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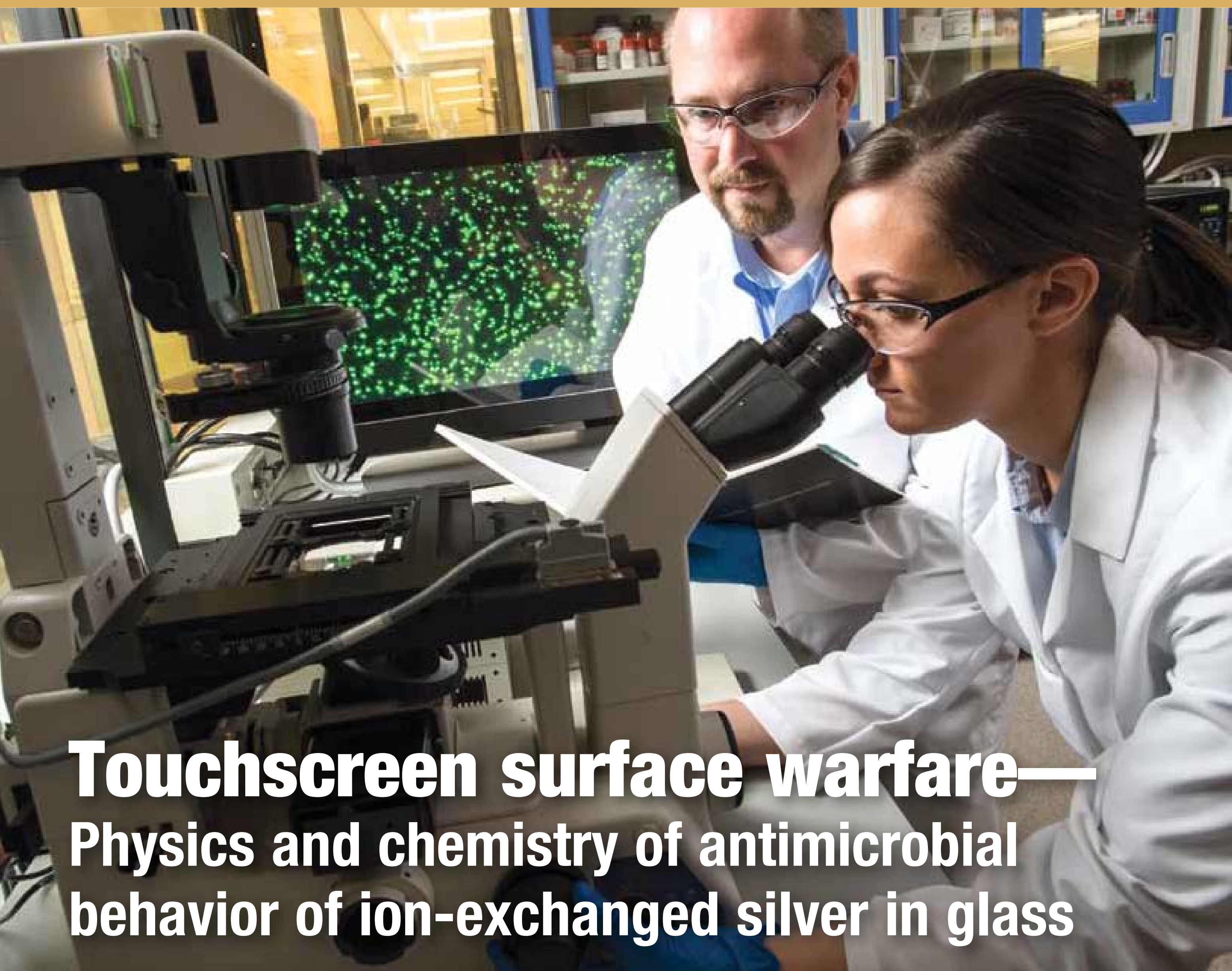

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Light intensity can vary dramatically in indoor spaces, which presents a challenge for photocatalytic air purification.

Passive purification—Effectiveness of photocatalytic titanium dioxide to convert pathogens and pollutants

By Karen Welch

Titanium dioxide has the potential to clean and disinfect under the right lighting conditions and environment.

Much has been written in mainstream and scientific sources about technologies that purify air or provide self-cleaning properties to clothing and other items by harnessing the oxidative power of light. Titanium dioxide (TiO_2) provides these exciting benefits, expanding its utility beyond its long history as a white colorant in paint and a common ingredient in cosmetics, sunscreens, ceramic tile, windows, and cement. When exposed to the correct wavelength and intensity of light, TiO_2 acts as a photocatalyst and oxidizes diverse contaminants that cause stains, odors, and air pollution. It also kills bacteria, fungi, and other microorganisms.

TiO_2 is a semiconductor and a photocatalytic material. It exists as anatase, rutile, and brookite polymorphs. All possess photocatalytic activity, but the anatase form (Figure 1) has proved to be the most effective photocatalyst for cleaning or purifying applications. When activated by light, electrons in the semiconductor are excited from the valence band to the conduction band. These electrons, and the holes they leave behind, react with oxygen and water to form superoxide and hydroxyl radicals (see sidebar, p. 28). These reactive oxygen species (ROS) and electron holes are powerful oxidants that provide self-cleaning and self-sanitizing properties to TiO_2.[1]

The use of photocatalytically derived ROS to oxidize organic and inorganic compounds has many real world applications. For example, TiO_2 has been incorporated into window glass to fabricate self-cleaning windows. Pilkington, Saint-Gobain, PPG, Cardinal Glass Industries, and Nippon Sheet Glass offer commercial self-cleaning window products. Another self-cleaning application uses the photocatalyst within the light covers in highway tunnels, where activation occurs because of the proximity and intensity of the lamps themselves.[2] Also, "Wendy," an outdoor interactive art installation at the Museum of Modern Art (New York), in summer 2012, took advantage of the activity of sunlight-powered TiO_2 nanoparticles sprayed on its nylon pyrometric-cone-shaped appears to decrease the levels of nitrogen dioxide and other airborne pollutants (Figure 2). In the future, TiO_2 coatings may be applied to surgical implants to prevent bacterial colonization and growth, while not threatening native bone and tissue growth.

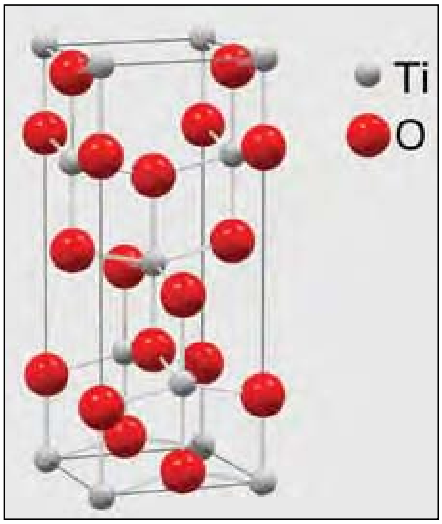

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Figure 1. TiO_2 anatase crystal structure.

This article briefly reviews TiO_2 photocatalytic technology and the research that led to its potential as an environmental purifier. The article also attempts to provide perspective to these claims by discussing the technology's current capabilities for use in the home environment and technical issues surrounding its use.

History—From water splitter to germ killer

Fujishima and Honda[3] demonstrated the photocatalytic effect in 1972 when they split water molecules into hydrogen and oxygen molecules using TiO_2 activated with light wavelengths <415 nm. Light with wavelengths from 320 to 400 nm is in the ultraviolet A (UVA) range. In 1985, Matsunaga et al.[4] reported that TiO_2–platinum semiconductor powder could kill bacteria and yeast.

Since that time, the effectiveness of TiO_2 has been demonstrated against a wide range of organisms. In 2003, Ibáñez et al.[5] demonstrated bacterial concentration reductions of almost 4 to 5 orders of magnitude in 40 min for individual strains of gram-negative bacteria. (Gram-negative bacteria cause infections, such as pneumonia and wound infections. They are increasingly resistant to antibiotic treatment.) The light source was a long-wavelength UV lamp, and light intensity ranged from 14 W/m^2 for *Pseudomonas aeruginosa* to 55 W/m^2 for *E. coli, Enterobacter cloaceae, and Salmonella typhimurium.* Another study by Dunlop et al.[6] in 2010 showed the effectiveness of TiO_2-treated surfaces activated with UVA light against clinically relevant organisms, including *E. coli, Pseudomonas aeruginosa*, methicillin-resistant *Staphylococcus aureus* (MRSA), and spores of *Clostridium difficile*. (Figure 3 shows typical bacterial colony growth in a petri dish.)

UVA irradiation of 30 W/m^2 was used to achieve a 3 log kill (99.9% reduction) within 60 min for all but the clinically relevant *E. coli* strain (3 log kill in 80 min) and a 2.6 log kill in 5 h for the *Clostridium* spores. (The unit log kill represents a 90% kill rate or 10% survival rate. Thus, 3 log kill represents 1,000-fold reduction of pathogens, or 99.9% kill rate.) These results strongly support the antibacterial potential of photoactivated TiO_2 under robust lighting conditions. They also highlight the differences in susceptibility to the photocatalytic activity of TiO_2 among various organisms.

Light intensity and phase stability

Researchers report a direct relationship between the photocatalytic activity of TiO_2 and UVA intensity.[7] One 2009 study examining photocatalytic action on organic vapors using commercially available TiO_2-treated tile showed that decreasing UVA light intensity from 10 to 1 W/m^2 decreased photocatalytic efficiency to 15% of the original value.[8] This need for relatively intense UVA light exposure is a concern for indoor applications of photocatalytic technology. Because UVA is known to cause skin cancer and premature skin aging, domestic lighting products are currently designed and manufactured to minimize emissions in this range. As a result, product designers do not expect the light energy needed to generate and sustain photocatalytic activity to be present consistently in the typical home.

We demonstrated this variability in UVA intensity with measurements taken during the late morning of a fall day in North Carolina. The UVA intensity of direct sunlight streaming through a home window was 60 W/m^2. However, the UVA light intensity measured 10 ft away from the same window was 0.033 W/m^2, a decrease by a factor of more than 1,800. A similar room on p. 25 shows the wide variability of light intensity typical of indoor spaces.

We took additional measurements at night in the presence of typical fluorescent indoor lighting with all of the light fixtures in a master bedroom/bath suite turned on. Under these conditions UVA intensity varied from 0.073 W/m^2 at the sink surface to 0.002 W/m^2 in a corner of the shower enclosure. Again, the UVA intensity levels were 2 to 4 orders of magnitude below those found in outdoor or high-intensity UV exposure applications. These measurements

(Credit: Wikimedia Commons)

Figure 2. 'Wendy,' the winning design of MoMA's Young Architects Program in 2012. TiO_2 nanoparticles sprayed on its surfaces neutralize nitrogen dioxide air pollution.

Figure 3. Bacterial colonies growing on an agar plate.

indicate that the levels of UVA lighting indoors can be weak and highly variable, even within the same room. Therefore, depending on photocatalytic technology activated by UVA light at levels that are not common or safe for indoor spaces is clearly a limitation and technical challenge.

To address this limitation, researchers are working to achieve photocatalytic activation under visible-light conditions by incorporating other elements, such as carbon, nitrogen, silver, or copper within or on the surface of the TiO_2 crystal structure.[9] Many of these studies demonstrate photocatalytic activity under lighting conditions not consistently or universally found in the home.

However, a few have demonstrated antibacterial activity under weaker UV light exposure. Sunada et al.[10] made antibacterial surfaces that responded to weak UV light at intensities of 0.01 to 0.4 W/m^2. The study described the use of a thin film of TiO_2 prepared by dip coating followed by calcination in a furnace at 500°C. The authors added copper to the surface by liquid deposition followed by a UV light treatment. They measured a 1.6-log bacterial decrease after 3 h of illumination at 0.4 W/m^2. At the lowest UVA light level, 0.01 W/m^2, the bacterial decrease was ~80% after 3 h and was not significantly different from the decrease achieved in the dark by the effect of the added copper.

Sato and Taya[11] used a similar copper-doped TiO_2-coated glass plate (prepared by spin coating and drying at 100°C) with visible light intensity levels of 3 and 28 W/m^2 provided by a white fluorescent tubular lamp. They measured a 3 log kill (99.9% reduction) at 28 W/m^2 in 30 min. However, this light intensity is not significantly lower than what could be produced from sunlight exposure. The authors demonstrated that a significant portion of the antimicrobial effect was caused by copper ions that leached from the photocatalyst surface. Sato and Taya demonstrated that a concentration of 10 $mmol/m^3$ copper in solution provided the optimal photocaytalytic activity. This concentration was comparable with the amount of copper that leached into the aqueous solution in contact with the tile after 6 h while under irradiation. They further demonstrated that once the amount of available copper decreased below a threshold concentration, the TiO_2 film became much less effective under visible light conditions.

High-temperature manufacturing processes, such as those needed to produce ceramics and sanitary ware with high-touch or durable surface properties, present another technical challenge to incorporating photocatalytic TiO_2. The phase transition from the more photoactive anatase form of TiO_2 to the more stable rutile form begins at ~600°C for pure anatase, which is well below conventional firing temperatures.[12] Unregulated polymorphic transformations such as this would limit the ability to incorporate photocatalytic materials. Added dopants—metallic and nonmetallic—and the impurities present in TiO_2 can affect the phase stability of the anatase form. However, the high-temperature stability of anatase TiO_2 also depends on many other factors involved in TiO_2 synthesis and preparation. Aluminum, silicon, and zirconium oxides are effective at stabilizing the anatase form at increased temperatures.

However, photocatalytic TiO_2 is applied to ceramics during postfiring to avoid the phase transition from anatase to rutile. Optical properties and durability of the surface as well as maintaining photocatalytic activity are key concerns. One reported method involves depositing cold nano-TiO_2 powder on glazed ceramic articles as they exit the heat zone of the kiln.[13] Dopants may be added in this step, or in a separate step. Liquid-phase depositions with secondary firings also are used. A recent report describes a scale-up study in which a TiO_2 coating was applied by ink jet or roller printing.[14] Several postapplication firing temperatures were explored, and the authors identified a compromise between the photocatalytic activity achieved with lower temperature firing and the surface durability achieved at a higher temperature. Another report describes a liquid-phase deposition of a silver-containing TiO_2 film by immersion in an aqueous solution followed by annealing at an optimal temperature of 600°C.[15]

Standard testing methodology

One important aspect in the evaluation of new technologies is the establishment and acceptance of standardized testing to measure relevant

Table 1. ISO standards for testing photocatalytic activity

Standard	Title
ISO 10677:2011	Fine ceramics (advanced ceramics, advanced technical ceramics)—Ultraviolet light source for testing semiconducting photocatalytic materials
ISO 10678:2010	Fine ceramics (advanced ceramics, advanced technical ceramics)—Determination of photocatalytic activity of surfaces in an aqueous medium by degradation of methylene blue
ISO 13125:2013	Fine ceramics (advanced ceramics, advanced technical ceramics)—Test method for antifungal activity of semiconducting photocatalytic materials
ISO 22197-1:2007	Fine ceramics (advanced ceramics, advanced technical ceramics)—Test method for air-purification performance of semiconducting photocatalytic materials—Part 1: Removal of nitric oxide
ISO 27447:2009	Fine ceramics (advanced ceramics, advanced technical ceramics)—Test method for antibacterial activity of semiconducting photocatalytic materials
ISO 27448:2009	Fine ceramics (advanced ceramics, advanced technical ceramics)—Test method for self-cleaning performance of semiconducting photocatalytic materials—Measurement of water contact angle

effects. Because of questions surrounding indoor light activation of TiO_2, appropriate standards are essential for evaluating the performance of materials under conditions that are representative of the home or other indoor environments. There are several ISO protocols for the photocatalytic activity of ceramic tile, including standards for antibacterial and antifungal activity as well as degradation of organic and inorganic molecules.

Table 1 lists the International Organization for Standards (ISO) standards reviewed at the time of this writing. Each of these standards specifies the use of a light source whose primary output is in the UVA range. The antifungal standard (ISO 13125:2013) specifies two light levels, 4 and 8 W/m^2. It further indicates that higher-intensity light is required, because fungal spores are more resistant to photocatalytic action than bacteria. The antibacterial standard (ISO 27447:2009) covers four possible regimes ranging from low indoor light to a level approximating an indoor area with sunlight exposure. The other standards surveyed at present specify light intensities of ≥10 W/m^2. Thus, we can assess only the antibacterial activity of TiO_2 catalysts under lower light levels. Moreover, visible-light active photocatalysts do not have a comparable set of standard procedures to test their performance.

Photocatalysis and the science of defects

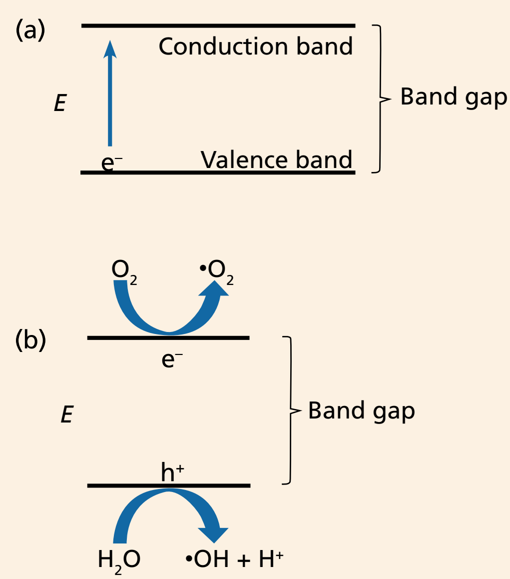
Two important factors that determine the effectiveness of a photocatalytic material, such as TiO_2, are the rate of formation of charge carriers—electrons and holes—and the rate of recombination of those charge carriers.[12] After the charge carriers form, conditions must be right for them to react with water, oxygen, or other chemical compounds.

Understanding of photocatalytic activity requires more, namely, to identify defects in the lattice structure of the material as sites that stabilize charge carriers to produce a more photoactive material. In TiO_2, titanium and oxygen atoms are arranged as TiO_6 octahedra. The lattice defects result at edges and boundaries in the material where octahedra are not complete. The defects may be in the form of an oxygen vacancy or a titanium atom in a reduced state.

A discussion of defects can be extended to the incorporation of dopants into the TiO_2 structure. Substitutions of cations or anions in the material can increase or decrease the number of oxygen vacancies in the material, in addition to the chemical effect of the dopant itself. These lattice changes modulate the material's band gap (the difference in energy between the valence band and the conduction band) or introduce midgap states. Dopants also can increase the lifetimes of electrons and holes and promote absorption of species on the TiO_2 surface.[12]

(a) When a semiconductor absorbs light with energy (E) that is equal to or greater than its band gap, an electron is promoted from the valence band to the conduction band. This electron (e^-), as well as the hole (h^+) in the valence band, can participate in chemical reactions.

(b) The electron can react with oxygen to produce a superoxide radical, while the hole can react with water to form a hydroxyl radical, or it can react with an organic molecule.



More air quality questions

Air purification by oxidation of organic and inorganic compounds is one of the important benefits claimed for TiO_2-based technologies. Thus, questions about the effect of TiO_2 on air quality in the home are of utmost importance. The environment in enclosed spaces can be more polluted than what is found outdoors, and indoor pollutants can irritate the eyes and respiratory tract and exacerbate allergies and asthma. Hydroxyl radical, one of the ROS generated by photocatalytic TiO_2, forms in the home from the action of ozone on the chemical compounds found in natural home-cleaning products.[16] Once formed, the hydroxyl radical participates in oxidation reactions that contribute to the mix of chemicals that constitute indoor pollution.

Studies on the action of photocatalytic TiO_2 for air purification have approximated the indoor environment by including more than one compound to be oxidized.[17,18] However, air in the home may contain more than 60 volatile organic compounds (VOCs).[19] Studies with multiple compounds indicate that these compounds may be oxidized at various rates based on their affinity for the TiO_2 surface. Water also "competes" with organic molecules for sites on the TiO_2 surface, and relative humidity is accordingly an important factor in the oxidation rates of gaseous molecules by photocatalytic oxidation. Thus, in a mixture of organic molecules, one or more may be oxidized completely through several reactions to carbon dioxide as a final product, while another group is partially oxidized and other molecules are unaffected. Because partially oxidized VOCs may be more harmful or toxic than their precursors, this question deserves careful attention.[16,20] The potential for TiO_2 photocatalysts to produce toxic products from household cleaners or other sources also is a concern.[21]

Another important question is the rate of oxidation of VOCs at the levels that are found in the home—typically in the parts-per-billion. Multiple studies demonstrate that the rate at which TiO_2-treated surfaces convert organic compounds decreases as the ambient concentration of the compounds decreases.[17,18] An evaluation of commercial TiO_2-treated paints revealed no oxidation of a mixture of organic compounds each at levels of 30–100 ppb with 1 W/m^2 UVA light.[22] The authors further demonstrated that air exchange was more effective in removing these VOCs from the 1-m^3 sample chamber. Observation of the oxidation of formaldehyde was complicated, because the illuminated painted surfaces gave off formaldehyde. Compounds that were offgassed from the paint samples in the presence of light were oxidized by the TiO_2 in the paint, although complete oxidation to carbon dioxide was not discussed.

A final question results from the tendency of photocatalytic surfaces to become fouled by the products of photocatalytic reactions.[23,24] Heating, or prolonged periods of strong UV irradiation may be needed to clean the catalyst surface. Washing with water may suffice in other cases.

Summary

Photocatalytic TiO_2 has significant potential in applications where high-intensity UV light or the UVA component of sunlight provides sufficient energy to promote photocatalytic reactions. In lower-light environments, such as those found in the home, photocatalytic activity is significantly decreased in areas where sufficient light is not consistently available during daytime and nighttime hours. In a survey of several ISO standards pertaining to photocatalytic ceramics, only the antibacterial standard includes lower-light-activity measurements.

The claims regarding the activity of TiO_2 are broad and far-reaching, including bacteria, fungi, and a diverse group of volatile compounds, all found in indoor environments. Limited testing of multiple chemical or biological species simultaneously means that it is not certain how photocatalytic TiO_2-based materials will perform indoors in the presence of multiple challenges. Moreover, questions about the effect of TiO_2-based materials on indoor air quality should be addressed, because a photocatalyst made ineffective by inadequate lighting or other means may have little to no effect on indoor air quality, or it may serve to increase the concentrations of potentially harmful indoor pollutants. Although its potential for cleaning and disinfecting surfaces remains, there is a strong indication that TiO_2 photocatalytic technology will not "shine" in every light or in every environment.

About the author

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References

[1]O.K. Dalrymple, E. Stefanakos, M.A. Trotz, and T.D. Goswami, "A review of the mechanisms and modeling of photocatalytic disinfection," *Appl. Catal. B*, **98**, 27–38 (2010).

[2]H. Honda, A. Ishizaki, R. Soma, K. Hashimoto, and A. Fujishima, "Application of photocatalytic reactions caused by TiO_2 film to improve the maintenance factor of lighting systems," *J. Illum. Eng. Soc.*, **28**, 42–47 (1998).

[3]A. Fujishima and F. Honda, "Electrochemical photolysis of water at a semiconductor electrode," *Nature*, **238**, 38–39 (1972).

[4]T. Matsunaga, R. Tomoda, T. Nakajima, and H. Wake, "Photoelectrochemical sterilization of microbial cells by semiconductor powders," *FEMS Microbiol. Lett.*, **29**, 211–14 (1985).

[5]J.A. Ibáñez, M.I. Litter, and R.A. Pizarro, "Photocatalytic bactericidal effect of TiO_2 on *Enterobacter cloacae*: Comparative study with other Gram (–) bacteria," *J. Photochem. Photobiol. A*, **157**, 81–85 (2003).

[6]P.S. Dunlop, C.P. Sheeran, J.A. Byrne, M.A.S. McMahon, M.A. Boyle, and K.G. McGuigan, "Inactivation of clinically relevant pathogens by photocatalytic coatings," *J. Photochem. Photobiol. A.*, **216**, 303–10 (2010).

[7]A. Mills, S. Hodgen, and S.K. Lee, "Self-cleaning titania films: An overview of direct, lateral, and remote photo-oxidation processes," *Res. Chem. Intermed.*, **31**, 295–308 (2005).

[8]E. Land, M. Bergin, and G. Huey, "Photocatalytic degradation of VOCs by TOTO's hydrotect (TiO_2-impregnated) surfaces: Technical report on TiO_2-impregnated tiles," School of Earth and Atmospheric Science and School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Ga., Dec. 9, 2009.

[9]M. Pelaez, N.T. Nolan, S.C. Pillai, P. Seery, A.G. Falaras, A.G. Kontos, P.S.M. Dunlop, J.W.J. Hamilton, J.A. Byrne, K. O'Shea, M.H. Entezari, and D.D. Dionysiou, "A review on the visible light active titanium dioxide photocatalysts for environmental applications," *Appl. Catal., B*, **125**, 331–49 (2012).

[10]K. Sunada, T. Watanabe, and K. Hashimoto, "Bactericidal activity of copper-deposited TiO_2 thin film under weak UV light illumination," *Environ. Sci. Technol.*, **37**, 4785–89 (2003).

[11]T. Sato and M. Taya, "Copper-aided photosterilization of microbial cells on TiO_2 film under irradiation from a white fluorescent lamp," *Biochem. Eng. J.*, **30**, 199–204 (2006).

[12]D.A.H. Hanaor and C.C. Sorrell, "Review of the anatase to rutile phase transition," *J. Mater. Sci.*, **46**, 855–74 (2011).

[13]J. Prochazka, "Manufacturing of photocatalytic, antibacterial, and self-cleaning and optically noninterfering surfaces on tiles and glazed ceramic products," WO Pat. Application PCT/CZ2003/000019, 2004-09-23.

[14]M. Raimondo, C. Zanelli, G. Guarini, M. Dondi, F. Marani, and L. Fossa, "Photocatalytic ceramic tiles: Key factors in industrial scale-up (and the open question of performance)"; presented at Qualicer'12, Global Forum on Ceramic Tile, Castellón, Spain, Feb. 13–14, 2012.

[15]S.-Q. Sun, B. Sun, W. Zhang, and D. Wang, "Preparation and antimicrobial activity of Ag–TiO composite film by liquid-phase deposition (LPD) method," *Bull. Mater. Sci.*, **31**, 61–66 (2008).

[16]C.J. Weschler and H. Shields, "Measurements of the hydroxyl radical in a manipulated but realistic indoor environment," *Environ. Sci. Technol.*, **31**, 3719–22 (1997).

[17]T. Noguchi, A. Fujishima, P. Sawunyama, and K. Hashimoto, "Photocatalytic degradation of gaseous formaldehyde using TiO_2 film," *Environ. Sci. Technol.*, **32**, 3831–33 (1998).

[18]T.N. Obee, and S.O. Hay, "The estimation of photocatalytic rate constants based on molecular structure: Extending to multicomponent systems," *J. Adv. Oxid. Technol.*, **4**, 147–52 (1999).

[19]P. Wolkoff, P.A. Clausen, B. Jensen, G.D. Neilsen, and C.K. Wilkins, "Are we measuring the relevant indoor pollutants?" *Indoor Air*, **7**, 92–106 (1997).

[20]A.T. Hodgson, D.P. Sullivan, and W.J. Fisk, "Evaluation of ultraviolet photocatalytic oxidation (UVPCO) for indoor air applications: Conversion of volatile organic compounds at low part-per-billion concentrations," Technical Report LBNL-58936, Indoor Environment Department, Environmental Energy Technologies Division, E.O. Lawrence Berkeley National Laboratory, Berkeley, Calif., Sept. 2005.

[21]M.A. Kebede, M.E. Varner, N.K. Scharko, R.B. Gerber, and J.D. Raff, "Photooxidation of ammonia on TiO_2 as a source of NO and NO_2 under atmospheric conditions," *J. Am. Chem. Soc.*, **135**, 8606–15 (2013).

[22]T. Salthammer and F. Fuhrmann, "Photocatalytic surface reactions on indoor wall paint," *Environ. Sci. Technol.*, **41**, 6573–78 (2007).

[23]W.A. Zeltner and D.T. Tompkins, "Shedding light on photocatalysis," *ASHRAE Trans.*, **111**, 523–34 (2005).

[24]L. Cao, Z. Gao, S.L. Suib, T.N. Obee, S.O. Hay, and J.D. Freihaut, "Photocatalytic oxidation of toluene on nanoscale TiO_2 catalysts: Studies of deactivation and regeneration," *J. Catal.*, **196**, 253–61 (2000). ■