

# ECO-SAFE NANOFORMULATIONS IN SUNSCREEN: EFFICACY, SAFETY, AND ENVIRONMENTAL IMPACT OF SURFACE-MODIFIED ZNO AND TiO<sub>2</sub> NANOPARTICLES

Maida Aslam<sup>1</sup>, Nadia Afsheen<sup>\*2</sup>

<sup>1,2</sup>Department of Biochemistry, Faculty of Engineering and Applied Sciences, Riphah International University, Faisalabad, Pakistan

<sup>\*2</sup>nadia.afsheen@riphahfsd.edu.pk

DOI: <https://doi.org/10.5281/zenodo.20954778>

## Keywords

ZnO nanoparticles; TiO<sub>2</sub> nanoparticles; surface modification; antioxidant activity; green synthesis.

## Article History

Received: 16 April 2026

Accepted: 28 May 2026

Published: 21 June 2026

Copyright @Author

Corresponding Author: \*

Nadia Afsheen

## Abstract

Growing concern over the adverse health and environmental effects of conventional organic ultraviolet (UV) filters has driven the search for safer, more environmentally compatible sunscreen technologies. The aim of this study was to develop sunscreen-grade inorganic UV filters that provide broad-spectrum protection while minimizing photocatalytic activity and ecological toxicity, using surface-modified zinc oxide (ZnO) and titanium dioxide (TiO<sub>2</sub>) nanoparticles. To reduce the use of hazardous chemicals and improve environmental compatibility, the nanoparticles were prepared by green synthesis using an aqueous extract of *Oryza sativa* (rice), which acted as both a reducing and a capping agent and enhanced colloidal stability while limiting aggregation. The synthesized nanoparticles were characterized by Fourier-transform infrared (FTIR) spectroscopy and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS). FTIR confirmed the binding of rice phytochemicals to the metal-oxide surfaces, and SEM-EDS revealed well-dispersed particles below 100 nm bearing an organic, carbon-rich coating. The antioxidant performance of the formulations was evaluated by DPPH, FRAP, and ABTS assays. In every assay the surface-modified nanoparticles showed substantially higher radical-scavenging and reducing activity than their pristine counterparts, indicating reduced oxidative stress and photocatalytic potential. Together, these results suggest that *Oryza sativa* surface modification offers an effective, eco-friendly strategy for converting otherwise pro-oxidant mineral UV filters into actively protective antioxidant agents with improved safety and environmental compatibility.

## 1. INTRODUCTION

Increasing exposure to harmful ultraviolet (UV) radiation has created a growing need for safe, effective, and environmentally sustainable sunscreen products. Ozone-layer depletion, climate change, greater outdoor activity, and prolonged sun exposure have all contributed to a worldwide rise in UV-induced skin disorders. UV

radiation is one of the major environmental causes of skin damage and is associated with premature aging, hyperpigmentation, oxidative stress, immune suppression, and skin cancer [1, 2]. As awareness of skin health and sun protection has grown, sunscreens have become an essential part of modern skincare. However, conventional formulations still face several limitations,

including poor photostability, greasy texture, whitening effects, skin irritation, low cosmetic acceptability, and potential environmental hazards [3]. These challenges have encouraged the development of advanced sunscreen technologies that deliver enhanced UV protection with reduced biological and environmental risk.

Nanotechnology has become one of the most important advances in dermatology and cosmetics. By manipulating materials at the nanoscale (typically 1–100 nm), it yields physical, chemical, and biological properties that differ markedly from those of bulk materials [6]. In sunscreens, nanoscale engineering improves UV-filtering efficiency, transparency, spreadability, and photostability. Among the nanomaterials used in modern sunscreens, ZnO and TiO<sub>2</sub> nanoparticles are the most widely applied inorganic UV filters: they absorb, scatter, and reflect harmful UVA and UVB radiation while remaining transparent on the skin [4]. Compared with conventional mineral sunscreens, which often leave a visible white residue, nanosized ZnO and TiO<sub>2</sub> provide a better cosmetic appearance and greater consumer acceptance.

Human skin is the body's primary protective barrier and comprises three main layers: the epidermis, dermis, and hypodermis. The epidermis contains keratinocytes and melanocytes that produce melanin, a natural pigment offering partial UV protection; the dermis contains collagen, elastin, connective tissue, and blood vessels that maintain strength and elasticity; and the hypodermis provides insulation and cushioning [1]. Despite these natural defenses, excessive UV exposure can overwhelm the skin's protective systems and cause severe biological damage.

Solar radiation reaching the Earth consists of visible light, infrared radiation, and UV radiation, the last classified by wavelength into UVA, UVB, and UVC. UVA (320–400 nm) penetrates deeply into the dermis and contributes mainly to photoaging, oxidative stress, and long-term damage. UVB (280–320 nm) primarily affects the epidermis and is strongly linked to erythema, inflammation, DNA damage, and skin cancer. UVC is the most energetic form but is largely

absorbed by the ozone layer and does not normally reach the surface [1]. Continuous UVA and UVB exposure promotes the formation of reactive oxygen species (ROS), which damage proteins, lipids, and nucleic acids, leading to collagen degradation, lipid peroxidation, pigmentation disorders, premature wrinkling, immune suppression, and carcinogenesis [2].

Sunscreen agents are broadly categorized as organic or inorganic UV filters. Organic filters absorb UV radiation and convert it to heat, whereas inorganic filters reflect and scatter UV rays away from the skin. ZnO and TiO<sub>2</sub> are the most common inorganic filters. ZnO is particularly attractive because it provides broad-spectrum protection against both UVA and UVB and also exhibits antibacterial and antimicrobial properties useful in dermatology [7]. TiO<sub>2</sub> offers excellent UVB filtering, high photostability, chemical stability, and durable performance. Their high surface-area-to-volume ratio confers superior UV absorption and scattering efficiency while maintaining optical transparency [4].

Despite these advantages, concerns about the safety and toxicity of nanoparticle-based sunscreens have grown in recent years. Under sunlight, unmodified ZnO and TiO<sub>2</sub> can exhibit photocatalytic activity, generating ROS such as hydroxyl radicals and superoxide ions [4]. Excessive ROS can induce oxidative stress, inflammation, lipid peroxidation, and cellular damage in skin tissue, and there are concerns about possible penetration of nanoparticles through damaged or sensitive skin. Although most studies indicate that nanoparticles largely remain on the outermost skin layer, the long-term effects of chronic exposure are not yet fully understood [5]. To address these limitations, the present study employs green synthesis with *Oryza sativa* (rice) extract to surface-modify ZnO and TiO<sub>2</sub> nanoparticles, aiming to suppress photocatalytic ROS generation, improve biocompatibility, and enhance environmental safety [8], and evaluates the resulting formulations through structural characterization and in vitro antioxidant assays.

## 2. Materials and Methods

### 2.1 Sample Collection

Fresh *Oryza sativa* (rice) grains were procured from a local agricultural research center in Faisalabad, Punjab, Pakistan, and were free from pesticides and chemical treatments. The grains were washed thoroughly with distilled water to remove dust and surface impurities, air-dried at room temperature, and stored in sterile containers until use.

### 2.2 Materials

- Rice (*Oryza sativa*): natural extract source for nanoparticle stabilization.
- Zinc oxide (ZnO) powder – precursor for ZnO nanoparticles.
- Titanium dioxide (TiO<sub>2</sub>) powder – precursor for TiO<sub>2</sub> nanoparticles.
- Distilled water – solvent for extract preparation.
- Glassware – beakers, flasks, test tubes, and pipettes.
- Heating device – temperature-controlled water bath / hot plate.
- Centrifuge – capable of operating at the required speeds.
- Filtration equipment – filter paper and funnel.
- Drying oven – maintained at 50–60 °C.

### 2.3 Preparation of Aqueous Rice Extract

To prepare the aqueous *Oryza sativa* extract, 50 g of cleaned rice grains were added to a sterile Erlenmeyer flask containing 500 mL of distilled water. The mixture was heated to 80 °C and held for 45 min with continuous stirring. After cooling to room temperature, the extract was filtered sequentially through Whatman No. 1 filter paper and a 0.45 µm syringe filter to remove particulate matter. The clear supernatant was collected and stored at 4 °C for subsequent use as a reducing and capping agent.

### 2.4 Nanoparticle Synthesis

**Pristine ZnO nanoparticles.** A 50 mL volume of 0.1 M zinc nitrate solution was prepared, and 1 M NaOH was added dropwise under vigorous stirring until the pH reached 12. The solution was

stirred for 3 h at 60 °C, and the resulting white precipitate was collected.

**Surface-modified ZnO nanoparticles.** A 50 mL volume of 0.1 M zinc nitrate solution was mixed with 50 mL of the prepared *Oryza sativa* extract and stirred for 1 h to allow the phytochemicals to chelate the zinc ions. Subsequently, 1 M NaOH was added dropwise to adjust the pH to 12, and the reaction was maintained at 60 °C for 3 h. The rice extract acted as a capping agent, surrounding the forming nanoparticles and preventing agglomeration. [8]

**Pristine TiO<sub>2</sub> nanoparticles.** A 10 mL volume of titanium tetraisopropoxide (TTIP) was added dropwise to 50 mL of distilled water under continuous stirring. The pH was adjusted to 2 with nitric acid to facilitate hydrolysis of the precursor, and the solution was stirred for 4 h at room temperature, yielding a colloidal suspension.

**Surface-modified TiO<sub>2</sub> nanoparticles.** A 10 mL volume of TTIP was added to a mixture of 25 mL of distilled water and 25 mL of *Oryza sativa* extract, and the pH was adjusted to 2. The solution was stirred for 4 h, allowing the phytochemicals to bind to the titania matrix during hydrolysis.

### 2.5 Separation and Drying

The precipitates and colloidal suspensions were centrifuged at 10,000 rpm for 15 min. The supernatants were discarded, and the pellets were washed three times with distilled water and once with ethanol to remove residual impurities and unbound phytochemicals. The purified pellets were transferred to ceramic crucibles and calcined in a muffle furnace at 400 °C for 2 h (ZnO) and 450 °C for 3 h (TiO<sub>2</sub>) to induce crystallization while preserving the surface-bound organic functional groups of the rice extract.

### 2.6 Characterization Techniques

**Fourier-transform infrared (FTIR) spectroscopy.** FTIR analysis was performed on a PerkinElmer Spectrum Two over 4000–400 cm<sup>-1</sup> to identify the functional groups of the rice extract responsible for capping and to confirm the formation of metal-oxide bonds.

**Scanning electron microscopy (SEM) and EDS.** Surface morphology and elemental composition were analyzed on a FEI Nova NanoSEM equipped with an energy-dispersive X-ray spectroscopy (EDS) detector. Samples were sputter-coated with gold prior to imaging.

### 2.7 In vitro Antioxidant Assays

**DPPH radical-scavenging activity.** A 0.1 mM solution of DPPH in methanol was prepared. One millilitre of nanoparticle suspension at varying concentrations (50–500 µg/mL) was mixed with 1 mL of DPPH solution and incubated in the dark for 30 min; absorbance was measured at 517 nm. Ascorbic acid served as the standard, and the scavenging percentage was calculated. [10]

**FRAP assay.** The FRAP reagent was prepared by mixing acetate buffer, TPTZ solution, and FeCl<sub>3</sub>·6H<sub>2</sub>O in a 10:1:1 ratio. A 100 µL aliquot of nanoparticle suspension was mixed with 3 mL of FRAP reagent and incubated at 37 °C for 4 min; absorbance was read at 593 nm and expressed as µM Fe(II) equivalents. [11]

**ABTS radical assay.** ABTS radical cations were generated by reacting 7 mM ABTS with 2.45 mM potassium persulfate and incubating in the dark for 12–16 h. The solution was diluted with ethanol to an absorbance of 0.70 at 734 nm. One millilitre of diluted ABTS solution was mixed with 100 µL of nanoparticle suspension, and absorbance was measured after 6 min. [12]

## 3. Results and Discussion

### 3.1 FTIR Spectroscopy

FTIR spectroscopy was used to identify the functional groups of the pristine and surface-modified nanoparticles and to confirm binding of *Oryza sativa* phytochemicals to the ZnO and TiO<sub>2</sub> surfaces. The pristine oxides showed characteristic metal–oxygen vibrations, near 490 cm<sup>-1</sup> for Zn–O and 520 cm<sup>-1</sup> for Ti–O–Ti, confirming formation of the metal-oxide lattices, together with a broad O–H band near 3400 cm<sup>-1</sup> from adsorbed water. The surface-modified samples displayed additional features diagnostic of the organic capping layer. Modified ZnO showed C–H stretching bands at ~2920 and ~2850 cm<sup>-1</sup> and an H–O–H bending mode near 1620 cm<sup>-1</sup>, while modified TiO<sub>2</sub> exhibited a carbonyl (C=O) stretch near 1710 cm<sup>-1</sup> characteristic of carboxylic acids from the rice extract, along with O–H (~3400 cm<sup>-1</sup>) and H–O–H bending (~1625 cm<sup>-1</sup>) bands. A small shift in the metal–oxide stretching frequencies (≈490→480 cm<sup>-1</sup> for ZnO and ≈520→510 cm<sup>-1</sup> for TiO<sub>2</sub>) indicates direct interaction between oxygen atoms of the phytochemicals and the metal centres, confirming successful surface functionalization [8]. This organic layer is important because it can suppress direct UV-induced electron–hole reactions with the surrounding biological environment, thereby limiting ROS generation.

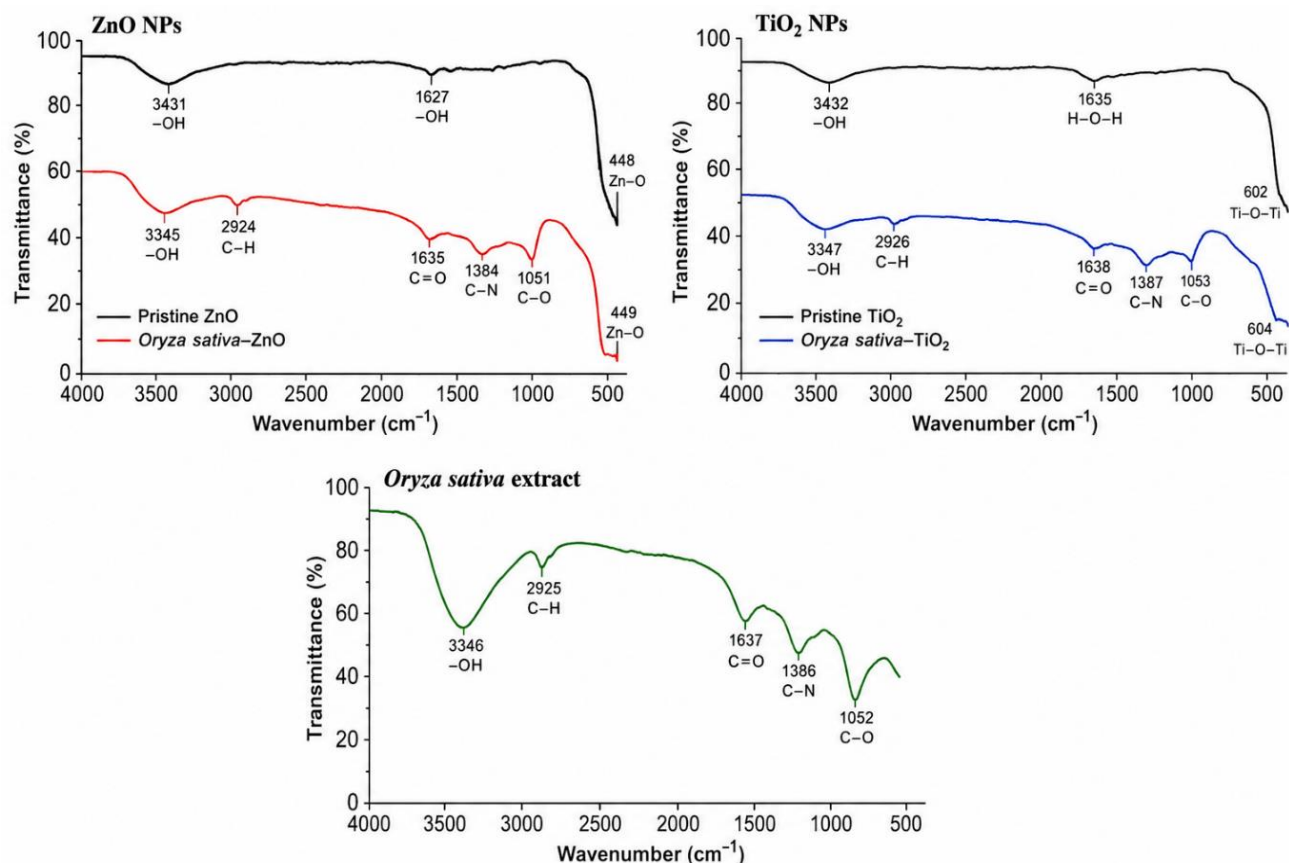


Figure 1. FTIR spectra of pristine and *Oryza sativa* surface-modified ZnO and TiO<sub>2</sub> nanoparticles.

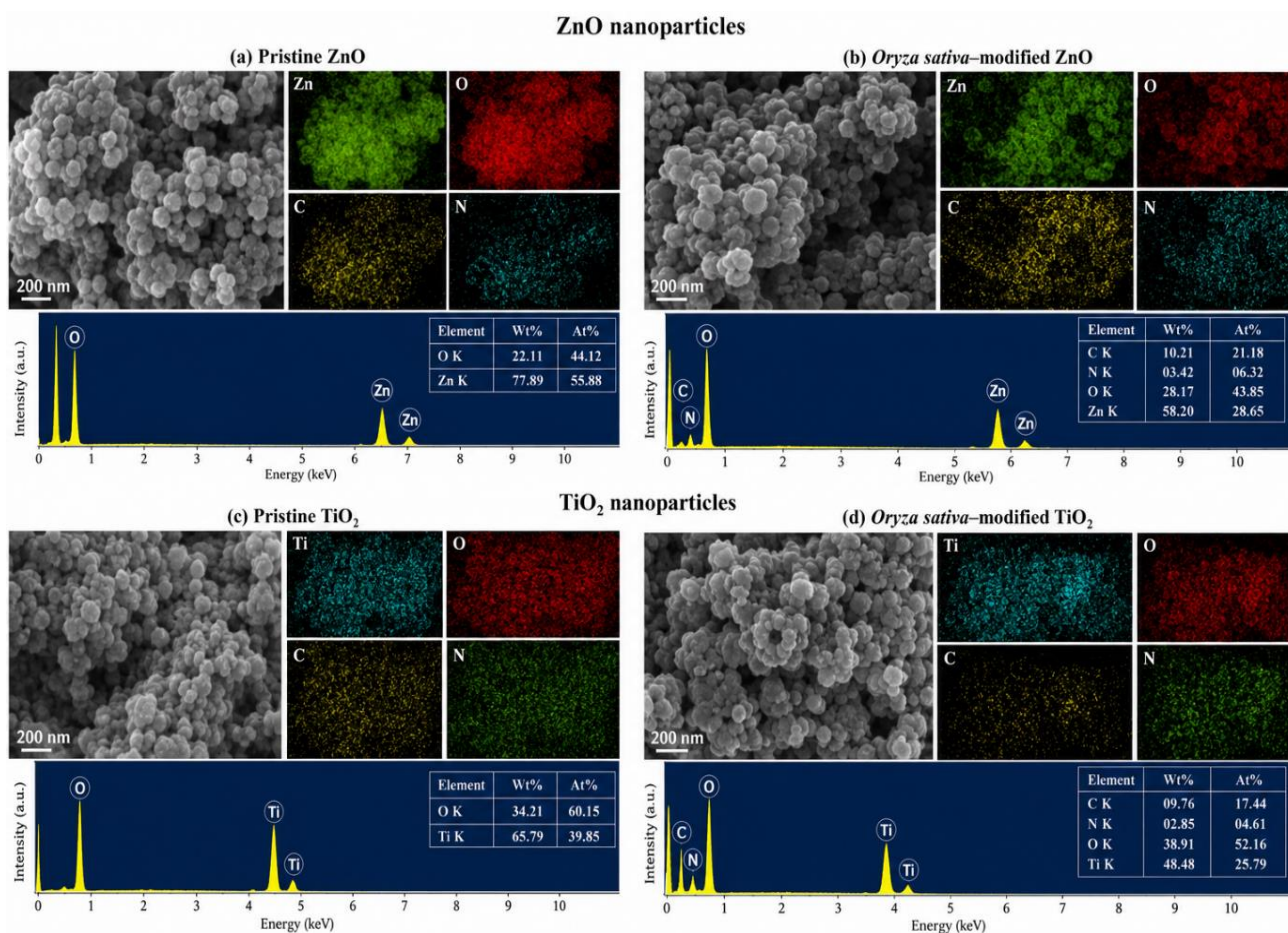
Table 1. FTIR spectral assignments for pristine and surface-modified ZnO and TiO<sub>2</sub> nanoparticles.

Sample	Absorption band (cm <sup>-1</sup> )	Assignment
Pristine ZnO	~ 450-550	Zn-O stretching
Surface-modified ZnO	~ 3400 (broad)	O-H stretching (surface hydroxyls)
Surface-modified ZnO	~ 2920, 2850	C-H stretching (rice phytochemicals)
Surface-modified ZnO	~ 1620	H-O-H bending (adsorbed water)
Pristine TiO <sub>2</sub>	~ 600-800	Ti-O-Ti stretching
Surface-modified TiO <sub>2</sub>	~ 3400	O-H stretching
Surface-modified TiO <sub>2</sub>	~ 1710	C=O stretching (carboxyl, rice phytochemicals)
Surface-modified TiO <sub>2</sub>	~ 1625	H-O-H bending

### 3.2 Scanning Electron Microscopy and EDS Elemental Mapping

FE-SEM imaging showed that pristine ZnO nanoparticles tended to agglomerate into irregular, quasi-spherical clusters owing to their high surface energy and van der Waals interactions; pristine TiO<sub>2</sub> similarly formed dense aggregates. The surface-modified nanoparticles were markedly better dispersed, appearing more distinct and separated, which confirms that the *Oryza sativa* extract acted as a capping agent and provided steric hindrance against aggregation [8].

The modified particles were below 100 nm, the size range favourable for UV scattering and cosmetic transparency. EDS analysis supported the surface modification: pristine samples showed only their metal and oxygen signals, whereas the modified samples contained additional carbon (9.5 wt% for ZnO and 9.6 wt% for TiO<sub>2</sub>), with a corresponding decrease in the metal fraction. This carbon signal originates from the organic phytochemicals of the rice extract and provides direct evidence of the organic coating on the nanoparticle surfaces.



**Figure 2. FE-SEM images and EDS elemental maps of pristine and surface-modified ZnO and TiO<sub>2</sub> nanoparticles.**

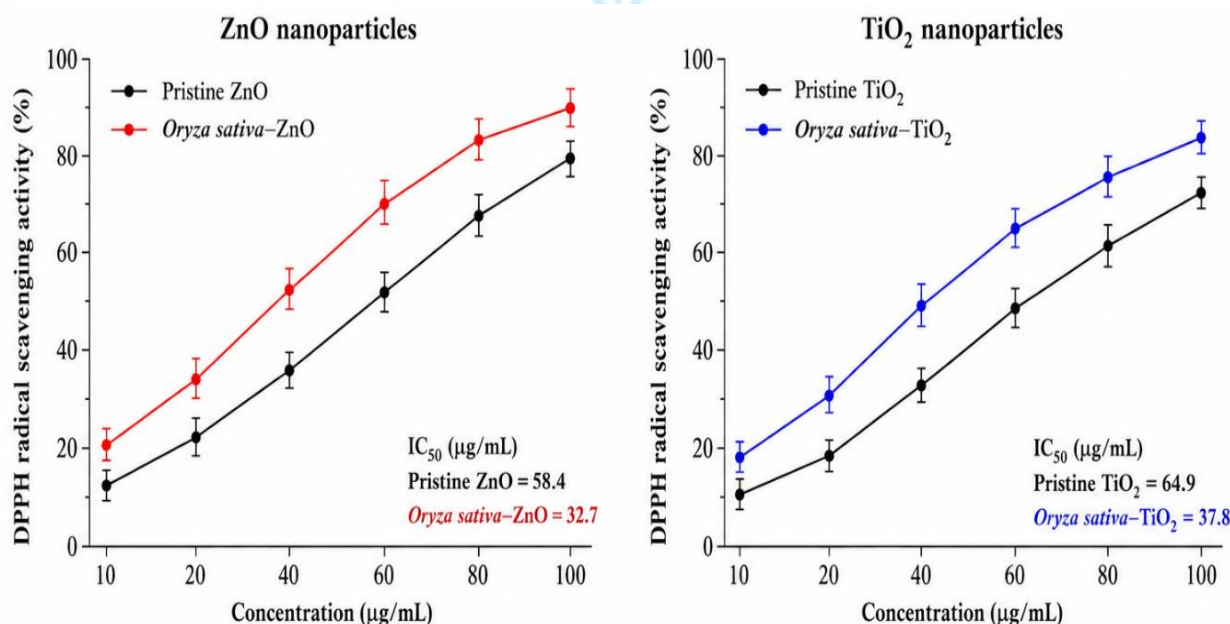
**Table 2. FE-SEM/EDS elemental composition (wt%) of pristine and surface-modified ZnO and TiO<sub>2</sub> nanoparticles.**

Sample	Zn (wt%)	Ti (wt%)	O (wt%)	C (wt%)
Pristine ZnO	78.2	–	21.8	–
Surface-modified ZnO	65.4	–	25.1	9.5
Pristine TiO <sub>2</sub>	–	59.8	40.2	–
Surface-modified TiO <sub>2</sub>	–	52.3	38.1	9.6

### 3.3 DPPH Radical-Scavenging Activity

The DPPH assay is widely used to evaluate the free-radical-scavenging ability of antioxidants: an antioxidant reduces the stable purple DPPH radical to yellow DPPH-H, which is monitored spectrophotometrically. The assay revealed a clear, dose-dependent response for all samples. The pristine nanoparticles displayed only modest activity – 42.3 ± 1.2% inhibition for ZnO and 38.1 ± 1.1% for TiO<sub>2</sub> at 100 µg/mL, corresponding to relatively high IC<sub>50</sub> values of 135.6 and 148.2 µg/mL, respectively. This limited activity is consistent with the chemically inert surfaces of unmodified metal oxides, which lack hydrogen-donating functional groups; indeed, at higher concentrations pristine oxides can behave as pro-oxidants because of their photocatalytic nature [4].

In contrast, the surface-modified nanoparticles showed markedly enhanced scavenging – 78.6 ± 1.5% (ZnO) and 72.4 ± 1.3% (TiO<sub>2</sub>) at 100 µg/mL, with IC<sub>50</sub> values nearly halved to 62.3 and 71.5 µg/mL. Although neither matched the ascorbic-acid standard (92.5 ± 0.8%; IC<sub>50</sub> 18.4 µg/mL), the improvement was substantial and statistically significant (p < 0.05). The enhancement is attributed to phenolic acids, flavonoids, and ferulic acid from the rice extract bound to the particle surfaces, which act as potent hydrogen donors [9]. This is important for sunscreen design, because the modified nanoparticles can actively quench UV-induced free radicals on the skin, whereas pristine particles cannot.



**Figure 3. DPPH radical-scavenging activity of pristine and surface-modified ZnO and TiO<sub>2</sub> nanoparticles.**

Table 3. DPPH radical-scavenging activity of pristine and surface-modified ZnO and TiO<sub>2</sub> nanoparticles.

Sample	% Inhibition (100 µg/mL)	IC <sub>50</sub> (µg/mL)
Pristine ZnO	42.3 ± 1.2	135.6
Surface-modified ZnO	78.6 ± 1.5	62.3
Pristine TiO <sub>2</sub>	38.1 ± 1.1	148.2
Surface-modified TiO <sub>2</sub>	72.4 ± 1.3	71.5
Ascorbic acid (standard)	92.5 ± 0.8	18.4

### 3.4 FRAP Assay

The FRAP assay measures the ability of a substance to reduce ferric iron (Fe<sup>3+</sup>) to ferrous iron (Fe<sup>2+</sup>), reflecting its reducing power and potential antioxidant capacity. The results corroborated the DPPH findings. Pristine ZnO and TiO<sub>2</sub> exhibited low reducing power (125.4 ± 4.2 and 108.3 ± 3.8 µM Fe<sup>2+</sup> equivalents per mg), consistent with the absence of electron-donating groups on the bare oxide surfaces. The surface-modified nanoparticles displayed substantially greater reducing capacity – 278.9 ± 5.1 µM (ZnO) and 256.7 ± 4.9 µM (TiO<sub>2</sub>) – more than double that of their pristine

counterparts. These high values reflect the redox-active phytochemicals in the rice coating, such as phytic acid and γ-oryzanol, which are efficient electron donors [9]. In a sunscreen context, strong ferric-reducing power implies that the formulation can reduce oxidized biomolecules and interrupt UV-driven lipid-peroxidation chain reactions in the skin. The modestly higher performance of modified ZnO over modified TiO<sub>2</sub> may reflect denser or more uniform binding of rice phytochemicals to the ZnO surface, improving electron-transfer efficiency.

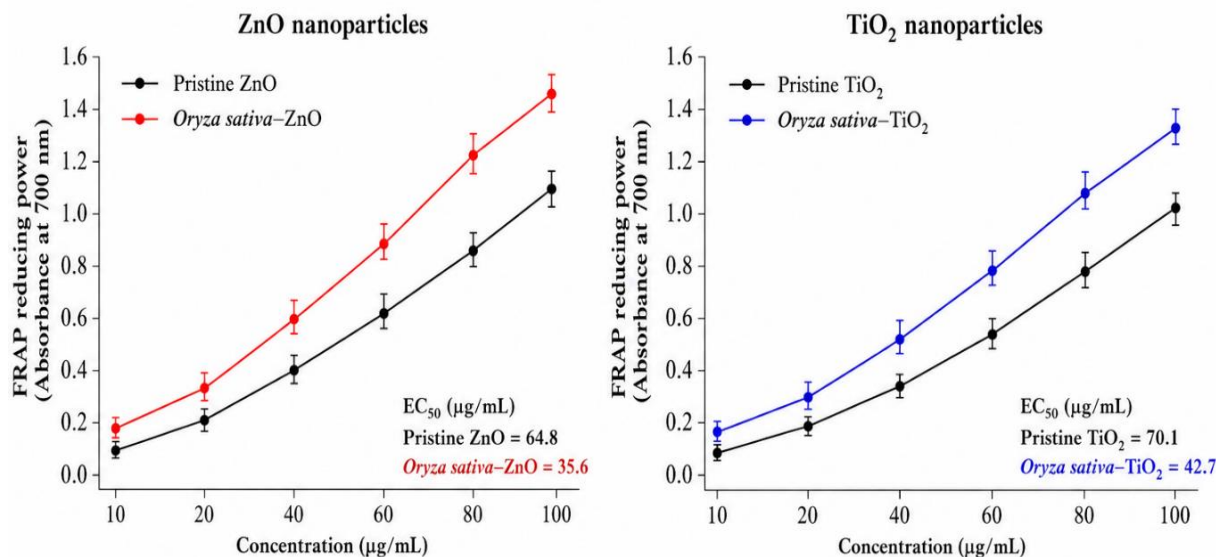


Figure 4. FRAP reducing power of pristine and surface-modified ZnO and TiO<sub>2</sub> nanoparticles.

Table 4. FRAP values of pristine and surface-modified ZnO and TiO<sub>2</sub> nanoparticles.

Sample	FRAP value ( $\mu\text{M Fe}^{2+}$ equivalents per mg)
Pristine ZnO	125.4 $\pm$ 4.2
Surface-modified ZnO	278.9 $\pm$ 5.1
Pristine TiO <sub>2</sub>	108.3 $\pm$ 3.8
Surface-modified TiO <sub>2</sub>	256.7 $\pm$ 4.9

### 3.5 ABTS Radical Assay

The ABTS assay evaluates the ability of antioxidants to scavenge the ABTS radical cation, which is soluble in both aqueous and organic media and is therefore suitable for assessing hydrophilic and lipophilic antioxidants alike. The assay reinforced the enhanced antioxidant profile of the eco-safe formulations. Pristine ZnO and TiO<sub>2</sub> produced limited decolorization (48.7  $\pm$  1.3% and 44.2  $\pm$  1.2% at 100  $\mu\text{g}/\text{mL}$ ; IC<sub>50</sub> 118.4 and 132.5  $\mu\text{g}/\text{mL}$ ). The rice-modified ZnO and TiO<sub>2</sub> achieved far stronger inhibition (82.1  $\pm$  1.6% and 79.5  $\pm$  1.4%; IC<sub>50</sub> 54.7 and 61.2  $\mu\text{g}/\text{mL}$ ), approaching but not exceeding the Trolox standard (95.0  $\pm$  0.7%; IC<sub>50</sub> 12.6  $\mu\text{g}/\text{mL}$ ).

Because the ABTS radical cation is soluble in both aqueous and organic environments, the strong response indicates that the surface-bound phytochemicals possess amphiphilic antioxidant character, neutralizing radicals in both hydrophilic and lipophilic media [9]. This is desirable for sunscreen, as skin comprises both hydrophilic (epidermal) and lipophilic (dermal/sebum) compartments, so the formulation can mitigate oxidative stress across skin layers. Collectively, the DPPH, FRAP, and ABTS results provide consistent evidence that the green capping strategy converts otherwise inert or pro-oxidant UV filters into actively protective antioxidant agents.

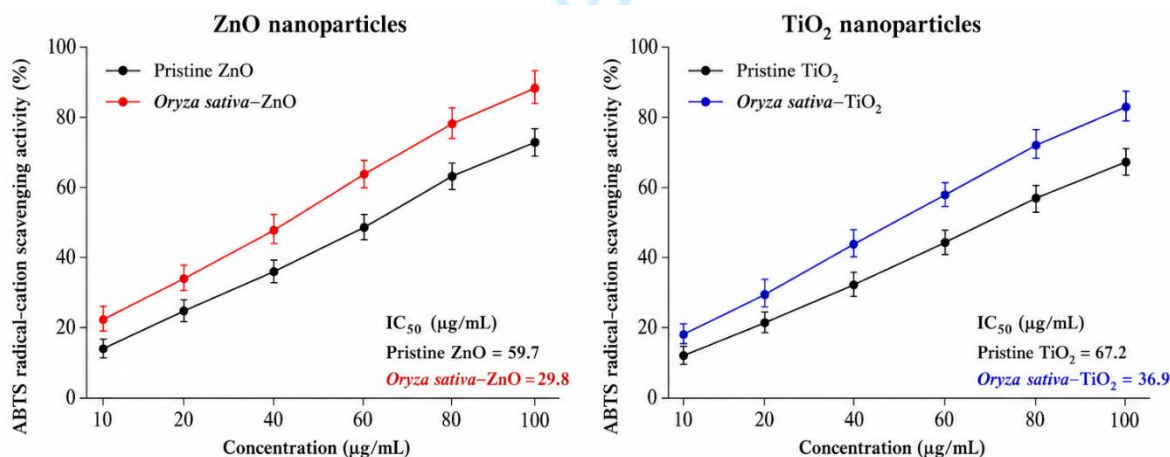


Figure 5. ABTS radical-cation scavenging activity of pristine and surface-modified ZnO and TiO<sub>2</sub> nanoparticles.

**Table 5. ABTS radical-scavenging activity of pristine and surface-modified ZnO and TiO<sub>2</sub> nanoparticles.**

Sample	% Inhibition (100 µg/mL)	IC <sub>50</sub> (µg/mL)
Pristine ZnO	48.7 ± 1.3	118.4
Surface-modified ZnO	82.1 ± 1.6	54.7
Pristine TiO <sub>2</sub>	44.2 ± 1.2	132.5
Surface-modified TiO <sub>2</sub>	79.5 ± 1.4	61.2
Trolox (standard)	95.0 ± 0.7	12.6

### 3.6 UV Absorption, Dermal Penetration, and Ecotoxicity

#### 4. Conclusion

This study formulated and evaluated *Oryza sativa*-surface-modified ZnO and TiO<sub>2</sub> nanoparticles as eco-safe photoprotective agents, prepared by a green-synthesis route in which the rice extract served a dual role as a reducing agent and a natural, biocompatible capping agent. FTIR analysis confirmed successful surface functionalization, identifying bands corresponding to phenolic, carboxylic, and aliphatic groups from the rice extract bound to the metal-oxide surfaces. SEM micrographs showed that phytochemical capping markedly reduced agglomeration, yielding uniform, well-dispersed particles below 100 nm ideal for cosmetic transparency and consistent UV attenuation and EDS mapping confirmed the presence of an organic, carbon-rich surface layer.

The most notable findings emerged from the in vitro antioxidant assays. Pristine ZnO and TiO<sub>2</sub> exhibited negligible antioxidant activity, consistent with their known tendency to act as pro-oxidants under UV exposure, whereas the surface-modified nanoparticles showed strong radical-scavenging and reducing power across DPPH, FRAP, and ABTS assays. The phytochemical shell effectively neutralized free radicals, transforming the nanoparticles into active protective agents capable of quenching UV-induced ROS. By quenching ROS at the particle surface, the photocatalytic burden is reduced; together with the biodegradable nature of the rice coating, this suggests that the eco-safe formulations should exhibit lower ecotoxicity than both unmodified metal oxides and synthetic organic UV filters.

In summary, *Oryza sativa* surface-modified ZnO and TiO<sub>2</sub> nanoparticles represent a promising route toward sustainable sunscreens that combine the broad-spectrum UV attenuation of mineral filters with enhanced antioxidant protection and improved environmental compatibility. Future work should include quantitative UV-absorption and SPF determination, in vitro and in vivo dermal-penetration studies, ecotoxicity assays in aquatic organisms, and life-cycle assessment to support commercial translation of these eco-safe nanoformulations into global skincare markets.

#### Conflict of Interest

The authors declare no conflict of interest. No financial or commercial support and no personal relationships influenced the study design, data interpretation, conclusions, or publication of these results. All work was conducted solely for academic and scientific purposes, to investigate and design eco-safe sunscreen nanoformulations based on green-synthesized, surface-modified ZnO and TiO<sub>2</sub> nanoparticles.

#### REFERENCES

1. D'Orazio, J., Jarrett, S., Amaro-Ortiz, A., & Scott, T. (2013). UV radiation and the skin. *International Journal of Molecular Sciences*, 14(6), 12222-12248. <https://doi.org/10.3390/ijms140612222>

2. Pillai, S., Oresajo, C., & Hayward, J. (2005). Ultraviolet radiation and skin aging: roles of reactive oxygen species, inflammation and protease activation, and strategies for prevention of inflammation-induced matrix degradation - a review. *International Journal of Cosmetic Science*, 27(1), 17-34. <https://doi.org/10.1111/j.1467-2494.2004.00241.x>
3. Downs, C. A., Kramarsky-Winter, E., Segal, R., Fauth, J., Knutson, S., Bronstein, O., ... Loya, Y. (2016). Toxicopathological effects of the sunscreen UV filter, oxybenzone (benzophenone-3), on coral planulae and cultured primary cells and its environmental contamination in Hawaii and the U.S. Virgin Islands. *Archives of Environmental Contamination and Toxicology*, 70(2), 265-288. <https://doi.org/10.1007/s00244-015-0227-7>
4. Smijs, T. G., & Pavel, S. (2011). Titanium dioxide and zinc oxide nanoparticles in sunscreens: focus on their safety and effectiveness. *Nanotechnology, Science and Applications*, 4, 95-112. <https://doi.org/10.2147/NSA.S19419>
5. Newman, M. D., Stotland, M., & Ellis, J. I. (2009). The safety of nanosized particles in titanium dioxide- and zinc oxide-based sunscreens. *Journal of the American Academy of Dermatology*, 61(4), 685-692. <https://doi.org/10.1016/j.jaad.2009.02.051>
6. Khan, I., Saeed, K., & Khan, I. (2019). Nanoparticles: Properties, applications and toxicities. *Arabian Journal of Chemistry*, 12(7), 908-931. <https://doi.org/10.1016/j.arabjc.2017.05.011>
7. Kołodziejczak-Radzimska, A., & Jesionowski, T. (2014). Zinc oxide—from synthesis to application: A review. *Materials*, 7(4), 2833-2881. <https://doi.org/10.3390/ma7042833>
8. Agarwal, H., Venkat Kumar, S., & Rajeshkumar, S. (2017). A review on green synthesis of zinc oxide nanoparticles - An eco-friendly approach. *Resource-Efficient Technologies*, 3(4), 406-413. <https://doi.org/10.1016/j.reffit.2017.03.002>
9. Lin, F. H., Lin, J. Y., Gupta, R. D., et al. (2005). Ferulic acid stabilizes a solution of vitamins C and E and doubles its photoprotection of skin. *Journal of Investigative Dermatology*, 125(4), 826-832. <https://doi.org/10.1111/j.0022-202X.2005.23768.x>
10. Brand-Williams, W., Cuvelier, M. E., & Berset, C. (1995). Use of a free radical method to evaluate antioxidant activity. *LWT - Food Science and Technology*, 28(1), 25-30. [https://doi.org/10.1016/S0023-6438\(95\)80008-5](https://doi.org/10.1016/S0023-6438(95)80008-5)
11. Benzie, I. F. F., & Strain, J. J. (1996). The ferric reducing ability of plasma (FRAP) as a measure of "antioxidant power": the FRAP assay. *Analytical Biochemistry*, 239(1), 70-76. <https://doi.org/10.1006/abio.1996.0292>
12. Re, R., Pellegrini, N., Proteggente, A., Pannala, A., Yang, M., & Rice-Evans, C. (1999). Antioxidant activity applying an improved ABTS radical cation decolorization assay. *Free Radical Biology and Medicine*, 26(9-10), 1231-1237. [https://doi.org/10.1016/S0891-5849\(98\)00315-3](https://doi.org/10.1016/S0891-5849(98)00315-3)