5

Other Applications of Photo Catalyst in Dental Treatments in Diverse Fields

Seung-Ho Ohk[1] and Hyeon-Shik Hwang[2]
[1]*Department of Oral Microbiology,*
[2]*Department of Orthodontics and Dental Science Research Institute, Chonnam National University*
Korea

1. Introduction

Photocatalysts do not make the light faster. The term ‘photocatalyst’ represents chemical substances that act as a catalyst when exposed to light. For several decades numerous studies have been published about photocatalyst in water treatment process and air pollution control. Among several photocatalysts, TiO_2 has been considered as the most useful and harmless substance. With the illumination of UV-A light, TiO_2 photocatalysts decompose organic compounds through oxidation, with hydroxyl radicals (HO·) being produced by the oxidation of water. Various methods have been introduced for the surface modification of orthodontic treatment devices. Among them, Sol-gel dip-coating, CVD and PE-CVD methods were applied to coat photocatalytic TiO_2 on the surface of orthodontic wires and brackets. The antibacterial activities of the surface-modified orthodontic wires and brackets were demonstrated on *Streptococcus mutans* and *Porphyromonas gingivalis*. Viable cell counts with dilution-agar plate method and spectrophotometry were carried out to evaluate the antibacterial effect of photocatalytic TiO_2. Besides the photocatalytic degradation of organic compounds, there are several unique characteristics of photocatalytic TiO_2 were reported. In virtue of those characteristics it can be used in various ways such as preventing air contamination, anti-fog glasses and anti-bacterial paints. Sometimes many useful points are considered as handicaps in other point of view and vice versa. For example, to show photocatalytic activity for the TiO_2, usually it needs illumination with wavelength of less than 380. However, this drawback could be, in turn, used as a useful tool to control the release of hydroxyl radical from water since there is not much of UV-A in normal sun light.

The definition of photocatalysts and basic mechanism of photocatalytic activity will be described in this chapter.

Application and evaluation methods of photocatalyst, antibacterial efficiency on oral pathogens and safety of photocatalyst will be mentioned also. With the advantage of photocatalytic TiO_2, safety, versatile applications and other important remarkable characteristics of photocatalytic TiO_2 will be described in this section.

2. What is photocatalyst?

2.1 Photochemical reaction

Does the ‘photocatalyst’ catalyze photo-reaction or catalyze reactions with the exposure of light? Literally, both of the meanings are correct. However, the later will be explained in this chapter.The term ‘photocatalyst’ represents chemical substance that act as a catalyst when exposed to light. ‘Photocatalytic reaction’ again can be classified as one of photo-reactions. The most popular example of photo-reaction is a photographic film. Although digital imaging technique is popular these days, one of the most excellent inventions was the development of photography. In a traditional way of taking photo, a target image was exposed to a roll of film installed in the dark space of camera. This photographic film is a sheet of plastic paper such as polyester, nitrocellulose or cellulose acetate coated with a light-sensitive silver bromide emulsion. When the emulsion is exposed to sufficient light, bromide ion (Br^-) produces brom-atom and electron (e^-). This electron, in turns, binds to silver ion (Ag^+) to make metallic silver, which blocks light and appears as the black part of film negative.

$$Br^- + [light] \rightarrow Br + e-$$

$$Ag^+ + e^- \rightarrow Ag$$

In 1972, Honda and Fujishima have reported electrochemical decomposition of water (Fujishima & Honda, 1972). They have found that when platinum and titanium dioxide (TiO_2) were connected as cathode and anode, respectively, water is decomposed with a illumination of xenon lamp to make hydrogen and oxygen molecules (Fig.1).

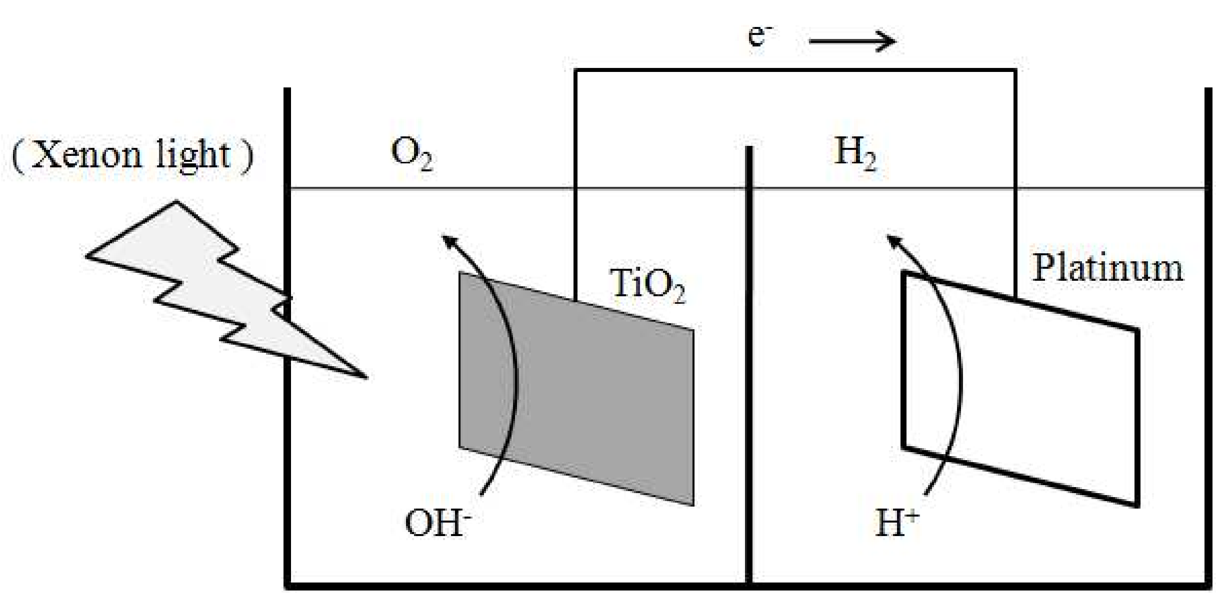

Fig. 1. Decomposition of water with photocatalytic TiO_2.

$$2H_2O + [Light, < 400\ nm] + TiO_2 \rightarrow 2H + O_2$$

This is a coupled reaction of reduction ($4H^+ \rightarrow 2H_2$) and oxidation ($4OH^- \rightarrow O_2 + 2H_2O$) with four molecules of water ($4H_2O$, $4H^+ + 4OH^-$) producing hydrogen and oxygen molecules.

Titanium dioxide can absorb light energy of below 400 nm and emits electrons to catalyze the decomposition of water.

2.2 Photocatalytic TiO_2

Several substances have been known to have photocatalytic activities such as ZnO, Nb_2O_5, WO_3, SnO_2, ZrO_2, CdS, ZnS, CdSe, and GaP. One of the most important reason that titanium dioxide is widely used is that it is chemically stable in most of acid, base and organic solvents. In the contrary, ZnO has similar energy band and high photocatalytic activity. However, when it is illuminated with light in aqueous solution, it can be easily dissolved in water as a Zn^+ ion. It also can be easily melt with sulfuric acid or nitric acid. Therefore, ZnO cannot be used separately.

3. Surface modification of orthodontic treatment devices

3.1 Anodic oxidation

When metal or silicon plates are immersed in an appropriate electrolyte a fine and rigid thin oxidized film will form on the surfaces plates. Anodic oxidation of aluminum is commonly introduced for their (semi-) transparent, anti-corrosion characteristics. The film composed by anodic oxidation usually shows stable conductivity. Neutral or acidic electrolytes are commonly used for aluminum, but there are not many options for other metals. Several dental implants have used anodic oxidation method for the surface modification to enhance their bone integration efficiency (Schupbach *et al.*, 2005).

3.2 Sol-gel dip-coating method

Dip-coating method is the oldest and most commonly used technique in deposition of thin film. Jenaer Glaswerk Schott & Gen are the first who have filed a patent with dip-coating technique for silica film in 1939. Sol-gel coatings, on the other hand, are being studied and applied in a diverse way such as protective coatings, passivation layers, ferroelectrics, sensors and membranes. The sol-gel dip-coating method uses inorganic precursors in aqueous or organic solvents. Those precursors are hydrolyzed and condensed to form polymers. Solid substrates are usually taken out of coating bath vertically at a constant speed. While taken out of the bath, the substrate entrains the liquid. Along with the evaporation of the solvent, wedge shaped film is formed on the surface of substrate. A lot of researchers have used sol-gel dip-coating method to study the application of the photocatalytic TiO_2 (Dongare *et al.*, 2003; Lee *et al.*, 2004; Zainal *et al.*, 2005).

3.3 CVD (Chemical vapor deposition) and PE-CVD (Plasma enhanced-CVD) method

Chemical vapor deposition method is the most widely used technique in semiconductor industries. It can form thin films from different precursors onto a substrate. In a CVD technique, a substrate is exposed to multiple volatile precursors with an inert gaseous carrier at high temperature and pressure. Those volatile precursors react or decompose on the surface of desired substrates, which form a thin film. Since CVD is one of the most well studied, and set up techniques, it is good for mass production.

Plasma enhanced CVD (PE-CVD) is a more progressed and important technique in VLSI (Very-large-scale integration) and TFT (Thin film transistor) manufacturing. The most important advantage of PE-CVD is low process temperature, which enables lower the manufacturer's budget. It uses plasma energy instead of heat energy for the reaction between precursors and substrates. Due to the wide range of applications of photocatalytic TiO_2, much of studies have been reported with CVD and PE-CVD technique for the application (Giavaresi *et al.*, 2003; Gluszek *et al.*, 1997; Gonzalez-Elipe *et al.*, 2004; Mills *et al.*, 2002).

4. Antibiotic effect of photocatalytic TiO_2

After Fujishima and Honda (Fujishima & Honda, 1972) reported the photolytic effect of TiO_2 in 1972, a series of efforts have been carried out to apply in various ways. Among them Matsunaga *et al*. have first reported photocatalytic TiO_2 has antibacterial effect on *Lactobacillus acidophilus, Saccharomyces cerevisiae* and *Escherichia coli* (Matsunaga *et al.*, 1985). Since hydroxyl radical (HO•) became of interest in decomposing organic compounds, it is no wonder to try antibacterial effect on various microorganisms. It was well documented that chemical oxidation with hydroxyl radical has a high activity in degradation of organic compounds (Ireland & Valinieks, 1992). Accordingly, antibacterial effect of photocatalytic TiO_2 that could efficiently produce hydroxyl radical in aqueous solution with illumination of light was demonstrated. Major microorganisms that have tested with photocatalytic TiO_2 were listed in Table 1.

According to the early report presented by Ireland *et al*. *Escherichia coli* showed rapid cell death in a mixture with the anatase crystalline form of titanium dioxide (Ireland *et al.*, 1993). Cho *et al*. also explained correlation between HO• radicals and the rate of *E. coli* inactivation which indicates that the HO• radical is the primary oxidant species responsible for inactivating *E. coli* in the UV/TiO_2 process (Cho *et al.*, 2004). Effort to clarify the antibacterial effect of titanium plate by surface modifications has been also reported. Yoshinari *et al*. tried to modify the surface of titanium plate by ion implantation (Ca^+, N^+, and F^+), oxidation (anode oxidation, titania spraying), ion plating (TiN, alumina), and ion beam mixing (Ag, Sn, Zn, Pt) with Ar^+ (Yoshinari *et al.*, 2001). Among them they have reported that F^+-implanted specimens significantly inhibited the growth of both *Porphyromonas gingivalis* and *Actinobacillus actinomycetemcomitans*. However, this antibacterial effect might be caused by the formation of a metal fluoride complex on the surfaces.

Since orthodontic wires and brackets provide a sufficient habitat for oral infectious microorganisms, orthodontic patients might have a higher risk of contracting other dental diseases (Balenseifen & Madonia, 1970; Sakamaki & Bahn, 1968; Scheie *et al.*, 1984). Therefore, as well as the orthodontic patients, clinicians should pay attention to reduce the chances for oral microorganisms to adhere to the surfaces of teeth and orthodontic wires. Chun *et al*. have tried to apply photocatalytic TiO_2 to orthodontic wires (Chun *et al.*, 2007). They used sol-gel dip coating method to modify the surfaces of wires. Special device for efficient illumination of UV-light to TiO_2-coated orthodontic wires using quartz cylinder was designed and used for the adhesion assay (Fig. 2). Since *Streptococcus mutans* that causes dental caries can easily adhere to tooth surface or orthodontic devices attached to tooth surfaces anti-adhesion effect of photocatalytic TiO_2 was monitored. Modified surface of wires showed effectively reduced adhesion of bacterial cells. Surface modification with photocatalytic TiO_2 enabled orthodontic wires to have effective anti-adherent characteristics. Using Scanning electron microscope damaged bacterial cell surfaces could be observed when treated with TiO_2. Similar effect was observed in *Porphyromonas gingivalis*, which is known as one of the major pathogen of periodontitis.

	Species	References
Bacteria	*Escherichia coli*	(Cho *et al.*, 2004; Ireland *et al.*, 1993; Kuhn *et al.*, 2003; Matsunaga *et al.*, 1985; Salih, 2002)
	Lactobacillus acidophilus	(Matsunaga *et al.*, 1985)
	Saccharomyces cerevisiae	(Matsunaga *et al.*, 1985)
	Streptococcus mutans	(Chun *et al.*, 2007; Elsaka *et al.*, 2011)
	Porphyromonas gingivalis	(Chun *et al.*, 2007; Yoshinari *et al.*, 2001)
	Bacillus atrophaeus	(Muranyi *et al.*, 2010)
	Kocuria rhizophila	(Muranyi *et al.*, 2010)
	Pseudomonas aeruginosa	(Kuhn *et al.*, 2003)
	Staphylococcus aureus	(Kuhn *et al.*, 2003)
	Enterococcus faecium	(Kuhn *et al.*, 2003)
Fungi	*Aspergillus niger*	(Muranyi *et al.*, 2010)
Yeast	*Candida albicans*	(Kuhn *et al.*, 2003)
Viruses	Rota virus	(Sang *et al.*, 2007)
	Astrovirus	(Sang *et al.*, 2007)
	Feline calcivirus (FCV)	(Sang *et al.*, 2007)
	Bacteriophage	(Gerrity *et al.*, 2008; Liga *et al.*, 2011)
Prion	PrP^{SC}	(Paspaltsis *et al.*, 2006)

Table 1. Major microorganisms that have positive results with photocatalytic TiO_2.

Other than antibacterial effect, the efficacies of TiO_2 on viruses and prion have also demonstrated. Sang *et al*. have tested rotavirus, astrovirus, and feline calcivirus (FCV) to verify the inactivation effect of TiO_2 with irradiation of visible light (Sang *et al.*, 2007). According to the report, light activated TiO_2 could partially degrade dsRNA of the rotavirus particles. They have found that activated TiO_2 with illumination of light in aqueous solution produces a significant amount of reactive oxygen species such as superoxide anions (O_2^-) and hydroxyl radicals (•OH) after activation for 8, 16, and 24 hrs. Destruction of nucleic acid was also confirmed by Ashikaga *et al*. (Ashikaga *et al.*, 2000). Those reactive oxygen species affect not only nucleotides but also other organic compounds such as peptides or proteins. With this special features, Paspaltsis *et al.* have examined the photocatalytic TiO_2 to prion protein, which is known to cause transmissible spongiform encephalopathy (TSB) (Paspaltsis *et al.*, 2006). Inoculation of prion protein (PrP^{SC}) with a TiO_2/H_2O_2 treatment to Syrian hamsters showed higher survival rate than control group and retarded presentation of clinical symptom for 50 days later. Since prion is strongly resistant to commonly used conventional decontamination methods, they have presented photocatalytic TiO_2 as a potential disinfecting agent for liquid waste and TSE infectious agent.

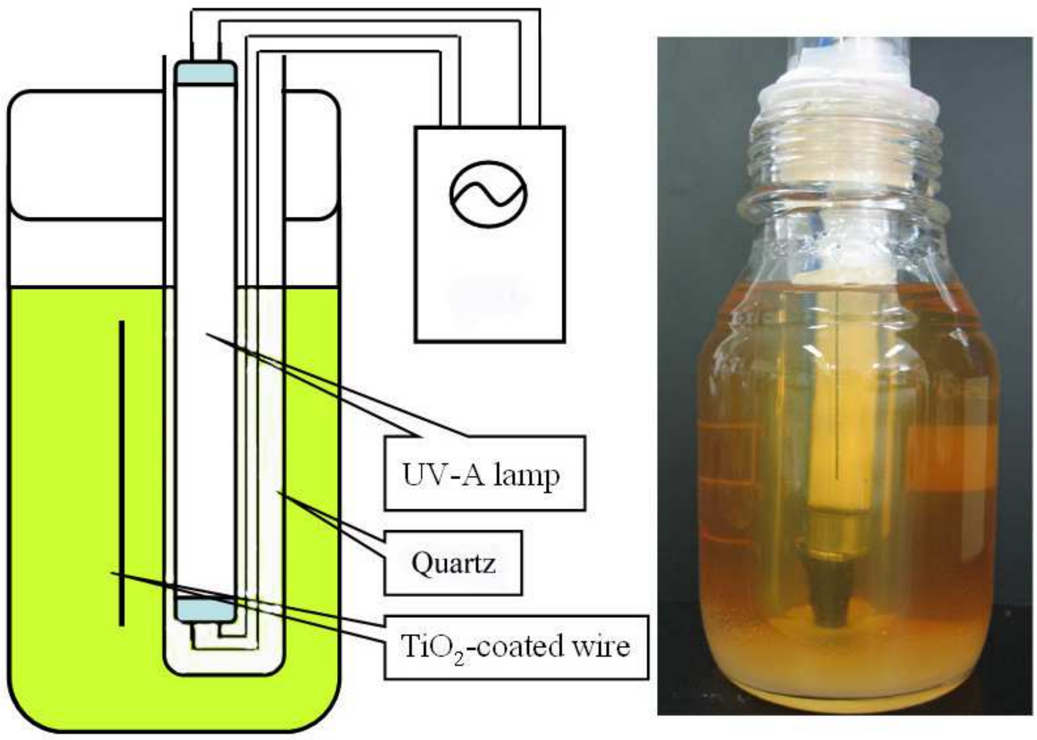

Fig. 2. Apparatus for the assay of anti-adhesion effect of TiO_2-coated orthodontic wire.

5. Other applications of photo catalyst in dental treatments

We are unconsciously in contact with diverse form of titanium dioxide these days. It is now commonly used in making papers, fabrics, toothpastes and wall paints. Photocatalytic TiO_2 has a broad spectrum of applications in virtue of its almighty capability of degrading almost every organic compounds. It has been realized that TiO_2 can absorb energy from light (usually UV light) and react with water molecules to produce reactive oxygen species.

One of the main focuses of applying photocatalytic TiO_2 was decontamination of polluted environments such as air cleaning system, decomposition of waste water. At the beginning of studies on the photocatalytic TiO_2, it was mainly applied to degrade highly toxic dyes from textile industries (Muneer *et al.*, 1997; Saquib & Muneer, 2003). However, its scope has been gradually expanded to various areas such as herbicides (Singh *et al.*, 2003) or pesticides (Daneshvar *et al.*, 2004) and other industrial waste water (Makino *et al.*, 2007).

Several companies producing ceramic tiles are using TiO_2 on the very surface of their products which is so-called self-cleaning tiles. Due to the ability to decompose organic molecules, these self-cleaning tiles can disinfect contamination of their surfaces by themselves only if there's a little portion of moisture and enough sun light. It might be very useful in hospitals, public restrooms, and household bathrooms. This unique advantage can be expanded to trivial devices used in most of clinics such as forceps, spatulas, scissors, and any rigid ceramic or metal surfaces to reduce the opportunity of cross infection.

Another useful aspect of TiO_2 is the hydrophilic property. Coating with photocatalytic TiO_2 layer on rigid ceramic or metal surfaces provides super-hydrophilic property that might dramatically reduce contact angle. Ohdaira *et al*. in Department of General Surgery, Jichi Medical Universitym Japan have designed special laparoscope that has antifogging effect (Ohdaira *et al.*, 2007). This property also can be applied to dental mirrors, bathroom mirrors, and car windows to impose antifogging characteristics.

6. Limitations and drawbacks of photocatalytic TiO_2

Even though photocatalytic TiO_2 has various utilities and potentials, still it has some limitations and drawbacks. It still needs improvements in reaction rate, broad spectrum of light source, specificity (or wide range of target) and stability. Several limitations and expected solutions are listed in Table 2. However, many of these are not solved yet.

Limitations	Solutions
Low reaction rate	Increasing surface area
Incomplete reaction	Fluid type reactor
Low efficiency	Increasing surface area
	Gas type reactor
Low specificity	Reactor design for specifically adsorption of target substances
Light source	Mixing with other inorganic compounds

Table 2. Several limitations of photocatalytic TiO_2.

6.1 Surface area

Since photocatalytic reaction occurs at the solid surface of TiO_2, it is very easy to separate substrates or products from photocatalyst. However substrates should be in contact with photocatalyst, which causes relatively low reaction rate and less homogeneity compared to other reactions such as gas-gas, or liquid-gas reactions. The first way to manage this problem is to increase surface area of the catalysts and the way to increase surface area is to reduce the particle sizes. Some solid catalysts are used in a unique three dimensional structure such as 'honey comb structure' to increase surface area. However it is not suitable for the photocatalytic TiO_2 because it needs illumination of UV or day light to activate. Therefore making round shaped particles and reduction in size may be the only way to increase surface area. Average diameter of commonly used TiO_2 ranges from 20 nm to 0.5 µm. Ultrafine particles of even below 10 nm of diameter are now developed and used in some fields. The average surface area of some ultrafine particle is reduced down to 7 nm which has about 300 m^2/g of surface area. Photocatalytic activity of this particle is 2 – 4 times higher than the particle that has 50 m^2/g of surface area. The activity did not increase as much as the surface area because ultrafine particles usually can aggregate each other. But there is no reason not to use ultrafine particles if it shows higher activity even though increasing fold of activity is not high as that of surface area.

6.2 Crystalline forms

Titanium dioxide forms three kinds of crystals: those are rutile, anatase, and brookite (Fig. 3). It is usually said that anatase crystal has higher photocatalytic activity than others. Depending on the crystalline type, binding structure of T-O and characteristics of crystal surface varies of course. However, the reason is unclear until now. Anatase crystal of TiO_2 can be formed between 400 – 500 ℃ and transformed to rutile at more than 900 ℃.

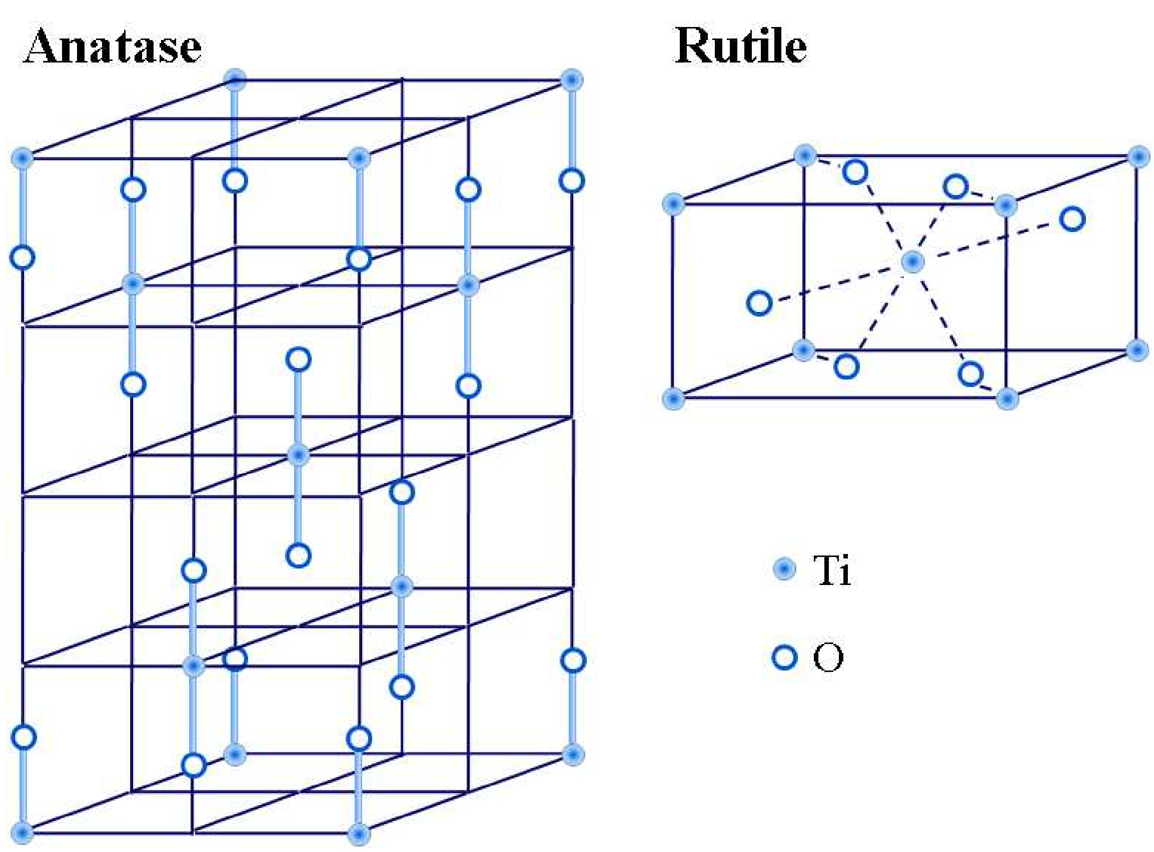

Fig. 3. Anatase and rutile forms of crystalline TiO_2.

6.3 Light sources

As the term 'photo-' represents, illumination of light is essential for the photocatalytic TiO_2 to get catalytic activity. It is the most important limitation in designing reactors with photocatalytic TiO_2. Even worse is the fact that most of photocatalytic TiO_2 can only utilize UV rather than visible light. It may not be a drawback of TiO_2, if any devices or reactors use natural sun light as a light source. However, in the view point of energy efficiency, if the reactor can utilize only a part of natural sun light and cannot utilize visible light, energy efficiency of the reactor will be less than 5% at most. Some of physical or chemical changes of titanium dioxide should be necessary to absorb and utilize visible light. Otherwise, photocatalytic TiO_2 can utilize visible light by mixing a small amount of other inorganic substances such as chromic oxide (Cr_2O_3, VI). However, in this case, reduced photocatalytic activity should be expected.

Limitation of light source may not always be a drawback of photocatalytic TiO_2. Since it produces hydroxyl radicals in aqueous solution and hydroxyl radical can decompose most of organic compounds, prolonged release of hydroxyl radical might be harmful in living organisms such as human. In case of antibacterial orthodontic wire described in section 3, it was coated with photocatalytic TiO_2 for its additional feature. The fact that releases of hydroxyl radicals from the photocatalytic TiO_2 for decomposition of bacterial cell wall compartments may imply a negative supposition. Hydroxyl radicals may also act on normal oral epithelial cells. In this case, the limitation of TiO_2 could, in turn, be a simple solution for the problem. The fact that relatively low intensity of UV light in normal day light is an advantage in this case. Since, photocatalytic activity of TiO_2 is usually activated by UV light, it can be regulated by manually controlling the illumination time and period in dental clinics.

7. Conclusion

When Fujishima and Honda reported the remarkable characteristics of titanium dioxide in 1972, few people have noticed the potentials of this white powder. Combined with the powerful effect of reactive oxygen species it became an almost almighty substance that can be used in environmental cleanup industries, personal hygiene products and even food industries. Not many substances have been interested in such diverse fields. However, there are still some drawbacks to overcome in the application of photocatalytic TiO_2. That means it is still worthy of challenge in the field of photocatalysis research.

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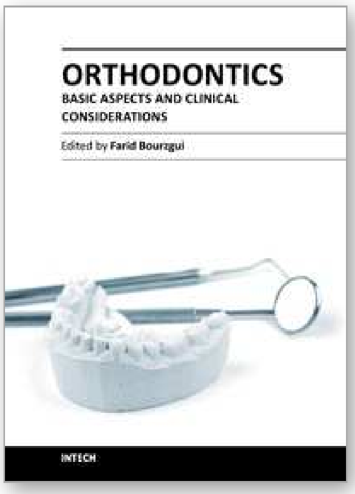

Orthodontics - Basic Aspects and Clinical Considerations

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The book reflects the ideas of nineteen academic and research experts from different countries. The different sections of this book deal with epidemiological and preventive concepts, a demystification of cranio-mandibular dysfunction, clinical considerations and risk assessment of orthodontic treatment. It provides an overview of the state-of-the-art, outlines the experts' knowledge and their efforts to provide readers with quality content explaining new directions and emerging trends in Orthodontics. The book should be of great value to both orthodontic practitioners and to students in orthodontics, who will find learning resources in connection with their fields of study. This will help them acquire valid knowledge and excellent clinical skills.