on the inactivation of airborne pathogens by means UV light[1] [8,9]. This is a cost-effective and environmentally-compatible alternative to frequently used chemical processes. UV irradiation has been found to consume little energy as compared to thermal treatments and can be simply applied by installing and turning on a UV lamp. In this regard, UV lamps are often installed in the ceilings of

[1] UV-A (λ = 315 - 400 nm); UV-B (λ = 280 - 315 nm) UV-C (λ = 100 - 280 nm)

surgery rooms in hospitals and health care facilities and function to inactivate nearby bioaerosols [10]. Of note, germicidal UV light allows the inactivation of both drug-sensitive and multi-drug-resistant bacteria [11], as well as different viral strains [12]. However, the widespread use of germicidal UV lighting systems in public space has been very limited because conventional UV light sources are a human health hazard as well [13].

To date, one of the most promising technologies for environmental disinfection is photocatalysis (or UV photocatalytic oxidation (PCO)), which is one of the most important advanced oxidation technologies available [14]. PCO has many advantages over the other technologies, including the simultaneous treatment of mixtures of diverse pollutants, relatively low costs, and ease of operation and maintenance [1,15,16].

1. UV-activated photocatalysis: working principle

Photocatalysis using semiconductor (SC) has been proven to effectively degrade a vast array of pollutants. Although the detailed mechanism of photocatalysis varies with different pollutants, it is commonly agreed that the primary reactions responsible for the photocatalytic effect are interfacial red-ox reactions of electrons and holes that are generated when the SC catalyst is exposed to light of sufficient energy (**Figure 1A**). It is well known that a SC is characterized by a band energetic structure, with a band gap between the lower valence band (VB), entirely filled with electrons, and the unoccupied, higher energetic conduction band (CB). The adsorption of a photon with sufficient energy (hv) by the SC promotes electrons from the valence band (e_{vb}^-) to the conduction band (e_{cb}^-), leaving a positively charged hole in the valence band (h_{vb}^+) (**Figure 1B**). The electrons (e•) are then free to migrate within the conduction band. The holes (h^+) may be filled by the migration of an electron from an adjacent molecule, leaving the latter with a hole, and the process may be repeated.

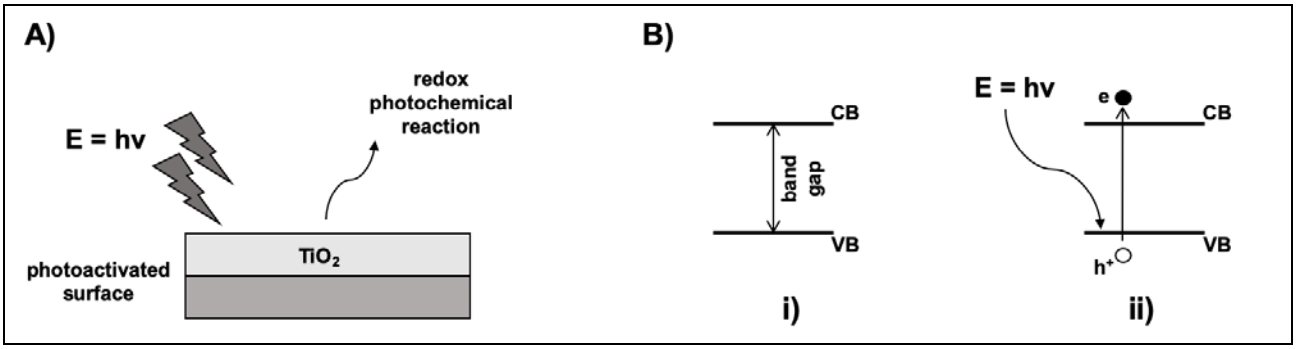


Figure 1. A) Schematic representation of a photoactivated antimicrobial surface. **B)** Band energetic structure (i) and mechanism of photoirradiation of a SC (ii).

Electrons and holes may recombine (bulk recombination) a non-productive reaction, or, when reaching the surface, they react to give reactive oxygen species (ROS) such as $O_2^{-}\cdot$ (**Figure 2**, reaction 2) and ·OH (**Figure 2**, reaction 3). When in aqueous solution, these can react to give H_2O_2 (**Figure 2**, reaction 4), further hydroxyl (**Figure 2**, reaction 5) and hydroperoxyl (**Figure 2**, reaction 6) radicals. Reaction of the radicals with organic compounds ultimately results in their mineralization (**Figure 2**, reaction 7), that is the degradation of organic contaminants due to their total oxidation [17,18].

Compared to other SC photocatalysts, titanium dioxide (TiO_2) is the most promising material because of its high photoactivity behavior and stability, relatively low cost, and non-toxicity. For these reasons, TiO_2 mediated photocatalytic inactivation of a large number of organic contaminants, including bacteria and viruses, has been extensively investigated [19–25]. Noteworthy, there are three main polymorphs of TiO_2: anatase, rutile and brookite. The majority of studies showed that anatase was the most effective photocatalyst and that rutile was the less active form. This is probably due to differences in the extent of recombination of electron and hole between the two forms. However, studies have shown that mixtures of anatase and rutile were more effective photocatalysts than 100% anatase [26]. In this context, Degussa P25 (Degussa Ltd., Germany) is a widely used, commercially available preparation of TiO_2 which contains approx. 80% anatase and 20% rutile.

$$TiO_2 + h\nu \rightarrow e_{cb}^{-} + h_{vb}^{+} \quad (1)$$

$$O_2 + e_{cb}^{-} \rightarrow O_2^{-}\cdot \quad (2)$$

$$h_{vb}^{+} + H_2O \rightarrow \cdot OH + H^{+}_{aq} \quad (3)$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \quad (4)$$

$$O_2^{-}\cdot + H_2O_2 \rightarrow \cdot OH + OH^{-} + O_2 \quad (5)$$

$$O_2^{-}\cdot + H^{+} \rightarrow \cdot OOH \quad (6)$$

$$\cdot OH + \text{Organic} + O_2 \rightarrow CO_2, H_2O \quad (7)$$

Figure 2. Mechanism of photocatalytic oxidation (POC). POC is based on the interaction between light and semiconductor particles, which produce the highly reactive oxygen species (ROS), such as OH•, OH^{-}, O_2^{-}•, HO_2•, capable of destroying organic (chemical and biological) contaminants

TiO_2 photocatalysts generate strong oxidizing power when illuminated with UV light with wavelengths (λ) of less than 385 nm [27]. On the other hand, doping TiO_2 with C, N, S, and metals such as Sn, Pd, and Cu has been found to increase the λ radiation adsorption so that also visible light can be used to trigger the photocatalysis [28]. Generally speaking, photocatalytic TiO_2 particles can be used in the form of *i)* powder, usually dispersed in aqueous solutions, *ii)* film/coating applied to various substrates or *iii)* immobilized on surfaces [29–34].

As photocatalytic inactivation of contaminants is a synergistic bactericidal effect of UV light and oxidative radicals generated at the TiO_2-based illuminated surface, some parameters, such as light intensity, extent of irradiation, catalyst concentration, play a role on the disinfection behavior. The UV dose (referred to as fluence) is generally expressed as the product of UV light intensity (I) and irradiation time (T_{irr}), according to **Eq. 1**:

$$\text{UV dose} = I \times T_{irr} \qquad \text{(Eq. 1)}$$

where UV dose is commonly expressed as $J/cm^2 = W\ sec/cm^2$.

It is worthy of note that UV dose is a key parameter when UV radiation (whether or not used in combination with TiO_2) is used as an antimicrobial mean.

2. Antibacterial effects of UV light in combination or not with TiO_2

The antimicrobial activity of UV-activated TiO_2 was first demonstrated by Matsunaga and coworkers in 1985 [35]. Since then, a substantial body of literature has addressed the antimicrobial effects of photocatalytic TiO_2 nanoparticles against both Gram negative and Gram positive bacteria. The most relevant examples of TiO_2 nanoparticles and microparticles used in the form of powder, and typically dispersed in aqueous solutions (**Table 1**)**,** or immobilized onto surfaces (**Table 2**) are reported in the tables herein below.

Table 1. Studies on the photocatalytic activity of TiO_2 used as nanoparticle and microparticle suspensions against bacteria.

target	[photocatalyst]	light parameters	irradiation time	antibacterial efficiency	Estimated minimum UV dose (according to Eq. 1)	Ref.
S. choleraesuis, *V. parahaemolyticus*, *L. monocytogenes*	10 mg/mL (Petri dish)	λ = 360 nm (UV-A); I = 0.4 mW/cm^2	30 min 1 hr 1.5 hrs 2 hrs	100% at T_{irr} ≥ 2hrs	0.3 J/cm^2 (or W sec/cm^2)	[36]
	0.25 - 1.25 mg/mL (batch reactor)	λ = 360 nm (UV-A); I = 0.1 mW/cm^2	3 hrs 4 hrs	100% at T_{irr} ≥ 3hrs	0.1 J/cm^2	
E. coli	0.025 - 1 mg/mL	λ = 400 - 800 nm (Visible – IR); I = 0.04 mW/cm^2 I = 0.1 mW/cm^2	2 hrs	100% at T_{irr} ≥ 40 min 100% at T_{irr} ≥ 25 min	96 J/cm^2 150 J/cm^2	[37]
S. aureus, S. typhimurium, P. aeruginosa, E. coli	1 mg/mL	λ = 368 nm (UV-A); I = n.d.	30 min 1 hr 1.5 hrs 2 hrs 2.5 hrs	100% at T_{irr} ≥ 1 hr	/	[38]

E. coli	1 mg/mL	λ = 310 - 400 nm (UV-A); I = 0.5 mW/cm^2	30 min 1 hr 1.5 hrs 2 hrs 2.5 hrs 3 hrs 3.5 hrs 4 hrs	100% at T_{irr} ≥ 4 hrs	1.8 J/cm^2	[39]

POLITECNICO
MILANO 1863

Table 2. Studies on the photocatalytic activity of TiO_2-based phoreactors against bacteria.

target	photoreactor	light parameters	irradiation time	antibacterial efficiency	Estimated minimum UV dose (according to Eq. 1)	Ref.
E. coli	TiO_2-coated Petri dish	λ = 310 - 400 nm (UV-A); I = 0.25 mW/cm^2	2 hrs 4 hrs 6 hrs	100% at T_{irr} ≥ 2 hrs	7.2 J/cm^2	[39]
M. smegmatis, *B. thuringiensis*	TiO_2 and Pt/TiO_2-coated glass	λ = 350 - 400 nm (UV-A); I = 0.65 mW/cm^2	10 min 20 min 30 min	99.8% at T_{irr} ≥ 30 min	1.1 J/cm^2	[40]
E. coli	TiO_2-coated glass	λ = 315-400 nm (UV-A); I = 1 mW/cm^2	15 min 30 min 1 hr 1.5 hrs	100% at T_{irr} ≥ 30 min	1.8 J/cm^2	[41]
E. coli	TiO_2-coated filter	λ = 355–375 nm (UV-A) λ = 280–320 nm (UV-B) λ = 254 nm (UV-C); I = 3.6 mW/cm^2	2 hrs 4 hrs 6 hrs	100% at T_{irr} ≥ 4 hrs	518 J/cm^2	[21]
E. coli, *P. aeruginosa,* *C. freundii,* *S. aureus,* *S. saprophyticus* *MRSA*	TiO_2-coated cellulose acetate monoliths	λ = 365 nm (UV-A); I = n.d.	5 min 10 min 15 min 20 min	100% at T_{irr} = 20 min	/	[22]

E. coli	TiO_2 film	λ = 365 nm (UV-A); I = n.d.	1 hr 3 hrs 6 hrs 8 hrs	100% at T_{irr} ≥ 6 hrs	/	[42]
E. coli	continuous annular reactor with TiO_2-coated filter	λ = 365 nm (UV-A); I = 0.5 mW/cm^2 I = 3.4 mW/cm$_2$	1.1 min	100%	0.03 J/cm^2 0.204 J/cm^2	[24]

Generally speaking, the UV photocatalytic inactivation of bacteria is mainly due to damage of the cell wall, membrane, enzymes, and nucleic acids by ROS and their stable byproducts [43]. In particular, Sunada *et al.* proposed a three-step mechanism for photokilling of bacteria on irradiated TiO_2-surfaces (**Figure 3**): i) attack of cell walls by ROS; ii) disordering of the inner cytoplasmic membrane and killing of the cell; iii) degradation of the intracellular components [44].

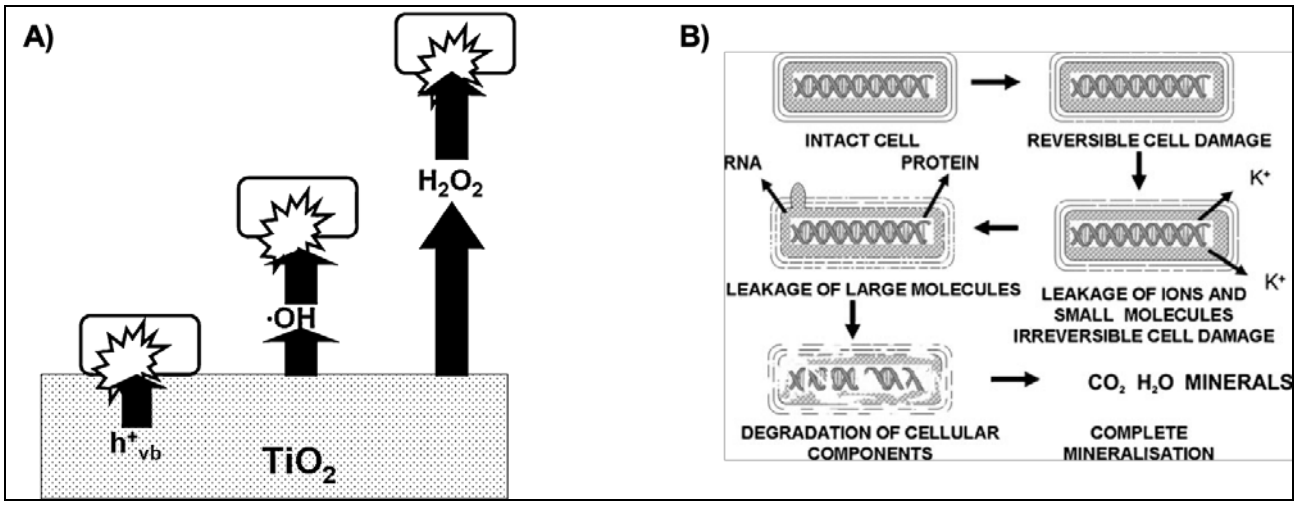


Figure 3. A) Role of ROS in the photocatalytic-induced killing mechanism of bacteria. Direct oxidation of cell components can occur when cells are in direct contact with the catalyst. Hydroxyl radicals and H_2O_2 are involved close to and distant from the catalyst, respectively. **B)** Scheme for photocatalytic killing and destruction of bacteria on TiO_2. Contact between the cells and TiO_2 may affect membrane permeability (reversible process). This is followed by increased damage to all cell wall layers, allowing leakage of small molecules such as ions. Damage at this stage may be irreversible, and it accompanies cell death. Furthermore, membrane damage allows leakage of higher molecular weight components such as proteins, which may be followed by protrusion of the cytoplasmic membrane into the surrounding medium through degraded areas of the peptidoglycan and cell lysis. Degradation of the internal components of the cell then occurs, followed by complete mineralization. The degradation process may occur progressively from the side of the cell in contact with the catalyst (adapted by [45]).

By contrast, it has been shown that far-UV-C light (λ = 207 - 222 nm; UV dose = 135 mJ/cm^2) efficiently inactivates drug-resistant bacteria, without apparent harm to exposed mammalian skin [46,47]. Short-wave UV-C radiation is highly disinfectant because the light can efficiently pass through and inactivate microorganisms as their size is typically of μm or smaller. This means that UV-C has an intensive biocidal effect and may render harmless viruses, bacteria, yeasts and fungi within seconds. Moreover, the microorganisms cannot gain resistance to UV radiation. Based on literature data, the radiant exposure of UV-C (i.e., UV dose) needed for complete sterilization was usually in the order of tens to hundreds of mJ/cm^2 [11,48,49].

3. Antiviral effects of UV light in combination or not with TiO_2

UV-activated photocatalysis has been found to inactivate mammalian viruses including poliovirus 1, avian and human influenza viruses, and SARS coronavirus, as reported in **Table 3**.

Experimantal findings demonstrate that the photocatalysis induced by TiO_2 significantly inactivates the influenza virus by degrading viral proteins, and the degradation depends on the UV-A intensity (I) and irradiation time (T_{irr}).

Besides, simple exposition to UV light has been reported to be an efficient way to inactivate viruses. It has been shown that effective inactivation occurs under an environmental level of UV-A intensity, as reported in literature [50]. Moreover, using a conventional UV-C lamp at λ = 254 nm capable of providing a UV dose of 1.1 mJ/cm^2, McDevitt *et al.* [51] found an inactivation of ~95% of airborne influenza virus H1N1 virus. Similar results were found by Welch D *et al.* [52], but in different conditions (i.e., 30 min-exposure at far UV-C light (λ = 207 - 222 nm), corresponding to a very low dose of 2 mJ/cm^2), and by Tsunetsugu-Yokota [53] (i.e., 20 min-exposition at UV-A light intensity of 1.3 mW/cm^2, corresponding to a UV dose of 1.6 J/cm^2).

POLITECNICO
MILANO 1863

Table 3. Studies on the photocatalytic activity of TiO_2-based phoreactors against viruses.

target	photoreactor	light parameters	irradiation time	antiviral efficacy	Estimated minimum UV dose (according to Eq. 1)	Ref.
influenza virus H1N1	TiO_2-coated porous ceramic substrate	λ = 365 nm (UV-A); I = 1 mW/cm^2	5 min 10 min 15 min 30 min	100% at T_{irr} ≥ 5 min	0.3 J/cm^2	[19]
vaccinia virus, influenza virus H3N3	TiO_2 and Pt/TiO_2-coated glass	λ = 350-400 nm (UV-A); I = 0.65 mW/cm^2	10 min 20 min 30 min	99.8% at T_{irr} ≥ 30 min	1.1 J/cm^2	[40]
influenza virus H1N1	TiO_2-coated glass	λ = 352 nm (UV-A); I = 0.001 mW/cm^2 I = 0.01 mW/cm^2 I = 0.1 mW/cm^2 I = 1 mW/cm^2	2 hrs 4 hrs 6 hrs 8 hrs	100%	0.8-14.4 J/cm^2	[50]
HSV-1 virus	TiO_2 film	λ = 365 nm (UV-A); I = n.d.	6 hrs	100%	/	[42]
noravirus	TiO_2 photocatalytic reactor	λ = 254 nm (UV-B)	5 min 10 min 15 min 20 min	100% at T_{irr} ≥ 10 min	2.7 J/cm^2	[54]

POLITECNICO
MILANO 1863

4. Conclusions

Photocatalytic inactivation of microorganisms is a synergistic bactericidal effect of light and oxidative radicals generated by TiO_2. The extent of each one varies as a function of different physical parameters.

A positive effect was observed and depended on:

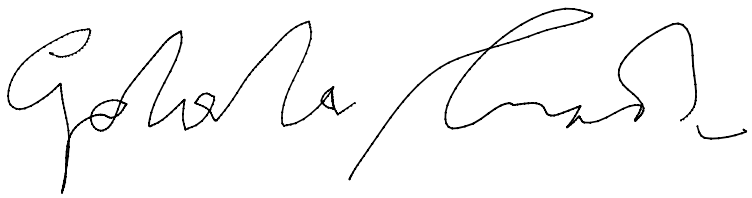
- UV light intensity (optimal range: 0.5 – 3.5 mW/cm^2)
- irradiation time (optimal range: 30 min - 2 hrs)
- TiO_2 concentration in solution (optimal range: 0. 5 – 1.0 mg/mL)

Other parameters which affect the photocatalytic bacterial inactivation are:

- Immobilization of catalyst onto a surface
- The crystalline form of catalyst was studied using suspended and immobilized TiO2.

In conclusion, according to the data shown in the tables herein above, UV-A-induced photocatalysis of TiO_2 or TiO_2-based surface at a suitable light intensity (I) has the potential to provide a powerful tool in the fight against transmission of infectious disease in a very short irradiation time (T_{irr}) of about 30 min. As a valuable alternative, inactivation of airborne microorganisms can be reached by using 30-min UV light irradiation time (T_{irr}) across the UV-C spectrum, depending on the UV light intensity (I).

Prof. Gabriele Candiani



POLITECNICO
MILANO 1863

References

1. Kim, J.; Jang, J. Inactivation of airborne viruses using vacuum ultraviolet photocatalysis for a flow-through indoor air purifier with short irradiation time. *Aerosol Sci. Technol.* **2018**, *52*, 557–566.
2. Xu, Z.; Wu, Y.; Shen, F.; Chen, Q.; Tan, M.; Yao, M. Bioaerosol Science, Technology, and Engineering: Past, Present, and Future. *Aerosol Sci. Technol.* **2011**, *45*, 1337–1349.
3. Candiani, G.; Del Curto, B.; Cigada, A. Improving indoor air quality by using the new generation of corrugated cardboard-based filters. *J. Appl. Biomater. Funct. Mater.* **2012**, *10*, 157–162.
4. Yu, B.F.; Hu, Z.B.; Liu, M.; Yang, H.L.; Kong, Q.X.; Liu, Y.H. Review of research on air-conditioning systems and indoor air quality control for human health. *Int. J. Refrig.* 2009, *32*, 3–20.
5. Ryan, K.; Mccabe, K.; Clements, N.; Hernandez, M.; Miller, S.L. Inactivation of Airborne Microorganisms Using Novel Ultraviolet Radiation Sources in Reflective Flow-Through Control Devices. *Aerosol Sci. Technol.* **2010**, *44*, 541–550.
6. Lee, B.U. Life Comes from the Air: A Short Review on Bioaerosol Control. *Aerosol Air Qual. Res.* **2011**, *11*, 921–927.
7. Hwang, G.B.; Jung, J.H.; Jeong, T.G.; Lee, B.U. Effect of hybrid UV-thermal energy stimuli on inactivation of S. epidermidis andB. subtilis bacterial bioaerosols. *Sci. Total Environ.* **2010**, *408*, 5903–5909.
8. Hollaender, A.; Du Buy, H.G.; Ingraham, H.S.; Wheeler, S.M. Control of air-borne microorganisms by ultraviolet floor irradiation. *Science (80-.).* 1944, *99*, 130–131.
9. Kowalski, W. *Ultraviolet germicidal irradiation handbook : uvgi for air and surface disinfection.*; Springer, 2014; ISBN 9783642424809.
10. Kujundzic, E.; Matalkah, F.; Howard, C.J.; Hernandez, M.; Miller, S.L. UV air cleaners and upper-room air ultraviolet germicidal irradiation for controlling airborne bacteria and fungal spores. *J. Occup. Environ. Hyg.* **2006**, *3*, 536–546.
11. Conner-Kerr, T.A.; Sullivan, P.K.; Gaillard, J.; Franklin, M.E.; Jones, R.M. The effects of ultraviolet radiation on antibiotic-resistant bacteria in vitro. *Ostomy. Wound. Manage.* **1998**, *44*, 50–56.
12. Budowsky, E.I.; Bresler, S.E.; Friedman, E.A.; Zheleznova, N. V. Principles of selective inactivation of viral genome - I. UV-induced inactivation of influenza virus. *Arch. Virol.* **1981**, *68*, 239–247.
13. Setlow, R.B.; Grist, E.; Thompson, K.; Woodhead, A.D. Wavelengths effective in induction of malignant melanoma. *Proc. Natl. Acad. Sci. U. S. A.* **1993**, *90*, 6666–6670.
14. Benabbou, A.K.; Derriche, Z.; Felix, C.; Lejeune, P.; Guillard, C. Photocatalytic inactivation of Escherischia coli. Effect of concentration of TiO2 and microorganism, nature, and intensity of UV irradiation. *Appl. Catal. B Environ.* **2007**, *76*, 257–263.
15. Gaya, U.I.; Abdullah, A.H. Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems. *J. Photochem. Photobiol. C Photochem. Rev.* 2008, *9*, 1–12.
16. Pelaez, M.; Nolan, N.T.; Pillai, S.C.; Seery, M.K.; Falaras, P.; Kontos, A.G.; Dunlop, P.S.M.; Hamilton, J.W.J.; Byrne, J.A.; O'Shea, K.; et al. A review on the visible light active titanium dioxide photocatalysts for environmental applications. *Appl. Catal. B Environ.* 2012, *125*, 331–349.
17. Friedmann, D.; Mendive, C.; Bahnemann, D. TiO2 for water treatment: Parameters affecting the kinetics and mechanisms of photocatalysis. *Appl. Catal. B Environ.* **2010**, *99*, 398–406.
18. Visai, L.; de Nardo, L.; Punta, C.; Melone, L.; Cigada, A.; Imbriani, M.; Arciola, C.R.

Titanium oxide antibacterial surfaces in biomedical devices. *Int. J. Artif. Organs* **2011**, *34*, 929–946.
19. Daikoku, T.; Takemoto, M.; Yoshida, Y.; Okuda, T.; Takahashi, Y.; Ota, K.; Tokuoka, F.; Kawaguchi, A.T.; Shiraki, K. Decomposition of Organic Chemicals in the Air and Inactivation of Aerosol-Associated Influenza Infectivity by Photocatalysis. *Aerosol Air Qual. Res.* **2015**, *15*, 1469–1484.
20. Josset, S.; Taranto, J.; Keller, N.; Keller, V.; Lett, M.C. Photocatalytic Treatment of Bioaerosols: Impact of the Reactor Design. *Environ. Sci. Technol.* **2010**, *44*, 2605–2611.
21. Pigeot-Remy, S.; Lazzaroni, J.C.; Simonet, F.; Petinga, P.; Vallet, C.; Petit, P.; Vialle, P.J.; Guillard, C. Survival of bioaerosols in HVAC system photocatalytic filters. *Appl. Catal. B Environ.* **2014**, *144*, 654–664.
22. Rodrigues-Silva, C.; Miranda, S.M.; Lopes, F.V.S.; Silva, M.; Dezotti, M.; Silva, A.M.T.; Faria, J.L.; Boaventura, R.A.R.; Vilar, V.J.P.; Pinto, E. Bacteria and fungi inactivation by photocatalysis under UVA irradiation: liquid and gas phase. *Environ. Sci. Pollut. Res.* **2017**, *24*, 6372–6381.
23. Lin, W.C.; Chen, C.N.; Tseng, T.T.; Wei, M.H.; Hsieh, J.H.; Tseng, W.J. Micellar layer-by-layer synthesis of TiO2/Ag hybrid particles for bactericidal and photocatalytic activities. *J. Eur. Ceram. Soc.* **2010**, *30*, 2849–2857.
24. Pal, A.; Pehkonen, S.O.; Yu, L.E.; Ray, M.B. Photocatalytic inactivation of airborne bacteria in a continuous-flow reactor. *Ind. Eng. Chem. Res.* **2008**, *47*, 7580–7585.
25. Keller, N.; Rebmann, G.; Barraud, E.; Zahraa, O.; Keller, V. Macroscopic carbon nanofibers for use as photocatalyst support. In Proceedings of the Catalysis Today; Elsevier, 2005; Vol. 101, pp. 323–329.
26. Miyagi, T.; Kamei, M.; Mitsuhashi, T.; Ishigaki, T.; Yamazaki, A. Charge separation at the rutile/anatase interface: A dominant factor of photocatalytic activity. *Chem. Phys. Lett.* **2004**, *390*, 399–402.
27. Fujishima, A.; Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* **1972**, *238*, 37–38.
28. Fujishima, A.; Zhang, X. Titanium dioxide photocatalysis: present situation and future approaches. *Comptes Rendus Chim.* 2006, *9*, 750–760.
29. Kikuchi, Y.; Sunada, K.; Iyoda, T.; Hashimoto, K.; Fujishima, A. Photocatalytic bactericidal effect of TiO2 thin films: Dynamic view of the active oxygen species responsible for the effect. *J. Photochem. Photobiol. A Chem.* **1997**, *106*, 51–56.
30. Sunada, K.; Kikuchi, Y.; Hashimoto, K.; Fujishima, A. Bactericidal and detoxification effects of TiO2 thin film photocatalysts. *Environ. Sci. Technol.* **1998**, *32*, 726–728.
31. Kühn, K.P.; Chaberny, I.F.; Massholder, K.; Stickler, M.; Benz, V.W.; Sonntag, H.G.; Erdinger, L. Disinfection of surfaces by photocatalytic oxidation with titanium dioxide and UVA light. *Chemosphere* **2003**, *53*, 71–77.
32. Yu, J.C.; Ho, W.; Lin, J.; Yip, H.; Wong, P.K. Photocatalytic activity, antibacterial effect, and photoinduced hydrophilicity of TiO2 films coated on a stainless steel substrate. *Environ. Sci. Technol.* **2003**, *37*, 2296–2301.
33. Brook, L.A.; Evans, P.; Foster, H.A.; Pemble, M.E.; Steele, A.; Sheel, D.W.; Yates, H.M. Highly bioactive silver and silver/titania composite films grown by chemical vapour deposition. *J. Photochem. Photobiol. A Chem.* **2007**, *187*, 53–63.
34. Ditta, I.B.; Steele, A.; Liptrot, C.; Tobin, J.; Tyler, H.; Yates, H.M.; Sheel, D.W.; Foster, H.A. Photocatalytic antimicrobial activity of thin surface films of TiO 2, CuO and TiO2/CuO dual layers on Escherichia coli and bacteriophage T4. *Appl. Microbiol. Biotechnol.* **2008**, *79*, 127–133.
35. Matsunaga, T.; Tomoda, R.; Nakajima, T.; Wake, H. Photoelectrochemical sterilization of microbial cells by semiconductor powders. *FEMS Microbiol. Lett.* **1985**, *29*, 211–214.

36. Kim, B.; Kim, D.; Cho, D.; Cho, S. Bactericidal effect of TiO2 photocatalyst on selected food-borne pathogenic bacteria. *Chemosphere* **2003**, *52*, 277–281.
37. Rincón, A.G.; Pulgarin, C. Photocatalytical inactivation of E. coli: Effect of (continuous-intermittent) light intensity and of (suspended-fixed) TiO 2 concentration. *Appl. Catal. B Environ.* **2003**, *44*, 263–284.
38. Cushnie, T.P.T.; Robertson, P.K.J.; Officer, S.; Pollard, P.M.; McCullagh, C.; Robertson, J.M.C. Variables to be considered when assessing the photocatalytic destruction of bacterial pathogens. *Chemosphere* **2009**, *74*, 1374–1378.
39. Verdier, T.; Coutand, M.; Bertron, A.; Roques, C. Antibacterial activity of TiO 2 photocatalyst alone or in coatings on E. coli: The influence of methodological aspects. *Coatings* **2014**, *4*, 670–686.
40. Kozlova, E.A.; Safatov, A.S.; Kiselev, S.A.; Marchenko, V.Y.; Sergeev, A.A.; Skarnovich, M.O.; Emelyanova, E.K.; Smetannikova, M.A.; Buryak, G.A.; Vorontsov, A. V. Inactivation and mineralization of aerosol deposited model pathogenic microorganisms over TiO2 and Pt/TiO2. *Environ. Sci. Technol.* **2010**, *44*, 5121–5126.
41. Kim, D.; Kwak, S.Y. Photocatalytic inactivation of e coli with a mesoporous Ti0 2coated film using the film adhesion method. *Environ. Sci. Technol.* **2009**, *43*, 148–151.
42. Hajkova, P.; Spatenka, P.; Horsky, J.; Horska, I.; Kolouch, A. Photocatalytic effect of TiO2 films on viruses and bacteria. *Plasma Process. Polym.* **2007**, *4*, 397–401.
43. Guo, Q.; Xu, C.; Ren, Z.; Yang, W.; Ma, Z.; Dai, D.; Fan, H.; Minton, T.K.; Yang, X. Stepwise photocatalytic dissociation of methanol and water on TiO 2(110). *J. Am. Chem. Soc.* **2012**, *134*, 13366–13373.
44. Sunada, K.; Watanabe, T.; Hashimoto, K. Studies on photokilling of bacteria on TiO 2 thin film. *J. Photochem. Photobiol. A Chem.* **2003**, *156*, 227–233.
45. Foster, H.A.; Ditta, I.B.; Varghese, S.; Steele, A. Photocatalytic disinfection using titanium dioxide: Spectrum and mechanism of antimicrobial activity. *Appl. Microbiol. Biotechnol.* **2011**, *90*, 1847–1868.
46. Buonanno, M.; Randers-Pehrson, G.; Bigelow, A.W.; Trivedi, S.; Lowy, F.D.; Spotnitz, H.M.; Hammer, S.M.; Brenner, D.J. 207-nm UV Light - A Promising Tool for Safe Low-Cost Reduction of Surgical Site Infections. I: In Vitro Studies. *PLoS One* **2013**, *8*, 1–7.
47. Buonanno, M.; Stanislauskas, M.; Ponnaiya, B.; Bigelow, A.W.; Randers-Pehrson, G.; Xu, Y.; Shuryak, I.; Smilenov, L.; Owens, D.M.; Brenner, D.J. 207-nm UV light - A promising tool for safe low-cost reduction of surgical site infections. II: In-vivo safety studies. *PLoS One* **2016**, *11*, 1–12.
48. Sullivan, P.K.; Conner-Kerr, T.A. A comparative study of the effects of UVC irradiation on select procaryotic and eucaryotic wound pathogens. *Ostomy. Wound. Manage.* **2000**, *46*, 28–34.
49. Mohr, H.; Steil, L.; Gravemann, U.; Thiele, T.; Hammer, E.; Greinacher, A.; Müller, T.H.; Völker, U. A novel approach to pathogen reduction in platelet concentrates using short-wave ultraviolet light. *Transfusion* **2009**, *49*, 2612–2624.
50. Nakano, R.; Ishiguro, H.; Yao, Y.; Kajioka, J.; Fujishima, A.; Sunada, K.; Minoshima, M.; Hashimoto, K.; Kubota, Y. Photocatalytic inactivation of influenza virus by titanium dioxide thin film. *Photochem. Photobiol. Sci.* **2012**, *11*, 1293–1298.
51. McDevitt, J.J.; Rudnick, S.N.; Radonovich, L.J. Aerosol susceptibility of influenza virus to UV-C light. *Appl. Environ. Microbiol.* **2012**, *78*, 1666–1669.
52. Welch, D.; Buonanno, M.; Grilj, V.; Shuryak, I.; Crickmore, C.; Bigelow, A.W.; Randers-Pehrson, G.; Johnson, G.W.; Brenner, D.J. Far-UVC light: A new tool to control the spread of airborne-mediated microbial diseases. *Sci. Rep.* **2018**, *8*, 1–7.
53. Tsunetsugu-Yokota, Y. Large-scale preparation of UV-inactivated SARS coronavirus virions for vaccine antigen. *Methods Mol. Biol.* **2008**, *454*, 119–126.

54. Kim, S.H.; Shahbaz, H.M.; Park, D.; Chun, S.; Lee, W.; Oh, J.W.; Lee, D.U.; Park, J. A combined treatment of UV-assisted TiO2 photocatalysis and high hydrostatic pressure to inactivate internalized murine norovirus. *Innov. Food Sci. Emerg. Technol.* **2017**, *39*, 188–196.