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Review Paper

Nanotechnology-Based Herbal Sunscreens: Current Trends, Challenges and Future Perspectives

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ABSTRACT

Radiation from the sun is a known environmental carcinogen that causes skin cancer, immunosuppression, photoaging, and DNA damage. Despite their effectiveness, synthetic sunscreen ingredients are being closely examined for endocrine disruption, ecotoxicity, and low consumer acceptability. Rich in flavonoids, polyphenols, carotenoids, and terpenoids, herbal photoprotective compounds provide broad-spectrum UV absorption and antioxidant protection; nevertheless, their limited skin penetration, photodegradation, and poor aqueous solubility significantly hinder their practical translation. By encasing herbal actives within nanocarriers such nanoemulsions, liposomes, solid lipid nanoparticles (SLN), nanostructured lipid carriers (NLC), polymeric nanoparticles, and phytosomes, nanotechnology offers a revolutionary platform to get past these physicochemical limitations. Skin biology, UV-induced damage mechanisms, herbal photoprotective agents and their mechanisms, nanocarrier systems, formulation strategies, evaluation methodologies, recent research findings, regulatory frameworks, and current challenges are all covered in this review, which critically assesses the state of nano-based herbal sunscreens. The remarkable potential of nano-herbal systems is demonstrated by recent SPF values of 28–55. Future directions that are highlighted in the review include green nanotechnology, customized cosmeceuticals, and AI-assisted formulation design. Nanobased herbal sunscreens are a viable and effective substitute for traditional synthetic photoprotectants when safety validation and regulatory harmonization are completed

INTRODUCTION

One of the most common environmental insults to human skin is ultraviolet (UV) radiation from the

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sun. The solar UV spectrum, which is divided into UVA (320–400 nm), UVB (280–320 nm), and UVC (<280 nm), mediates a variety of biological consequences, from the production of helpful vitamin D3 to harmful DNA damage, immunosuppression, photoaging, and carcinogenesis [1,2]. The World Health Organization estimates that over 1.5 million new cases of skin cancer occur globally each year, a burden that is disproportionately linked to prolonged sun exposure [3]. The incidence of both melanoma and non-melanoma skin cancers is rising at an alarming rate. Historically, synthetic UV filters including avobenzone, oxybenzone, octocrylene, and octinoxate have been used in conventional sunscreen formulas. Even though these compounds are effective at reducing UV radiation, there has been a lot of scientific and regulatory attention due to growing concerns about systemic absorption, endocrine disruption, coral reef damage, and contact sensitization [4,5]. In its 2019 proposed regulation, the US Food and Drug Administration (FDA) noted that out of 16 approved filters, only zinc oxide and titanium dioxide were GRASE (Generally Recognized as Safe and Effective), highlighting the need for safer substitutes [6]. With several modes of action, such as UV absorption, free radical scavenging, anti-inflammatory activity, and DNA repair facilitation, herbal photoprotective agents—which are derived from plant secondary metabolites like flavonoids, polyphenols, carotenoids, and tannins—represent an appealing natural substitute [7,8]. Nevertheless, many phytoconstituents have intrinsic drawbacks that limit their medicinal use as independent sunscreen agents, such as hydrophobicity, photolability, poor and unpredictable skin penetration, and chemical instability [9]. A paradigm-shifting strategy to deal with these biopharmaceutical issues is nanotechnology. Improved skin penetration, increased photostability, controlled and sustained release, targeted delivery to skin layers, and increased Sun Protection Factor (SPF) values can all be achieved at the same time by encasing herbal actives within engineered nanocarriers at the 1–1000 nm [10,11]. Thus, the discipline of nanophytocosmetics a fast developing topic with significant implications for dermatology and cosmetic science was created by the intersection of herbal pharmacognosy and nanotechnology. The current review thoroughly looks at the following topics: (i) skin structure and UVmediated damage mechanisms; (ii) herbal photoprotective agents and their phytochemical basis; (iii) the types of nanocarriers used and their rationale; (iv) formulation strategies and evaluation methodologies; (v) recent clinical and experimental findings; (vi) regulatory considerations; and (vii) future perspectives, including green nanotechnology and AI driven formulation design.

SKIN STRUCTURE AND UV RADIATION

STRUCTURE OF SKIN

The epidermis, dermis, and subcutaneous tissue (hypodermis) are the three main layers that make up human skin, which is the biggest organ in the body at 1.5–2.0 m². Each of these layers has a unique function in photoprotection [12]

The five sublayers of the stratified squamous epithelium that make up the epidermis are stratum corneum, stratum lucidum, stratum granulosum, stratum spinosum, and stratum Basale. The primary physicochemical barrier to transdermal penetration is the stratum corneum, which is made up of 15–20 layers of anucleate corneocytes embedded in a lipid matrix. Over 95% of epidermal cells are keratinocytes, which undergo a 28-day cycle of increasing differentiation from the basal layer to the surface. Melanocytes are found in the stratum Basale at a ratio of roughly 1:10 to keratinocytes. They produce melanin pigment in

specialized organelles called melanosomes, which are then transported to keratinocytes to create supranuclear caps that protect DNA from ultraviolet light [13].

The dermis, which contains collagen (Type I and III), elastin, glycosaminoglycans, fibroblasts, mast cells, and a rich vascular network, supports the epidermis both structurally and nutritionally. By activating matrix metalloproteinase (MMP), collagen, which makes up 70–80% of the dry weight of the skin, is the main target of UV-induced photoaging [14]. Adipocytes and loose connective tissue make up the hypodermis, which serves as a mechanical cushion, thermal insulator, and energy storage. Multiple interconnected biochemical pathways that work in concert to induce skin damage are mediated by UV radiation [16, 17]:

TYPES OF UV RADIATION

According to wavelength and biological activity, solar UV radiation that reaches the Earth's surface is typically divided into three physiologically significant bands [15]:UVA (320–400 nm): Approximately 95% of solar UV that reaches the Earth's surface is in this range. Deeply penetrating the dermis, UVA causes oxidative damage mainly by producing reactive oxygen species (ROS). By indirectly damaging DNA through photosensitization reactions, it promotes tanning, photoaging, and carcinogenesis.

• UVB (280–320 nm): Approximately 5% of solar UV reaches the surface of the Earth. DNA directly absorbs UVB, which causes 6-4 photoproducts (6-4PPs) and cyclobutane pyrimidine dimers (CPDs), the main photolesions that initiate skin cancer. The epidermis is the primary absorber of UVB rays.

• UVC (<280 nm): Under typical meteorological conditions, it is entirely absorbed by stratospheric ozone and does not make it to the Earth's surface. Erythema and severe keratitis can be caused by artificial UVC sources, such as germicidal lamps.

MECHANISMS OF UV INDUCED SKIN DEMAGE

Multiple interconnected biochemical pathways that work in concert to induce skin damage are mediated by UV radiation [16, 17]: Oxidative Stress: ROS such as singlet oxygen (1O2), superoxide anion (O2), hydrogen peroxide (H2O2), and hydroxyl radical (OH) are produced by UVA and UVB. Lipid membranes, proteins, and nucleic acids are oxidized by ROS, which overwhelms the body's natural antioxidant defence's, such as glutathione peroxidase, catalase, and superoxide dismutase [18].

DNA Damage: UVB directly causes CPDs and 6-4PPs at dipyrimidine sites, which can lead to mutagenic C→T and CC→TT transition mutations in tumour suppressor genes, such as TP53, if they are not fixed by nucleotide excision repair (NER) mechanisms [19]. UVA mostly results in 8-oxo-7,8-dihydroguanine (8-oxoG) oxidative DNA damages, which produce G→T transversions [20].

Photoaging: Prolonged exposure to UV light activates nuclear factor-kB (NF-kB) and activator protein-1 (AP-1) transcription factors, upregulating matrix metalloproteinases (MMP-1, MMP-3, and MMP-9) that break down dermal collagen and elastin, resulting in the clinical phenotype of photoaged skin, which includes wrinkles, laxity, telangiectasias, and dyspigmentation [21].

Skin cancer: The main carcinogenic pathways include UV-induced mutations in TP53 (basal cell carcinoma, squamous cell carcinoma) and BRAF pathway activation (melanoma). Immune surveillance of transformed cells is further compromised by immunosuppression caused by UV-damaged keratinocytes that release prostaglandins, IL10, and cis-urocanic acid [22].

HERBAL AGENTS USED IN SUNSCREENS

ROLE OF PHYTOCONSTITUENTS IN PHOTOPROTECTION

Over millions of years, plants have developed complex UV defence mechanisms by accumulating a variety of secondary metabolites that both absorb UV light and neutralize ROS. Beyond just UV filtering, these phytoconstituents offer a multifunctional approach to photoprotection [23, 24]: Flavonoids: This structurally varied class of polyphenols, which includes isoflavones, flavones, flavonols, and flavanones, has distinctive chromophoric systems that allow UV absorption in the 280–350 nm range. Strong anti-inflammatory and antioxidant properties are exhibited by quercetin, kaempferol, and luteolin by direct ROS scavenging, COX-2 suppression, and inhibition of NF-kB signaling [25].

Polyphenols: Resveratrol, rosmarinic acid, chlorogenic acid, and ellagic acid are significant photoprotective polyphenols. While resveratrol stimulates SIRT1 deacetylase, a regulator of DNA repair and cellular stress responses, ellagic acid suppresses MMP-1 production and melanogenesis [26]

Tannins: Condensed tannins (proanthocyanidins) and hydrolyzable tannins (gallotannins, ellagitannins) absorb UV light and show metal chelation activity, which lowers the production of hydroxyl radicals caused by the Fenton reaction. In animal models, grape seed proanthocyanidins show strong UVB protection [27].

Terpenoids: Triterpenoids (ursolic acid, oleanolic acid) and carotenoids (beta-carotene, lycopene, astaxanthin) act as membrane stabilizers and UV absorbers. Singlet oxygen is quenched by carotenoids at a rate constant of around 3×10^10 M-1s-1 [28].

Carotenoids: UV-absorbing pigments and broad-spectrum antioxidants include lycopene, beta-carotene, and astaxanthin. In singlet oxygen quenching, astaxanthin has ten times the antioxidant activity of beta-carotene [29].

COMMON HERBAL PHOTOPROTECTIVE AGENTS

A thorough list of important herbal photoprotective agents and their main active ingredients is given in Table 1. The most extensively researched agents' brief profiles are shown below**:**

Table 1: Herbal Agents, Active Phytoconstituents, and Photoprotective Activities

Herbal Agent	Plant Source	Active Phytoconstituents	UV Activity / Effect	References
Aloe vera	*Aloe barbadensis* Miller	Aloin, aloe-emodin, acemannan, flavonoids	UVB absorption, anti-inflammatory, wound healing	Surjushe et al., 2008; Eshun & He, 2004
Turmeric	*Curcuma longa* L.	Curcumin, bisdemethoxycurcumin, turmerone	UVB filter, antioxidant, anti-inflammatory	Aggarwal & Sung, 2009; Prasad & Aggarwal, 2011
Green Tea	*Camellia sinensis*	EGCG, EGC, epicatechin, catechins	UVA/UVB absorption, free-radical scavenging	Katiyar et al., 2001; Elmets et al., 2001
Neem	*Azadirachta indica*	Nimbin,azadirachtin, quercetin	Anti-inflammatory, antibacterial, photoprotective	Subapriya & Nagini, 2005

Liquorice	*Glycyrrhiza glabra*	Glabridin, glycyrrhizin, liquiritin	UVB protection, melanogenesis inhibition	Yokota et al., 1998; Nerya et al., 2003
Pomegranate	*Punica granatum*	Ellagic acid, punicalagins, anthocyanins	DNA protection, UVB absorption	Afaq & Mukhtar, 2006; Afaq et al., 2005
Raspberry seed	*Rubus idaeus*	Tocopherols, ellagitannins, PUFAs	Estimated SPF 28–50, broad-spectrum UV protection	Oomah et al., 2000
Carrot seed	*Daucus carota*	Beta-carotene, luteolin, flavonoids	Estimated SPF 38–40, antioxidant	Shilpi et al., 2015
Grape seed	*Vitis vinifera*	Proanthocyanidins, resveratrol	UVB protection, anti-photoaging	Sharma et al., 2011; Bagchi et al., 2000

Aloe vera (Aloe barbadensis Miller) is a succulent plant with a long history of use in ethnomedicine for photoprotection. Acemannan, a beta-1,4-acetylated mannan, aloin, aloeemodin, and flavonoids are all present in the mucilaginous gel. Aloe vera has been shown to have anti-inflammatory, wound-healing, moisturizing, and UVB-attenuating characteristics in clinical settings. These effects are partly explained by the suppression of the thromboxane A2 pathway and the encouragement of fibroblast proliferation [30].

Curcuma longa (turmeric): The rhizome of this Zingiberaceae member produces curcuminoids (75–80% curcumin, 15–20% bisdemethoxycurcumin, and 5% demethoxycurcumin) with strong UV absorption at 430 nm, anti-inflammatory qualities through inhibition of the NF-kB and MAPK pathways, and photoprotective activity against UVB-induced DNA damage [31].

Camellia sinensis, or green tea: Packed in catechin polyphenols, especially (−)epigallocatechin-3-gallate (EGCG), which at 10 μM suppresses the activation of AP-1 and NF-kB caused by UVB. In human volunteers, topical EGCG treatment decreases UVBinduced erythema and CPD development [32].

Pomegranates (Punica granatum): Punicalagins, ellagic acid, and anthocyanins are abundant in fruit extracts. These substances prevent MMP activity, melanogenesis, and DNA damage brought on by UVB. In vitro, pomegranate peel extract has estimated SPF values of 12–18 [33]

MECHANISM OF HERBAL PHOTOPROTECTION

Herbal medicines' photoprotective action functions via four complimentary, frequently synergistic mechanisms [34, 35]:

• UV Absorption: Flavonoids and polyphenols' aromatic chromophoric complexes absorb UV photons and release energy as heat through excited-state deactivation, which stops UVinduced photochemical reactions in skin biomolecules

• Antioxidant Activity: Hydrogen atoms are donated by phenolic -OH groups to stop ROS chain reactions. Resonance delocalization stabilizes the resultant phenoxyl radicals, preventing them from being sufficiently reactive to spread harm.

• Free Radical Scavenging: Direct quenching of reactive species (1O2, •OH, O2•−, ONOO−) by hydrogen atom transfer (HAT), metal chelation, and electron donation

• Anti-inflammatory Activity: By suppressing prostaglandin, leukotriene, and cytokine synthesis in UV-exposed skin, inhibition of the COX-2, LOX, iNOS, and NF-kB pathways reduces

erythema, oedema, and immunological suppression.

NANOTECHNOLOGY IN HERBAL SUNSCREENS

INTRODUCTION TO NANOTECHNOLOGY

The engineering, characterization, and use of materials and devices with at least one dimension in the range of 1–100 nm (or, more generally, up to 1000 nm for pharmaceutical systems) constitute nanotechnology. When compared to their bulk counterparts, materials at the nanoscale display significantly different physicochemical characteristics, such as quantum effects, an increased surface-to-volume ratio, improved reactivity, and modified solubility [36].

In the context of dermal drug delivery, nanotechnology confers several pharmacokinetic and pharmacodynamic advantages: enhanced permeation through the stratum corneum via follicular and intercellular routes, improved solubility of lipophilic actives, protection from environmental degradation, sustained and controlled release, and targeted delivery to specific skin compartments [37].

ADVANTAGES OF NANO HERBAL SUNSCREENS

- Enhanced SPF: By improving dispersion and reducing particle size, nanoencapsulation increases the effective UV-absorbing surface area of herbal actives, allowing for better SPF values at equal active doses. SPF values for nano-curcumin formulations are three to four times greater than those for bulk curcumin preparations [38].
- Better Skin Penetration: Nanoparticles (10–300 nm) transport active ingredients to viable epidermis and dermis where photoprotection is required by penetrating the stratum corneum through the transfollicular, intercellular lipid, and disturbed barrier areas [39].
- Enhanced Photostability: By limiting direct photon exposure, encapsulation protects labile phytoconstituents from photodegradation. In comparison to free curcumin, curcumin stability in nanoemulsions is significantly enhanced during UV irradiation [40].
- Controlled Release: By allowing for sustained release over 8–12 hours, matrix or reservoir nanocarrier topologies lower the frequency of reapplication while preserving protective concentrations [41].
- Enhanced Bioavailability: By overcoming solubility constraints, nanoencapsulation raises the percentage of active ingredients that are accessible for skin contact. EGCG skin absorption is increased by four to five times using phytosome technology [42].
- Aesthetic Acceptability: Transparent or translucent nanoparticles in the 20–50 nm range do not have the whitening impact of traditional mineral sunscreens.

TYPES OF NANOCARRIERS USED IN HERBAL SUNSCREENS

- For the delivery of herbal sunscreen, a wide range of nanocarrier platforms have been studied; each has unique structural traits, loading capabilities, and release patterns. A comparative overview is given in Table **2.**

Table 2: Nanocarriers Used in Herbal Sunscreen Formulations – Comparison

Nanocarrier	Composition	Advantages	Disadvantages	Key References
Nanoemulsion	Oil, water, surfactant, cosurfactant	High bioavailability; low viscosity; good thermodynamic stability	Surfactant toxicity; scale-up challenges	Sonneville-Aubrun et al., 2004; McClements, 2012
Liposomes	Phospholipid bilayers	Biocompatible; controlled release; enhanced dermal penetration	Physical instability; short shelf-life	Cevc & Vierl, 2010; Benson, 2005
SLN (Solid Lipid Nanoparticles)	Solid lipid matrix	Controlled release; scalable; UV protection	Polymorphic transitions; drug expulsion	Müller et al., 2000; Pardeike et al., 2009
NLC (Nanostructured Lipid Carriers)	Liquid + solid lipid blend	Higher loading capacity; better stability than SLN	Complex preparation	Wissing & Müller, 2003; Puglia & Bonina, 2012
Polymeric NPs	PLGA, chitosan, PLA	Controlled release; biodegradable	Expensive; regulatory concerns	Yildirimer et al., 2011; Kumari et al., 2010
Phytosomes	Phospholipid + herbal complex	Improved absorption; potential for patent protection	Limited commercial availability	Bhattacharyya et al., 2009; Kidd, 2009
Nanogels	Crosslinked polymer network	High water content; easy application	Preparation complexity	Vinod et al., 2019
ZnO NPs	Zinc oxide	Broad-spectrum UV protection; photostable	Potential cytotoxicity at nanoscale	Smijs & Pavel, 2011; Newman et al., 2009
TiO_2 NPs	Titanium dioxide	Photostable; broad-spectrum UV protection	Photocatalytic activity; whitening effect	Nohynek et al., 2008; Scientific Committee, 2014

NANOEMULSION

Nanoemulsions are thermodynamically or kinetically stable, optically isotropic disperse systems consisting of two immiscible liquids (typically oil and water) stabilized by a surfactant/cosurfactant interfacial film, with droplet sizes in the 20–500 nm range [43]. They are classified as oil-in-water (O/W) or water-in-oil (W/O) based on the dispersed phase. Their high surface area, low interfacial tension, and ability to solubilize lipophilic actives make them ideal vehicles for herbal phytoconstituents. Preparation methods include highpressure homogenization, microfluidization, and spontaneous emulsification. Curcumin nanoemulsions have demonstrated SPF values up to 42 with UVA:UVB critical wavelength ratios indicating broad-spectrum protection [44].

LIPOSOMES

Liposomes are spherical, self-assembling vesicles with sizes ranging from 25 nm to several micrometers that are made up of one or more concentric phospholipid bilayers encasing an aqueous core [45]. Hydrophilic (aqueous core) and lipophilic (bilayer) herbal actives can be encapsulated simultaneously thanks to their amphiphilic architecture. They have superior biocompatibility and skin compatibility since their composition resembles biological membranes. For

the delivery of macromolecular polyphenols like resveratrol and EGCG, deformable liposomes (transfersomes, ethosomes) with improved skin penetration show great promise [46].

SOLID LIPID NANOPARTICLES (SLN)

A solid lipid core (physiological lipids like stearic acid, cetyl palmitate, or beeswax) stabilized by an emulsifier monolayer makes up SLN, which was first developed in the early 1990s [47]. Superior chemical protection of encapsulated actives, regulated release, occlusive skin moisturization, and UV-scattering qualities that add extra SPF are all provided by the solid matrix. SLN are scalable for industrial production and can be created by either hot or cold homogenization. Drug ejection during lipid polymorphism transitions from the α to the more ordered β crystalline form is one of the main limitations [48].

NANOSTRUCTURED LIPID CARRIERS(NLC)

In order to produce structural disorder that allows for increased drug loading and minimizes polymorphic transitions seen in SLN, NLC, a second-generation lipid nanoparticle idea, incorporates a combination of solid and liquid lipids in the core matrix [49]. There are three types of structural models: the numerous type (oil nano compartments within solid lipid), the amorphous type (no crystalline structure), and the imperfect type (spatially flawed crystals). When compared to both free actives and SLN, NLC including curcumin, quercetin, and pomegranate extracts has shown noticeably improved photostability and SPF [50].

POLYMERIC NANOPARTICLES

Biodegradable polymers including poly(lactic-co-glycolic acid) (PLGA), polylactic acid (PLA), chitosan, and poly(epsilon-caprolactone) (PCL) can be used to manufacture polymeric nanoparticles (50–500 nm) as nanospheres (matrix systems) or nanocapsules (core-shell systems) [51]. Because of their mucoadhesive qualities, innate antibacterial activity, and capacity to form ionic complexes with anionic polyphenols, chitosan nanoparticles are very appealing for herbal administration. EGCG encapsulated in PLGA exhibits prolonged release over a 72-hour period while maintaining its antioxidant efficacy [52].

PHYTOSOMES

Polar phytoconstituents and phosphatidylcholine produce a 1:1 or 1:2 molar complex by coordinate covalent bonding in phytosomes (herbosome technology, Indena S.p.A.) [53]. Transcutaneous absorption is greatly improved by this complexation, which changes the hydrophilic polyphenol into a more lipophilic, membrane-compatible molecule. In comparison to uncomplexed extracts, green tea phytosomes, quercetin phytosomes, and grape seed proanthocyanidin phytosomes have shown gains in skin bioavailability of three to five times [54].

NANOGELS

Particle sizes in the 100–1000 nm range are found in nanogels, which are three-dimensional crosslinked polymeric networks inflated with solvent [55]. They have adjustable mechanical characteristics, a high water content (which makes them aesthetically pleasing), and the capacity to react to environmental cues (pH, temperature, ionic strength). Excellent spreadability, stability, and moderate SPF values have been shown by carbopol and HPMC based nanogels containing aloe vera and neem extracts (28–35) [56].

METALLIC NANOPARTICLES

Through both absorption and scattering mechanisms, inorganic metallic nanoparticles in particular, zinc oxide (ZnO) and titanium dioxide (TiO2) act as physical/mineral UV blockers. Compared to their micronized counterparts, they offer better cosmetic transparency and broad-spectrum UVA/UVB protection at the nanoscale (10–50 nm) [57]. Additionally, ZnO nanoparticles exhibit inherent antifungal and antibacterial qualities. Green nanotechnology and herbal pharmacognosy have come together to create green-synthesised ZnO and AgNPs utilizing plant extracts (neem, aloe vera, tulsi), where phytoconstituents act as both reducing/capping agents and photoprotective agents [58].

FORMULATION STRATERIGES NANO HERBAL SUNSCREENS

SELECTIONS OF HERBAL EXTRACTS

The following factors must be carefully taken into account when choosing herbal extracts for nanoformulation: (i) phytochemical standardization (HPLC marker compound quantification); (ii) UV absorption spectrum (identification of chromophoric constituents); (iii) antioxidant capacity (DPPH, FRAP, ABTS assays); (iv) physicochemical compatibility with chosen excipients; and (v) safety profile (cytotoxicity, allergenicity, phototoxicity data) [59]. Batch-to-batch repeatability, which is necessary for regulatory compliance, is ensured by standardized extracts represented as marker chemical equivalents (e.g., % curcumin, % EGCG, % quercetin).

PREPARATION TECHNIQUES

High-Pressure Homogenization (HPH): Uses cavitation, turbulence, and shear forces to reduce droplet/particle size by applying pressure differentials of 200–1500 bar. While cold HPH is better for thermolabile actives, hot HPH is used for SLN preparation (melted lipids, distributed in hot aqueous surfactant solution, homogenized at increased temperature). Narrow size distributions (PDI <0.2) are produced by HPH, which is scalable in the industrial setting [60].

Ultrasonication (Probe Sonication): Localized energy densities produced by acoustic cavitation are high enough to break apart interfacial layers and reduce particle size to nanoscale dimensions. extensively employed in the creation of nanoemulsions. Localized heat production and possible metal contamination from probe tip degradation are limitations that are addressed by titanium probe replacement schedules and pulse mode operation [61].

Solvent Evaporation/Emulsion Diffusion: This process involves dissolving lipophilic agents in a volatile organic solvent (such as ethanol or acetone), emulsifying the mixture into the aqueous phase, and then removing the solvent under low pressure. extensively utilized in the synthesis of lipid and polymeric nanoparticles (PLGA, PLA). Pharmaceutical applications require residual solvent monitoring using GC headspace analysis [62].

Microfluidization: A high-pressure method that creates very homogeneous nanodroplets (50200 nm) by repeatedly impinging emulsions at high speeds using an interaction chamber with fixed geometry microchannels. especially well-suited for producing nanoemulsions on a large scale with high consistency [63].

EVALUATION PARAMETERS

PHYSICOCHEMICAL EVALUATION

Particle Dimensions and Polydispersity Index (PDI): The most used method for determining particle size is dynamic light scattering (DLS), which measures hydrodynamic diameter in the range of 1-6000 nm. Pharmaceutical nanoparticles

are deemed acceptable if their PDI is less than 0.3. Complementary information on size and concentration is provided by Nanoparticle Tracking Analysis (NTA). Sunscreen nanocarrier acceptable ranges are usually between 20 and 500 nm [67].

Zeta Potential: Electrophoretic light scattering is used to quantify electrostatic surface charge, which is a predictor of colloidal stability. Adequate electrostatic stability against aggregation is indicated by absolute zeta potential values greater than ±30 mV. Steric stabilization with PEGylated or polymeric surfactants may be necessary for values between ±10–30 mV [68].

Entrapment Efficiency (%EE) is computed as [(total drug − free drug)/total drug] × 100 after the encapsulated and free active are separated using ultracentrifugation, ultrafiltration, or dialysis. For topical treatments, values greater than 70% are typically regarded as acceptable [69].

PHOTOPROTECTIVE EVALUATION

The Mansur equation is used to compute the in vitro SPF spectrophotometrically: $SPF = CF \times \Sigma[E(\lambda) \times I(\lambda) \times Abs(\lambda)]$, where $E(\lambda)$ is the erythemal action spectrum, $I(\lambda)$ is the sun spectral irradiance, $Abs(\lambda)$ is the absorbance, and CF is a correction factor (10). By simulating surface roughness, the PMMA (polymethylmethacrylate) plate method (ISO 24443) more closely resembles in vivo circumstances [70]. In vivo SPF is determined using minimal erythema dose (MED) measurement in human volunteers in accordance with ISO 24444:2010.

nm (FDA criteria). The in vitro UVAPF method or the persistent pigment darkening (PPD) method (ISO 24442) are used to calculate the UVA Protection Factor (UVAPF). UVAPF ≥1/3 of SPF is required by EU rules for a broad-spectrum claim [71].

ADVANCED CHARACTERIZATION

FTIR (Fourier Transform Infrared Spectroscopy): Determines the polymorphic state of lipid nanoparticles (crystallinity index from CH2 scissoring bands at ~1473 and ~1462 cm-1), encapsulation evidence (change in typical phytoconstituent peaks), and functional group interactions. For SLN/NLC characterisation, quantitative information on lipid crystallinity, melting enthalpy, and phase transitions is provided by Differential Scanning Calorimetry (DSC) [72]. Surface topography and spherical nanoparticle structure are morphologically confirmed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). X-ray diffraction (XRD) distinguishes between the crystalline and amorphous states of encapsulated active ingredients [73].

RECENT RESEARCH STUDIES AND MARKETED PRODUCTS

The creation and characterisation of herbal sunscreens based on nanotechnology are documented in a rapidly growing body of research. Table 4 contrasts the benefits and drawbacks of nanocarriers for herbal uses, whereas Table 3 provides a curated summary of representative recent formulation research.

Table 3: Recent Research Studies – Nano Herbal Sunscreen Formulations with SPF Values

Year	Herbal Agent	Nanocarrier	SPF Value	Method	Reference
2022	Curcumin	Nanoemulsion	42 ± 1.8	In vitro (PMMA plate)	Ganesan et al., 2022
2022	Green tea EGCG	SLN	38 ± 2.1	Spectrophotometric	Verma et al., 2022
2021	Aloe vera + Neem	Nanogel	35 ± 1.5	In vitro UV	Patel et al., 2021
2021	Pomegranate	NLC	45 ± 2.3	Diffey & Robson	Singh et al., 2021
2020	Resveratrol	Polymeric NPs	31 ± 1.9	In vitro Spectro	Zhao et al., 2020
2020	Liquorice extract	Phytosomes	28 ± 1.2	PMMA plate method	Sharma et al., 2020
2019	Curcumin + ZnO	Nanoemulgel	52 ± 2.5	In vitro/In vivo	Golmohammadzadeh et al., 2019
2019	Grape seed extract	Liposomes	36 ± 1.7	Spectrophotometric	Hassan et al., 2019
2018	Raspberry seed oil	Nanoemulsion	48 ± 2.0	Diffey & Robson	Negi et al., 2018
2018	*Camellia sinensis*	SLN + TiO_2	55 ± 3.1	In vitro hybrid	Kim et al., 2018

Table 4: Advantages and Disadvantages of Nanocarriers for Herbal Sunscreen Applications

Nanocarrier	Key Advantages	Key Disadvantages	Best Suited Herbal Application
Nanoemulsion	Transparent, easy to formulate, high skin penetration	Thermodynamic instability, surfactant irritation risk	Hydrophobic actives; curcumin, essential oils
Liposomes	Biocompatible, skin-identical bilayer structure, encapsulate hydrophilic & lipophilic compounds	Oxidation, hydrolysis, short shelf-life	Polyphenols; EGCG, resveratrol, vitamin C
SLN	Scalable, protects labile compounds, UV scattering	Polymorphic transitions, limited loading capacity	Lipophilic actives; carotenoids, curcumin
NLC	Higher drug loading, fewer polymorphic transitions than SLN	Regulatory gaps, complex characterization	Complex extracts; neem, aloe vera fractions
Polymeric NPs	Sustained release, biodegradable options	High cost, potential toxicity, complex scale-up	Quercetin, ellagic acid, plant alkaloids
Phytosomes	Improved oral/topical bioavailability, patentable	Limited scalability, expensive excipients	Green tea, milk thistle, *Centella asiatica*

(i) hybrid nanocarrier systems that combine organic carriers with inorganic UV-filters (e.g., SLN + TiO2) to achieve SPF values >50 with broad-spectrum protection; (ii) the increasing use of QbD and RSM for systematic optimization; (iii) the investigation of biopolymer-based carriers (chitosan, zein, gliadin) from renewable sources; (iv) the incorporation of photostabilizers (avobenzone, UV-quenchers) in herbal nanoformulations for use in aquatic and sports [74,75].

COMMERICAL HERBAL NANO SUNSCREENS

Commercialization of nano-based herbal sunscreens is still in its infancy, with the majority of products using nano-minerals (ZnO, TiO2) in combination with herbal extracts instead of phytoconstituents that are actually nano-encapsulated. Notable commercial brands and products include Badger Balm (nano-ZnO with herbal extracts), Coola Suncare (aloe vera and green tea), and several Ayurvedic brands (Himalaya, Forest Essentials) that use innovative delivery technologies to combine aloe vera, neem, and turmeric. The market for natural and organic sunscreen was estimated to be worth USD 3.2 billion in 2023, and it is expected to expand at a compound annual growth rate (CAGR) of 8.5% through 2030 due to the high demand from consumers for clean-label, environmentally friendly photoprotection [76].

REGULATORY AND SAFETY ASPECTS

SAFETY CONCERNS OF NANOPARTICLES

Three main factors must be considered when evaluating the safety of nanoparticles used in cosmetic applications: photocatalytic activity, nanotoxicity, and skin penetration [77]. Regarding dermal penetration, the scientific consensus from multiple human and animal studies indicates that ZnO and TiO2 nanoparticles do not penetrate through intact stratum corneum to reach viable skin layers, and systemic absorption is negligible [78]. However, further research is necessary to understand penetration via follicular routes and weakened barriers (eczema, psoriasis, abraded skin).

The lipid and phospholipid components of organic nanocarriers (nanoemulsions, liposomes, SLN) are widely acknowledged as biocompatible; their nanotoxicity has been thoroughly investigated. Cationic polymeric nanoparticles (poly-L-lysine, CTAB-capped systems) and metallic nanoparticles are the main sources of cytotoxicity concerns because they can disrupt mitochondrial membrane potential and cause apoptosis at high concentrations [79].

REGULATORY GUIDELINES

Table5summarizes the regulatory frameworks governing nano-basedherbal herbal sunscreens across major jurisdictions

Table 5: Regulatory Frameworks for Nano Herbal Sunscreens

Regulatory Body	Region	Classification	Key Requirements	Nanoparticle Guidance
US FDA	United States	OTC Drug (sunscreens)	Active ingredient monograph, NDA/ANDA	No specific nano guidance; GRASE evaluation for ZnO, TiO_2
EU Commission / SCCS	European Union	Cosmetic Regulation (EC) No. 1223/2009	Pre-market notification, safety assessment	Mandatory nano notification; SCCS opinions on nanoscale ZnO and TiO_2
CDSCO / BIS	India	Cosmetics (Drugs & Cosmetics Act)	BIS IS 16521, safety data submission	No dedicated nano regulation; follows EU guidance informally
TGA	Australia	Therapeutic Goods / Cosmetics	ARTG listing, ingredient assessment	Nano-specific review; ZnO/TiO_2 considered not absorbed through intact skin
Health Canada	Canada	Natural Health Products / Cosmetics	Ingredient declaration, safety testing	Policy statement on nanomaterials; case-by-case evaluation

Sunscreens are categorized as over-the-counter medications under US FDA regulations and are subject to the Final Monograph system (21 CFR Part 352), which is currently undergoing reform under the framework of the 2019 Sunscreen Innovation Act. Only TiO2 and ZnO are GRASE for the time being. Under the CARES Act approach, organic UV filters must submit an ANDA or NDA. The FDA's 2014 and 2018 advice memos advise case-bycase evaluation based on physicochemical characteristics and safety data [80], but there are no explicit nanotechnology guidelines

Pre-market safety evaluation by a certified safety assessor, CPNP notification, and particular nano-ingredients labeling ([nano] suffix) are required under the EU Cosmetics Regulation (EC 1223/2009). According to SCCS (Scientific Committee on Consumer Safety) safety opinions, ZnO and TiO2 nano-forms are allowed with certain size and coating limitations; Annex VI specifies 27 approved UV filters. A nanomaterial is defined by the EU as having at least 50% of particles with a single dimension between 1 and 100 nm [81].

CHALLENGES IN NANO HERBAL SUNSCREENS DEVELOPMENTS

Despite tremendous scientific advancements, there are a number of interrelated obstacles in the physicochemical, biological, manufacturing, and regulatory domains that must be overcome before nano herbal sunscreen research can be turned into commercial goods [82,83]:

• Stability Issues: Hydrolysis, oxidation, and photodegradation are inherent risks for herbal phytoconstituents. In watery settings, polyphenols undergo oxidative polymerization, while carotenoids are particularly vulnerable to oxidative breakage and isomerization. These degradation processes are lessened but not completely eliminated by nanoencapsulation, and oxidative rancidity, phase separation, and Ostwald ripening can affect nanocarriers

• Scale-up and Manufacturing: Without considerable process re-optimization, laboratoryscale preparation techniques (such as probe sonication and microfluidization) are not necessarily readily transferable to industrial scales. Because the composition of herbal extracts varies naturally, it is difficult to replicate the particle size distribution from batch to batch.

• Phytochemical Standardization: Herbal extracts show compositional heterogeneity based on extraction circumstances, harvest season, post-harvest processing, and geographic origin, in contrast to synthetic actives. This heterogeneity makes regulatory filings and dose-response interactions more difficult.

• High Production Cost: Compared to traditional sunscreens, formulation costs are significantly higher due to specialized equipment, pharmaceutical-grade lipids, phospholipids, and biodegradable polymers. This restricts economic viability in the absence of substantial optimization.

• Regulatory Uncertainty: Product development routes are unpredictable due to the lack of uniform global rules pertaining to nanotechnology in cosmetics. Multi-market regulation tactics are complicated by different definitions of "nanomaterial" in the EU, USA, and Canada.

• Safety Data Gaps: There is still a lack of long-term in vivo toxicological information on topical exposure to polymeric and lipid nanoparticles. Regulators are increasingly demanding ecotoxicological evidence for nanoparticles (especially ZnO and TiO2) that reach aquatic habitats through washing.

• Consumer Acceptance: In consumer-facing formulations, photoprotective effectiveness must be balanced with sensory qualities (greasiness, whitening, smell) and ecological/sustainability issues.

FUTURE PERSPECTIVES

The subject of nano herbal sunscreen is situated at an intriguing nexus of changing consumer desires and convergent technologies. There are a number of new directions that could be transformative [84,85].

AI-Assisted Formulation Design: Artificial intelligence and machine learning platforms are being used more and more to find synergistic herbal combinations, predict SPF values from molecular structure descriptors, and predict the ideal nanocarrier composition. Novel excipient combinations that enhance photoprotective action while reducing side effects can be suggested by generative AI models trained on formulation databases [86].

Green nanotechnology: Using plant extracts as reducing and capping agents, biosynthesized nanoparticles offer a sustainable substitute for chemically produced nanomaterials. Green-synthesised ZnO and TiO2 nanoparticles made from extracts of Aloe vera, Camellia sinensis, and Azadirachta indica show similar UV-blocking effectiveness with a less environmental impact and natural antioxidant activity from leftover phytoconstituents [87].

Personalized Herbal Sunscreens: The potential for customized photoprotective formulations based on skin phototype, UV sensitivity, microbiome composition, and genetic polymorphisms in melanogenesis and DNA repair pathways is suggested by developments in precision dermatology and skin microbiome research. This customization might be made possible by 3D-printed personalized sunscreen dose formulations [88].

Smart Sunscreen Systems: An inventive method of on-demand photoprotection is provided by stimuli-responsive nanocarriers that release active ingredients in reaction to changes in pH, skin temperature, or UV irradiation intensity. Temperature-responsive lipid carriers and UV-sensitive azo-polymer nanoparticles have been shown in experiments [89].

Sustainable & Eco-Friendly Products: The shift to mineral and herbal sunscreen substitutes is being accelerated by the "reef-safe" movement and growing legislative prohibitions on oxybenzone and octinoxate in coral reef ecosystems. Market expansion will be aided by certification systems (COSMOS, Ecocert, NaTrue) that acknowledge nano-herbal compositions as ecologically responsible.

Combination Photoprotective Strategies: UV absorption (herbal chromophores), physical blocking (mineral nanoparticles), antioxidant activity (polyphenols), DNA repair stimulation (enzymes like photolyase, T4 endonuclease V), and immunomodulation in single multifunctional nanocarrier systems are all likely to be included in future nano herbal sunscreens [90].

CONCLUSION

The scientific foundation, formulation landscape, evaluation technique, regulatory environment, difficulties, and future prospects of herbal sunscreens based on nanotechnology have all been thoroughly reviewed in this review. The overwhelming amount of data shows that nanoencapsulation of herbal photoprotective agents is a scientifically sound way to take advantage of the multimechanistic photoprotective properties of phytoconstituents while also overcoming their intrinsic biopharmaceutical limitations.

Herbal pharmacognosy and sophisticated nanocarrier platforms, such as nanoemulsions, SLN, NLC, liposomes, polymeric nanoparticles, and phytosomes, have come together to create formulations that achieve SPF values of 28–55 with proven broad-spectrum UVA/UVB protection, enhanced photostability, controlled release, and acceptable safety profiles. Beyond the

capabilities of synthetic UV filters, the addition of herbal actives from Aloe vera, Curcuma longa, Camellia sinensis, Punica granatum, and Vitis vinifera, among others, offers antioxidant, anti-inflammatory, and skin-healing properties in addition to photoprotection.

Phytochemical uniformity, long-term stability, industrial scale-up, safety validation for long-term topical exposure, ecotoxicological evaluation, and regulatory harmonization continue to be major obstacles. Transforming promising research formulations into safe, efficient, and commercially viable photoprotective products requires addressing these obstacles through cooperative efforts between academia, industry, and regulatory agencies.

The clever integration of AI-driven formulation design, green synthetic techniques, customized delivery systems, and multipurpose smart nanocarriers within a sustainable, legally compliant framework will determine the future of nano herbal sunscreens. Nanobased herbal sunscreens have the potential to raise the bar for safe, efficient, and ecologically friendly photoprotection with continued interdisciplinary research funding.

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