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Other Applications of Photo Catalyst in Dental Treatments in Diverse Fields

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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, TiO₂ has been considered as the most useful and harmless substance. With the illumination of UV-A light, TiO₂ 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 TiO₂ 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 TiO₂. Besides the photocatalytic degradation of organic compounds, there are several unique characteristics of photocatalytic TiO₂ 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 TiO₂, 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 TiO₂ safety, versatile applications and other important remarkable characteristics of photocatalytic TiO₂ 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.

\[
\text{Br}^{-} + \text{[light]} \rightarrow \text{Br} + \text{e}^{-} \\
\text{Ag}^{+} + \text{e}^{-} \rightarrow \text{Ag}
\]

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 an illumination of xenon lamp to make hydrogen and oxygen molecules (Fig. 1).

\[
\text{2H}_2\text{O} + \text{[Light, < 400 nm]} + \text{TiO}_2 \rightarrow 2\text{H} + \text{O}_2
\]

This is a coupled reaction of reduction (4H\(^{+}\) → 2H\(_3\)) and oxidation (4OH\(^{-}\) → O\(_2\) + 2H\(_2\)O) with four molecules of water (4H\(_2\)O, 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$_2$O$_5$, 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 Glaswerke 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
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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.

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

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 (TSE). Inoculation of prion protein (PrP$_{SC}$) with a TiO$_2$/H$_2$O$_2$ 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 photocatalyst in dental treatments

We are unconsciously in contact with diverse forms 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 compound. 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 systems, 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 sunlight. 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 University, 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.

<table>
<thead>
<tr>
<th>Limitations</th>
<th>Solutions</th>
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<tbody>
<tr>
<td>Low reaction rate</td>
<td>Increasing surface area</td>
</tr>
<tr>
<td>Incomplete reaction</td>
<td>Fluid type reactor</td>
</tr>
<tr>
<td>Low efficiency</td>
<td>Increasing surface area</td>
</tr>
<tr>
<td></td>
<td>Gas type reactor</td>
</tr>
<tr>
<td>Low specificity</td>
<td>Reactor design for specifically adsorption of target substances</td>
</tr>
<tr>
<td>Light source</td>
<td>Mixing with other inorganic compounds</td>
</tr>
</tbody>
</table>

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 TiO₂ 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 TiO₂ 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 m²/g of surface area. Photocatalytic activity of this particle is 2 – 4 times higher than the particle that has 50 m²/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 TiO₂ can be formed between 400 – 500 °C and transformed to rutile at more than 900 °C.

![Fig. 3. Anatase and rutile forms of crystalline TiO₂.](www.intechopen.com)
6.3 Light sources

As the term 'photo-' represents, illumination of light is essential for the photocatalytic TiO\textsubscript{2} to get catalytic activity. It is the most important limitation in designing reactors with photocatalytic TiO\textsubscript{2}. Even worse is the fact that most of photocatalytic TiO\textsubscript{2} can only utilize UV rather than visible light. It may not be a drawback of TiO\textsubscript{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\textsubscript{2} can utilize visible light by mixing a small amount of other inorganic substances such as chromic oxide (Cr\textsubscript{2}O\textsubscript{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\textsubscript{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\textsubscript{2} for its additional feature. The fact that releases of hydroxyl radicals from the photocatalytic TiO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2}. That means it is still worthy of challenge in the field of photocatalysis research.

8. References


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of diesel engines by means of thermally excited holes in titanium dioxide at high temperatures. *Ipn J Appl Phys* 1, 46, 6037-6042.


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.

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