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ISSN 2959-409X

TiO2 Nanoparticle-Modified Textiles for Sunscreen Applications: Advances and Challenges

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Abstract:
Under the backdrop of increasing ultraviolet radiation intensity and growing public concern about sun protection, the development of sun protection materials has become an important issue related to public health and quality of life. TiO2 nanoparticles, with their excellent light scattering and absorption properties, have shown great application potential in sun protection fabrics. Although current research has made certain progress in the preparation, testing and optimization of TiO2 nanoparticle-modified fabrics, there is a lack of comparative studies on the effects of different processes on the loading effect of TiO2 nanoparticles and the sun protection performance of fabrics. This study systematically summarizes the advantages and disadvantages of five modification methods and their impact on sun protection performance. At the same time, the research content will incorporate biological safety tests to reflect the impact of materials on human health and explore their potential in personalized sun protection, in line with the development trend of precision medicine. However, there are still problems to be solved in current research. The comparison of the loading effect of TiO2 nanoparticles and the sun protection performance of fabrics under different modification processes is not sufficient, and biological safety tests also need to be improved. Future research can further deepen process optimization, personalized customization, etc., to develop new types of sun protection fabrics with high efficiency, and promote the sustainable development and wide application of TiO2 nanomaterials in the field of sun protection.

Keywords: Titanium dioxide (TiO_2); Textiles; Sunscreen Applications.

ISSN 2959-409X

1. Introduction

With the intensification of global climate change, the intensity of ultraviolet (UV) radiation is increasing year by year. According to data from the World Health Organization, UVA can accelerate skin aging, while excessive exposure to UVB radiation can increase the risk of skin cancer by 30% to 50%, posing a serious threat to human skin health. Traditional sunscreen products have problems such as uneven application and easy detachment. TiO2 nanoparticles, with their excellent light scattering and absorption properties, show great application potential in the field of sunscreen fabrics.

Titanium dioxide (TiO_2) absorbs light with wavelengths ranging from 275 to 405 nm and effectively reflects light due to its high refractive index [1]. The excellent light scattering and absorption properties of TiO_2 lay the foundation for its potential applications in the field of sun protection fabrics. These two effects effectively protect the power of TiO_2 against ultraviolet rays. When the particle size of TiO_2 is less than a micron, the protection against ultraviolet UVA and UVB increases. The high specific surface area of TiO_2 increases the contact area with ultraviolet rays and the number of absorption sites, enabling it to absorb ultraviolet rays more fully and achieving good sun protection effects. In addition, TiO_2 can be compounded with materials such as ZnO, SiO_2, and polymers, demonstrating excellent anti-ultraviolet performance. Moreover, when TiO_2 is compounded with other ultraviolet absorbers, it can broaden the sun protection band and enhance the overall sun protection performance.

Although current research has made certain progress in the preparation, testing and optimization of TiO2 nanoparticle-modified fabrics, it lacks a comparison of the effects of different processes on the loading efficiency of TiO2 nanoparticles and the sun protection performance of the fabrics. This study will systematically summarize the advantages and disadvantages of five modification methods and their effects on sun protection performance in this paper. At the same time, biological safety tests will be integrated into the research content to reflect the impact of the materials on human health, explore its potential in personalized sun protection, and conform to the development trend of precision medicine.

2. Health Risks of Ultraviolet Radiation and the Rising Demand for Sun Protection

2.1 Background of the Increase in Global Ultraviolet Radiation and the Associated Health Threats

Since the 1980s, human industrial production and daily life have released large amounts of ozone-depleting substances such as chlorofluorocarbons (CFCs) and halons. These substances, when rising to the stratosphere, will undergo chemical reactions with ozone molecules. According to long-term monitoring data from the World Meteorological Organization, under the combined effect of ozone layer depletion and global climate warming, the intensity of ultraviolet radiation at the Earth's surface is increasing at a rate of 0.2% to 0.5% per year. This trend is particularly significant in mid- and high-latitude regions. 2024 is the peak year of the 25th solar activity cycle, which may enhance the ultraviolet radiation on the Earth's surface. According to statistics, except for the Arctic region, the global average ultraviolet index has increased by 23% compared to previous years.

Although moderate exposure to ultraviolet rays is beneficial to the human body, such as promoting the synthesis of vitamin D and having disinfectant and sterilizing effects, excessive ultraviolet rays pose great harm to human health. The research of the World Health Organization (WHO) has revealed the severe harm of different wavelength ultraviolet rays to human skin. Ultraviolet rays (wavelengths 10-400 nm), UVA (320-400 nm) have longer wavelengths and stronger penetrating power, and can easily pass through the epidermis layer to reach the dermis layer, causing the skin to lose its supporting structure and leading to phenomena such as skin relaxation and wrinkles due to photoaging. Studies have shown that the skin exposed to UVA for a long time has a collagen loss rate more than three times that of normal skin. UVB (280-320 nm) directly acts on the DNA of epidermal cells, and excessive exposure to UVB will trigger gene mutations, increasing the risk of skin cancer by 30%-50%. Data from 2024 shows that the incidence of malignant melanoma (the most fatal type of skin cancer) has significantly increased among young people.

According to the statistics of the International Agency for Research on Cancer (IARC), the number of new skin cancer cases worldwide has exceeded 3 million each year, and 80% of these cases are directly related to long-term excessive exposure to ultraviolet radiation. These data and cases indicate that the problem of enhanced ultraviolet radiation caused by ozone layer depletion has clearly become a major crisis threatening human health. Therefore, all people around the world need to take joint actions to strengthen the control of ozone and develop more efficient sun protection technologies.

2.2 Limitations of Traditional Sunscreen Products and Advantages of Textile-Based Sun Protection Materials

Products such as sunscreen and sunscreen spray rely on manual application. A survey shows that approximately 40% of users fail to form an effective sunscreen barrier due to improper application methods or insufficient usage. Moreover, these products are highly susceptible to external environmental factors: under the impact of sweat, rain, or friction from intense exercise, their protective performance will rapidly decline. For example, at water parks, after applying traditional sunscreen products, their protective efficiency will drop by 50%-70%, unable to provide continuous and effective protection for the skin. Additionally, some traditional sunscreen products also have problems such as being sticky and prone to causing skin allergies, which further limits the user experience for the general public.

Under such circumstances, textile-based sun protection materials have stood out due to their unique advantages and have become a research hotspot in the field of sun protection in recent years. These materials integrate sun protection functions into the fabric through special processes, featuring wide coverage, ease of use, water resistance, and resistance to friction. Whether for daily wear or outdoor activities, textile-based sun protection products can continuously provide protection, allowing people to enjoy long-term UV protection without the need for frequent reapplication.

Among the numerous components used for preparing textile-based sun protection materials, TiO_2 nanoparticles (TNPs) demonstrate an irreplaceable advantage due to their outstanding performance. The ability of TNPs to efficiently absorb ultraviolet energy (which I will elaborate on in the following text) makes them an ideal material for preparing high-performance sun protection fabrics, providing a strong support for meeting the increasingly stringent sun protection needs of the public.

3. The Sunscreen Mechanism and Application Potential of TNPs

From the rigorous experimental results, it can be clearly concluded that TiO_2, with its unique physical and chemical properties, can serve as an ideal filtering material to resist various UVA and UVB rays [1]. Moreover, the smaller the size of TiO_2 particles, the better the protection against UVA and UVB. According to theoretical calculations and experimental research, it has been proven that when the TiO_2 particle size is less than 1 micron, the protection against UVA and UVB increases. TiO_2 absorbs light with wavelengths ranging from 275 to 405 nm. At the same time, its refractive index of up to 2.76 enables it to have excellent light scattering ability, which can effectively reflect the ultraviolet rays that reach the fabric surface and reflect the light during the light exposure. The combination of light absorption and light scattering effects forms a solid protective barrier, significantly weakening the energy of ultraviolet rays and achieving effective protection for the skin or fabric. It is precisely due to this excellent light scattering and absorption performance that TiO_2 demonstrates great application potential in the field of sun protection fabrics. Nano TiO_2 is a common broadband-gap semiconductor material. When the energy is greater than or equal to the photon bandgap width, TiO_2 will excite from the ground state to generate photogenerated electron-hole pairs. Therefore, adding nano TiO_2 can exhibit excellent ultraviolet shielding effects over a long period of time [2]. In terms of chemical stability, TNPs have good resistance to light, heat, and chemical corrosion, and do not react with other substances, maintaining stable sun protection effects in various complex environments. Nowadays, many sun protection garments add TiO_2 to allow wearers to enjoy outdoor activities while avoiding the harm of ultraviolet rays, which further confirms the important value of TiO_2 in the field of ultraviolet protection.

The high specific surface area characteristic of TiO_2 is one of the key factors for its excellent sun protection performance. When the particle size of TiO_2 is reduced, its specific surface area will increase exponentially. This enables each unit mass of TiO_2 to have more surface areas in contact with ultraviolet rays, while also increasing a large number of absorption sites. As shown in Figure 1, it has a high (001) face exposure rate controlled by the reaction temperature, which significantly improves the photocatalytic activity. The absorption sites can quickly capture and absorb photon energy when exposed to ultraviolet rays, converting it into harmless heat energy or low-energy radiation, thereby significantly enhancing the sun protection effect [3].

ISSN 2959-409X

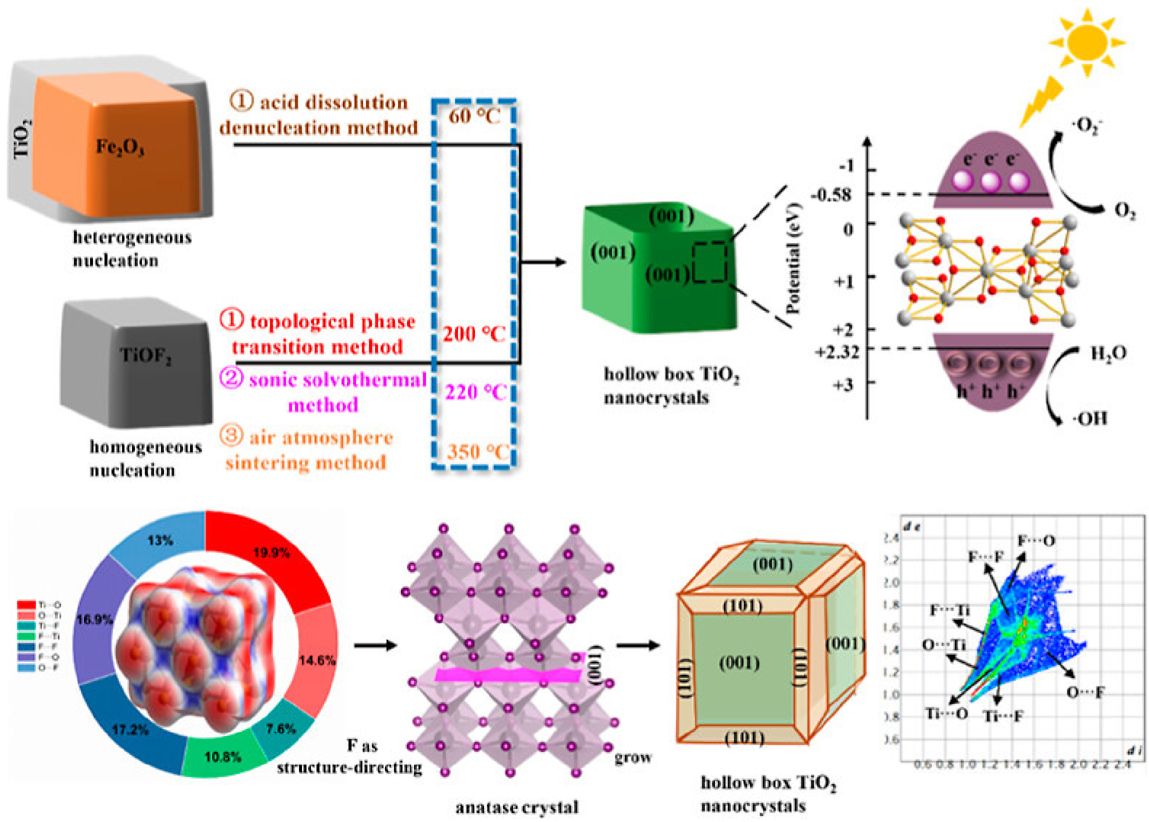

Fig. 1 The high (001) surface exposure rate significantly enhances the photocatalytic activity [3].

Furthermore, the synergistic effect of TiO_2 with other materials has opened up new paths for enhancing the sun protection performance. Taking ZnO, SiO_2, and polymer materials as examples, through scientific proportioning and process optimization, excellent composite systems can be created. Some research indicates that when the ratio of SiO_2 to TiO_2 is 1:1 and the mass fraction of PU is 20%, the SiO_2-TiO_2/PU coating prepared shows astonishing ultraviolet protection ability. Its absorption and reflection rates of ultraviolet rays reach their peak. At this time, after being exposed to ultraviolet light for 30 minutes, the fracture stress and fracture elongation of the SiO_2-TiO_2/PU coating decreased by 32.69% and 8.98% respectively, significantly lower than other coatings, demonstrating excellent anti-ultraviolet performance [4]. Moreover, when TiO_2 is combined with other ultraviolet absorbers, it can broaden the sun protection band through spectral complementation, effectively covering the protection blind spots of the original single material, and improving the overall sun protection performance from multiple dimensions, providing a broad innovative space for the research and application of sun protection products.

4. Research Status

4.1 Preparation Methods of TNPs Modified Fabrics

4.1.1 Rolling - Drying - High Pressure Steam Distillation

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This method involves pre-treating with 2.5 g/L coupling agent, and then processing the nano-TiO2 onto the cotton fabric through the rolling-drying-high-pressure steam treatment process. The whiteness and mechanical properties of the fabric are then measured. After the cotton fabric is treated, the whiteness increases, the tear strength changes little, the breaking strength increases, and the elongation at break decreases. This is because the nano-TiO2 itself has good white light-blocking properties, which increases the whiteness of the cotton fabric. The reactions between the coupling agents and between the coupling agents and the cotton fibers form chemical bonds, thereby increasing the breaking strength; however, due to the restricted movement of the basic units, the deformation ability decreases, which affects the elongation at break [5].

4.1.2 Hydrothermal Method

The deposition of nano TiO2 on the surface of silk fabric using the hydrothermal method or atomic deposition technology can enhance the absorption of ultraviolet rays, prevent the fabric from yellowing, and improve the mechanical properties.

High-intensity ultraviolet irradiation can cause the molecular structure of polyester fibers and chemically plated silver polyester fibers to be damaged in a short period of time, resulting in a decrease in crystallinity index, an increase in apparent grain size, and almost no change in crystal plane spacing and orientation. Due to the breakage of the large molecular chains, the crystallinity of polyester decreases, leading to a rapid decline in the mechanical properties of polyester fibers. Coating nano TiO2 particles on the surface of polyester fibers can largely protect polyester fibers from being damaged by high-intensity ultraviolet rays for a short period of time and extend their service life. However, long-term and high-intensity ultraviolet irradiation still causes relatively serious damage to polyester fibers [6].

4.1.3 Sol-Gel

The sol-gel method is a commonly used nanofunctional finishing technique. By coating TiO_2 in the form of a sol onto the surface of the fabric, and then undergoing gelation and heat treatment, a dense film is formed. After this process, the surface of the polyester fibers initially only shows a small amount of particle deposition. However, when using a modified TiO_2 system, the number of deposited particles significantly increases and the coverage is more uniform. After dyeing polyester fabric with this process, the sunfastness of the fabric improves with the increase in baking temperature, reaching the best performance at 120°C. Beyond this temperature, the performance decreases, indicating that excessively high temperatures may damage the nano-coating structure. In terms of color, the ordinary nano TiO_2 finishing significantly alters the appearance of the fabric, while the modified TiO_2 finishing has a smaller impact on color difference and is more suitable for occasions with higher requirements for color fidelity [7].

4.1.4 DC Magnetron Sputtering

Within the wavelength range of 340nm and below, the transmittance of the deposited nano TiO2 fabric sample was significantly lower than that of the original sample, with a relative difference of nearly 50%. This indicates the strong absorption ability of the TiO2 film for ultraviolet light. The transmittance of the samples at 60 minutes and 100 minutes was close to each other within the wavelength range below 340nm, and was significantly lower than that of the 20-minute sample. This suggests that within a certain range, as the sputtering time increases, the continuity, uniformity, and density of the film increase, and the absorption ability for ultraviolet light gradually strengthens. When a continuous, uniform, and dense film is formed, further increasing the sputtering time and depositing a thicker film does not significantly increase the ultraviolet light absorption ability [8].

4.1.5 Coating Method

The alloy sol can absorb a wider range of ultraviolet wavelengths and has a higher absorption intensity. By impregnating PP/PDA fibers with the optimized nano TiO2/ZnO alloy sol, a dense TiO2/ZnO alloy particle coating is formed on the surface of the PP/PDA fibers. After the fibers are irradiated with ultraviolet light, the loss rate of fiber strength is only 11.3%. The melting temperature of the modified fibers is higher than that of the PP/PDA fibers, and the anti-ultraviolet aging performance has significantly improved compared to before the modification. Through Fourier infrared spectroscopy, it can be observed that carbonyl groups are generated on the surface of the PP fibers, indicating aging, while no carbonyl groups were detected on the surface of the PP/PDA/TiO2/ZnO fibers. In conclusion, the anti-ultraviolet aging performance of the fibers after alloy sol modification has improved [9].

4.2 Evaluation of the Sunscreen Performance of TiO_2 Modified Fabrics

The cotton fabrics processed by the rolling-drying-high-pressure steam treatment have relatively high photocatalytic performance; depositing nano TiO_2 on the surface of silk fabrics using the hydrothermal method or atomic deposition technology can enhance the absorption of ultraviolet rays; after dyeing polyester fabrics with nano TiO_2 sol treatment, the fabric's resistance to sunlight fading increases with the increase of baking temperature. When the temperature reaches 120 °C, the sunfastness grade reaches the highest level, and after 120 °C, the sunfastness grade decreases with the increase of baking temperature; in a certain range, with the increase of sputtering time by direct current magnetron sputtering method, the continuity, uniformity and density of the film increase, and the absorption ability to ultraviolet light gradually strengthens. When a continuous, uniform and dense film is formed, increasing the sputtering time to increase the film deposition thickness does not significantly enhance the ultraviolet light absorption ability. The anti-ultraviolet aging performance of the fibers modified by alloy sol coating method is improved.

ISSN 2959-409X

5. Biological Safety and Toxicity Mechanisms of TNPs

5.1 Toxicity Mechanisms

In the field of biological safety, the potential risks of TiO_2 have gradually become the focus of scientific research. TiO_2 has been classified as a 2B class carcinogen by the International Agency for Research on Cancer [10]. Through precise experiments, it has been revealed that as the component ratio of rutile-type TiO_2 (TNPS-A) in the mixture continuously increases, its physical and chemical properties will undergo significant changes. Under ultraviolet exposure conditions, the sedimentation rate of the mixture of TNPS-A and rutile-type TiO_2 (TNPS-R) significantly accelerates, which makes TiO_2 particles more likely to aggregate around the cells. The main toxicity mechanism of TNPs is to induce oxidative stress in cells by generating reactive oxygen species, thereby causing cellular oxidative damage and even leading to cell death [11].

The research further revealed the biological toxicity mechanism of TiO_2 at the level of nerve cells. The experiments showed that TNPs could penetrate the blood-brain barrier and enter the central nervous system. In dopaminergic nerve cells, TiO_2-NPs disrupted the internal dynamic balance by affecting the expression of proteins related to the mitochondrial apoptosis pathway. As shown in Figure 2, the abnormal expression of these proteins activated the apoptotic signaling pathway, causing changes in the mitochondrial membrane permeability, releasing pro-apoptotic factors, and ultimately inducing the apoptosis of dopaminergic nerve cells [12]. The research clearly demonstrated from different perspectives and different cell types that TiO_2 has significant biological toxicity under certain conditions, and the toxic effects induced by TNPs are often related to their chemical structure, crystal phase, particle size, reaction surface, coating, dose, and exposure time. It warns people that while widely applying TiO_2, they must attach great importance to the potential hazards it may pose to the health of living organisms and strengthen the assessment and research on biological safety.

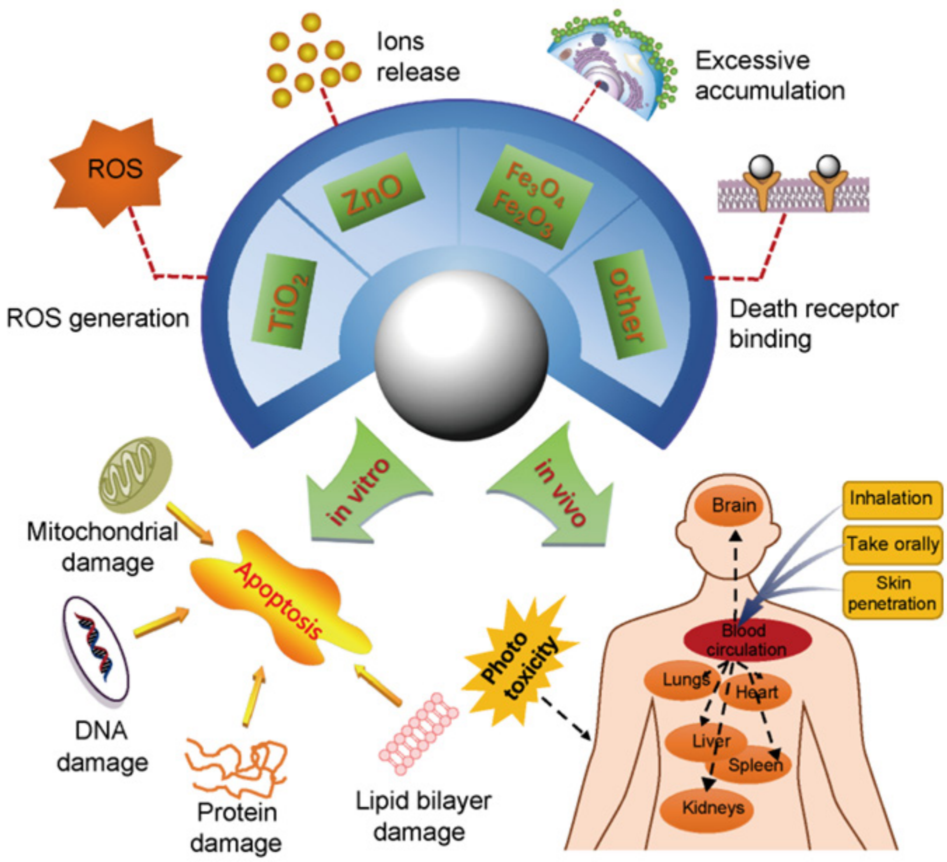

Fig. 2 TiO_2has significant biological toxicity to the human body [12].

5.2 Strategies for Reducing Toxicity

Recent studies have introduced the synthesis of a new type of nano-composite material $TiO2@Ti3C2Cl2$ using a one-step molten salt shielding method under a low-temperature air atmosphere of 1000 °C. This innovative process abandons the traditional synthesis mode that relies on chemical reagents and uses molten salt as the protective medium to form a stable physical shielding layer at high temperatures. It not only effectively inhibits the agglomeration and oxidation of the material during the synthesis process, but also simplifies the process flow and reduces production costs and environmental pollution risks. By coupling the synthesized $TiO2@Ti3C2Cl2$ with low-band-gap carbon nitride through ultrasonic technology, a ternary ($C3N5/TiO2@Ti3C2Cl2$) nano-composite material was formed. The synthesized ternary nano-composite material improved the photocatalytic and HER efficiency and reduced toxicity, which cleared the biological safety barriers for its large-scale application in environmental remediation and clean energy fields, and became a highly promising new generation of functional materials. (a and b) The results of MTT assay show that the cytotoxicity of the photocatalyst decreases with the increase of exposure time and the decrease of concentration. The addition of 2—Ti3C2Cl (tetra)2 to TiO leads to a gradual decrease in cytotoxicity [13]. The above research systematically revealed the biological safety risks of TNPs and their toxicity control strategies, providing key scientific basis for balancing the functional properties of the materials with biocompatibility.

From the perspective of toxicity mechanisms, the biological hazard of TNPs is closely related to their physical and chemical properties, confirming the "contact - aggregation - damage" toxicity pathway of TNPs, and the crystal phase composition is the core factor influencing the toxicity intensity [11]. Further research has revealed that TNPs pose a potential threat to the central nervous system, highlighting the hidden risks of long-term low-dose exposure [12].

In terms of biological safety improvement, there has been a breakthrough solution: the molten salt shielding synthesis process inhibits the aggregation and oxidation of TNPs, avoiding the risk of toxic residue introduced by traditional chemical reagents [13]. This "functional enhancement - toxicity reduction" dual-effect regulatory strategy has opened up a safe path for the application of TNPs in environmental remediation and the new energy field.

In conclusion, the research on the biological safety of TNPs presents two major trends: toxicity analysis: it is necessary to study the biological safety performance of TiO2 particles; green optimization: through methods such as crystal structure modification, surface coating design, and composite system construction, achieve "high efficiency and low toxicity" material optimization.

6. Personalized Sunscreen Applications and Precise Protection Design

The research involved synthesizing acrylic resin and blending it with modified nano-TiO2/SiO2 composite particles to prepare TiO2/SiO2-acrylic resins of different concentrations. Through comprehensive performance tests and UV absorption spectrum analysis, the results were remarkable. This resin exhibited excellent absorption and shielding capabilities in the two most harmful UV bands to human skin, UVB and UVA. As the concentration of nano TiO2/SiO2 composite particles increased from 1wt% to 10wt%, the material's UV shielding effect changed significantly. From an optical perspective, more nanoparticles provided a larger surface area and more light scattering and absorption sites, causing the completely shielded UV wavelength of the TiO2/SiO2-acrylic resin to shift from 310nm to approximately 350nm, effectively expanding the protection band. Even at high particle concentration filling, this resin could still maintain a visible light transparency of over 90%. Under the premise of ensuring transparency, choosing a composite particle concentration of 10% by mass not only ensures UV absorption performance but also ensures transparency [14]. This lays the foundation for personalized transparent sunscreen fabrics. This material is not only suitable for coating finishing of sunscreen fabrics but can also be applied to smart window films, outdoor equipment, and other scenarios that require both light transmittance and protection, providing the possibility for customized development of personalized sunscreen products.

The research employed an anhydrous solid-state method to prepare a new type of inorganic UV absorber - TiO_2 in SiO_2. Compared with traditional methods, the anhydrous solid-state method not only significantly reduced production costs and environmental pollution risks, but also avoided the influence of solvent residues on material performance, demonstrating remarkable advantages of being environmentally friendly and having a simple process. The samples were characterized using SEM-EDS (scanning electron microscope - energy dispersive X-ray spectroscopy), and the mapping images clearly and intuitively showed that TiO_2 was uniformly and stably distributed within the silica matrix. This uniform dispersion microstructure laid a solid foundation for the improvement of material performance. Further research revealed that when TiO_2 was combined with SiO_2, its photocatalytic behavior

ISSN 2959-409X

was effectively inhibited. Under different experimental conditions, the photocatalytic inhibition rate decreased from 86% to 31%. This research result has important reference value for the optimization of subsequent preparation processes [15]. By adjusting the ratio of TiO_2 to SiO_2 and reaction conditions, the degree of photocatalytic inhibition can be further precisely controlled. While retaining its excellent UV absorption performance, it avoids the possible side effects of photocatalytic action. With the advantages of a green and environmentally friendly process and controllable photocatalytic inhibition characteristics, it solves the problem of photocatalytic side effects in traditional nano TiO_2 applications, significantly improving the stability of the material over a long period of use, and opening up a new direction for the industrial production of high durability sunscreen products.

These studies collectively reveal the core value of nano-material composite modification and process innovation in achieving precise protection. In the future, by further optimizing the interface properties of nanoparticles and exploring the mechanism of multi-component synergy, it is expected to develop sunscreen materials that are not only highly effective in protection, environmentally friendly, functionally adaptable, but also personalized.

7. Conclusion

To sum up, TNPs, with their unique light scattering and absorption properties, demonstrate significant application potential in the field of sun protection fabrics. Through a systematic review of existing research, it can be seen that different preparation methods confer distinct sun protection properties to the fabrics: the rolling - drying - high-pressure steam treatment process can achieve a firm bonding of nano TiO_2 with cotton fabric, and has good durability; the direct current magnetron reactive sputtering method can enhance the ultraviolet shielding ability of the fabric by adjusting the sputtering time.

At the level of biological safety research, although traditional TiO_2 nanoparticles have certain biological toxicity, such as causing damage to human liver cells and dopaminergic nerve cells, recently through material composites and process innovations, new low-toxicity and highly efficient nano-composite materials like $TiO_2@Ti_3C_2Cl_2$ have been successfully developed, providing new ideas for addressing safety issues.

The combination of TiO_2 with materials such as ZnO and SiO_2, as well as the optimization of particle concentration, can effectively broaden the sunscreen spectrum and enhance the protection efficiency. Moreover, the research on the relationship between nanoparticle concentration and sunscreen performance has laid a theoretical foundation for the development of personalized sunscreen products. However, there are still unresolved issues in the current research. The comparison of the loading effect of TiO_2 nanoparticles and the fabric's sun protection performance under different modification processes is not sufficient, and the biological safety tests also need to be improved. Future research can further deepen process optimization, individualized customization, strengthen interdisciplinary integration, combine with the concept of precision medicine, and develop new types of sun protection fabrics that are both highly effective in protection, have low biological toxicity, and are customizable. This will promote the sustainable development and wide application of TiO_2 nanomaterials in the field of sun protection.

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