

# Nanoparticles in sunscreen: exploration of the effect and harm of titanium oxide and zinc oxide

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**Abstract.** In recent years, cosmetics have shown a positive development due to its own various properties, functionalities and applications. But as we know, microorganisms can cause the decomposition, deterioration and corruption of cosmetics, bringing economic losses. Therefore, commodities with bactericidal and antibacterial effects are attracting more and more people's attention. People found nanoparticles can be used in the cosmetics like sunscreen to have UV protection and prevent bacteria simultaneously. In this review, it firstly discuss the nanotechnology and different mechanisms of process of sun protection. In main body, it focused on the nano size of titanium dioxide and zinc oxide particles in sunscreen. Then taking a deeply research on their preparation, effectiveness and toxicity, respectively. In nano titanium dioxide part, because of specific functions, the antibacterial property of it is also been shown. Finally, having a summary and expectation of the nano particles in sunscreen.

**Keywords:** Titanium oxide, Zinc oxide, sunscreen, nanoparticles.

## 1. Introduction

Nanotechnology is a new generation of innovation in science and engineering, where we can observe and control individual atoms and molecules in the nanoworld. Everything on earth is made of atoms, which means that through nanotechnology we can change its properties by transforming its atoms. Nanotechnology has been developing rapidly in recent years and has been applied in many fields in the form of milestones. Nowadays we can use new technological means to manufacture materials, using nanotechnology to scale them down to nano size. Nanomaterials have nanoscale dimensions that allow the materials to have many distinct physical and chemical properties, such as a large specific surface area, high activity, and quantum effects. It is because of these properties that traditional materials are gradually being replaced by nanomaterials. They are now being used in a wide range of applications in the fields of medicine, cosmetics and energy, and have achieved a high degree of recognition. For example, they enable higher energy conversion rates, more accurate delivery of small molecule drugs and improved efficiency in cosmetics. In sunscreens, titanium dioxide and zinc oxide nanoparticles have become indispensable ingredients.

The most common sunscreens in the market today are divided into chemical sunscreens and physical sunscreens. The two types of sunscreens differ greatly in their active ingredients and mechanisms for protecting the skin, and their effects demonstrate different results. Chemical sunscreens contain oxybenzone. Its role is to decompose or blunt sunlight, producing a chemical reaction that converts UV radiation into heat, which is then released from the skin, but it takes about 20 minutes after application to start to act. Oxybenzone is harmful to the environment and its toxicity and effects on the human body can be significant if applied in large doses. By comparison, physical sunscreens are safer. They contain the effective constituent titanium dioxide and zinc oxide, which are less irritating to our skin and more friendly to the environment than oxybenzone, so physical sunscreens mainly dominate the sunscreen market.

The use of nanoscale materials has secured the position of physical sunscreens in the sunscreen market. Titanium dioxide and zinc oxide nanoparticles are smaller, apply more evenly on the skin, are less whitish, and increase the surface area for reflecting UV radiation. Physical sunscreens provide instant protection without waiting and are effective immediately. Physical sunscreens can also be applied over cosmetics and other skincare products as zinc oxide and titanium dioxide are chemically inert and do not react easily with other chemicals. Due to the adhesive nature of titanium dioxide and zinc oxide, physical sunscreens can easily be sweated off and thus lose their protective effect, so frequent and repeated applications are required. Zinc oxide is a naturally reflective material and due to the use of nanotechnology in sunscreens, zinc oxide has also been scaled down to the nanoscale and is almost invisible to the naked eye. Zinc oxide contains antibacterial factors, which also help wounds heal more quickly. The most notable benefit of zinc oxide is that it protects your skin from the sun and it is also one of the most effective types of active sunscreen ingredient, blocking short-wave and long-wave UVA radiation and all UVB radiation. The role of titanium dioxide in sunscreens is mainly shown by the whitening, thickening, and lubricating while protecting from the sun. Unlike zinc oxide, it does not protect against long-wave UVA radiation. Titanium dioxide is milder, less likely to cause acne and pimples, and is more friendly to consumers with sensitive skin.

Physical sunscreens incorporate both zinc oxide and titanium dioxide to achieve the benefits of these two minerals and to maximize the benefits of protection from UV radiation. Consumers are demanding more and more from sunscreens in terms of their effectiveness, safety, and functionality. After a long period of experimentation, the active ingredients in sunscreens are constantly updated and improved, combined with the weighting of factors such as cost and effectiveness, so that sunscreens achieve the highest sun protection effect and the lowest cost to mass-market sunscreens. In the meanwhile time, it is possible to try mixing other mineral ingredients to increase the stickiness of the physical sunscreen so that it stays on the skin for longer. There are still many problems with the use of nanotechnology in sunscreens, there are some safety concerns as to whether they can penetrate through the skin and react with molecules in our bodies to affect the normal operation of our tissues and organs. Also and a comparison can be made between ordinary sunscreens and nanotechnology sunscreens to test the extent to which titanium dioxide and zinc oxide nanoparticles can attenuate UV radiation.

## 2. The basic introduction of UV radiation

The ozone layer is a natural barrier to the earth, protecting humans from ultraviolet radiation. The ozone layer minimizes the effects of UV radiation by absorbing UVC radiation and reducing UVA and UVB radiation. However, in recent years, the massive use of chlorofluorocarbon chemicals by humans has reduced the concentration of ozone, thus causing serious damage to the ozone layer and increasing the amount of UV radiation reaching the earth. Exposure of the skin to UV radiation causes numerous severe health problems.

Ultraviolet light is a form of electromagnetic radiation that ranges in frequency from 30 PHz to 750 THz. UV radiation is mainly derived from sunlight, causes many complex chemical reactions that are not simply bond breaking and bond formation, and involves the formation of free radicals. UVA,UVB and UVC rays are collectively known as UV radiation, but as the atmospheric ozone absorbs UVC, ambient sunlight is mainly UVA and UVB, with UVA making up the largest proportion of the ambient content.

Most skin cancers are caused by exposure to UV light, in which the two most common types of skin cancer are basal cell carcinoma and squamous cell carcinoma. UV light is only absorbed by the skin but does not penetrate deeply into the body's internal tissues, so they are not expected to cause cancers of internal organs.

UVA has a higher wavelength but lower energy level than other UV rays, and UVA is more penetrative than UVB rays. They affect cells deep in the skin, causing premature aging, thus leading

to visible effects such as wrinkles. The effects of UVA rays often appear immediately as it causes tanning and sunburn.

UVB radiation can damage the outermost epidermis of the skin and can directly damage the DNA in the skin's epidermis, cause cancer. Overexposure to UVB rays also causes sunburn but the effects of UVB rays can be postponed, or appear several hours after sun exposure.

To prevent and reduce the harmful caused by UVA and UVB radiation to our skin, sunscreens have emerged. The protective strength of a sunscreen is measured by the SPF, which is an accepted indicator of UV radiation protection. Usually, manufacturers will add a large number of active sunscreen ingredients to increase the value of the SPF. Nonetheless, the addition of large amount of active sunscreen ingredients is not the greatest as they may raise some safety concerns, but these will need to be evaluated in future trials and studies.

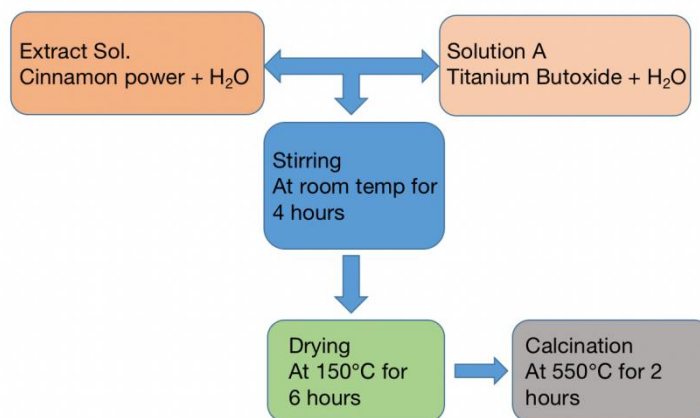
### **3. TiO<sub>2</sub> in sunscreen.**

#### **3.1. Effectiveness of nano-TiO<sub>2</sub> in sunscreen**

Nano titanium dioxide used in sunscreen cosmetics is safe, non-toxic and has high uv shielding efficiency. The capacity of nano titanium dioxide absorption and scattering is the main factor to have the UV shielding performance. The smaller the original particle size of nano-sized titanium dioxide, the stronger the UV absorption capacity. Experiments show that the longer the UV wavelength, the greater the effect of the shielding result on nano titanium dioxide ability of scattering. In contrast, the shorter the UV wavelength, the greater the effect of absorption shielding. Nano titanium dioxide size, however, is not minimal, because nanometer titanium dioxide particles exist inevitable agglomeration phenomenon leads to nanometer titanium dioxide for dispersion, help to plug the pores of our skin and is bad for skin breathing and sweat to eliminate defects. It shows that particle size is range from about 30 to 100nm, the effect of UV shielding is better, and the skin can be enriched with natural beauty through visible light. The powder of nano titanium dioxide is mainly used in the cosmetics, other formation is dispersion liquid.

#### **3.2. Preparation of nano-TiO<sub>2</sub>**

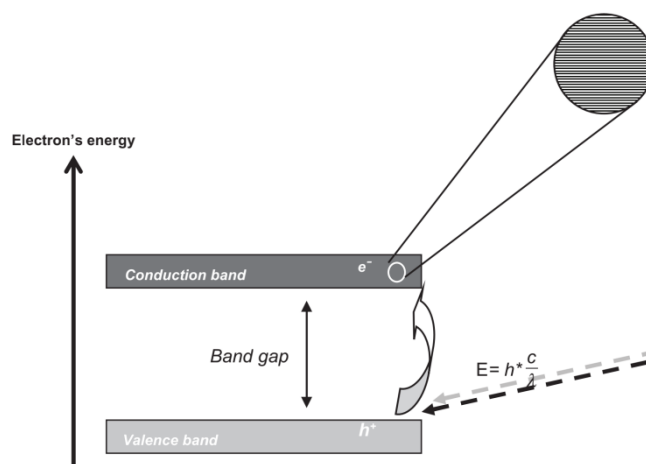
Titanium oxide is one of the functional nanoparticles which adding to the sunscreen. Titanium dioxide is composed of two types: crystalline and amorphous. And presents three crystal types: anatase, rutile and ash titanium. The anatase structure is the most stable one and is easy to be prepared in cosmetics. According to a series of experiments and researches, the chemical methods for the synthesis of titanium oxide nanoparticles have seemed toxic to our environment and had corresponding limitations. The chemical methods demanded high pressure and temperature conditions which was a difficulty in the synthesis process. Thus, a green nanotechnology for preparing the TiO<sub>2</sub> nanoparticles has been studied which was a biological synthesis.[1] The green synthesis can use the extracted material from leaves because of their high metabolites. Nabi et al.[2] have reported a method that utilized the aqueous extract from cinnamon powder. The prepared samples have applications for the photocatalytic field such as sunscreen in the cosmetics field. The synthesized nano particles are anatase phase TiO<sub>2</sub>, the particles are spherical which have band gap function under visible light. This contributes to its photocatalysis.



**Figure 1.** The experimental flow chart.

### 3.3. Antibacterial of nano-TiO<sub>2</sub>

The properties of TiO<sub>2</sub> are various, not only UV shielding but also antibacterial activity. The main antibacterial mechanism of titanium oxide is photocatalysis. ROS will have induction to generate oxidative stress which is another important mechanism by using nanoparticles. Titanium oxide generates reactive oxygen species. ROS are a normal product of cells with respiratory activity and can induce oxidative stress. This destroys cell membranes, genetic material and cell organelles and will have a deeper cell death. The electronic structure of titanium oxide has a full valence band (VB) and conduction band (CB). In light condition larger than its gap energy, electrons can be excited from VB to CB, and the holes can be generated in the valence band simultaneously. When there is a suitable trapping agent, it inhibits the interactions between electrons and holes, then have the redox reactions on the surface. The holes generally react with water or hydroxide ions adsorbed on the surface to form active hydroxyl groups (-OH). Hydroxyl groups have strong oxidation, while the electrons react with oxygen molecules to form superoxide ions which are O<sub>2</sub><sup>-</sup>. They may further react with water to generate super hydroxyl (·OOH) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). In addition, the active hydroxyl groups can also combine to form hydrogen peroxide. These active substances generated by the chemical reaction can react with biological macromolecules, directly damage or through a series of reactions cause extensive damage to biological cell structure. TiO<sub>2</sub> has a better shielding to UV light, so electrical conductivity is significantly enhanced, which activates the interactions between nanoparticles and bacteria, and photocatalytic antibacterial effect is enhanced with the increase of light intensity. After UV light is turned off, photoconductivity still occurs and the reason is that the surface electron-depletion region will combine with negative oxygen, such as O<sub>2</sub><sup>-</sup> and O<sub>2</sub><sup>2-</sup> adsorbed on the surface.[3]



**Figure 2.** The mechanism of transition of electrons.[4]

### 3.4. Toxicity of nano-TiO<sub>2</sub>

Turn to the safety of the nanoparticles, although the nanomaterials have antibacterial and anti-inflammatory effects, their toxicity of them should also be focused. It can focus on the skin's permeable properties and ways to combat the risks of NP sunscreens, such as sunscreen formulations. Clearly, toxicological effects are only possible under certain circumstances when sunscreen particles have the potential to penetrate the skin barrier, then enter the living skin layer. The toxicity of nanoparticles is associated with their photocatalytic activity. Specially, TiO<sub>2</sub> has gained much attention for its photo-induced reactions.[5] Free radicals produced during photocatalysis can be detected by electron spin resonance (ESR) or indirectly detecting photoinduced cell damage in cytotoxicity assay.[6][7] Uchino et al. and Sayes et al. Reported that titanium dioxide generally showed relatively higher photoactivity. And they reported higher OH content produced by UV irradiation of anatase compared to rutile type TiO<sub>2</sub> particles. Sayes et al. also observed higher phototoxicity of anatase. They measured the photodegradation of Congo red aqueous solution in the presence of 10nm spherical particles. Montero-riviere et al. confirmed the invalid test results by using NP-Dye interactions, the conclusion is that the datas were related to the interactions.[8][9] Thus, precise information of the mechanisms responsible for titanium dioxide nanoparticles toxicity is widely unknown.

## 4. ZnO in sunscreen

### 4.1. Effectiveness of nano-ZnO in sunscreen

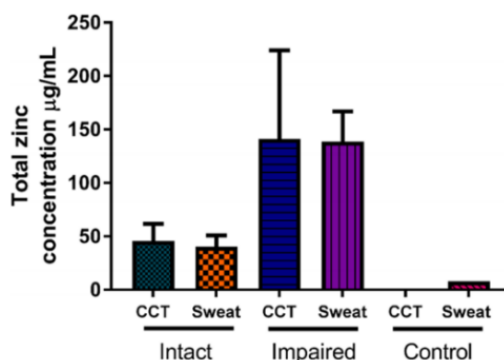
Zinc oxide and Titanium dioxide are always mentioned together, the distinction is that TiO<sub>2</sub> is more responsible for the UVB spectrum, whereas ZnO is more effective in the UVA range[10]. When microsized ZnO particles are used as sunscreens, they have a considerable impact on UV attenuation. Zinc oxide particles are found on the stratum corneum, the epidermis (the top layer of your skin), where the UV radiation is scattered, absorbed, and reflected, safeguarding the live skin underneath[11][12], so they act as a physical block. Additionally, the absorption of UV radian by ZnO depends on the size of the particle. The absorption ability increase with the diameter[13]. ZnO dispersions should preferably have small nanosized and huge micro sized particles to provide the essential balanced UVA and UVB protection, therefore the particle size is not as small as possible. Specifically, UVA-1 protection is influenced by aggregated ZnO particles of 130 nm were used, rather than primary 20nm ZnO nanoparticles. It has diverse forms (rod-like, star-like, and isometric) and a 30-150 nm size distribution range[14][15]. The normal spherical size particles are between 200 nm and 1 μm[16], and present in clusters. The ingredients in cosmetics are not allowed to be used in some countries because they are considered to be carcinogenic. But only after they react with UV rays.

### 4.2. Preparation of ZnO

ZnO is the other important functional ingredient in sunscreen. It is one of the few ceramic oxides that can be used as UV-protection films[17]. Spanhel and Anderson proposed the sol-gel method for producing ZnO nanoparticles in 1991, and it is widely utilized. The synthesis of a zinc precursor (Zn(Ac)<sub>2</sub>·2H<sub>2</sub>O) generated by boiling an ethanolic solution of zinc acetate dihydrate (Zn(Ac)<sub>2</sub>·2H<sub>2</sub>O) at 80°C under reflux for 3 hours is the essential step in this sol-gel approach[18]. This is the priority of preparation that shows the precursor involved in the Spanhel and Anderson route is the anhydrous Zn(Ac)<sub>2</sub>. To solve this, other simple and novel routes of preparation can also make ZnO nanorods successfully though it is not powder or particle, or with zinc sulfate and sodium hydroxide, zinc oxide nanoparticles can be made by utilizing a simple precipitation process. But, the drawback of production is also significant, like ZnO is believed to be easily dissolved in the environment due to its photocatalytically active; it will also cause air pollution and lead to “metal-fume fever” due to the inhalation of zinc oxide fumes[19].

### 4.3. Skin penetration of nano-ZnO

Nanoscale ZnO, so theoretically, it should be likely to sink into the skin. This has become the most concern for the majority. However, there is not much evidence supporting this idea, and experiments have been made by Mohammed, Yousuf H that shows the unlikeliness of the absorption of Zinc oxide in the human body. First, nano-ZnO particles collected on the surface of the skin and within skin furrows, but did not penetrate the live epidermis or produce cellular toxicity. Figure 1 shows the concentration of the absorption of Zinc particles, over a period.



**Figure 3.** Total zinc concentration over the condition of each trail [20]

Two conditions are required, one is to mix up with CCT (caprylic capric triglyceride, a common sunscreen formulation base) and with sweat to make the experiment more realistic. The result shows that if the skin sample is intact, a low concentration of Zinc is detected compared with the condition that the skin sample is impaired. Therefore, the concern of absorption of metal particles is overwhelming, as not much evidence is supporting this hypothesis, so the ZnO component will be detected inside the hair follicle and not under the skin. But one does need to make sure his skin isn't hurt when using sunscreen. This is different from TiO<sub>2</sub> which has higher toxic potential and skin penetration ability. It may pass the blood–brain barrier and be identified in several tissues, including the lung, brain, and spleen. The result comes from experiments on hairless mice in vivo.

### 4.4. Toxicology of nano ZnO

The cytotoxicity of ZnO is similar to that of TiO<sub>2</sub> [21]. In an aqueous solution, assess the photocatalytic (254 nm) breakdown of carbofuran. Mahalakshmi et al. employed Degussa p-25 (70 percent anatase, 30 percent rutile [Degussa Chemical, Germany]) TiO<sub>2</sub> and 0.1–0.4 m Zn[15]. And the result shows that ZnO is less photo reactive compared with TiO<sub>2</sub>, but it turns out to be more unstable during irradiation[22]. Besides opposite with TiO<sub>2</sub>, ZnO has a lower oxidation rate under the condition of whether being coated or not. Therefore, the results of genotoxicity differ greatly between the two due to the scarcity of detailed information on irradiation circumstances and dose measures. Because of their capacity to shed ions, nano-ZnO particles are more hazardous than other metallic oxide nanoparticles[23][24]. ZnO appears to be less photoreactive than TiO<sub>2</sub> but, unlike TiO<sub>2</sub>, may exhibit instability under irradiation, as demonstrated by Mitchnick et al[25]. Therefore, the toxicological properties of titanium dioxide have been studied in excess of zinc oxide. Also, nano-zinc particles are antimicrobial and prevent microbes from growing by penetrating the cell membrane. Lipids, carbohydrates, proteins, and DNA are all damaged by oxidative stress.

## 5. Conclusion

We illustrate how the active ingredients in physical sunscreens interact in sunscreens and assess the future market impacts of the use of nanotechnology in the cosmetics industry. We identify the benefits of scaling down materials to the nanoscale, such as the large specific surface area that makes sunscreens more effective, but also the safety concerns that they can cause blocked skin pores and pimples due to the polymerization of titanium dioxide nanoparticles. Zinc oxide is a relatively reactive

chemical that can cause damage to human organs. Whilst we enjoy the convenience of nanomaterials, we also need to be concerned about safety. As nanotechnology has only recently been applied to cosmetics, it is not possible to predict the long-term effects of these products, which may have a long latency period of 10 years or more. Sunscreens have become an essential part of UV protection and are used by almost all people. There is a huge market for them, but it is important to consider the economic and safety aspects of improving the effectiveness of sunscreens. As sunscreens tend to fail due to sweating, we can try new mineral ingredients to boost their consistency and make them stay on the body longer. The sunscreen market is becoming increasingly competitive, so don't overdo it by adding too many ingredients just to increase the SPF. We need to be concerned about the safety of new technology as we enjoy the convenience it brings.

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