Rev. Biol. Biomed. Sci. 2019 2 (1) 1-11
DOI: 10.31178/rbbs.2019.2.1.1

Current photocatalytic applications of nano-scaled titanium dioxide in the new era of "smart" technologies

Ionela Cristina Nica, Miruna Silvia Stan✉, Anca Dinischiotu

Department of Biochemistry and Molecular Biology, Faculty of Biology, University of Bucharest, 91-95 Splaiul Independentei, 050095 Bucharest, Romania

✉**Correspondence to**: Miruna Silvia Stan, Department of Biochemistry and Molecular Biology, Faculty of Biology, University of Bucharest, 91-95 Splaiul Independentei, 050095 Bucharest, Romania E-mail: miruna.stan@bio.unibuc.ro

Received: 2 March 2018 / **Revised**: 17 July 2018 / **Accepted**: 13 August 2018 / **Available online**: 22 August 2018

Abstract Over the past decades, nanotechnology has increasingly developed and reached to monopolize almost all of the human activity areas. Materials with nanoscaled dimensions are not only developed for technological or medical purposes, but also, they can be found in daily commercial products. So, nanoparticles' applications found a well-defined place in our modern life. Almost 70% of global pigment production is based on titanium dioxide (TiO_2), which represents also one of the top five nanoparticles used in consumer products. TiO_2 surrounds our lives, being always present whether we want to take care of our health, wash our teeth or protect ourselves from harmful ultraviolet (UV) radiation. Moreover, TiO_2 is commonly used as a white pigment in different inks, paints, varnishes, plastics, papers, cosmetic products, also being the most common food additive (E171). But, the main perspectives of TiO_2 nanoparticles are related to different photo-induced phenomena, leading to the complete mineralization of pathogens and toxic non-biodegradable compounds, with low costs and high efficiency. Here, the authors aimed to present a brief review mainly focused on the ability of TiO_2 to create surfaces with self-cleaning, anti-fogging and antibacterial properties, as well as on the current photocatalytic applications of TiO_2 in new medical sanitizing techniques and biomedical devices development, wastewater management and air purification, energy and hydrogen production, and for obtaining "smart" clothes.

Keywords: titanium dioxide, photocatalysis, self-cleaning

Introduction

Manufactured nanomaterials (MNMs) are increasingly used as they have many unique and improved properties compared to conventional materials. Different products are already available on the market, ranging from nano-composites used for car and aircraft construction, cosmetics, textiles or food packaging to medical applications (imaging techniques and nano-carrier pharmacological compounds). Nanoparticles' applications are widespread in all aspects of modern life, but photocatalysis received particular attention due to its capacity to convert solar energy with low costs and high efficiency (Wang et al., 2015; Fujishima et al., 2007). Furthermore, on the surfaces coated with a thin layer of photocatalyst, inactivation of microorganisms and mineralization of organic matter was noticed following advanced oxidation processes (AOPs) (Bogdan et al., 2015).

The photodegradation mechanism is a global research topic because photocatalytic mineralization is a complex process in which most of the involved chemical species are difficult to distinguish as a consequence of their very short lifetimes (Shi et al., 2013).

Titanium dioxide (TiO_2) is one of the most studied models for the photocatalytic process because it has ideal chemical properties, also being cheaper than other photocatalysts. A major disadvantage of TiO_2 is the limited absorption of radiation, only in the UV region of the solar spectrum (<400 nm) (Tryba 2008). For this reason, many researchers have successfully doped TiO_2 nanoparticles (NPs) with other metals (Cu, Fe) or non-metals (C, N) to extend their photocatalytic activity in visible light, and thus enhancing the efficiency of contaminant agents' degradation (Nica et al., 2016).

What is already known regarding MNMs toxicity is that the same properties that make them both fascinating and useful are also a cause of serious concern. The effects generated by TiO_2 NPs in mammalian systems are well correlated with their physicochemical properties, such as the size, shape and crystal phase (Wang and Fan 2014).

The main issue is that these nanomaterials are redox active and has small sizes, allowing them to be internalized through the cell membranes and to generate oxidative stress (Gurr et al., 2005). According to the scientific literature, the nanomaterials diversity is huge and moreover, their synthesis approaches are in continuous development, thanks to the efforts made to design new nanomaterials with improved properties. But the technological progress should be accompanied by a constant need to check whether these properties are safe for the environment safety and human health.

Titanium dioxide nanoparticles

Titanium dioxide started to gain interest in the second part of the 20th century, with the discovery of its photocatalytic activity induced by UV radiation (Hashimoto et al., 2005). Although the first who observed the photocatalytic oxidation capacity of TiO_2 was Kato, in 1964, (Kato and Masuo 1964) the event that propelled TiO_2 in this field of photocatalysis was the discovery of the "Fujishima-Honda effect" (Fujishima and Honda 1972). Photo-electrolysis of water in the presence of TiO_2 was initially described in Japanese (Fujishima et al., 1969), and three years later their findings were reported in English, making them accessible to the whole world.

A brief analysis of the global market of mostly used inorganic substances in the form of fine particles and nanoparticles in the new era of "smart" technologies reveals the presence of titanium dioxide (TiO_2). With a market size estimated at 13.3 billion USD in 2015 and per capita consumption of TiO_2 in Europe of about 2.7 kg, it is anticipated a progressive growth in the next years according to the report of "Titanium Dioxide (TiO_2) Market Analysis by Application – 2014 - 2025" published at the end of 2017.

1. Physicochemical properties of titanium dioxide

Titanium dioxide is a semiconductor material of the transition metal oxides family (Gupta and Tripathi 2011) and appears as a white, odorless and non-combustible powder characterized by a molecular weight of 79.9 g/mol and a relative density of 4.26 g/cm^3 (Shi et al., 2013). The melting point of titanium dioxide is recorded at 1855 °C (O'Neil 2013), while boiling temperature may vary between 2500 and 3000 °C (Weast 1988-1989). TiO_2 can be naturally found in three different crystalline forms: rutile, anatase and brookite (Le Guyader and Chen 2012). But besides these, there are also less common crystalline structures such as columbite, baddeleyite (Zhu and Gao 2014), monoclinic (Wu and Xu 2005), hollandite (Pérez-Flores et al., 2014) or ramsdellite (Kuhn et al., 2001) TiO_2 types, which occur only under very special conditions (Banerjee 2011).

Rutile, with a tetragonal structure, is the most stable TiO_2 crystal form, even at high temperatures and pressure values up to 60 kbar, where columbite becomes the thermodynamically favorable phase (Chen and Mao 2007). Its name is derived from the Latin word *rutilus*, which means "red", due to a deep red light that was observed to be transmitted by some minerals (Carp et al., 2004).

Anatase crystals also have a tetragonal structure, but TiO_6 octahedron is a little more distorted than rutile; in 1801, R.J. Hauy named this form based on the Greek word *anatasis* which means "extension" due to its elongated vertical axis (Spencer 1911). The anatase phase of TiO_2 has many photocatalytic applications and is also the most chemically reactive because of the lower oxygen adsorption capacity and the higher degree of hydroxylation (Xia et al., 2013).

Brookite, discovered by Armand Lévy and named in honor of the mineralogist Henry James Brooke (Lévy 1825), is characterized by an orthorhombic structure, more complicated and less dense than rutile or anatase, with a larger volume (Thompson and Yates 2006), but is rarely used experimentally. Usually, TiO_2 nanoparticles used in research contain an anatase-rutile mixture.

One of the unique features of TiO_2-based nanomaterials is that they possess two photo-induced properties: photocatalytic activity (Fig. 1) and superhydrophilicity/ superhydrophobicity (Lai et al., 2016). The term "photocatalysis" can be defined as an acceleration of a photoreaction in the presence of a catalyst (Castellote and Bengtsson 2011). Photocatalysts are materials that can absorb energy from exposure to electromagnetic radiation, more precisely from photons with an amount of energy equal or higher than the size of their band gap, which in case of TiO_2 is almost 3.2 eV. Following the energy leap of an electron from the valence band (lower energy) to the conduction band (higher energy) in the photocatalyst structure, an electron-hole pair is formed (Carcel 2011).

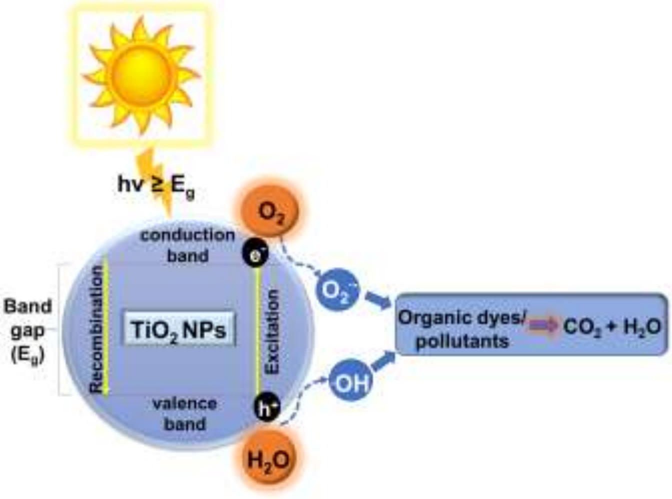

Fig. 1. The photocatalytic mechanism of TiO_2 nanoparticles.

2. Limits of exposure to titanium dioxide

Titanium is also found in biological systems, but only in very small quantities, as it is not an essential element for humans or animals. The concentration of titanium-based compounds in drinking water is generally low, and a typical diet can make a daily contribution of only 300-400 µg (Shi et al., 2013).

Food and Drug Administration Agency of the United States (FDA) approved TiO_2 as a food coloring additive with the requirement that the additive "does not exceed 1% of body weight (b.w.)". TiO_2 has also been approved by the FDA as a "food contact substance" in food packaging (FDA 2002). Taking into account the differences in physicochemical properties and the toxic effects of TiO_2 fine particles and nanoparticles, it is necessary to be established a specific exposure limit for these kinds of materials.

According to EU recommendation from October 2011, a “nanomaterial” is “a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm” (EU Directive 2011).

TiO_2 particles are synthesized and used in various fractions, including fine (~ 0.1-2.5 µm) and nano-sized (<0.1 µm) particles. Human exposure to TiO_2 nanoparticles may occur both during the manufacture processes and after the use of different nanoparticle-based products (Dankovic and Kuempel 2007).

American Conference of Governmental Industrial Hygienists (ACGIH) has set a threshold value of 10 mg/m^3 for TiO_2 fine particles in a normal 8-h workday and a 40-h workweek (ACGIH 2001). Occupational Safety and Health Administration (OSHA) has established the exposure limit for fine particles of TiO_2 at 15 mg/m^3. In November 2005, National Institute for Occupational Safety and Health (NIOSH) of the USA proposed a recommended exposure limit of 0.3 mg/m^3, which was ten times lower compared to the one set for fine particles (NIOSH 2011). New Energy and Industrial Technology Development Organization (NEDO) from Japan established an exposure concentration limit for TiO_2 nanoparticles of 1.2 mg/m^3 (Singh 2015).

3. Current applications of TiO_2 NPs

Owing to its very high refractive index, TiO_2 represents about 70% of the total amount of worldwide pigment production, being among the top five types of nanoparticles used in consumer products (Baan et al., 2006). Mostly, TiO_2 is used as a white pigment (CI 77891) and opacifier in paints, coatings, plastics, papers, as well as in most toothpaste brands, medicines (Allam and Kumar 2011), inks (Høgsberg et al., 2011), permanent make-up colorants (Wenzel et al., 2010), sunscreens and other cosmetics. Also, TiO_2 is a common food additive (E171) that is mainly found in sweets, candies and chewing gums (Weir et al., 2012).

TiO_2 and zinc oxide (ZnO) are commonly used as sunscreen agents because of their ability to absorb and scatter UV light. As TiO_2 is more efficient for long wave ultraviolet A (UVA) and ZnO in the short wave ultraviolet B (UVB) range, the combination of these particles provides protection on a wider UV spectrum (Smijs and Pavel 2011). Also, the effectiveness of these UV filters increases when they are used in the nano scale (Patel et al., 2011).

Even if the penetration by nanoparticles contained in sunscreen products through the epidermal layer has not been observed so far, human skin is not an impenetrable barrier. Hair follicles and abrasions offer opportunities for particles to reach the vasculature (Huang et al., 2013). However, scanning electron microscopy has shown that titanium penetrates the skin through vacant follicles, but does not penetrate into the dermis or deep layers of the epidermis (Senzui et al., 2010).

Considering the high thermodynamic stability, as well as the photocatalytic and anticorrosive properties of TiO_2 (Malhi 2012), besides the TiO_2 daily uses, there is also a distinct category of applications based on photocatalysis. Therefore, the main perspectives of nano-scaled TiO_2 take into account different photo-induced phenomena, such as antibacterial and self-cleaning effect, energy and hydrogen production, photo-oxidation of organic pollutants, wastewater management and air purification.

4. Antimicrobial effect and biomedical applications of TiO_2 NPs

In recent years, the medical field has faced a number of serious problems caused by harmful microorganisms, including *Legionella* infections in full-time baths, food poisoning by *Staphylococcus aureus*, and hospital infections caused by drug-resistant bacteria (Yadav et al., 2016). Nowadays, the ability of different microorganisms to share genetic determinants in stressful conditions, leading to a great antimicrobial resistance, represents an important healthcare issue (Nica et al., 2016). Moreover, the increasing number of modern clinical procedures requires the use of biomedical devices. One of the major problems of both short-term devices and implantable prostheses is represented by infections associated with the bacterial proliferation and colonization (Vasilev et al., 2009). Planktonic bacteria that colonize the surface of a device tend to form a biofilm, and sessile bacterial cells, enclosed in a polymeric matrix synthesized by them, can exhibit tremendous resistance to the immune response of the host and also to antibiotics (Costerton et al., 1999). For this reason, metal nanoparticles with their bactericidal and bacteriostatic effects became very useful to current medical requirements (Ahrari et al., 2015).

TiO_2 has been shown to be useful as a photocatalytic agent for killing various groups of microorganisms, such as bacteria, fungi and viruses, due to its high photoreactivity and broad-spectrum antibiosis (Gupta et al., 2013). In 1985, Matsunaga et al. reported for the first time the antimicrobial photocatalytic effect of TiO_2 on *Saccharomyces cerevisiae* (yeast), *Lactobacillus acidophilus* and *Escherichia coli* (bacteria), and *Chlorella vulgaris* (green algae) (Matsunaga et al., 1985). The antibacterial mechanism occurs as a result of the reaction between the reactive oxygen species (ROS) and the structural bacterial components, such as the cell wall and cell membrane. The most sensitive targets for ROS attack are the unsaturated phospholipids of cell membranes, while lipid peroxidation is considered to be the lethal mechanism of action for the antibacterial photocatalytic process (Cai et al., 2013).

Sunada and his collaborators proposed a three-step mechanism for photo-killing bacteria on TiO_2 coated surfaces following irradiation. According to this theory, the final step of total decomposition of bacterial toxins to CO_2 and H_2O makes photocatalytic sterilization the most efficient approach compared to classical antibacterial treatments (Sunada et al., 2003).

One of the main advantages of sterilization by photocatalytic oxidation is that it does not need electrical power or chemical reagents, light, oxygen and water being the only necessary ingredients. Also, TiO_2 surfaces are not toxic, are safety for use and do not cause environmental pollution. These features make TiO_2-based self-sterilizing materials ideal for future medical applications (Visai et al., 2011). Therefore, different approaches have been adopted to extend the photo-induced activity in visible light and remove possible electron-hole recombination, which are two major limitations for TiO_2 photocatalytic applications. The cooperative action of co-doping TiO_2 nanoparticles with transition metals (W, V, Ag or Cu) and non-metals (S, C or N), as well as combining it with other semiconductors, could be the most successful strategies to prepare composites with enhanced antibacterial properties (Yuan et al., 2010).

According to Bahadur et al., TiO_2 nanoparticles doped with silver (Ag) ions inactivated *Escherichia coli, Pseudomonas aeruginosa, Bacillus subtilis* and *Staphylococcus aureus* bacterial strains (Bahadur et al., 2016). Other studies suggested that copper (Cu) might be a more effective antimicrobial agent than Ag due to its low cytotoxicity (Norambuena et al., 2016), Cu-doped TiO_2 nanoparticles being able to inhibit the growth of *Mycobacterium smegmatis* (Wu et al., 2010). But, most of the studies focused on non-metal doped TiO_2 nanoparticles that showed remarkable photoactivity under visible light irradiation. Cheng et al. reported the visible light activity of carbon doped TiO_2 against *Staphylococcus aureus*, *Shigella flexneri* and *Acinetobacter baumannii* (Cheng et al., 2009). Moreover, Hamal et al. demonstrated that TiO_2 nanoparticles co-doped with silver, carbon and sulfur can act as a multifunctional biocide, proving strong antimicrobial properties against *Escherichia coli* and *Bacillus subtilis* spores without light activation (Hamal et al., 2010).

In the last years, nanotechnology has also expanded in the field of dentistry. Recently, the medical and dental literature paid more attention to the photocatalytic activity of TiO_2 nanoparticles. It was evidenced that TiO_2-containing resins exhibit significant antimicrobial effects (Arai et al., 2009), which may be very useful in preventing recurrent caries and enamel demineralization. The addition of TiO_2 nanoparticles to dental composites led to the development of new materials with improved mechanical characteristics, such as modulus of elasticity, microdurity and strength (Heravi et al., 2013) and improved its antibacterial effects without any changes in physical properties (Poosti et al., 2013).

5. Self-cleaning and anti-fogging surfaces based on TiO_2 NPs

Daily deposits of dirt, soot and other pollutants released by vehicles lead to a constant need of cleaning the buildings. Also, the growth of various microorganisms (bacteria, algae, fungi) disfigured facades of edifices, causing mechanical weakness and even destruction. To prevent this, constructions can be built or only covered using materials that incorporate photocatalysts. Commercial surfaces with self-cleaning properties are usually made of thin TiO_2 layers whose photo-induced catalytic performances are well-known (Jesus et al., 2015).

Titanium dioxide-coated surfaces are not contaminated even in the absence of light because nanoparticles create a rough superhydrophobic structure, which removes water drops and dust particles, preventing it from wetting or soiling. This phenomenon is inspired by nature and was observed for the first time in *Nelumbo nucifera* leaves, being called the "lotus effect" (Yamamoto et al., 2015). In contrast to hydrophobic surfaces that are kept clean due to water-repellent structures, the hydrophilic coatings use photocatalysis to break down dirt and any other kind of impurities or contaminants under light exposure (Ganesh et al., 2011). Although photo-induced suprehydrophilia and degradation of organic contaminants are two different processes, they occur in the same time. Pollutants gradually adsorbed from a surface covered with a TiO_2 film can be decomposed in the presence of light, and then removed by rain. The superhydrophilic surfaces coated with a thin layer of TiO_2 NPs have the ability to attract water, forming a continuous flowing film, washing away the dust particles or other contaminants (Jin et al., 2013).

Anti-fogging coatings also rely on the photo-induced hydrophilic property of TiO_2. On a superhydrophilic surface, the accumulation of small water drops leading to steaming and scattering of light is prevented, but instead, a uniform layer of water that will not disperse the light is formed (Tricoli et al., 2009).

Self-cleaning and anti-fogging properties of TiO_2 NPs not only remained at the research stage, they were adopted by large companies from building materials and glass industry and applied to the manufacture of their own products. For example, Activ^{TM} glass developed by Pilkington is one of the most successful commercial self-cleaning products, being used in different buildings around the world (Mills et al., 2003). Hydrotech^{TM}, introduced by the Japanese company TOTO Ltd., is another photo-induced superhydrophilicity based technology (Shimohigoshi and Saeki 2007). It is very impressive that self-cleaning windows and tiles are widely used in Japan. TiO_2 NPs containing glass and cements have also been used on the surface of National Opera Hall from China, in *Dives in Misericordia* Church from Rome and on the roof of Dubai Sports City's Cricket Stadium (Banerjee et al., 2015).

6. TiO_2 NPs-treated textiles with self-cleaning properties

Considering the important role of fabrics in human life from today's society, a new interesting research field involving both textile industry and nanotechnology has been developed over the last decades (Dastjerdi and Montazer 2010). It was found that by nano-decorating textiles with active particles, fibers properties are improved, gaining new features, such as water repellency (Bagherzadeh et al., 2007), increased mechanical strength (Davis et al., 2011), wrinkle resistance, antistatic, color change (Gorensek and Recelj 2007) or UV protection (Mondal and Hu 2016).

TiO_2 turned out to be the most effective and cheap alternative for textile coatings (Abidi et al., 2009; Mihailović et al., 2011). Recently, many articles focused on the functionalization of textiles with TiO_2 NPs and their self-cleaning properties (Bozzi et al., 2005; Lee et al., 2013; Afzal et al., 2013; Pakdel et al., 2015). Accordingly, various photocatalytic fibers based on cotton (Lam et al., 2010), polyester (Pasqui and Barbucci 2014), wool (Tang et al., 2011), and silk (Li et al., 2012) were designed. But, what is gratifying is that despite the changes that might have occurred during the functionalization process, these materials remain harmless to the skin cells. For example, nano TiO_2-coated fabrics exhibit a great antibacterial efficiency against *Escherichia coli* and *Staphylococcus aureus* and antifungal activity against *Candida albicans*, along with a significant self-cleaning capacity and no cytotoxic effects on human skin fibroblasts (Stan et al., 2016).

Self-cleaning fabrics can be obtained by applying an active photocatalytic layer containing the oxide of a transition metal. This coating reacts with organic compounds or pollutants deposited on the fabric, decomposing them under sunlight exposure to simple inorganic compounds (CO_2 and H_2O), which are subsequently removed by heat, wind or rain (Veronovski et al., 2009).

The hydrophobicity/hydrophilicity of textiles usually varies from one fabric to another, depending on the chemical composition and surface charges. Different treatments are needed to modify the physicochemical properties of the textile surface for improving the adhesion between photocatalyst and fiber, minimizing NPs losses in case of frequent washing (Kaihong et al., 2007). Another issue is about the photo-activity that TiO_2 might have on textiles and fiber degradation. In this regard, Veronovski and his team developed a titanium-silica composite shell that can be used to avoid the negative impact (Veronovski et al., 2009). However, any applied pre-treatment only modifies the outer superficial layers of the fabric without affecting its properties.

Finally, an actual application of these "smart" textiles was introduced by US Army in collaboration with the Massachusetts Institute of Technology. They have created a waterproof, lightweight and breathable uniform that has the ability to kill bacteria. Furthermore, the development of "nanopores" in soldiers' uniforms, which close when chemical or biological agents are detected, is attempted for the protection against chemical or biological weapons during wars (Karst and Yang 2006).

7. Photocatalytic applications of TiO_2 NPs for air treatment and purification

Breathing is a vital need not only for humans, but also for all aerobic forms of life on Earth, so the poor air quality is detrimental to both our health and environment. Indoor air pollution started to gain interest in the early 1990s when statistics showed that the most people spend more than 80% of the time indoors where the risk of exposure to pollutants is higher than outdoors (Le et al., 2015).

Pathogenic microorganisms spread through ventilation systems represent one of the main causes of air quality degradation inside buildings, offices or production units. Constant exposure to these contaminants can result into various health problems like irritation, systemic infections, allergies and other respiratory or skin disorders (Verdier et al., 2014). The accumulation of volatile organic compounds (VOCs) is another major pollutant in indoor environment, which induce several adverse effects on human health, including headache, excessive fatigue and skin irritations (Weon et al., 2017).

Car emissions have a particular impact on global air quality. The main emissions from motor vehicles are nitrogen oxides (NO_x), hydrocarbons (HC) and carbon monoxide (CO) (Nischk et al., 2014).

High-efficiency particulate arrestance (HEPA) and electrostatic filters are primarily used to purify indoor air. A preliminary study realized by Limmongkon and his collaborators showed that an electrostatic air filter could reduce fungal (*Aspergillus niger* and *Penicillium citrinum*) and bacterial (*Staphylococcus epidermidis* and *Bacillus subtilis*) growth from initial concentrations of 34.000-80.000 CFU/m^3 at the recommended concentration of 500 CFU/m^3 in just 30-40 minutes (Limmongkon et al., 2009). But besides conventional methods, it was demonstrated that photocatalytic oxidation can be an equally effective tool in removing both organic and inorganic compounds together with microorganisms from outdoor and indoor air (Binas et al., 2017). The use of an electrostatic air filter in combination with photocatalytic oxidation has not yet been studied, but it could be one of the most promising methods of air decontamination (Limmongkon et al., 2013). Instead, a glass fiber air filter coated with TiO_2 was proposed as a cheaper alternative to HEPA filters for *Mycobacterium tuberculosis* removal (Thunyasirinon et al., 2015).

Photocatalysis proved its efficiency in reducing a number of air contaminants, especially in places with high levels of pollution, such as intensely circulated streets, road tunnels or urban areas. In the last years, several projects have been launched in Belgium to improve air quality by building new photocatalytic sidewalks in industrial areas from Wijnegem and Lier (Boonen and Beeldens 2014).

The extensive use of TiO_2 NPs in building materials with photocatalytic properties is due to their low costs, compatibility with traditional building materials without any changes in original performance, high catalytic activity compared to other metal oxides, and efficiency even under weak solar irradiation in atmospheric environment (Chen and Poon 2009).

The European PhotoPAQ project was designed to demonstrate the usefulness of photocatalytic building materials for urban air purification purposes. Photocatalytic cement TX Active® developed by CTG Italcementi Group was applied to the side walls and the roof of one section of Leopold II tunnel from Brussels and the air purification system was activated by an UV illumination system (Gallus et al., 2015).

Since the first application of photocatalytic pavements in Antwerp (2004-2005), there has been a lot of progress in the field of photocatalysis. Newer, better and more effective materials are constantly developed, and research is increasingly focused on TiO_2-based materials photo-active in visible light.

8. Wastewater management using TiO_2 NPs

The exponential growth of the human population over the last decades has also led to an increasing need of drinking water supply. But, at the moment our society is facing various environmental issues including water pollution, which is a major worldwide cause of deaths. Incorrect management of water resources and the inefficiency of common chlorine-based disinfectants in water treatment are reflected in the increasing number of infectious diseases outbreaks (Bogdan et al., 2015).

The biggest threat to public health is represented by the toxic and non-biodegradable compounds that can be released into the environment through industrial wastewater (Nickheslat et al., 2013). Phenolic compounds represent the main group of wastewater pollutants produced by a wide range of industrial fields such as: chemicals, paints, textiles, pesticides, food processing, biotechnology, cosmetics, oil refineries, coal mines and cars` production, or released by natural processes (degradation of algae or vegetation) (Borji et al., 2014).

Other significant water contamination agents are the pharmaceutical products. As their variety has increased significantly over the past decades due to the rapid development of medical science, more and more anti-inflammatory drugs and antibiotics have been detected in surface water and effluents of the wastewater treatment plants (Farzdakia et al., 2015).

For this reason, the recent Directive of the European Parliament updated the water framework policy (EU Directive 2013). The new EU Directive promotes preventive actions, identifying the nature of different sources of pollution, and designing innovative wastewater treatment technologies with lower costs and higher efficiency. Furthermore, it pays attention to the importance of monitoring pollutants that are not usually considered hazardous but can have toxicological implications on humans' health and environment safety (Ribeiro et al., 2015).

Treatment of wastewater containing toxic organic compounds is usually done by physicochemical methods such as adsorption, sedimentation, filtration and chemical oxidation, but conventional techniques do not completely remove the pollutants, generating harmful secondary products that are high consumers of chemical reagents and time (Dong et al., 2015). Consequently, the development of new environmentally friendly technologies capable to mineralize and remove non-biodegradable compounds and pathogens from water became an urgent requirement (Martínez-Huitle et al., 2015).

Photocatalysis with TiO_2 NPs proved to be useful for the complete photodegradation of hazardous pollutants in wastewater (Morales-Torres and Pastrana- Martínez 2014). The spectrum of compounds that are sensitive to the destructive power of TiO_2 NPs is remarkable (Lazar et al., 2012). Even the most resistant organic compounds can be degraded by photocatalysis into harmless products (H_2O and CO_2) (Patel et al., 2014).

TiO_2 applications in water purification require the synthesis of TiO_2 films on suitable substrates, reducing their surface area and, subsequently, their photocatalytic activity. Therefore, three-dimensional nanoarchitectures, such as porous TiO_2 nanotubes are among the most attractive approaches due to their excellent performances (Lee et al., 2014). A novel cylindrical multi-column photocatalytic reactor (CMCPR) packed with TiO_2-coated silica gel beads has been obtained and efficiently applied for the degradation of different classes of water pollutants (Li et al., 2015).

9. Energy and hydrogen production using TiO_2 NPs

It is extremely difficult to estimate exactly what are the remaining reserves of fossil fuels on earth and when exactly they will be exhausted, but the trend is clear and the world is heading for a major energy crisis.

Fast depletion of the natural resources and the increasing rate of environmental pollution are highly debated issues, leading to a critical need for the development of innovative clean energy resources. Hydrogen is considered the ideal candidate as an energy carrier in the future since it is renewable and can be easily transformed into electricity by fuel cells (Dholam et al., 2009). There are a number of attempts to find alternative ways to hydrogen gas production from solar radiation and wind power, avoiding the emission of greenhouse gases. Photocatalytic water-splitting using sunlight could be a promising solution for the environmental issues caused by hydrogen production. Photocatalytic hydrogen production is based on two essential elements: a semiconductor, absorbing the light that generates electron–hole pairs, and a metal that acts as an electron trapper or a co-catalyst (Chen et al., 2012). Among all the semiconductors with great potential for photocatalysis that have been explored so far, TiO_2 still remains the most suitable material for hydrogen production, owing to its intrinsic properties (Chiarello et al., 2017). But the hydrogen production rate using TiO_2 is quite low due to fast charge recombination and its capacity to use only UV light from solar spectrum (Ni et al., 2007).

In the last decades, several methods have been developed to improve the photocatalytic activity of TiO_2, expanding it into visible light. Although it has been observed that noble metal deposition on its surface (Yu and Jaroniec 2010), metal and nonmetal ion doping (Yoong et al., 2009), or the preparation of composite semiconductors (Xiang et al., 2012) can enhance hydrogen production, combination of different techniques is required for an increased efficiency.

For a better understanding and assumption of the photocatalytic hydrogen production mechanism, more work still needs to be done. Moreover, the development of a photo-reactor for photocatalytic water splitting in an inexpensive and environmentally friendly manner will play an essential role in developing the future hydrogen economy.

Conclusions

Realizing how essential it is to keep our planet clean, researchers are constantly working to develop new eco-friendly alternative technologies for all fields of human activity. Sustainable energy production and pollutants` degradation are two of the most intensively researched areas. Titanium dioxide is a semiconductor with multiple applications that can be used as an energy catalyst (to produce hydrogen from photocatalytic water splitting), an environmental catalyst (for water and air purification) or a biomedical catalyst (in antimicrobial and self-cleaning surfaces and coatings).

In conclusion, titanium dioxide is the most suitable photocatalyst, considering its lack of biological and chemical reactivity, its strong oxidizing capacity, low toxicity, insolubility, relatively low costs, and long-term stability against photo- and chemical corrosion. Researchers` efforts for improving the photo-activity of TiO_2 by modifying its surface and expanding its activity in the visible light spectrum will enable the full potential of this photocatalyst to be exploited.

Acknowledgments

This work was supported by the project NANO-BIO-INT (PN-III-P1-1.1-PD-2016-1562) funded by UEFISCDI.

References

Abidi N., Cabrales L., Hequet E. 2009. Functionalization of a cotton fabric surface with titania nanosols: applications for self-cleaning and UV-protection properties. *ACS Appl. Mater. Interfaces* 1, 2141–2146.

ACGIH 2001. Titanium dioxide. In: Documentation of the threshold limit values for chemical substances. 7th edition. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

Afzal S., Daoud W.A., Langford S.J. 2013. Photostable self-cleaning cotton by a copper (II) porphyrin/TiO2 visible-light photocatalytic system. *ACS Appl. Mater. Interfaces* 5, 4753–4759.

Ahrari F., Eslami N., Rajabi O., Ghazvini K., Barati S. 2015. The antimicrobial sensitivity of *Streptococcus mutans* and *Streptococcus sangius* to colloidal solutions of different nanoparticles applied as mouthwashes. *Dent. Res. J.* 12, 44–49.

Allam K.V., Kumar G.P. 2011. Colorants-the cosmetics for the pharmaceutical dosage forms. *Int. J. Pharm. Pharm. Sci.* 3, 13–21.

Arai T., Ueda T., Sugiyama T., Sakurai K. 2009. Inhibiting microbial adhesion to denture base acrylic resin by titanium dioxide coating. *J. Oral Rehabil.* 36, 902–908.

Baan R., Straif K., Grosse Y., Secretan B., El Ghissassi F., Cogliano V. 2006. Carcinogenicity of carbon black, titanium dioxide, and talc. *Lancet Oncol.* 7, 295–296.

Bagherzadeh R., Montazer M., Latifi M., Sheikhzadeh M., Sattari M. 2007. Evaluation of comfort properties of polyester knitted spacer fabrics finished with water repellent and antimicrobial agents. *Fiber. Polym.* 8, 386–392.

Bahadur J., Agrawal S., Panwar V., Parveen A., Pal K. 2016. Antibacterial properties of silver doped TiO_2 nanoparticles synthesized via sol-gel technique. *Macromol. Res.* 24, 488–493.

Banerjee A.N. 2011. The design, fabrication, and photocatalytic utility of nanostructured semiconductors: focus on TiO_2-based nanostructures. *Nanotechnol. Sci. Appl.* 4, 35–65.

Banerjee S., Dionysiou D.D., Pillai S.C. 2015. Self-cleaning applications of TiO_2 by photo-induced hydrophilicity and photocatalysis. *Appl. Catal. B: Environmental* 176, 396–428.

Binas V., Venieri D., Kotzias D., Kiriakidis G. 2017. Modified TiO_2 based photocatalysts for improved air and health quality. *J. Materiomics* 3, 3–16.

Bogdan J., Jackowska-Tracz A., Zarzyńska J., Pławińska-Czarnak J. 2015. Chances and limitations of nanosized titanium dioxide practical application in view of its physicochemical properties. *Nanoscale Res. Lett.* 10, 57–67.

Boonen E., Beeldens A. 2014. Recent photocatalytic applications for air purification in Belgium. *Coatings* 4, 553–573.

Borji S.H., Nasseri S., Mahvi A.H., Nabizadeh R., Javadi A.H. 2014. Investigation of photocatalytic degradation of phenol by Fe(III)-doped TiO_2 and TiO_2 nanoparticles. *J. Environ. Health Sci. Eng.* 12, 101–121.

Bozzi A., Yuranova T., Kiwi J. 2005. Self-cleaning of wool-polyamide and polyester textiles by TiO_2-rutile modification under daylight irradiation at ambient temperature. *J. Photochem. Photobiol. A* 172, 27–34.

Cai Y., Strømme M., Welch K. 2013. Photocatalytic antibacterial effects are maintained on resin-based TiO_2 nanocomposites after cessation of UV irradiation. *PLoS ONE* 8, e75929.

Cârcel R.A. 2011. Metal oxide photocatalysts for the treatment of wastewaters resulted in the textile industry. *PhD thesis*. Transilvania University of Brașov, Brașov, Romania.

Carp O., Huisman C.L., Reller A. 2004. Photoinduced reactivity of titanium dioxide. *Prog. Solid State Chem.* 32, 33–177.

Castellote M., Bengtsson N. 2011. Principles of TiO_2 photocatalysis. In: Application of Titanium Dioxide Photocatalysis to Construction Materials. Ohama Y., Van Gemert D. (Eds.), Dordrecht: Springer Netherlands, 5–10.

Chen J., Poon C. 2009. Photocatalytic construction and building materials: From fundamentals to applications. *Build. Environ.* 44, 1899–1906.

Chen X., Li C., Grätzel M., Kostecki R., Mao S.S. 2012. Nanomaterials for renewable energy production and storage. *Chem. Soc. Rev.* 41, 7909–7937.

Chen X., Mao S.S. 2007. Titanium dioxide nanomaterials: Synthesis, properties, modifications, and applications. *Chem. Rev.* 107, 2891–2959.

Cheng C.L., Sun D.S., Chu W.C., Tseng Y.H., Ho H.C., Wang J.B., Chung P.H., Chen J.H., Tsai P.J., Lin N.T., Yu M.S., Chang H.H. 2009. The effects of the bacterial interaction with visible-light responsive titania photocatalyst on the bactericidal performance. *J. Biomed. Sci.* 16, 7.

Chiarello G.L., Dozzi M.V., Selli E. 2017. TiO_2-based materials for photocatalytic hydrogen production. *Journal of Energy Chemistry* 26, 250–258.

Costerton J.W., Stewart P.S., Greenberg E.P. 1999. Bacterial biofilms: a common cause of persistent ınfections. *Science* 284, 1318–1322.

Dankovic D., Kuempel E., Wheeler M. 2007. An approach to risk assessment for TiO_2. *Inhal. Toxicol.* 19, 205–212.

Dastjerdi R., Montazer M. 2010. A review on the application of inorganic nano-structured materials in the modification of textiles: Focus on anti-microbial properties. *Colloids Surf. B: Biointerfaces* 79, 5–18.

Davis D.C., Wilkerson J.W., Zhu J., Hadjiev V.G. 2011. A strategy for improving mechanical properties of a fiber reinforced epoxy composite using functionalized carbon nanotubes. *Compos. Sci. Technol.* 71, 1089–1097.

Dholam R., Patel N., Adami M., Miotello A. 2009. Hydrogen production by photocatalytic water-splitting using Cr- or Fe-doped TiO_2 composite thin films photocatalyst. *Int. J. Hydrog. Energy* 34, 5337–5346.

Dong H., Zeng G., Tang L., Fan C., Zhang C., He X., He Y. 2015. An overview on limitations of TiO_2-based particles for photocatalytic degradation of organic pollutants and the corresponding countermeasures. *Water Res.* 79, 128–146.

EU Directive, 2011. Directive 2011/696/EU of the European Parliament and of the Council of 18 October 2011 as regards the Comission recommendation on the definition of nanomaterial. *Off. J. Eur. Union* L275, 38–40.

EU Directive, 2013. Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. Off. J. Eur. Union L226, 1–17.

Farzadkia M., Bazrafshan E., Esrafili A., Yang J.K., Shirzad-Siboni M. 2015. Photocatalytic degradation of metronidazole with illuminated TiO_2 nanoparticles. *J. Environ. Health Sci. Eng.* 13, 35–43.

FDA 2002. Listing of color additives exempt from certification. In: Code of Federal Regulations Title 21-Food and Drugs. 21 CFR 73.2575. Washington, DC: US Government Printing Office.

Fujishima A., Honda K. 1972. Electrochemical photolysis of water at a semiconductor electrode. *Nature* 238, 37–38.

Fujishima A., Honda K., Kikuchi S. 1969. Photosensitized electrolytic oxidation on semiconducting n-type TiO_2 electrode. *Kogyo Kagaku Zasshi* 72, 108–113 [in Japanese].

Fujishima A., Zhang X., Tryk D.A. 2007. Heterogeneous photocatalysis: From water photolysis to applications in environmental cleanup. *Int. J. Hydrog. Energy* 32, 2664–2672.

Gallus M., Akylas V., Barmpas F., Beeldens A., Boonen E., Boréave A., Cazaunau M., Chen H., Daële V., Doussin J.F., Dupart Y., Gaimoz C., George C., Grosselin B., Herrmann H., Ifang S., Kurtenbach R., Maille M., Mellouki A., Miet K., Mothes F., Moussiopoulos N., Poulain L., Rabe R., Zapf P., Kleffmann J. 2015. Photocatalytic de-pollution in the Leopold II tunnel in Brussels: NOx abatement results. *Build. Environ.* 84, 125–133.

Ganesh V.A., Raut H.K., Nair A.S., Ramakrishna S. 2011. A review on self-cleaning coatings. *J. Mater. Chem.* 21, 16304–16322.

Gorensek M., Recelj P. 2007. Nanosilver functionalized cotton fabric. *Text. Res. J.* 77, 138–141.

Gupta K., Singh R.P., Pandey A., Pandey A. 2013. Photocatalytic antibacterial performance of TiO_2 and Ag-doped TiO_2 against *S. aureus*, *P. aeruginosa* and *E. coli*. *Beilstein J. Nanotechnol.* 4, 345–351.

Gupta S.M., Tripathi M. 2011. A review of TiO_2 nanoparticles. *Chinese Sci. Bull.* 56, 1639−1657.

Gurr J.R., Wang A.S.S., Chen C.H., Jan, K.Y. 2005. Ultrafine titanium dioxide particles in the absence of photoactivation can induce oxidative damage to human bronchial epithelial cells. *Toxicology* 213, 66–73.

Hamal D.B., Haggstrom J.a, Marchin G.L., Ikenberry M.a, Hohn K., Klabunde K.J.. 2010. A multifunctional biocide/sporocide and photocatalyst based on titanium dioxide (TiO_2) codoped with silver, carbon, and sulfur. *Langmuir* 26, 2805–2810.

Hashimoto K., Irie H., Fujishima A. 2005. TiO_2 photocatalysis: a historical overview and future prospects. *Jpn. J. Appl. Phys.* 44, 8269–8285.

Heravi F., Ramezani M., Poosti M., Hosseini M., Shajiei A., Ahrari F. 2013. In vitro cytotoxicity assessment of an orthodontic composite containing titanium-dioxide nano-particles. *J. Dent. Res. Dent. Clin. Dent. Prospects* 7, 192–199.

Høgsberg T., Loeschner K., Löf D., Serup J. 2011. Tattoo inks in general usage contain nanoparticles. *Br. J. Dermatol.* 165, 1210–1218.

Huang Y., Lenaghan S.C., Xia L., Burris J.N., Stewart C.N.Jr, Zhang M. 2013. Characterization of physicochemical properties of ivy nanoparticles for cosmetic application. *J. Nanobiotechnology* 11, 3–15.

Jesus M.A., Silva J.T., Timò G., Paiva P.R.P., Dantas M.S., Ferreira A.M. 2015. Superhydrophilic self-cleaning surfaces based on TiO_2 and TiO_2/SiO_2 composite films for photovoltaic module cover glass. *Appl. Adhes. Sci.* 3, 5–14.

Jin L., Kuo C., Suib S.L. 2013. Heterogeneous catalysts for biomass conversion. In: New and future developments in catalysis. Suib S.L. (ed.), Elsevier B.V., 253–270.

Kaihong Q., Xin J.H., Daoud W.A. 2007. Functionalizing polyester fiber with a self cleaning property using anatase TiO_2 and low-temperature plasma treatment. *Int. J. Appl. Ceram. Technol.* 4, 554–563.

Karst D., Yang Y. 2006. Potential advantages and risks of nanotechnology for textiles. *AATCC Review* 6, 44–48.

Kato S., Masuo F. 1964. Titanium dioxide-photocatalyzed liquid phase oxidation of tetralin. *Kogyo Kagaku Zasshi* 67, 42–50.

Kuhn A., Amandi R., Garcìa-Alvarado F. 2001. Electrochemical lithium insertion in TiO_2 with the ramsdellite structure. *J. Power Sources* 92, 221–227.

Lai Y., Huang J., Cui Z., Ge M., Zhang K.Q., Chen Z., Chi L. 2016. Recent advances in TiO_2-based nanostructured surfaces with controllable wettability and adhesion. *Small* 12, 2203–2224.

Lam Y.L., Kan C.W., Yuen C.W.M. 2010. Effect of concentration of titanium dioxide acting as catalyst or co-catalyst on the wrinkle-resistant finishing of cotton fabric. *Fiber. Polym.* 11, 551–558.

Lazar M.A., Varghese S., Nair S.S. 2012. Photocatalytic water treatment by titanium dioxide: recent updates. *Catalysts* 2, 572–601.

Le Guyader L., Chen C. 2012. Characterization of TiO_2 nanoparticles cytotoxicity. In: Controlled Nanofabrication: Advances and Applications, Ru-Shi, L. (ed.), Singapore, Pan Stanford Publishing Pte. Ltd., 103–154.

Le T.S., Dao T.H., Nguyen D.C., Nguyen H.C., Balikhin I.L. 2015. Air purification equipment combining a filter coated by silver nanoparticles with a nano-TiO_2 photocatalyst for use in hospitals. *Adv. Nat. Sci.: Nanosci. Nanotechnol.* 6, 015016.

Lee H.J., Kim J., Park C.H. 2014. Fabrication of self-cleaning textiles by TiO_2-carbon nanotube treatment. *Text. Res. J.* 84, 267–278.

Lee H.U., Lee C.S., Lee Y.C., Son B., Park S.Y., Lee J.W., Oh Y.K., Kim Y., Choi S., Lee Y.S., Lee J. 2014. Innovative three-dimensional (3D) eco-TiO_2 photocatalysts for practical environmental and bio-medical applications. *Sci. Rep.* 4, 6740–6748.

Lévy M.. 1825. An account of a new mineral. *Ann. Philos.* 9, 140–142.

Li G., Liu H., Li T.D., Wang J. 2012. Surface modification and functionalization of silk fibroin fibers/fabric toward high performance applications. *Mater. Sci. Eng. C* 32, 627–636.

Li G., Nie X., Chen J., Jiang Q., An T., Wong P.K., Zhang H., Zhao H., Yamashita H. 2015. Enhanced visible-light-driven photocatalytic inactivation of *Escherichia coli* using g C_3N_4/TiO_2 hybrid photocatalyst synthesized using a hydrothermal-calcination approach. *Water Res.* 15, 343–354.

Limmongkon Y., Johns J., Charerntanyarak L. 2013. Preparation of a TiO_2-coated photocatalytic air filter for use with an electrostatic air filter pack for xylene removal. *ScienceAsia* 39, 284–293.

Limmongkon Y., Sribenjalux P., Chuaybamroong T. 2009. Capability of electrostatic-filter air purifier on airborne microorganism removal. *J. Med. Tech. Phys. Ther.* 21, 246–256.

Malhi G.S. 2012. The chronic toxicity of titanium dioxide nanoparticles to the freshwater amphipod *Hyalella azteca*. *PhD thesis*, Wilfrid Laurier University, Ontario, Canada.

Martínez-Huitle C.A., Rodrigo M.A., Sirés I., Scialdone O. 2015. Single and coupled electrochemical processes and reactors for the abatement of organic water pollutants: a critical review. *Chem. Rev.* 115, 13362–13407.

Matsunaga T., Tomoda R., Nakajima T., Wake H. 1985. Photoelectrochemical sterilization of microbial cells by semiconductor powders. *FEMS Microbiol. Lett.* 29, 211–214.

Mihailović D., Šaponjić Z., Radoičić M., Lazović S., Baily C.J., Jovančić P., Nedeljković J., Radetić M. 2011. Functionalization of cotton fabrics with corona/air RF plasma and colloidal TiO_2 nanoparticles. *Cellulose* 18, 811–825.

Mills A., Lepre A., Elliott N., Bhopal S., Parkin I.P., O’Neill S.A. 2003. Characterisation of the photocatalyst Pilkington Activ^{TM}: a reference film photocatalyst? *J. Photochem. Photobiol. A* 160, 213–224.

Mondal S., Hu J.L. 2006. A novel approach to excellent UV protecting cotton fabric with functionalized MWNT containing water vapor permeable PU coating. *J. Appl. Polym. Sci.* 103, 3370–3376.

Morales-Torres S., Pastrana- Martínez L.M. 2014. Nanostructured carbon–TiO_2 photocatalysts for water purification: an overview. *Bol. Grupo Espanol Carbon* 32, 9−15.

Ni M., Leung M.K.H., Leung D.Y.C., Sumathy K. 2007. A review and recent developments in photocatalytic water-splitting using TiO_2 for hydrogen production. *J. Renew. Sustain. Energy* 11, 401–425.

Nica I.C., Stan M.S., Dinischiotu A., Popa M., Chifiriuc M.C., Lazar V., Pircalabioru G.G., Bezirtzoglou E., Iordache O.G., Varzaru E., Dumitrescu I., Feder M., Vasiliu F., Mercioniu I., Diamandescu L. 2016. Innovative self-cleaning and biocompatible polyester textiles nano-decorated with Fe–N-doped titanium dioxide. *Nanomaterials* 6, 214.

Nickheslat A., Amin M.M., Izanloo H., Fatehizadeh A., Mousavi S.M. 2013. Phenol photocatalytic degradation by advanced oxidation process under ultraviolet radiation using titanium dioxide. *J. Environ. Public Health* 23, 1–10.

NIOSH 2011. Occupational Exposure to Titanium Dioxide. In: Current Intelligence Bulletin 63. Cincinnati: National Institute for Occupational Safety and Health.

Nischk M., Mazierski P., Gazda M., Zaleska A. 2014. Ordered TiO_2 nanotubes: The effect of preparation parameters on the photocatalytic activity in air purification process. *Appl. Catal. B: Environmental* 144, 674–685.

Norambuena G., Patel R., Karau M., Wyles C., Jannetto P., Bennet K., Hanssen A., Sierra R. 2016. Antibacterial and biocompatible titanium-copper oxide coating may be a potential strategy to reduce periprosthetic ınfection: An *in vitro* study. *Clin. Orthop. Relat. Res.* 475, 722–732.

O'Neil M.J. 2013. The Merck Index - An Encyclopedia of Chemicals, Drugs, and Biologicals. Cambridge, UK: Royal Society of Chemistry, 1755.

Pakdel E., Daoud W.A., Afrin T., Sun L., Wang X. 2015. Self-cleaning wool: effect of noble metals and silica on visible-light-induced functionalities of nano TiO_2 colloid. *J. TEXT. I.* 106, 1348–1361.

Pasqui D., Barbucci R. 2014. Synthesis, characterization and self cleaning properties of titania nanoparticles grafted on polyester fabrics. *J. Photochem. Photobiol. A* 274, 1–6.

Patel A., Prajapati P., Boghra R. 2011. Overview on application of nanoparticles in cosmetics. *Asian J. Pharm. Clin. Res.* 1, 40–55.

Pérez-Flores J.C., Baehtz C., Kuhn A., Garcìa-Alvarado F. 2014. Hollandite-type TiO_2: a new negative electrode material for sodium-ion batteries. *J. Mater. Chem. A* 2, 1825–1833.

Poosti M., Ramazanzadeh B., Zebarjad M., Javadzadeh P., Naderinasab M., Shakeri M.T. 2012. Shear bond strength and antibacterial effects of orthodontic composite containing TiO_2 nanoparticles. *Eur J Orthod.* 35, 676–679.

Ribeiro A.R., Nunes O.C., Fereira M.F.R., Silva A.M.T. 2015. An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU. *Environ. Int.* 75, 33–51.

Senzui M., Tamura T., Miura K., Ikarashi Y., Watanabe Y., Fuji M. 2010. Study on penetration of titanium dioxide (TiO_2) nanoparticles into intact and damaged skin in vitro. *J. Toxicol. Sci.* 35, 107–113.

Shi H., Magaye R., Castranova V., Zhao J. 2013. Titanium dioxide nanoparticles: a review of current toxicological data. *Part. Fibre Toxicol.* 10, 15–48.

Shimohigoshi M., Saeki Y. 2007. Research and applications of photocatalyst tiles. In: International RILEM Symposium on Photocatalysis, Environment and Construction Materials – TDP, P. Baglioni, L. Casssar (Eds.), RILEM Publications SARL, 291–297.

Singh A.K. 2015. Engineered nanoparticles: structure, properties and mechanisms of toxicity. Elsevier Inc.

Smijs T.G., Pavel S. 2011. Titanium dioxide and zinc oxide nanoparticles in sunscreens: focus on their safety and effectiveness. *Nanotechnol. Sci. Appl.* 4, 95–112.

Spencer L.J. 1911. Anatase. In: Encyclopædia Britannica (11th ed.) Cambridge, UK, Cambridge University Press, 919.

Stan M.S., Nica I.C., Dinischiotu A.,Varzaru E., Iordache O.G., Dumitrescu I., Popa M., Chifiriuc M.C., Pircalabioru G.G., Lazar V., Bezirtzoglou E., Feder M., Diamandescu L. 2016. Photocatalytic, antimicrobial and biocompatibility features of cotton knit coated with Fe-N-doped titanium dioxide nanoparticles. *Materials* 9, 789.

Sunada K., Watanabe T., Hashimoto K. 2003. Studies on photokilling of bacteria on TiO_2 thin film. *J. Photochem. Photobiol. A.* 156, 227–233.

Tang B., Wang J., Xu S., Afrin T., Xu W., Sun L., Wang X. 2011. Application of anisotropic silver nanoparticles: Multifunctionalization of wool fabric. *J. Colloid Interface Sci.* 356, 513–518.

Thompson T.L., Yates Jr J.T. 2006. Surface science studies of the photoactivation of TiO_2-new photochemical processes. *Chem. Rev.* 106, 4428–4453.

Thunyasirinon C., Sribenjalux P., Supothina S., Chuaybamroong P. 2015. Enhancement of air filter with TiO_2 photocatalysis for *Mycobacterium tuberculosis* removal. *AEROSOL AIR QUAL. RES.* 15, 600–610.

Tricoli A., Righettoni M., Pratsinis S.E. 2009. Rapid synthesis of anti-fogging coatings. *NSTI-Nanotech* 3, 192–193.

Tryba B. 2008. Increase of the photocatalytic activity of TiO_2 by carbon and ıron modifications. *Int. J. Photoenergy* 2008, ID 721824, doi:10.1155/2008/721824.

Vasilev K., Cook J., Griesser H.J. 2009. Antibacterial surfaces for biomedical devices. *Expert Rev. Med. Devices* 6, 553–567.

Verdier T., Coutand M., Bertron A., Roques C. 2014. Antibacterial activity of TiO_2 photocatalyst alone or in coatings on *E. coli*: the influence of methodological aspects. *Coatings* 4, 670–686.

Veronovski N., Rudolf A., Smole M.S., Kreze T., Gersak J. 2009. Self-cleaning and handle properties of TiO_2-modified textiles. *Fiber. Polym.*10, 551–556.

Visai L., Nardo L., Punta C., Melone L., Cigada A., Imbriani M., Arciola C.R. 2011. Titanium oxide antibacterial surfaces in biomedical devices. *Int. J. Artif. Organs* 34, 929–946.

Wang J., Fan Y. 2014. Lung injury induced by TiO_2 nanoparticles depends on their structural features: size, shape, crystal phases, and surface coating. *Int. J. Mol. Sci.* 15, 22258–22278.

Wang W., Huang G., Yu J.C., Wong P.K. 2015. Advances in photocatalytic disinfection of bacteria: Development of photocatalysts and mechanisms. *J. Environ. Sci.* 1, 232–247.

Weast R.C. 1988-1989. Handbook of Chemistry and Physics (69th ed.) Boca Raton, FL: CRC Press Inc., B-140.

Wenzel S.M., Welzel J., Hafner C., Landthaler M., Bäumler W. 2010. Permanent make-up colorants may cause severe skin reactions. *Contact Dermatitis* 63, 223–227.

Weon S., Choi J., Park T., Choi W. 2017. Freestanding doubly open-ended TiO_2 nanotubes for efficient photocatalytic degradation of volatile organic compounds. *Appl. Catal. B.* 205, 386–392.

Wu B., Huang R., Sahu M., Feng X., Biswas P., Tang Y.J. 2010. Bacterial responses to Cu-doped TiO(2) nanoparticles. *Sci. Total Environ.* 408, 1755–1758.

Wu Y., Xu B. 2005. Synthesis and characterization of monoclinic TiO_2 nanosheets. *Chin. Sci. Bull.* 50, 2153–2156.

Xia Y., Zhu K., Kaspar T.C., Du Y., Birmingham B., Park K.T., Zhang Z. 2013. Atomic structure of the anatase TiO_2(001) surface. *J. Phys. Chem. Lett.* 4, 2958–2963.

Xiang Q., Yu J., Jaroniec M. 2012. Synergetic effect of MoS2 and graphene as cocatalysts for enhanced photocatalytic H_2 production activity of TiO_2 nanoparticles. *J. Am. Chem. Soc.* 134, 6575−6578.

Yadav H.M., Kim J.S., Pawar S.H. 2016. Developments in photocatalytic antibacterial activity of nano TiO_2: A review. *Korean J. Chem. Eng.* 33, 1989–1998.

Yamamoto M., Nishikawa N., Mayama H., Nonomura Y., Yokojima S., Nakamura S., Uchida K. 2015. Theoretical explanation of the lotus effect: superhydrophobic property changes by removal of nanostructures from the surface of a lotus leaf. *Langmuir* 31, 7355–7363.

Yoong L.S., Chong F.K., Dutta B.K. 2009. Development of copper-doped TiO_2 photocatalyst for hydrogen production under visible light. *Energy* 34, 1652–1661.

Yu J., Qi L., Jaroniec M. 2010. Hydrogen production by photocatalytic water splitting over Pt/TiO_2 nanosheets with exposed (001) facets. *J. Phys. Chem. C* 114, 13118–13125.

Yuan Y., Ding J., Xu J., Deng J., Guo J. 2010. TiO_2 nanoparticles co-doped with silver and nitrogen for antibacterial application. *J. Nanosci. Nanotechnol.* 10, 4868–4874.

Zhu T., Gao S.P. 2014. The stability, electronic structure, and optical property of TiO_2 polymorphs. *J. Phys. Chem. C* 118, 11385–11396.