An Overview Of The Photo-Catalysis Of Titanium Dioxide Nanotubes And Their Effect On Human Life

Basma Esam Jasim 1,*, Nibras Abdul-Ameer Aboud 1

1 Department of Chemical Industrial, Institute of Technology/Baghdad, Middle Technical University, Iraq.

Abstract
Nanomaterials are engineered materials with extremely small particle sizes with at least one dimension ranging from one to one hundred nanometers. Nanoscale materials contain unique electrical, magnetic, catalytic, and optical properties that can be applied in various fields, including engineering, medicine, and the environment. Nanomaterials with appealing chemical and physical properties are being researched for potential energy and environmental applications. Nanomaterials have grabbed people's interest due to their ability to enhance efficiency through-beam gap control, chemical composition, structural diagram, light propagation, and charge/transport collection, among other things. Titanium dioxide (TiO₂) nanoparticles are mass-produced all over the world for use in a range of applications. TiO₂ nanostructured materials have aroused much interest in the energy and environmental sectors due to their future applications in photocatalysis, solar cells, and pollution remediation. Furthermore, because TiO₂ nanoparticles are widely available, inexpensive, and non-toxic, they are routinely employed in various products, including cosmetics, where they are used as a UV filter in sunscreens, face creams, foundation, and lipstick. Analgesics. Because of the relevance of titanium dioxide, we will discuss it in this review by demonstrating its characteristics, photocatalysis mechanism, and uses that come into direct contact with human existence.

1. Introduction

Nanotechnology is the study of tiny structures. "Nano" is derived from the Greek word for "dwarf." The second interpretation of the word "Nano," which is a small thing in size, is that the word Nano can only be used for very small sizes. Engineering science is defined as a science that involves the treatment of atoms, molecules, or compounds within structures to provide specified properties to materials and electronics. As a result, engineering science is concerned with materials with dimensions ranging from [1 - 100] nanometers. Because of their small size, these nanomaterials exhibit drastically different properties than bulk materials, such as electrical, mechanical, magnetic, and optical effects [1].
2. Applications of Nanotechnology
Among the most important fields that nanotechnology has entered into its applications [2]:
1. Electronics field.
2. Transportation field.
3. The field of energy and the environment.
4. The field of space exploration

3. Titanium Dioxide Nanoparticles
Titanium dioxide (TiO₂) is one of the most important metal oxides known for a long time, as it has been known since ancient times for its ability to act as a photocatalyst, and as a result of these two properties, its applications have expanded as it has become used in self-cleaning of building windows, and in the manufacture of cement, paints, and anti-dirt paints and dirt, as a result of these two properties (air purification system and water filters). TiO₂'s most important applications are dye applications [2, 3].

One of the most important characteristics of TiO₂ nanoparticles that have drawn the world's attention is that it is a white solid, thermally stable, non-flammable, and poorly soluble, in addition to being cheap and non-toxic or (environmentally and human-friendly). Thus it is not classified, and They are not hazardous according to the United Nations Globally Harmonized System of Classification and Labeling of Chemicals (GHS) [4]. Because of the extraordinary qualities of TiO₂ nanoparticles, we can today find it in almost every white surface and thing in our civilization. As a result, we are surrounded by TiO₂-containing materials in our homes, workplaces, and public spaces. Since the commercialization of TiO₂ in 1923, there have been no identified health risks connected with consumer and general public exposure to titanium dioxide [5].

TiO₂ is a transition metal oxide in three forms: anatase, brookite, and rutile. Titanium dioxide nanoparticles have recently been identified as widely used as photocatalysts due to their non-toxicity and chemical stability. According to a laboratory study, using molecular molecular can also successfully convert organic compounds such as alcohol, carboxylic acid, phenolic derivatives, and chlorinated aromatics can also be successfully converted by TiO₂ into harmless carbon dioxide, water, and simple mineral acids oxygen as the primary oxidizing agent [6].

4. Photocatalytic mechanism of TiO₂
The photocatalytic process of titanium dioxide nanoparticles primarily includes the step of generating electron pairs and holes (h + / e⁻), which results from the exposure of titanium dioxide nanoparticles to ultraviolet rays of less than 400 nm, where a series of Photochemical reactions on the surface of a solid catalyst, represented by the redox reactions, are illustrated in Figure 1 [7–9].

The photocatalytic mechanism of titanium dioxide nanoparticles is simple to understand. When titanium dioxide nanoparticles are exposed to UV light, electrons in the valance band are immediately stimulated into the conduction band, leaving holes behind. These holes, in turn, will participate in the oxidation processes by generating hydroxyl radicals (OH⁻), which are strong oxidizing agents capable of breaking down organic pollutants and converting them to carbon dioxide and water. In contrast, the excited electrons in the conduction band will participate in the reduction process by generating superoxide radicals (O₂⁻), considered one of the most important factors contributing to breaking down organic pollutants [8, 10].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ + hv → h⁺ + e⁻</td>
<td>Photochemical reaction</td>
</tr>
<tr>
<td>O₂ + e⁻ → 'O₂⁻</td>
<td>Generation of oxygen radicals</td>
</tr>
<tr>
<td>H₂O + h⁺ → H + + 'OH</td>
<td>Generation of hydroxyl radicals</td>
</tr>
<tr>
<td>OH⁻ + h⁺ → 'OH</td>
<td>Generation of hydroxyl radicals</td>
</tr>
<tr>
<td>2 'O₂⁻ + 2H⁺ → H₂O₂ + O₂</td>
<td>Reaction of oxygen radicals with water</td>
</tr>
<tr>
<td>'OH + 'O₂⁻ → H₂O₂</td>
<td>Reaction of hydroxyl radicals with oxygen radicals</td>
</tr>
<tr>
<td>H₂O₂ + 'O₂⁻ → 'OH + OH⁻ + O₂</td>
<td>Reaction of hydrogen peroxide with oxygen radicals</td>
</tr>
<tr>
<td>Substrate + 'O₂⁻ + 'OH → CO₂ + O₂ + by-product</td>
<td>Conversion of substrate to harmless products</td>
</tr>
</tbody>
</table>

Figure 1. Photocatalytic mechanism of TiO₂.
5. Titanium Dioxide Nanoparticles Application

In recent years, it has been observed that the application of nanotechnology has expanded in all fields, especially titanium dioxide nanoparticles, as it has been observed that it has become used in the field of personal care products such as sunscreens that are either creamy or in the form of sprays and cosmetics, of which I especially mention compact powder and skin whitening. And lip balms and other personal care creams, which raised the question of many scientists and even users about the danger of these nanomaterials on the health of the user of these products, either through direct contact with the skin or through products that are inhalable by the user, and on this Basis the International Agency for Research on Cancer stated that it is possible titanium dioxide nanomaterials can be carcinogenic to humans when they are inhalable, and this, in turn, depends on the amount of dose that was inhaled, the duration of inhalation and the number of inhalation. While at the same time, the International Agency for Research on Cancer stated that no injury or real threat to human life has been recorded due to the use of titanium dioxide nanoscale in all products. Still, on the contrary, it has become used to remove pollutants from water and air in addition to the field of medicine in which it has achieved unparalleled success, so we will present some applications of titanium dioxide nanoparticles. Through these applications, we will [11].

6. Removal of Air Pollutants By Titanium Dioxide Nanoparticles

Several air pollutants are found in the atmosphere, which can have major consequences for the ecosystem and human health. Most of them are made of inorganic materials. They can be removed using ordinary procedures, but the other group is made of organic materials and is difficult to remove, necessitating the development of new removal methods. The most harmful organic chemicals are those that are volatile. The harm caused by these substances, which can be found indoors and outdoors, varies depending on the exposure dose and exposure time. They are mostly derived from combustion plants, motor vehicles, and various industrial items. When all of these factors are considered, eliminating VOCs becomes critical [12].

In this field, titanium dioxide nanoparticles lead the way in treating organic dirty air via a photocatalytic mechanism that operates as follows: To eliminate air pollutants, the photocatalytic oxidation method employs hydroxyl radicals formed by water cleavage. The air stream in this system goes through the entrance of a reactor containing a semi-conductive substance and is exposed to light at a specific humidity level. During this process, the semiconductor material absorbs light and causes electrons to travel. Moving electrons cause charge separation between the valence and conduction bands. The semiconductor material gains photocatalytic characteristics as a result of charge separation. Both excited electrons and positively charged holes interact with O2 and H2O in the air stream, creating hydroxyl radicals, which are classified as (powerful oxidizing agents) that interact with the absorbed oxygen. air pollutants (VOC) and lead to their breakdown into CO2 and H2O [13, 14].

Breakdown products change according to the inorganic or organic composition of air pollutants. Figures (2) and (3) illustrated of photocatalytic oxidation process for organic air pollutants.

Figure 2 illustrated photocatalytic oxidation process for organic air pollutants [9]
Titanium dioxide nanoparticles in sunscreens

The increased usage of nanomaterials in the consumer products industry has resulted in a re-evaluation of the safety of these nanomaterials on consumer health, including titanium dioxide (TiO$_2$) nanoparticles, which are widely employed in the creation of cosmetics, skincare, and sunscreens. They are also employed as colorants in processed foods and a variety of other consumer goods. This necessitated the need to ask numerous critical questions, the most essential of which are: Is it safe to use sunscreens containing titanium dioxide nanoparticles? Do titanium dioxide nanoparticles vary from other nanomaterials in their behavior?

Based on available scientific evidence, the Scientific Committee on Consumer Safety (SCCS) has confirmed that titanium dioxide nanoparticles, whose safety has been assessed, used at a concentration of up to 25% as a UV filter in sunscreens, can be considered safe for human life at this concentration if used on healthy or sunburned skin, and on this basis, it became necessary for all manufacturers of this type of skincare product (sunscreen) [15, 16].

Inhaling nanoparticles can result in toxicity and pneumonia, which can progress to lung cancer. As a result, SCCS advises against using titanium dioxide nanoparticles in applications that involve significant inhalation of nanomaterials, such as powders or sprayable products, while the expected risks from contacting this nanomaterial with the skin or eyes, which is represented by skin or eye irritation, are very low (eczema with dry itchy skin). Furthermore, there is no relevant information about so-called reproductive toxicity at this time, but some scientific research suggests that if titanium dioxide nanomaterial penetrates the body, it may cause damage to the genetic material of the cells (for example, damage to cells in some organs may lead to cancer and damage to sperm cells may lead to infertility) [17].

The photocatalytic feature of titanium dioxide nanoparticles, thanks to which its luster shines in a variety of applications, has occupied the minds of scientists and researchers as they considered the prospect of titanium dioxide nanoparticles acting as a photo-catalyst in some circumstances. This means that it can interact with ultraviolet light (such as the sun or any other source of ultraviolet radiation) to speed up photosynthesis, resulting in the oxidation of some biological components and the formation of free radicals. This, in turn, may exacerbate the harmful consequences indicated above, however this does not apply to titanium dioxide particles used in cosmetics when adequately encapsulated such that the nanoparticles do not operate as photocatalysts while still serving as a UV filter. However, manufacturers of sunscreens are advised to avoid using titanium dioxide nanoparticles that have a significant photocatalytic activity or to properly treat the surface of these nanoparticles with a stable and safe coating material [18].

TiO$_2$ and inhibition bacterial Infections

Who among us is not afraid of bacteria, and who does not think of a way to get rid of bacterial reproduction, which has become one of the most important problems that plague our daily lives. For example, he is largely responsible for the noticeable damage in many industries, including the manufacture of fabrics and bed linen and in industries based on water treatment, biomedicine, and packaging. Food and many other industries are facing a fierce war with so-called bacterial reproduction, also concerns about the emergence of microorganisms that have become resistant to antibiotics have encouraged the search for new treatments for infectious diseases. For example, some Gram-positive (for example, Staphylococcus aureus) and Gram-negative (Escherichia coli, Pseudomonas) bacteria have mutated into multi-drug resistant (MDR) pathogens and are a major cause of hospital-acquired infections. Therefore, new, cheap and effective antimicrobial agents are urgently needed to control bacterial activity, and nanomaterials constitute a very promising approach in this field [19, 20].

Some nanomaterials exhibit antimicrobial properties not found in ordinary materials. Among these nanomaterials
are silver nanoparticles (Ag NPS), which are now used in wound dressings, medical device coatings, and even in food packages. A large number of studies also demonstrate the antimicrobial properties of titanium dioxide nanoparticles due to the photocatalytic effect of this material, which includes the creation of free radicals such as O₂⁻, OH⁻, and H₂O₂. It is the product of the redox reactions that occur between the absorbent material (water or oxygen) and the TiO₂ electrons when illuminated by UV light with a wavelength shorter than 385 nm. The most important defect of TiO₂ is its necessity for ultraviolet irradiation to activate the photo-catalyst [21, 22].

9. TiO₂ NPs and foodstuffs

As a result of the expansion of the applications of nanotechnology in recent years and its entry into many consumer industries, it has become necessary to conduct a careful study to follow up the proportions of these manufactured materials and the extent of their impact on human health, especially about the field of food and beverages and methods of their packaging. For this according to the Consumer Products Inventory of Nanotechnology (CPI), as of March 2015, the global market introduced about 1,814 products based on nanomaterials, including 117 products in the food and beverage industry, and in the USA, TiO₂ NPs can be used in food if their content does not exceed 1% of the total weight of the TiO₂-containing product.

Among the foodstuffs that a person consumes daily and titanium dioxide particles are added to them are (skimmed milk, chewing gum, sauces, chocolate, ice cream, cheese, and other sweets to which titanium dioxide is added as a food color, and observed the ratio of TiO₂ in these products about 2.5 mg TiO₂ / g of the weight of Food, It’s estimated that a child can consume up to 2-4 times more TiO₂ NPs per 1 kg of body weight per day compared to an adult [23].

10. Safety of TiO₂ NPs and Foodstuffs

On May 11, 2010, the European Union published a new law requiring premarket risk assessment for novel meals containing nanoparticles. Once cleared for ingestion, all Nano-sized components must be labeled “Nano” (nanotechnology). The safety of nanoparticles in food has received a lot of attention. Because TiO₂ nanoparticles are one of the most widely used nanomaterials in the food industry, research on the health and safety implications of TiO₂ NPs in food is crucial [24].

Despite extensive research into TiO₂ NPs' oral toxicity, no definitive conclusion on their food safety has been reached. TiO₂ NPs absorb very little through the gastrointestinal tract after oral consumption, and the bulk is excreted in feces. TiO₂ NPs can be transported and stored in a variety of organs when exposed for a short period of time and at a high dose, but there is no evidence of transport or accumulation when exposed for a long period of time and at a low dose. The major target organ is the liver, but damage to the GI tract, heart, spleen, kidneys, and central nervous system have also been reported [25].

Nanomaterials have two biological effects: one that is known as the direct path and one that is known as the indirect path. The direct method involves TiO₂ NPs accumulating in organs and tissues and causing direct damage, whereas the indirect method involves activating oxidative stress and inflammatory responses, as well as the action of the gut microbiota, which results in future organ damage. In addition, 12 clinical trials on TiO₂ NPs discovered that the acute oral toxicity of TiO₂ NPs was low. The effects of subacute and subchronic toxicity were dramatically amplified with increased exposure time and number of exposures, indicating that long-term toxicity of TiO₂ NPs may be more detrimental than short-term toxicity. Nanomaterials have two biological effects: one known as the direct path and one known as the indirect path. The direct method involves TiO₂ NPs accumulating in organs and tissues and directly causing damage, whereas the indirect method involves activating oxidative stress and inflammatory responses, as well as the action of the gut microbiota, which leads to future organ damage. Furthermore, 12 clinical trials on TiO₂ NPs discovered that the acute oral toxicity of TiO₂ NPs was negligible. The effects of subacute and subchronic toxicity were dramatically amplified with increased exposure time and number of exposures, indicating that long-term toxicity of TiO₂ NPs may be more detrimental than short-term toxicity [26].

Most recent studies have primarily focused on the toxicity of nanomaterials, specifically titanium dioxide nanomaterials, by conducting toxicity experiments at high doses and for a short period of time, whereas studies of low doses of nanomaterials by the general public are still limited, and few studies have shown that human exposure to TiO₂ NPs orally and in different regions varies greatly, ranging from 0.19 to 13.5 mcg/kg BW / day. However, no population study or epidemiological study on the safety of foods containing TiO₂ NPs has been reported, thus more research is needed to determine the health consequences of TiO₂ NPs consumed orally by humans in a real-world exposure environment [27].

In the future, research on TiO₂ NPs' food safety must focus on the combined effects of TiO₂ NPs with other compounds. The human body's dietary intake of TiO₂ NPs is frequently a complicated mechanism. The interaction of
TiO₂ NPs with other chemicals, particularly nutrients in food, is worth investigating. Many in vitro tests have revealed that TiO₂ NPs are easily interacting with various substances. It has been observed that TiO₂ NPs are commonly ingested with a significant amount of sugar [28].

In vivo, we found that TiO₂ NPs and high hyperglycemia had a substantial impact on toxicity. Furthermore, Because of their sweet tooth, youngsters were shown to have the most exposure to TiO₂ through foods. In a prior investigation, we discovered that the oral toxicity of TiO₂ NPs was greater in young rats than in adult rats. As a result, when scientists investigate the safety of TiO₂ NPs in food, they should pay special attention to youngsters as a vulnerable demographic. Furthermore, TiO₂ NPs had a substantial antibacterial effect on intestinal bacteria, which was reasonable given that the vast majority of orally consumed TiO₂ NPs were not digested and merely went through the alimentary canal [29].

Despite what has been said previously about potential concerns and toxic effects from direct consumer exposure to nanomaterials, in its most recent assessment on the safety of E171 (titanium dioxide) used in food, done in 2016, the European Food Safety Authority (EFSA) determined that data on consumer exposure to titanium dioxide nanoparticles in food is not cause for concern. Due to a paucity of study data, the suggested daily consumption of TiO₂ NPs has not been determined [30, 31].

11. Conclusion

Nanotechnology is a science and engineering field that investigates, comprehends, and manipulates materials with dimensions ranging from 1 to 100 nanometers. Its applications include physics, chemistry, biology, materials science, and engineering. Nanotechnology is the fundamental study of physical, chemical, and biological properties at the atomic and molecular scales and the manipulation of these properties to build functional materials and systems with unique capabilities. On this basis, we have highlighted that one of the most important nanomaterials is Titanium dioxide nanoparticles. We have reviewed its most important applications and the extent of its impact on human life.

Perhaps one of its most important applications appeared in the field of medicine and pharmacology, where titanium dioxide nanoparticles entered strongly, starting with diagnosing pathological conditions and tumors (Diagnosis) and were also used as drug delivery and considered very important. Its advantage over traditional drug conductors is that the body absorbs them very quickly. Thus the doses given to patients can be reduced in addition to reducing time and money. experiments are still ongoing to prove its success in treating cancerous diseases and its ability to address microorganisms by producing antibiotics, which is the new alternative to antibiotics. They can be assembled in the form of nanotubes. When millions of these sticky tubes enter the gelatinous root of bacteria, they are chemically attracted to each other and assemble themselves into long, self-assembled tubes that puncture the cell membrane. These groups of adjacent tubes open larger pores in the bacterial cell wall, and within a few minutes they die. The bacterial cell is a result of the dispersal of the external electrical potential of its membrane, and this practice ends the life of the cell.

In food, titanium dioxide nanoparticles have been used in some food industries, whether as food coloring or preserving and canning, because of their ability to reduce the risks of harmful bacteria to health by killing bacteria from safe boxes.

In the field of cosmetics, titanium dioxide played a major role, as it was used in the manufacture of sunscreen, skin moisturizers, and lipstick, but in limited proportions, according to what was permitted by the World Food and Drug Organization. Therefore, through all that we reviewed previously, we can say that nanoscale titanium dioxide has a bright and promising future in our lives.

Conflict of Interest
The authors declare that they have no conflict of interest.

References


