Journal of Kerbala University, Vol. 22, Issue 4, December , 2025

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Review Article

A Review on Reducing TiO_2 Photocatalysis in Sunscreens: Perspectives on $TiO_2@Zn_2SnO_4$ Composites

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Article Info
Article history:
Received 18 -9-2025
Received in revised form 1-11-2025
Accepted 24-11-2025
Available online 31 - 12 -2025

Keywords: TiO_2, Zn_2SnO_4, ROS, UV filters, Sunscreen, free radicals.

Abstract:

This review examines the most important strategies to enhance titanium dioxide (TiO_2) as an ultraviolet (UV) filter by mitigating its photocatalytic activity in terms of suppressing the risk of harmful reactive oxygen species (ROS) (free radicals). As Zn_2SnO_4 has been reported recently to exhibit promising UV filter properties similar to TiO_2 while producing a very low amount of ROS. This review also provides insight into and compares Zn_2SnO_4 and TiO_2 for incorporation into sunscreen. Zn_2SnO_4 is potentially expected to maintain the high sun protection factor (SPF) of TiO_2, allowing for effective sunscreen formulation. To the best of our knowledge, this review summarizes for the first time the recent advancements in reducing the high photocatalytic activity of TiO_2, and explores the suitability of using a composite of $TiO_2@Zn_2SnO_4$ as a promising UV filter in sunscreen.

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1. Introduction

Long-term exposure to Ultraviolet (UV) rays in sunlight can cause skin cancer. UV spectrum is divided into three categories, UVA (320-400 nm), UVB (290–320 nm), and UVC (100–290 nm) [1]. UVA rays are also divided into two ranges, UVAI (340-400 nm) and UVAII (320-340 nm) can penetrate the ozone layer and cause sunburn and premature skin aging by suppressing the immune function. Although the ozone layer partially blocks UVB rays, they can still cause severe sunburn and skin cancer. UVC rays are filtered and fully blocked by the ozone layer; however, UVC can be produced by artificial sources such as welding operations [2]. All UV rays can eventually lead to skin cancer. The harmful effects of UV rays on normal skin can be categorized into two main types: acute reactions, including sunburn and tanning, and delayed reactions, including photocarcinogenesis and photoaging [3]. Many studies have shown that 65% to 90% of skin cancer is caused by UV exposure [4]. Although UVA and UVB rays have lower energy than UVC rays, they can penetrate human skin and cause various diseases and skin aging. In particular, they can penetrate the human dermis and promote the formation of ROS, which can cause DNA damage and lipid peroxidation [5].

Sunscreen is an essential complement for UV protection. According to several studies, regular use has been shown to reduce the risk of developing skin cancer [6]. Sunscreens often contain both inorganic elements that operate as physical UV filters and organic ingredients. Inorganic filters are more effective in terms of UV blocking [7],[8]. It is well known that ZnO exhibits a wide range of UV-blocking properties across a broad spectrum over the UVB and both UVA II and UVAI, while TiO_2 blocks UVB and part of UVA (UVA II) [8], [9]. Hybrid combinations include inorganic and organic filters that are used to effectively extend the UV blocking range of sunscreen. However, sunscreen based on inorganic filters (mineral) is preferred in terms of photostability and safe ingredients [10].

Despite TiO_2 and ZnO being widely considered as effective ingredients in sunscreen formulation, they have some limitations that need to be resolved and overcome. Such as (1) the limited UV protection range of TiO_2, (2) the high photocatalytic activity of TiO_2 and ZnO, producing high levels of harmful free radical species ROS, and (3) the inherent toxicity and the phototoxicity of ZnO make it an inappropriate UV filter in sunscreen [11]. TiO_2 has been incorporated with other inorganic materials as composite materials to broaden the UV protection range. For example, an improvement in UV blocking in TiO_2@ZnO composite has been reported through the effectiveness of nanosized TiO_2 and microsized ZnO for achieving higher SPF [9]. However, ZnO has recently been eliminated from sunscreen ingredients due to its inherent toxicity [12]. ZnO nanoparticles have two types of toxicity: solubility and photoreactivity. ZnO size and composition influence solubility, while photoreactivity intensifies when exposed to UV rays. Micro-sized ZnO particles can reduce toxicity by decreasing dissolution or penetration into the skin. The crystal structure also affects UV-blocking, with orthogonal structures showing the highest efficiency [12] ,[7].

Another research demonstrated that the TiO_2@SiO_2 composite absorbs more UVB and UVA than pure TiO_2. The photocatalytic activity of TiO_2 decreased from 87% to 31% when incorporated into SiO_2, suggesting that TiO_2@SiO_2 might be an alternate UV absorber [13].

Recently, efficient UV filters have been reported to enhance photostability, reduce toxicity, and broaden UV range protection. For example, calcium phosphate doped with iron showed promising performance compared to either TiO_2 or ZnO [14]. Hydrotalcite, an inorganic substance, has the potential to serve as a base for various UV filters, offering a viable solution to photostability issues [15]. Cerium oxide CeO_2 has recently been reported to show good UV blocking when combined with TiO_2; however, CeO_2 also generates a high amount of free radicals [16]. The combination of CeO_2-coated CaO and TiO_2 appears to be a superior option for traditional TiO_2@ZnO sunscreens due to its higher SPF and superior UVA protection [16].

In this review, the issues of reducing the high photocatalytic activity of the TiO_2 as UV filter in sunscreen that potentially cause skin cancer through generating harmful ROS, and its UV protection efficiency were outlined. Furthermore, the review introduced Zn_2SnO_4 as a non-toxic material with similar optical properties to TiO_2 in terms of using it as a UV filter as a composite. Zn_2SnO_4 is expected to significantly reduce the photocatalytic activity of TiO_2 while maintaining very low inherent toxicity, and to retain the required UVB and UVA blocking properties. Further research is required on Zn_2SnO_4 to develop it as an abundant and low-cost UV filter material that can be combined with TiO_2 for safer sunscreen applications [17]. The review gives an insight into the compared Zn_2SnO_4 properties against TiO_2 in terms of their UV blocking properties. Despite many researchers reporting either suppressing the photocatalytic activity or enhancing the sun protection factor (SPF) of TiO_2 through compositing with other inorganic filters, herein, these studies are summarized together (details will be presented in tables throughout the text) for a better understanding of overcoming these limitations in TiO_2.

2.Sun Protection Factor (SPF)

SPF is a quantitative measure of the sunscreen's effectiveness in protecting against UV rays .It is recommended to have higher numbers for sensitive skin or those with a skin cancer history [18]. The effectiveness of the protective sunscreen is related to the amount of rays that are allowed to enter through the skin, and these are specific standards in laboratories. For example, the SPF number, 30, means that the cream allows 1 out of 30 of the burning rays to penetrate the skin, meaning that it protects it from 97 percent of the harmful UV rays. While the SPF-50 number indicates that it allows 1 out of 50 of the rays to penetrate the skin, meaning that it protects it from 98 percent [19].

2.1Sun Protection Factor (SPF) of Sunscreen in the Laboratory

Mansur and his colleagues created a simple mathematical method for estimating in vitro SPF using UV spectroscopy in 1986. [20] This equation is inexpensive, fast, and effective for calculating SPF in the UVB spectrum. Mansur's equation applies in the UVB wavelength range of 290-320 nm, which corresponds to the erythemal response zone that is predominantly responsible for skin redness [20].The general formula for calculating SPF is:

$$\mathbf{SPF=CF\sum_{290}^{320} EE\,(\lambda)\;I\,(\lambda)\;Abs\,(\lambda)} \qquad \ldots\ldots\ldots\ (1)$$

Where**:**

EE (λ): Erythema effect spectrum. I (λ) : Solar intensity spectrum. Abs (λ): Absorbance of sunscreen product. CF: Correction equal to (10) λ:Wavelength (nm).

This approach is entirely laboratory-based and does not involve human or animal testing. SPF assessment is typically performed in vitro using the Mansour equation, employing polymethyl methacrylate (PMMA) sheets, which are often used as synthetic substrates to mimic the surface roughness of human skin. Because the measurement relies solely on the spectral absorption of UV radiation from the sunscreen layer deposited on the PMMA, it does not require consideration of the skin's phototype, pigmentation level, or individual skin tolerance [21]. Consequently, while it provides a rapid and reliable estimate of SPF, the values obtained in vitro may differ from in vivo results due to the absence of the biologically observable components in human skin [22].

2.2 Discrete Transmittance Integration Method

The discrete transmittance integration method is one way to test SPF. It measures the SPF over the whole UV spectrum (290–400 nm), including both UVA and UVB radiation. The Mansour method, on the other hand, only measures SPF over the UVB range (290–320 nm) and uses spectral absorbance with a correction factor [23]. This method uses transmittance data instead of absorbance to figure out the SPF. This means that a correction factor is not needed, and it gives a more accurate physical measurement of sunscreen UV protection. As a result, the Mansour method is a quick and cheap way to figure out the SPF. The SPF can be determined by the following discrete transmittance integration equation [24]:

$$\mathbf{SPF} = \frac{\sum_{290}^{400} \mathrm{EE}\,(\lambda) \times \mathrm{I}(\lambda)}{\sum_{290}^{400} \mathrm{EE}\,(\lambda) \times \mathrm{I}(\lambda) \times \mathrm{T}\,(\lambda)} \quad \text{.........} \ (2)$$

Where:

EE (λ): Erythema effect spectrum, I (λ): Solar intensity spectrum, T (λ): Transmittance of the sunscreen film, T (λ):$10^{-\mathrm{Abs}\,(\lambda)}$, and Δλ: Wavelength interval (nm)

In this method, the numerator represents the reddening-weighted ultraviolet radiation incident on unprotected skin, while the denominator represents the radiation transmitted through the sunscreen layer. Therefore, a higher SPF indicates a lower transmitted SPF.

Mansur's equation is a simple and easy empirical equation that can be used in vitro to quantify SPF of the sunscreen cast on a substrate, i.e, PMMA, which simulates the skin. While the discrete method can also be used in vitro, covering the whole UVB-UVA range. The Mansur equation can approximately evaluate the SPF in the lab for the materials that mostly block UVB, such as TiO_2 or ZTO. While the Discrete method can be used in the industry standardization for materials that block a wider range of UVB and UVA, such as ZnO.

3. UV filters in sunscreens

3.1. Physical UV Filters

Inorganic compounds in sunscreens reflect and scatter UV photons. Inorganic sunscreens typically contain ZnO and TiO_2, which both reflect and absorb UV rays [8]. To provide optimal skin coverage, inorganic UV filter materials must meet certain properties, such as a large surface area of their nanoparticles. This can be achieved using nanomaterials (up to 100 nm) [25]. Inorganic UV filters must also have a large bandgap in the UV region to absorb UVB and UVA rays (290–400 nm).

Another essential feature of inorganic UV filters is their ability to scatter and reflect UV rays [8]. These filters are considered safer and recommended because the skin does not absorb them. They have been shown to have less penetration into living skin, posing a lower chance of causing allergic reactions [26]. Although the dispersion performance of these compounds is important, the particle size must be carefully chosen to minimize unwanted whitening of the sunscreen formulation [27]. Some of the physical ingredients in sunscreen make the formula opaque, which may make the skin appear white when applied topically. Physical sunscreen ingredients also add opacity to the topical formulation, making the prepared creams visually undesirable and leaving a white cast on the skin [8].

3.2. Chemical UV Filters

Organic filters are often used in conjunction with inorganic filters. These filters work by scattering and absorbing rays through chemical reactions that generate heat and/or organic byproducts [8]. Many organic sunscreens contain compounds (e.g., PABA and its derivatives, cinnamates, avobenzone, octocrylene, salicylates including homosalates, benzophenones including oxybenzone, octisalates, and others) with one or more aromatic rings that can absorb and scatter energy from incident UV rays. They act as binders and contribute to the blocking/absorption of UV rays [26]. However, most organic filters are chemical formulations and have a limited UV-blocking range; for example, octinoxate and octocrylene can block UV rays reliably in the UVC-UVA range, while avobenzone can only block UVA and UVB [28]. In addition, organic filters have low photostability and degrade easily under sunlight, producing further harmful free radicals [29].

3.3. Hybrid UV Filters

Hybrid UV filters in sunscreen formulations combine nanoparticles (e.g., TiO_2 or ZnO) with chemical components (e.g., octyl methoxycinnamate, Oxybenzone, octocrylene, and octothon. By using these filters together, a broad-spectrum sun protection is achieved while also making the skin more compatible with the sunscreen. Organic filters soak up UV rays and turn them into heat, which is not harmful. Physical filters, on the other hand, block and scatter UV rays. Hybrid formulations often use advanced encapsulation technologies that make the product look better and give it a lighter texture and less white colour than regular mineral sunscreens [30], [31]. Tables 1 and 2 represent the comparison among the factions of UV filters, inorganic, organic, and hybrid formulations.

Table 1: General properties of different types of UV filters [8], [26], [29], [30], [31].

Feature	Physical Filters	Chemical Filters	Hybrid Filters
Mechanism	Reflect + Scatter + Absorb	Absorb + Convert to Heat	Combined action
UV Range	UVB + partial UVA	Targeted (depends on molecule)	Broad-spectrum
Photostability	High	Low–Moderate	Improved
Safety	High (low absorption)	Possible irritation/allergy	Balanced
Aesthetic	May leave a white cast	Transparent	Improved aesthetics

Table 2: UV protection range for common organic/inorganic UV filters [32].

UV Filter	UV Protection Range (nm)	UV Protection Types
Octinoxate	240 - 320	UVC, UVB
Octocrylene	240 - 340	UVC, UVB, UVA II
Octisalate	260 - 320	UVC, UVB
Oxybenzone	260 - 340	UVC, UVB, UVA II
Avobenzone	320 - 400	UVAII, UVA I
TiO_2	260 - 340	UVC, UVB, UVA II
ZnO	260 - 400	UVC, UVB, UVA II, UVA 1

4. TiO_2 as a UV Filter

TiO_2 belongs to the class of transition metals, a white inorganic solid that is insoluble in water, highly thermally stable, chemically inactive, and nonflammable. It is widely used in the manufacture of catalyst supports, dye-sensitized solar cells, and other industrial applications (cosmetics, coatings, paints, ceramics, printing inks, textiles, etc.) [33]. In addition to its strong oxidation capacity for photogenerated holes, it has excellent photocatalyst properties due to its high charge separation and non-toxicity [34], [35]. TiO_2 nanoparticles in nanosize less than (100 nm) are widely used in sunscreens due to their unique physical and chemical properties at concentrations up to10-17% (w/w). TiO_2 nanoparticles are generally considered to be inert and safe [36]. TiO_2 has a high refractive index and, therefore, is a good reflector and scatterer of UV light when applied to the skin. It blocks the whole UVB rays (290-320 nm), and also partially blocks UVA rays (absorbs the most penetrating UVA rays) in sunlight as well as all, thereby preventing sunburn and other photodamage [33]. TiO_2 in nanosize has the cosmetically acceptable advantage of not being opaque on the skin (because it is transparent to visible light) and being easily incorporated into lotions. Additionally, it is non-sensitizing, unlike some organic UV filters in sunscreens that can trigger photosensitivity and lead to skin sensitization. As a result, TiO_2 is particularly useful to us in sunscreen, childcare products, and facial cosmetics [37].

4.1 The crystalline structure and photocatalytic behavior of TiO_2

TiO_2 exhibits three common phase structures: brookite, anatase, and rutile. Among these phases, anatase displays the strongest photoactivity. The electron-hole recombination rate of rutile is higher than that of anatase, which may explain the excellent performance of anatase in photocatalysis [38]. The photocatalytic performance of anatase is better than that of brookite. Since rutile has the highest thermodynamic properties, stable, phase-pure anatase photocatalysts can be synthesized at sintering temperatures below 450 °C [39]. Table 3 shows the general properties of different TiO_2 phases. Anatase TiO_2 is a more favourable phase for photocatalysts and UV filter applications due to its high surface area and photoactivity. Figure 1 shows the crystalline unit cell structure of anatase TiO_2.

Table 3: Physical properties of anatase, rutile, and brookite polymorphs of TiO_2 [39].

Property	Anatase	Rutile	Brookite
Crystal structure	Tetragonal	Tetragonal	Orthorhombic
lattice constants (Å)	a=3.784 c=9.515	a=4.5936 c=2.9587	a=9.184 b=5.447 c=5.145
Band Gap Energy (eV)	3.20	3.00	3.10-3.40
Density (g/cm^3)	3.79	4.13	3.99
Refractive Index	2.52	2.72	2.63

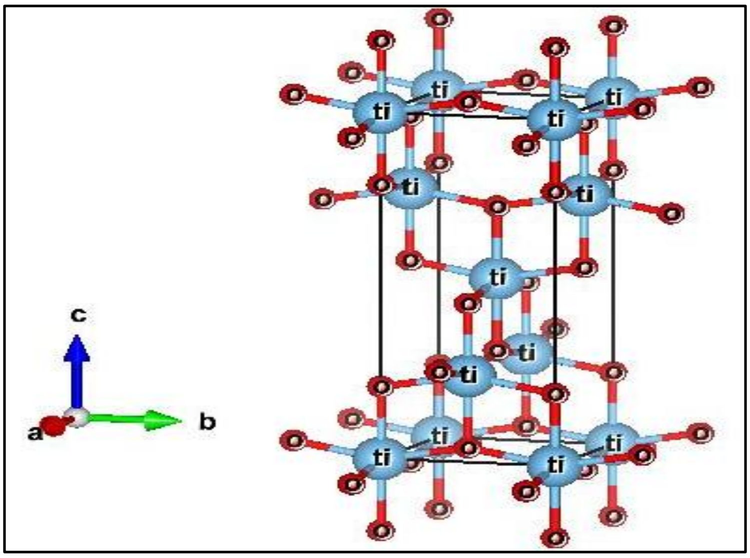

Figure 1: Crystal structures of anatase TiO_2 phase.

4.2 Photocatalytic mechanism in TiO_2

TiO_2 generates ROS, which can affect skin cells and the stability of sunscreens [40]. TiO_2 can absorb UV with energy that is equal to or greater than its band gap. Then, as shown in the inset in Figure 2, the electrons move from the valence band (VB) to the conduction band (CB), leaving behind an equal amount of positive charge (gap) in the valence band. When photons are absorbed, pairs of electrons and holes (e-h+) form. If the excited state (e-h+) pairs come back together, the lost energy could be released as heat from surface traps. Alternatively, the pairs could interact with donor and acceptor electrons that are absorbed on the surface of the semiconductor [41]. Generally, hydroxide ions (OH^-) or water adsorbed on the surface of TiO_2 can react with holes (h^+) in the VB to form hydroxyl radicals (OH•) as shown in Figure 2 [42]. The ROS formation, including superoxide, hydroxyl radicals, and singlet oxygen, can damage the cell and then change its DNA, developing skin cancer [7].

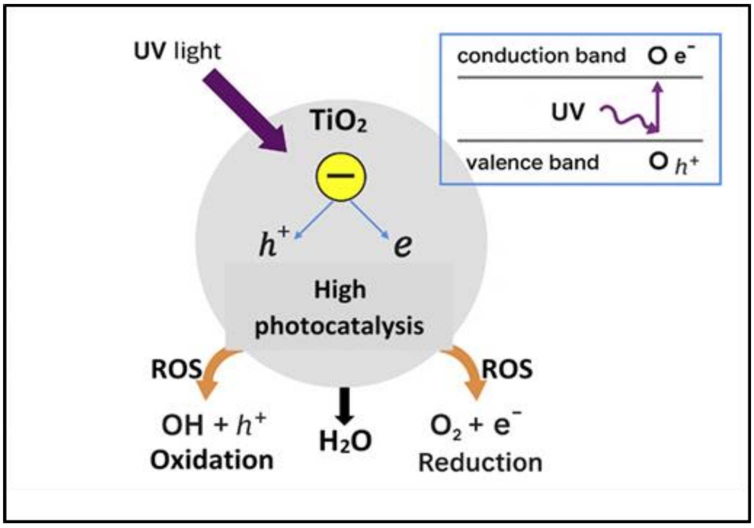

Figure 2: Mechanism of photocatalysis of TiO_2. Modified from [43].

5. Approaches to Reduce the Photoactivity of TiO_2

Many ways have been developed to lessen the effects of free radical production while keeping TiO_2's ability to protect skin from UV radiation. Some of these strategies are surface modification and coating, doping with elements, and putting things inside hybrid matrices. These methods aim to reduce the recombination of electrons and holes, limit the generation of oxygen species, or block the surface reactions responsible for photocatalysis. The common ways to reduce the photocatalytic activity of TiO_2 nanoparticles are through the addition of dopants, surface passivation, organic functionalization, and encapsulation. These processes make TiO_2-based UV filters safer and more biocompatible.

Mixing TiO_2 with inert metal oxides such as SiO_2 lowers its photocatalytic activity. The SiO_2 (silica coating) acts as a protective layer as a physical barrier, preventing direct contact between the TiO_2 surface and the surrounding environment, leading to a reduction in the production of ROS during UV exposure. Many studies show that nanocomposites composed of TiO_2 and SiO_2 reduce ROS levels and increase photostability without compromising UV absorption [13]. Cerium dioxide (CeO_2) is a promising coating material. Doping TiO_2 with CeO_2 changes its electrical structure, which slows down the formation of photoexcited electron-hole pairs and thus slows down the photocatalytic processes. Adding CeO_2 to broaden UV absorption in sunscreen formulas [44].

When nanosized TiO_2 and microsized ZnO are added to TiO_2@ZnO composites, the UV-blocking properties are improved, which raises the SPF. The size and content of ZnO determine how well it dissolves, and exposure to UV light makes it more photoreactive [9]. The size and content of ZnO determine its solubility, while exposure to UV light increases its photoreactivity. ZnO nanoparticles can reduce toxicity by slowing their disintegration or skin penetration ,[7] [12].

Surface modification and coating methods, for example, using 3-Isocyanatopropyltrimethoxysilane (IPTMS) and 3-aminopropyltrimethoxysilane (APTMS) to modify the surface of TiO_2 nanoparticles and reduce its photocatalytic activity, and then the surface reactivity of TiO_2. The modification creates a hydrophobic organic layer on the TiO_2 nanoparticle surface. This layer reduces the formation of ROS during UV exposure by inhibiting the reaction between the TiO_2 surface and the surrounding water or oxygen molecules [45].

Adding nitrogen (N) and iron (Fe^{3+}) to TiO_2 can greatly lower its ability to photocatalyze. This also reduces the photocatalytic activity and the energy bandgap. Elemental doping is used to change the electrical properties of the TiO_2 crystal lattice by adding nonmetallic or transition metal ions. Interestingly, some doped materials in sunscreens can limit photocatalytic activity by acting as recombination sites for pairs of photoexcited electrons and holes. Co-doping TiO_2 with nitrogen and Fe^{3+} significantly reduces the formation of ROS and improves UV protection [46].

Methods for encapsulating TiO_2 in hybrid matrices, such as using mesoporous silica structures loaded on TiO_2. The compounds showed the presence of the anatase phase of TiO_2, which reduces the photocatalytic activity and increases the specific surface area and thermal stability of the compound [47] . Table 4 shows a summary of the literature review on suppressing the photocatalytic activity of TiO_2.

Table 4: A summary of previous studies enhancing the SPF or reducing the photocatalytic activity of TiO_2 as a UV filter in sunscreen.

Author (Year)	Composite type	Preparation Method	Reducing photoactivity	SPF Value
Smijs G. et al. (2011) [48]	TiO_2 & ZnO nanoparticles	Particle size control + silica coating	Reducing photoactivity	Not mentioned
Barbosa J. et al. (2018) [49]	TiO_2@SiO_2, Al_2O_3, ZrO_2	Sonochemistry	Reduces photoactivity, colloidal stability	SPF Preserved
Yu J. et al. (2018) [50]	LS@TiO_2 composite	Hydrothermal esterification	Reduce photoactivity, improve stability	SPF = 16 (5 wt%), 26 (10 wt%), 48 (20 wt%), and 50+ at (10 wt% LS@TiO_2-1M)
Jiménez J. et al. (2018) [51]	ZnO@TiO_2 hierarchical composite	Sol-gel	Reducing recombination e^-/h^+ High photoactivity	SPF high
Allende P. et al. (2019) [13]	TiO_2-SiO_2 composite	Solvent-less solid state (pyrolysis)	Photosynthetic activity decreased from 85% to 31%.	Not mentioned Improve absorption UVA/UVB
Cubellos M. et al. (2019) [52]	TiO_2 with metal additives (Fe, Co, Ga, Bi, W, Mo, V, Ni)	Sol-gel	Modification with iron and other metal species affected the phase structure and catalytic behavior.	Not mentioned
Lategan M. et al. (2019) [53]	Zn–Ti LDH nanostructures	Hydrothermal	ROS reduction	SPF $\approx$ 18
Nicoara A. et al. (2020) [54]	Ag/Fe-doped TiO_2	Sol-gel + Microwave hydrothermal	Reducing photoactivity	SPF = 27 (TiO_2-SG), 37 (Ag-SG), 14 (Fe-SG), 42 (TiO_2-H), 40 (Ag-H), 16 (Fe-H)
Morlando A. et al. (2020) [55]	CeO_2@TiO_2 composite	Precipitation	Significantly reduced photoactivity and improved biocompatibility	Not mentioned
Bansal J. et al. (2020) [56]	Cu-doped TiO_2	Low-temperature sol–gel hydrothermal	Reducing photoactivity	Not mentioned
Bousiakou L. et al. (2022) [57]	Mn-doped rutile TiO_2	Doping (introducing Mn^{3+} into the Rutile phase)	Reduce ROS >95%	Not mentioned
Ghamarpoor R. et al. (2023) [58]	Commercial TiO_2 nanoparticles (142–263 nm	Milling + Ultrasonic homogenization	The photochemical activity decreased with increasing size; at 142.6 nm, MB degradation was 22% (higher than for larger sizes).	SPF = 6-7.5 (lowest values at some pH); visible improvement at 142.6 nm at 5–10% concentration.

6. Zn_2SnO_4 as a potential composite material

Zn_2SnO_4 belongs to the family of ternary metal oxides and has recently gained substantial attention. It crystallizes in a cubic spinel form, as illustrated in Figure 3. It is defined as a large band gap, typically between 3.0 and 3.7 eV [59]. Zn_2SnO_4 also shows n-type conductivity, which means it has an excess of electrons that act as charge carriers. The broad band gap makes it transparent to visible light, allowing its potential usage in optoelectronic applications [59]. Because of its versatile physical, chemical, electrical, and mechanical properties, Zn_2SnO_4 has recently been used in a variety of applications, including gas sensors, optical devices, solar cells, lithium-ion batteries, transparent conductive electrodes, and thermoelectric materials. It is also reported to have good UV-blocking properties [43, 44]. Zn_2SnO_4 showed very low photoactivity compared to TiO_2 and inherent toxicity compared to ZnO, while maintaining similar UVB and UVA blocking properties as TiO_2 [60]. Table 5 shows some studies that explored the preparation of Zn_2SnO_4 and the analysis of its structural and optical properties.

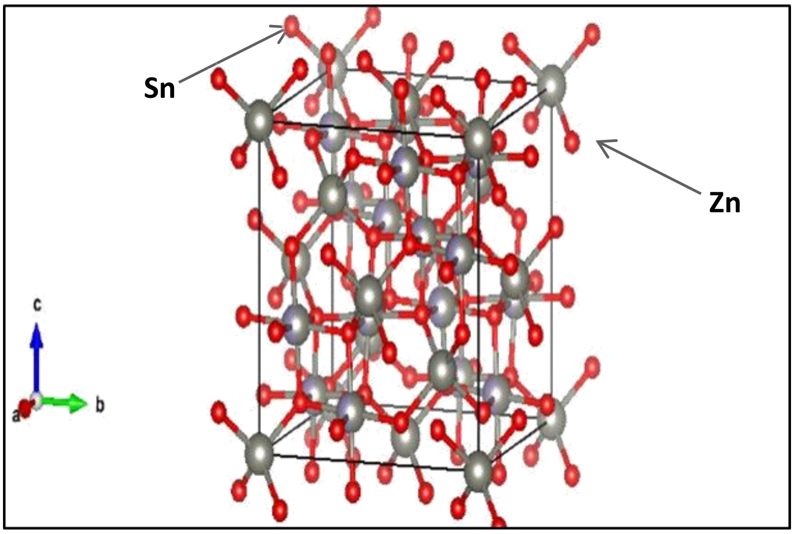

Figure3: The cubic spinel structure of Zn_2SnO_4.

Table 5: Some selected research on the preparation of Zn_2SnO_4 compound and analysis of its structural and optical properties.

Compound	Preparation method	Energy gap (eV)	Morphology and size	Performance
Zn_2SnO_4 [61]	Thermal treatment	3.6 - 3.8	Nanocubes 50-100 nm	Highly responsive to UV photodetectors
Zn_2SnO_4 [62]	Hydrothermal	~3.35	20-30 nm Nanoparticles	Weak Photocatalysis Due to Small Band Gap
Zn_2SnO_4 [63]	Hydrothermal (Nanocrystals)	~3.4	Single Crystalline NPs ~10 nm	High Efficiency in Photovoltaic Devices
Zn_2SnO_4 [64]	Hybrid with Oxide Composite	~3.3 - 3.6	Porous Structures	Improve Light Absorption in Solar Cells
Zn_2SnO_4 [65]	Nanobeads	~3.6	Homogeneous spheroids with a size of 200-300 nm	Conversion Efficiency 6.1% in DSSCs
Zn_2SnO_4/SnO_2 [66]	Heterojunction	~3.4 (Zn_2SnO_4)	SnO_2 (Core-Shell) Alkali Particles	Enhanced Photocatalysis for Dye Degradation
$Zn_2SnO_4/SnoO_2$ [67]	Hollow Spheres	~3.5	| 500 nm Hollow Structures	4.5% Efficiency in DSSCs
Zn_2SnO_4 [68]	Thin Films	~3.8	Compact Layers	Fast-response UV photodetectors

Table 6: lists a comparison between tetragonal anatase TiO_2 and cubic spinel Zn_2SnO_4 for sunscreen formulation.

Property	**Anatase TiO_2**	**Cubic Zn_2SnO_4**
Crystal Structure	Tetragonal (Anatase phase)	Cubic spinel-type
Band Gap (eV)	Wide bandgap ~3.1-3.3 eV	Wide bandgap ~3.1-3.6 eV
Particle Size (nano-form)	10–100 nm (adjustable for cosmetic use)	10–100 nm (nanostructured for sunscreen)
Color	White	White to pale beige
Photostability	Moderate (can produce ROS under UV)	High (less prone to ROS generation)
UV Absorption Range	Mainly UVB (~280–320 nm) and some UVA (~320–400 nm)	Expected to show similar UV absorption to TiO_2 (especially UVA)
Refractive Index	~2.5–2.9 (high, suitable for opacity)	~2.0–2.2 (lower than TiO_2)
Surface Charge (pHzpc)	~6.0–6.8	~8.0–9.0
Optimal pH Stability	Stable at pH 3–9	Stable at pH 6–11
Solubility in Water	Insoluble	Insoluble
Solubility in Organic Solvents	Insoluble (requires dispersion agents)	Insoluble (but dispersible in emulsions)
Toxicity/ROS Generation	Can generate ROS under UV (photo-reactive)	Low ROS generation (more photochemically inert)
Biocompatibility	Generally good (can cause oxidative stress)	Higher (safer alternative in some studies)
Common Surface Modifications	Silica and alumina coatings to reduce photoactivity	Rarely needed due to inherent stability
Regulatory Approval	FDA-approved UV filter (≤25% w/w in EU)	Not yet approved as a UV filter (research stage)

Table 6: Comparison between TiO_2 and Zn_2SnO_4 in terms of use in UV filter applications [35], [59].

7. Current research on Zn_2SnO_4 as UV filter

A recent study looked into the UV filtering properties of Zn_2SnO_4 and compared them to those of TiO_2 and ZnO [11]. This study looks at the main problems with both materials and suggests Zn_2SnO_4 as a good replacement for traditional inorganic UV filters like TiO_2 and ZnO. TiO_2 blocks UVB efficiently, but it also has a high photocatalytic activity, which makes harmful free radicals (ROS). On the other hand, ZnO can block a wide range of UV radiation (UVA and UVB), but once again produces a high amount of ROS in addition to its inherent toxicity. Zn_2SnO_4-assembled cubic nanoparticles and Zn2SnO4 nanoparticles can block the UVB and partial UVA. Noteably, their optical absorption and reflection properties are similar to those of hybrid TiO_2@ZnO. It found that Zn_2SnO_4 generated a very low amount of ROS and very low inherent toxicity (more than 95% of cells survive). Therefore, Zn_2SnO_4 is an important UV filter candidate to be used in sunscreen products. The cubic spinel phase of Zn_2SnO_4 makes it less photoactive, and its small nanoparticle size helps block UV rays while maintaining the visible light transparency. Overall, Zn_2SnO_4 has similar UV-blocking abilities to TiO_2, with much less photocatalytic activity and inherent toxicity compared to TiO_2 and ZnO, respectively. These factors make it a safer and more stable UV filter.

8. Some synthesis methods of TiO_2 and Zn_2SnO_4

8.1 Sol-Gel Method

The sol–gel method is a well-established wet chemical method for the synthesis and processing of inorganic and organic hybrid materials. A sol is a colloidal suspension of liquid or solid particles with diameters ranging from 1 to 100 nanometers, which are so small that they can overcome gravity. A gel is a continuous solid structure with a continuous liquid phase [69].

The sol-gel method is suitable for preparing solid host materials and has several advantages, including processing at low temperatures, excellent product homogeneity, and the ability to form complex shapes of materials in the gel state. Due to the ability to combine different chemical species at the molecular level, a wide variety of host materials can be prepared using the sol–gel method. For example, several studies have used sol–gel techniques to synthesize a variety of optical materials [70].

8.2. Hydrothermal method

The hydrothermal method is a process for crystallizing a substance in an aqueous solution under relatively high temperature and pressure. The process is carried out in a polytetrafluoroethylene autoclave in a stainless steel container, which is placed in an oven at a temperature above 100 °C (i.e., above the boiling point of the solvent (e.g., water)) and a pressure above 1 atmosphere [71]. This approach provides easy control over the form and size of the produced nanostructures. It is distinguished by its capacity to manufacture nanoparticles with excellent crystallinity, homogeneity in size and shape, and better purity than traditional procedures. It is also a good option for making high-quality nanomaterials at a lower cost because it doesn't require very high temperatures or complicated post-processing. There are two main types of hydrothermal methods: acidic hydrothermal methods and alkaline hydrothermal methods. These types are based on the reagent solution used in the synthesis process [72].

8.3. Solvothermal method

This process is slightly different from the hydrothermal method because it uses a special solvent. This process uses a special non-aqueous solvent. This process uses several organic solvents with higher temperatures and boiling points than the hydrothermal method. The solvothermal method allows for better control over the composition distribution, size, and crystallinity of the TiO_2 nanopowder. This process is used to produce nanoscale metals, ceramics, polymers, and semiconductors using solvents under heat and pressure treatment [73].

8.4. Co-precipitation method

It is a chemical method used to prepare nanomaterials or to precipitate specific compounds from a solution. It is widely used in analytical chemistry, industrial chemistry, and in the manufacture of oxides or nanomaterials. Co-precipitation precipitates a desired substance from an aqueous solution with other substances that precipitate simultaneously or with the help of these substances. These other substances may be impurities or intentionally added to improve the properties of the final product.

When a special reagent is added to a solution containing metal ions, these ions form a solid (usually a hydroxide or oxide). During this process, small amounts of other substances may be trapped in the solid due to (1) Adsorption - adhesion to the surface of the solid, (2) Inclusion - the substance entering the crystal structure, (3) Embedding - being trapped between the forming crystals [74].

8.5. Solid-state synthesis

It is a method of preparing materials, particularly inorganic compounds, directly from solid reactants without the use of solvents or liquid phases. This technique is commonly used to prepare ceramics, metals, and semiconductors, and it often involves high-temperature reactions [75]. However, this method can produce inhomogeneous particle sizes and poor crystallinity of synthesized materials.

Based on the above literature, the high photocatalytic activity of TiO_2 can be reduced by incorporating other materials into TiO_2 composites. As Zn_2SnO_4 demonstrates excellent UV blocking properties, very low photocatalytic activity, and very low toxicity, it can be used either as a composite with TiO_2 or by itself as an efficient UV filter in sunscreens. Among the synthesized methods mentioned above, the hydrothermal approach can produce the desired nanomaterials (TiO_2, Zn_2SnO_4) with designed properties in terms of controlling the particle size, crystalline phase, and purity.

9. Conclusions

In this review, several approaches have been discussed to suppress the high photocatalytic activity of TiO_2, which is widely used in sunscreens as a UV filter while maintaining high SPF. To further support these efforts, Zn_2SnO_4 has been proposed as a potential alternative to zinc oxide (ZnO), which is commonly used as a composite with TiO_2. However, ZnO suffers from the inherent toxicity and high photocatalytic activity. Zn_2SnO_4 has recently demonstrated lower toxicity and good UV blocking properties, most notably its ability to reduce the photocatalytic activity of TiO_2, making more safer as a UV filter in sunscreen.

10. References

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