SUNJIN BEAUTY SCIENCE

Oxidation of Metal-Phenolic Network on Rod shaped Zinc Oxide for Broad-spectrum Sunscreen

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Rising Demand for Mineral-Only Sunscreens

❖ FDA's proposed GRASE* rule (2019)

Status	UV filters
GRASE (2)	**Zinc Oxide, Titanium Dioxide**
Non-GRASE (2)	PABA; Para-Aminobenzoic Acid, Tolamine Salicylate
More tests required (12)	Cinoxatye, Dioxybenzone, Ensulizole, Homosalate, Meradimate, Octinoxate, Octisalate, Octocrylene, Padimate, Sulisobenzone, Oxybenzone, Avobenzone

***GRASE : Generally Recognized As Safe and Effective**

❖ Island Ban

Location	Banned Organic UV Filter
Hawaii	oxybenzone, octinoxate
Palau	oxybenzone, octinoxate, octocrylene, 4-methylbenzylidene camphor
U.S. Virgin Islands	oxybenzone, octinoxate, octocrylene
Aruba	oxybenzone
Bonaire	oxybenzone, octinoxate
Key West Florida	oxybenzone, octinoxate
Thailand (marine national parks)	oxybenzone, octinoxate 4-methylbenzylidene camphor

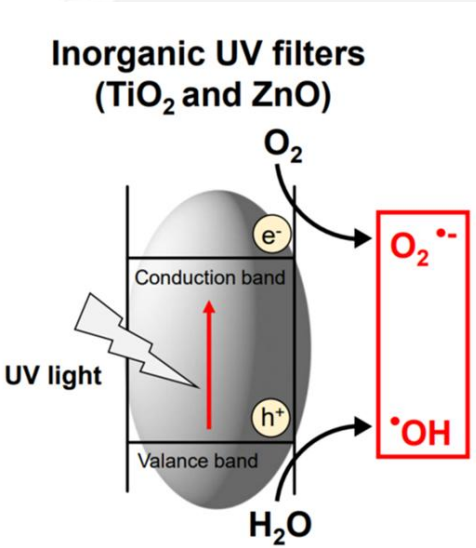
Driven by Environmental Imperatives and Skin Safety,
the Sunscreen Market is Rapidly Shifting toward Mineral-Only Formulations

Limitations of Conventional Mineral Filters

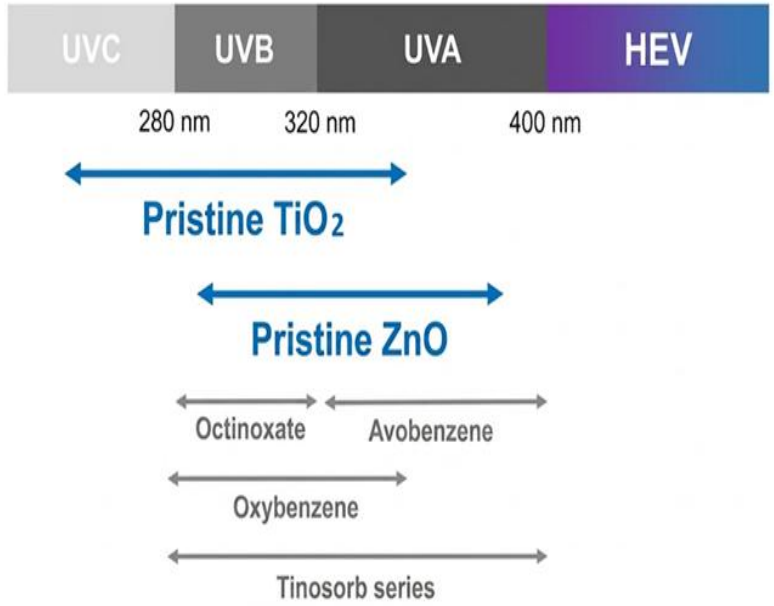
❖ Poor Spreadability

❖ White Cast

❖ Photocatalytic Activity



❖ Spectral Protection Gap

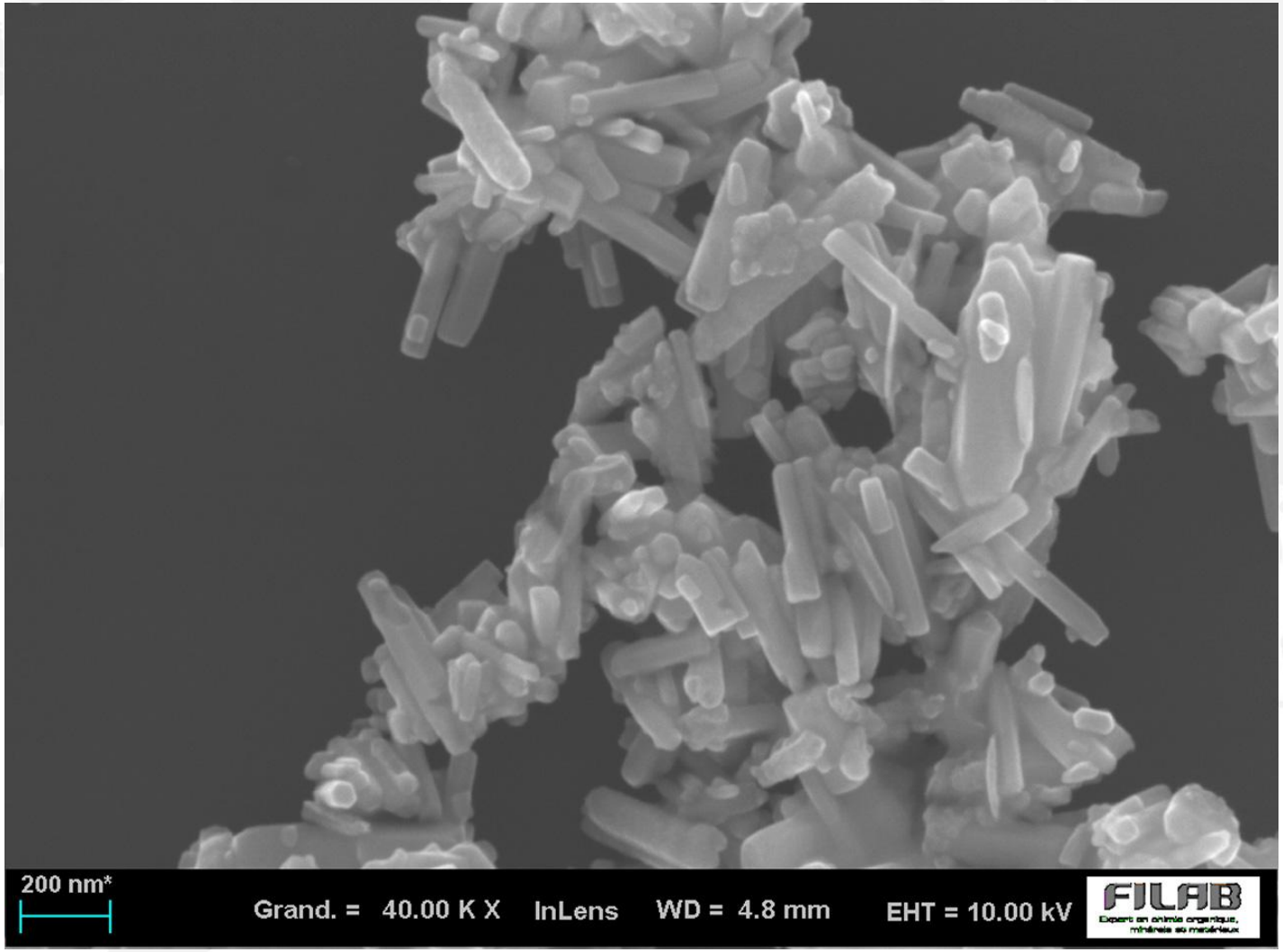


Proposed Breakthrough Solutions

Innovation 1. Rod-Shaped Morphology Control

Innovation 2. Metal Phenolic Network (MPN) Coating Technology

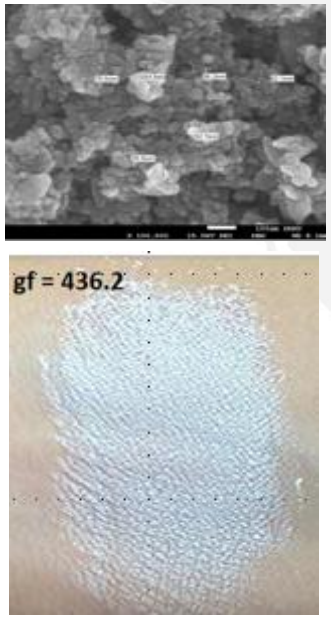
Innovation 1. Rod-shaped ZnO



Innovation 1. Rod-shaped ZnO

Spherical ZnO

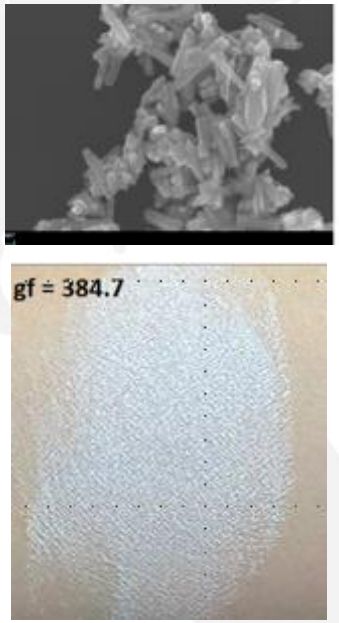
30nm



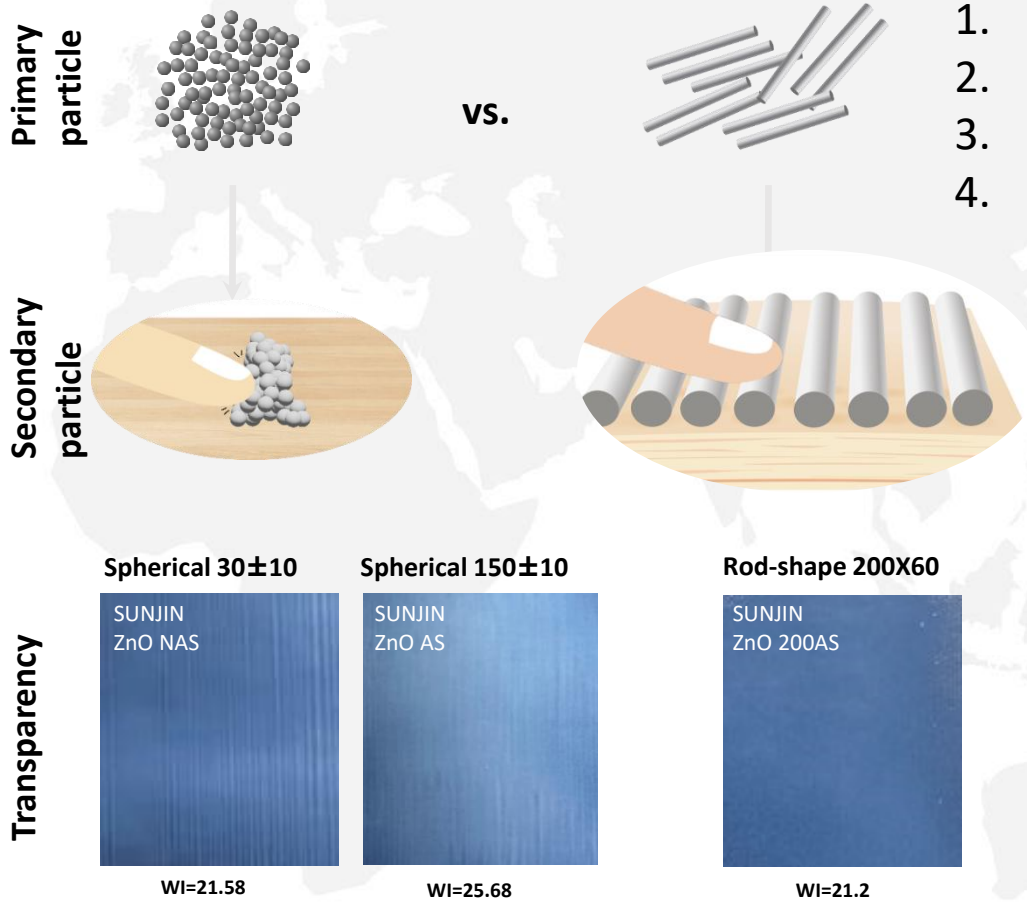
Rough

Rod-shaped ZnO

200*60nm



Creamy



Why Rod Shape?

1. More Creamy Feeling
2. Better Spreadability
3. Better Transparency
4. Better UV performance

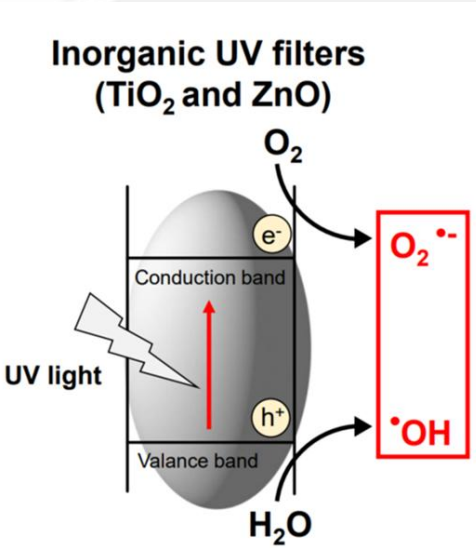
Innovation 2. MPN Coating Technology

❖ Poor Spreadability

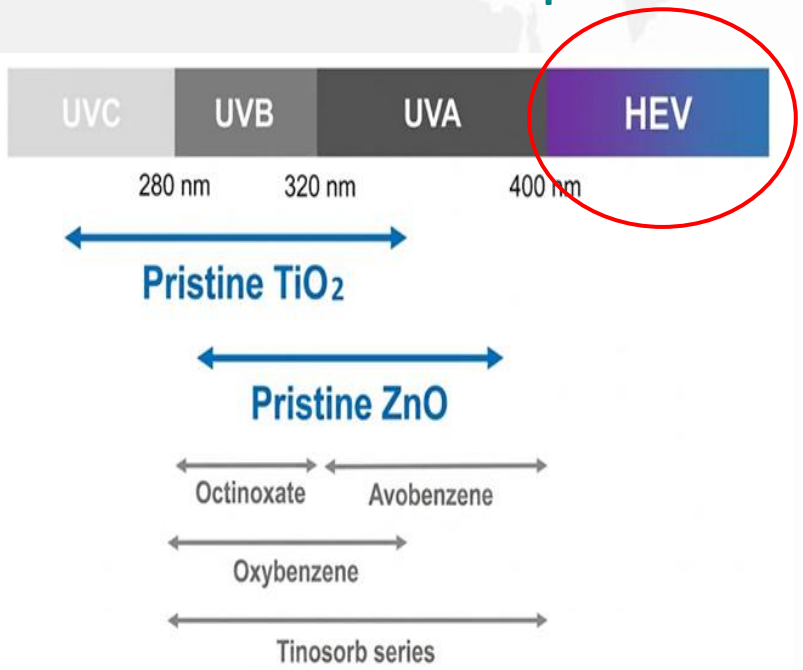
❖ White Cast

Rod-Shaped Morphology

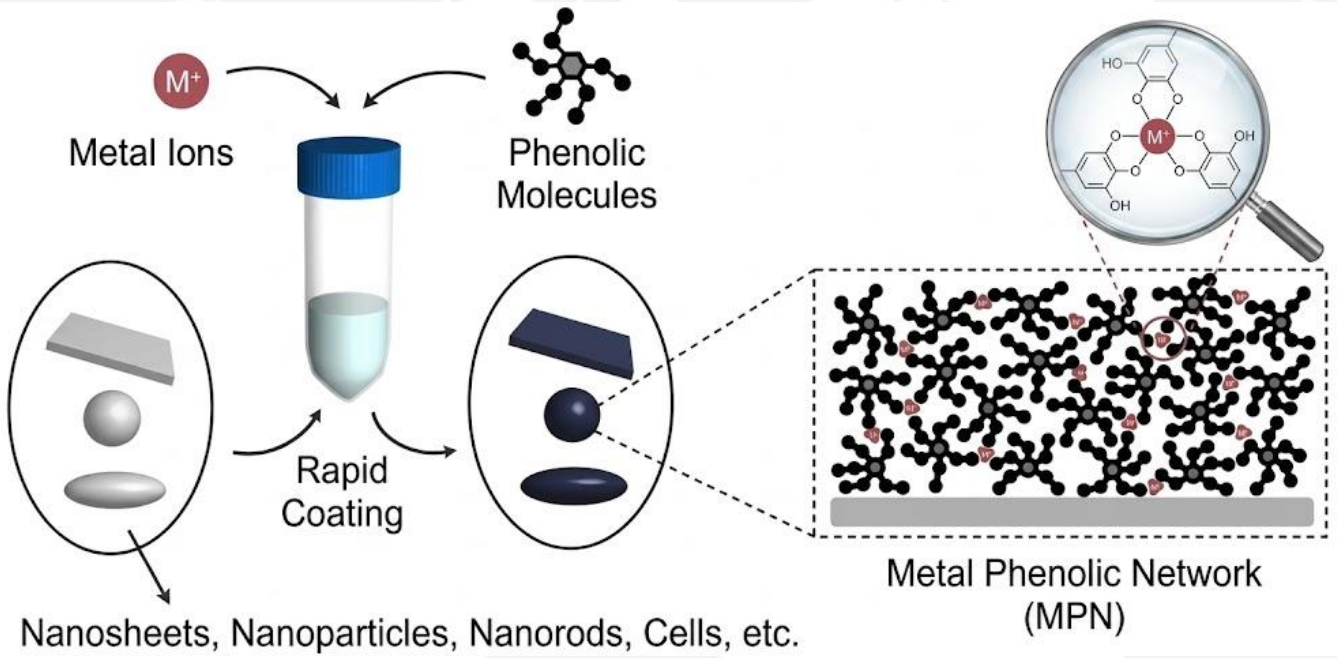
❖ Photocatalytic Activity



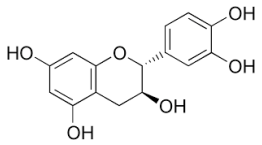
❖ Spectral Protection Gap



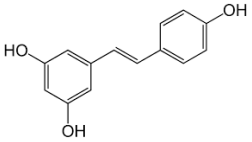
Bio-inspired Coating Platform: Metal-Phenolic Network (MPN)



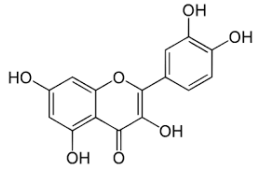
Polyphenols



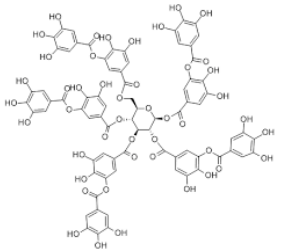
Catechin



Resveratrol



Quercetin



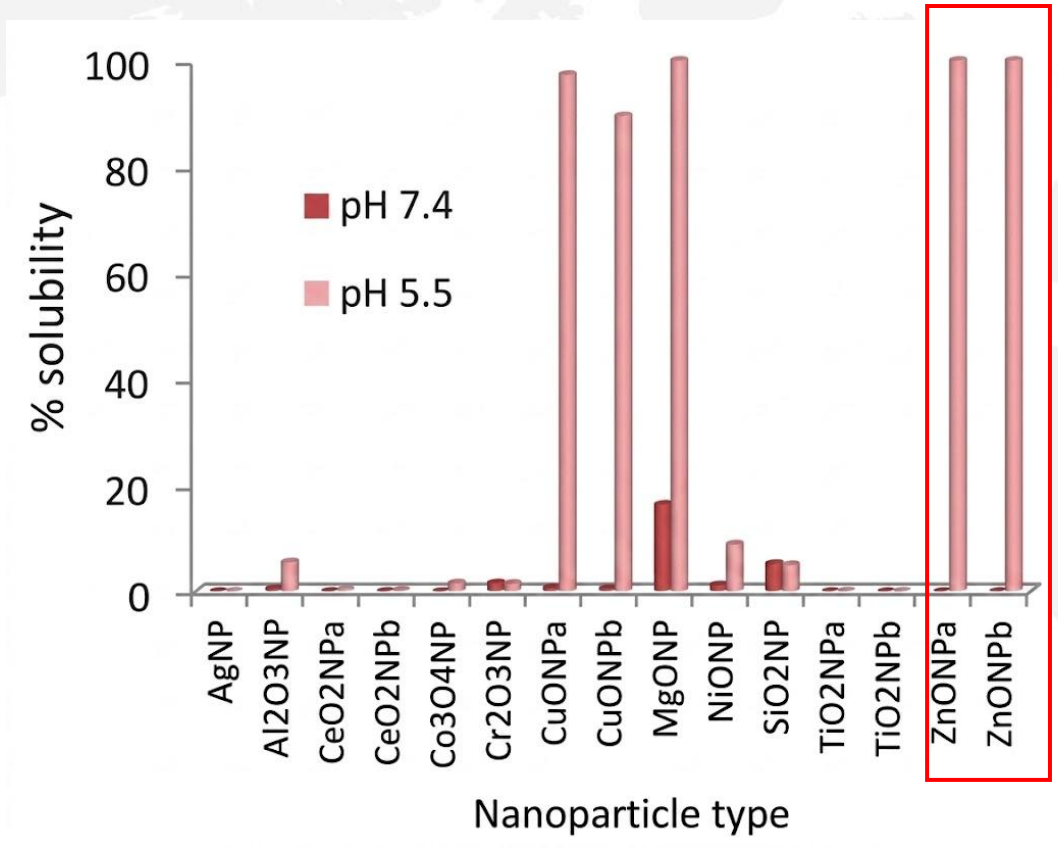
Tannic acid

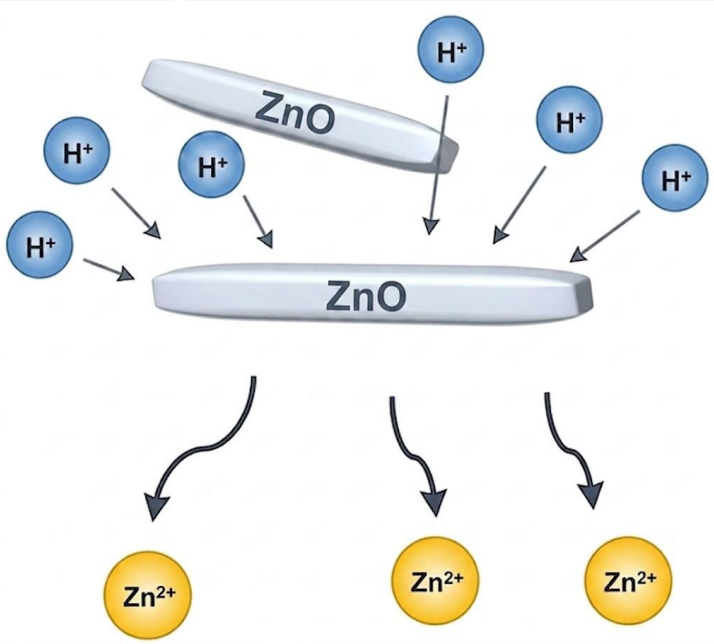
- Excellent antioxidant property
- Abundant metal chelation sites

- Defensive mechanisms found in plant polyphenols (e.g., Tannins) and mussel adhesive proteins.
- **Spontaneous Self-assembly** driven by **Coordination Bonding** between polyphenolic ligands and metal ions.
- High binding affinity through **Multidentate Chelation** (Multiple -OH groups binding to a single metal ion).

H. Ejima, J. J. Richardson, F. Caruso (2017). Metal-phenolic networks as a versatile platform to engineer nanomaterials and biointerfaces, Nano Today, 12, 136–148.

Zn^{2+} Ion Release from ZnO Nanoparticles



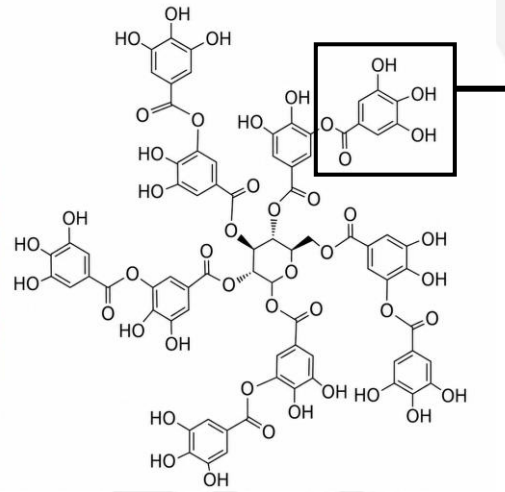


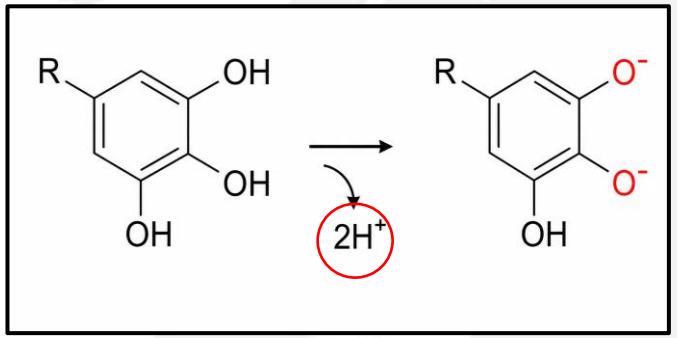
$$ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O$$

Donaldson, Schinwald, Murphy, Cho, Duffin, Tran, Poland (2013). The biologically effective dose in inhalation nanotoxicology. Accounts of chemical research, 46(3), 723-732.

Hypothesis of Spontaneous Formation of MPN

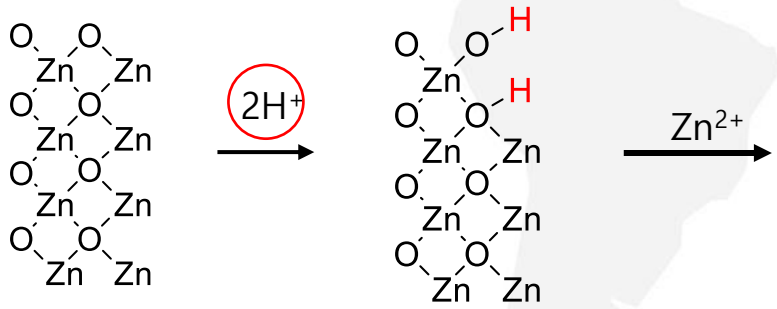
Polyphenol: Tannic acid (TA)



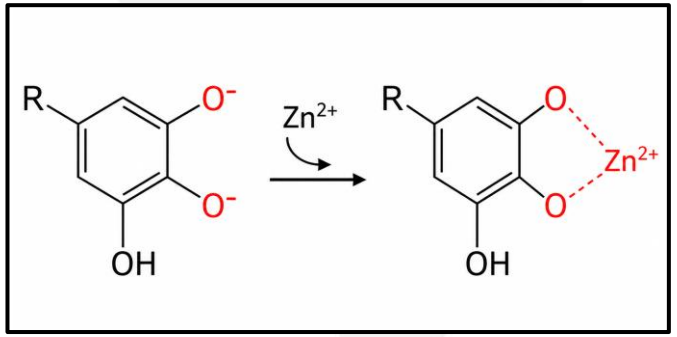


- TA is weak acid.
- Easy to give proton to surround substance and form deprotonation form.

Metal Oxide: ZnO

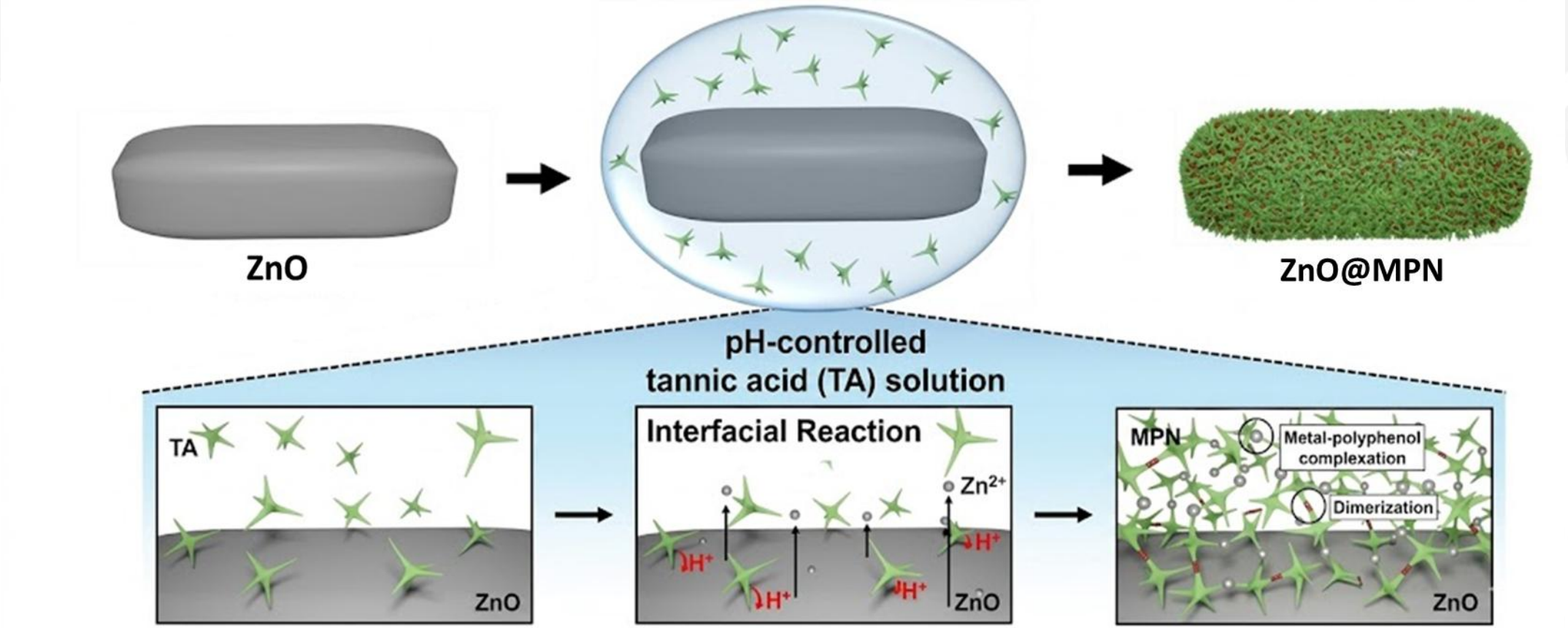


MPN Formation



- TA can give proton to the ZnO and induce Zn^{2+} ion release from ZnO.
- Zn^{2+} ion and deprotonated TA can from metal phenolic networks (MPN).
- MPN-coated ZnO can be formed without adding extra metal ions

Spontaneous Formation of Metal-phenolic Networks

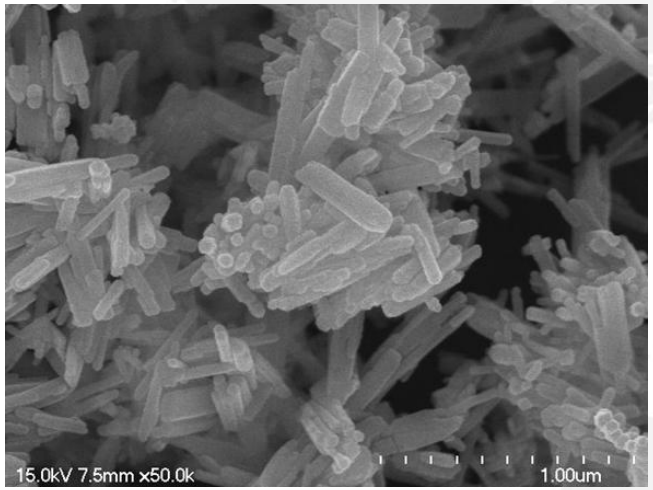


Simple & Efficient One-pot Coating Process

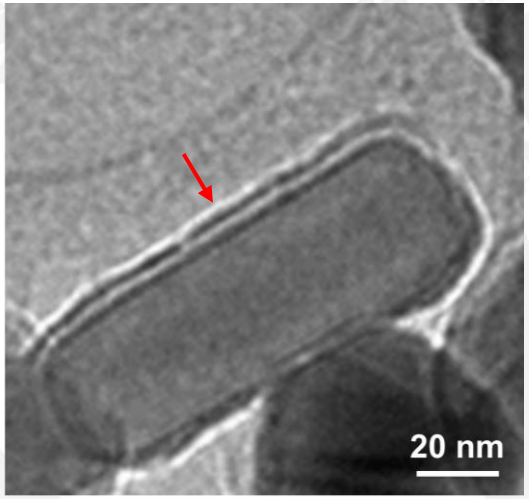
Saehan Choi et. al (2025). Spontaneous Formation and Oxidation of Metal-Phenolic Networks by Zinc Oxide: Expanding Photoprotection and Suppressing Photoreactivity, Chemical Engineering Journal 515, 163210.

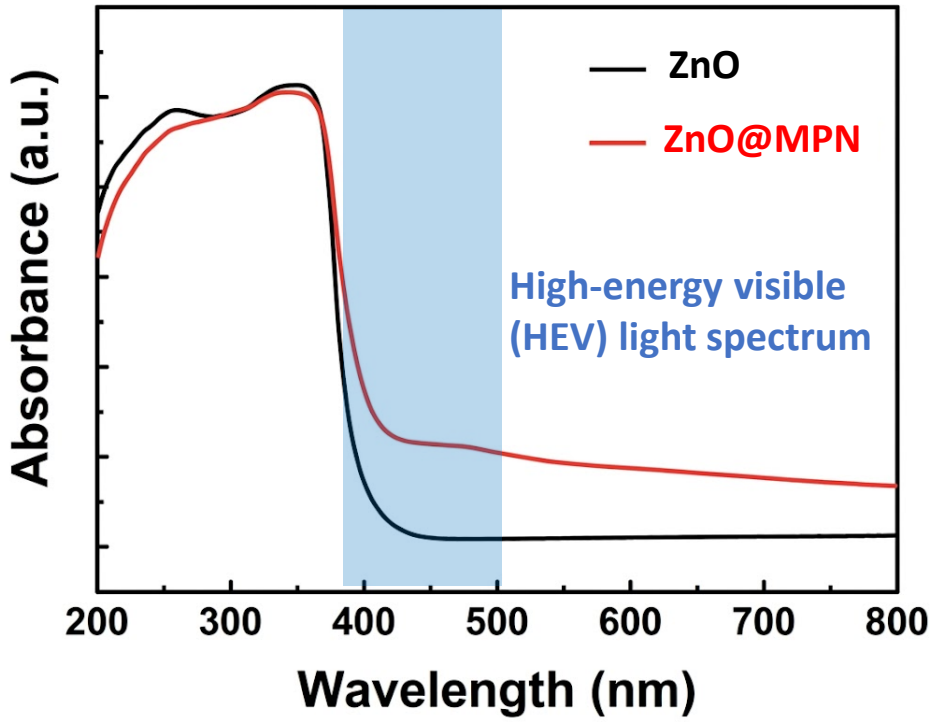
UV-visible Absorbance of ZnO@MPN Particles

ZnO
Long axis: ~200 nm
Short axis: ~60 nm



Coating layer
Thickness: 3-5nm
MPN: Zn^{2+} & Dimerized TA





There is no HEV blocking property
at the ZnO@MPN interface.

Synthesis of ZnO@MPN
ZnO 100 mg + TA solution (20 mM) 0.8 mL + PBS 9.2 mL
Coating Time: 1 min by vortexing

Browning Effect of Polyphenol via Oxidation

Browning of Apple with Oxygen

Oxidation Mechanism of Polyphenol

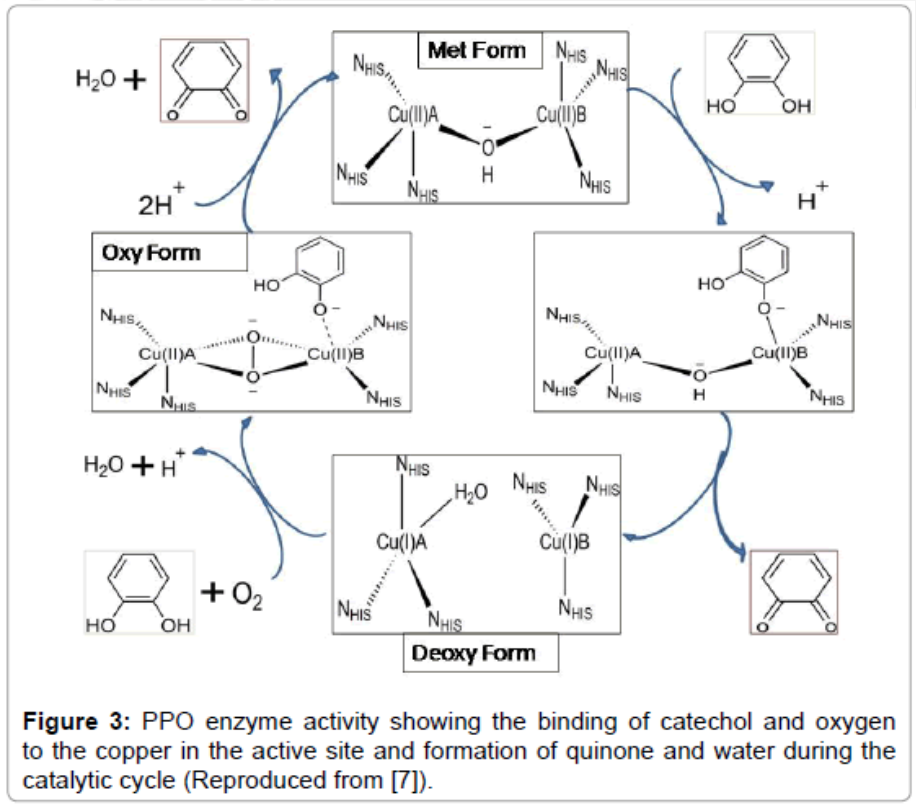
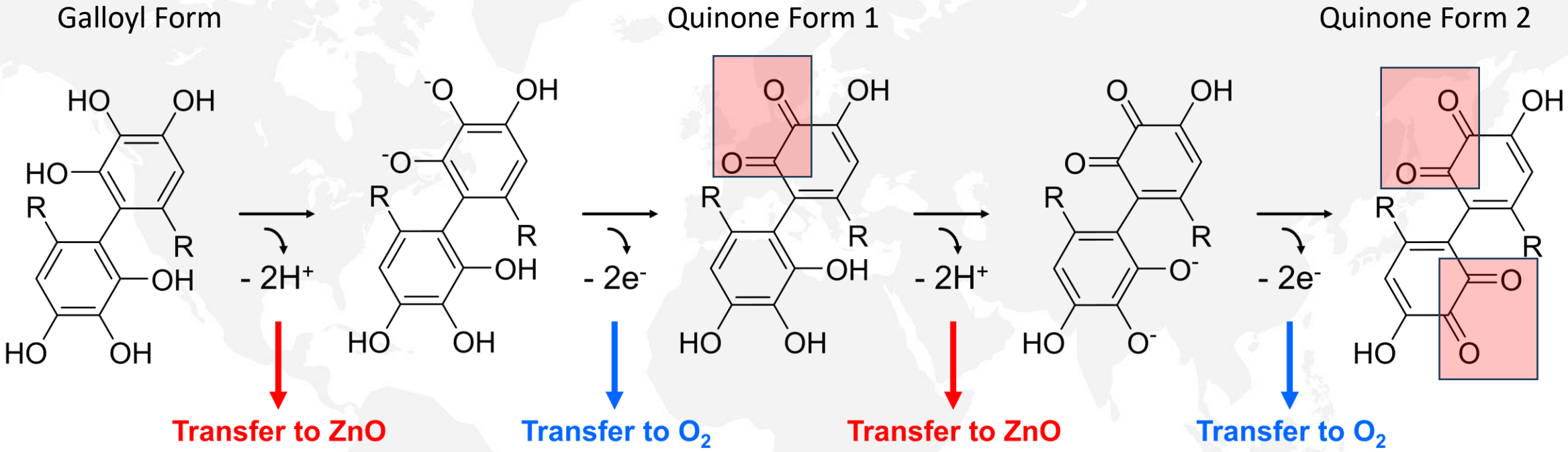


Figure 3: PPO enzyme activity showing the binding of catechol and oxygen to the copper in the active site and formation of quinone and water during the catalytic cycle (Reproduced from [7]).

Quinone tanning of polyphenol can enhance HEV light absorption of ZnO@MPN interface.

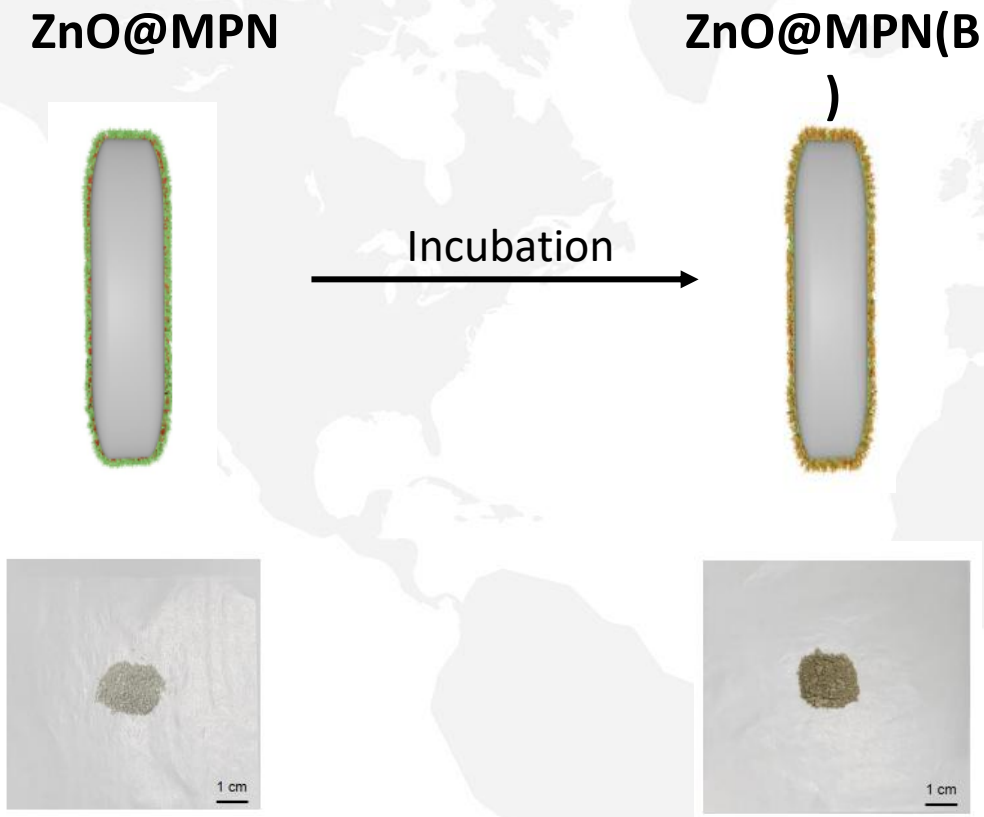
Tang, Chen, Liu, He, Yang, Liu, Yan (2020). Controlled reactivity of metastable n-Al@ Bi (IO3) 3 by employment of tea polyphenols as an interfacial layer. Chemical Engineering Journal, 381, 122747.

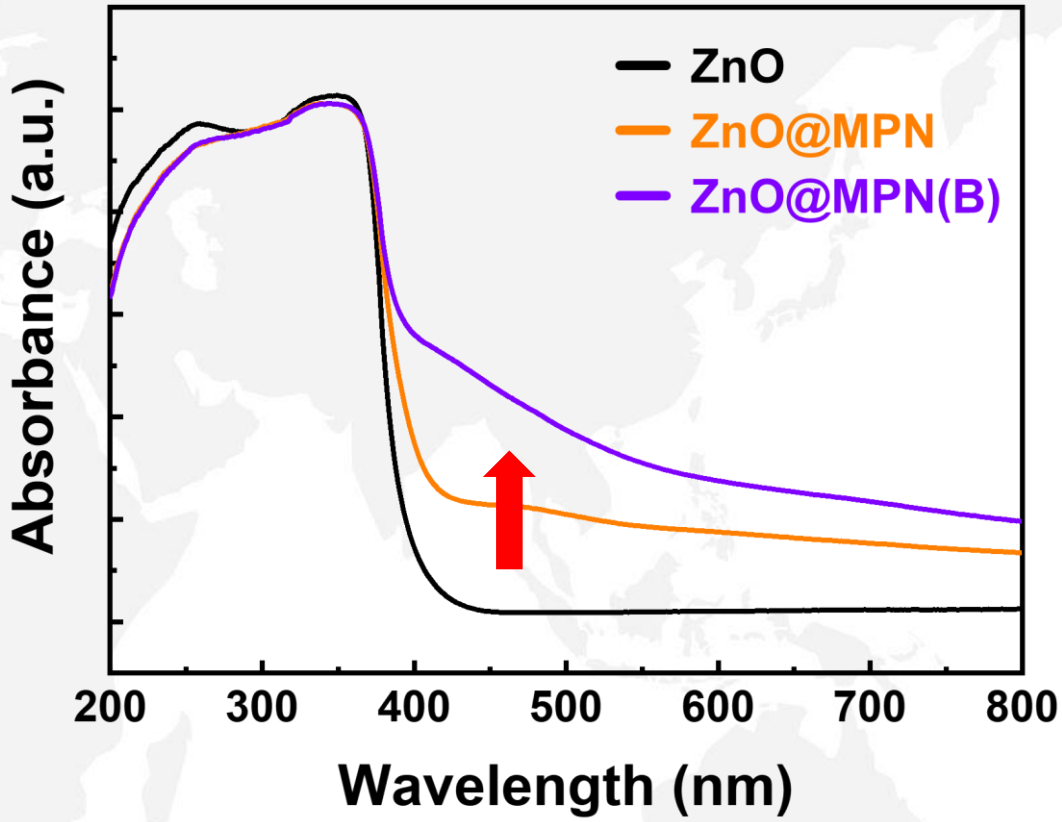
Proposed Mechanism of MPN Browning Effect



Quinonoid structures enhance π-electron delocalization, thereby broadening the absorption spectrum of the material to encompass the HEV light region.

UV-visible Absorbance of ZnO@MPN with Incubation

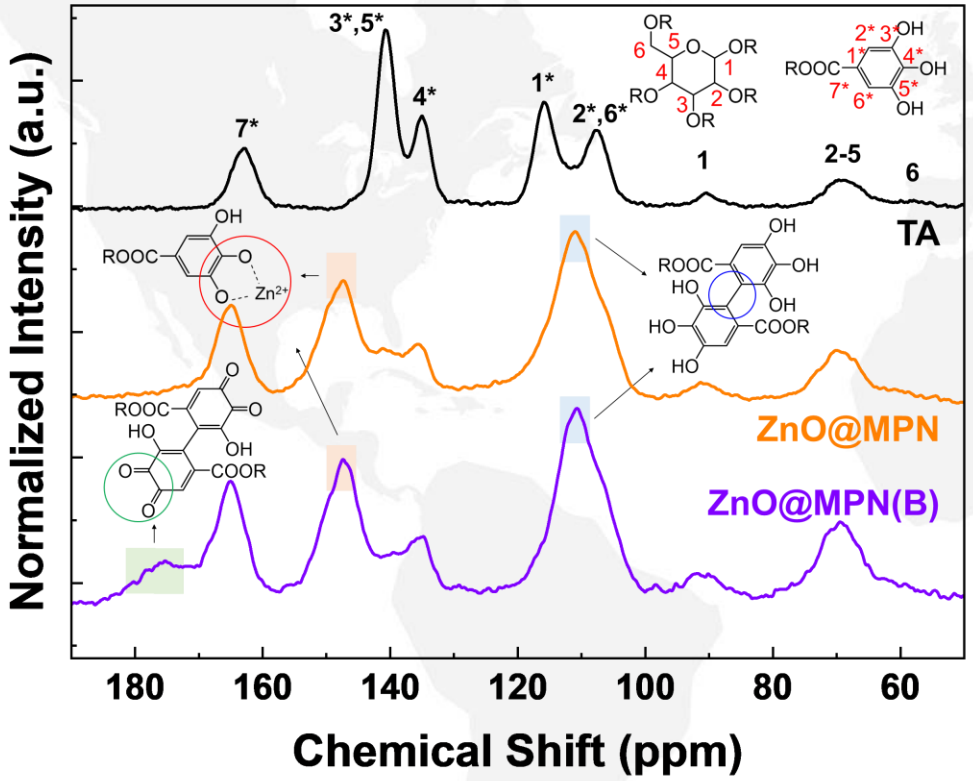




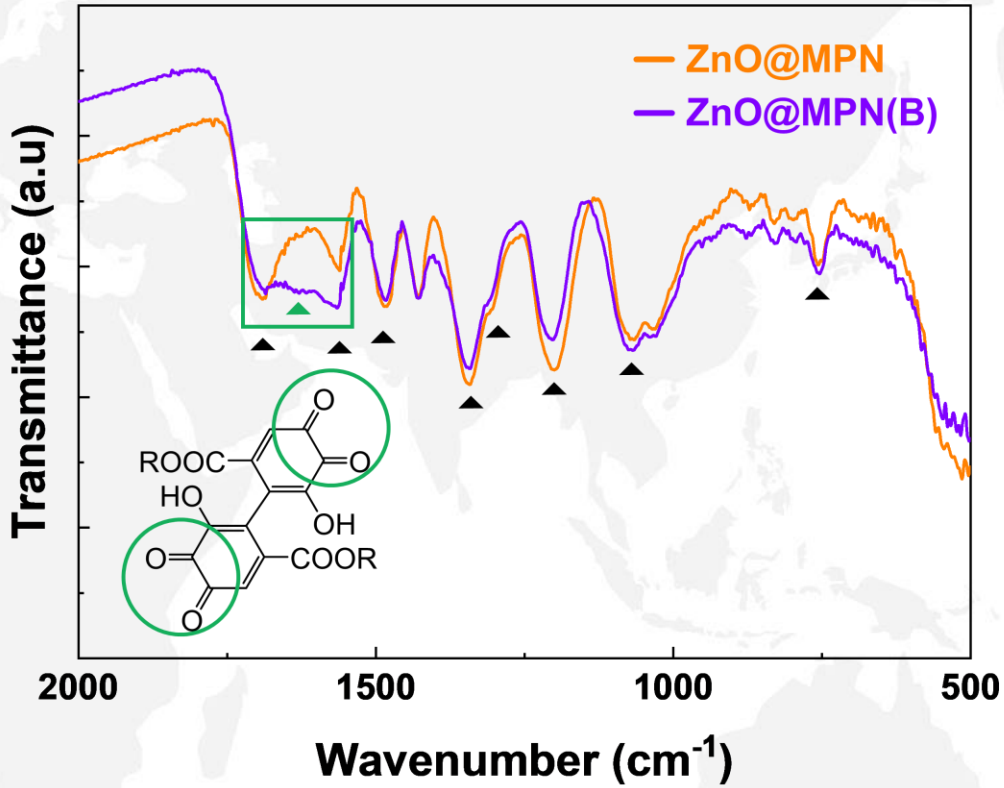
Incubation Condition
Atmospheric condition
Humidity: ~50%, Pressure: 0.1 Mpa, Time: 7days

Structural characterization of ZnO@MPN Particles

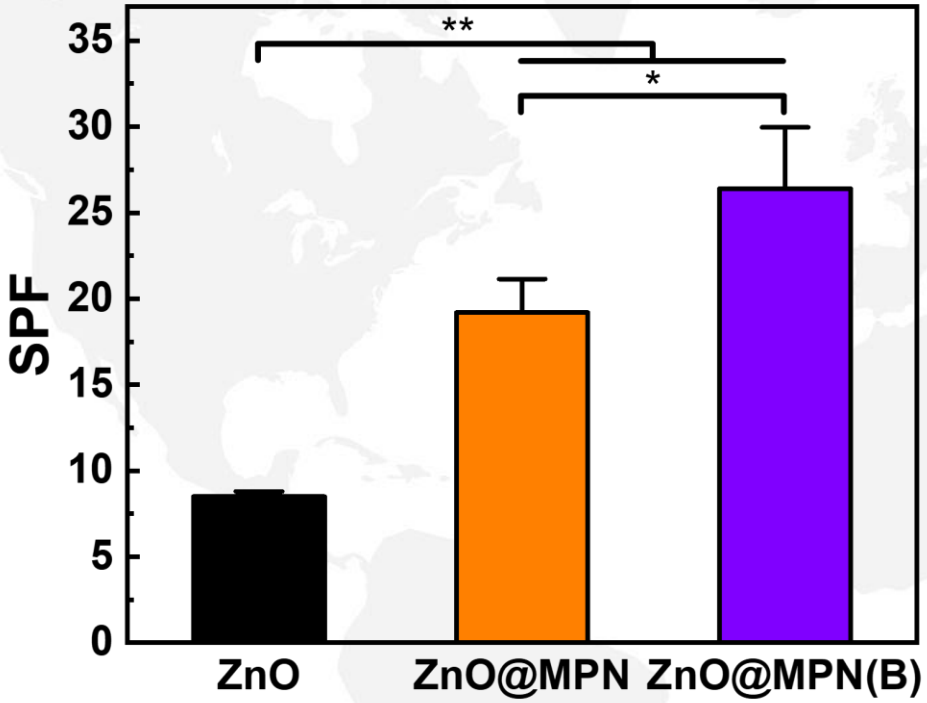
^{13}C CPMAS NMR spectra

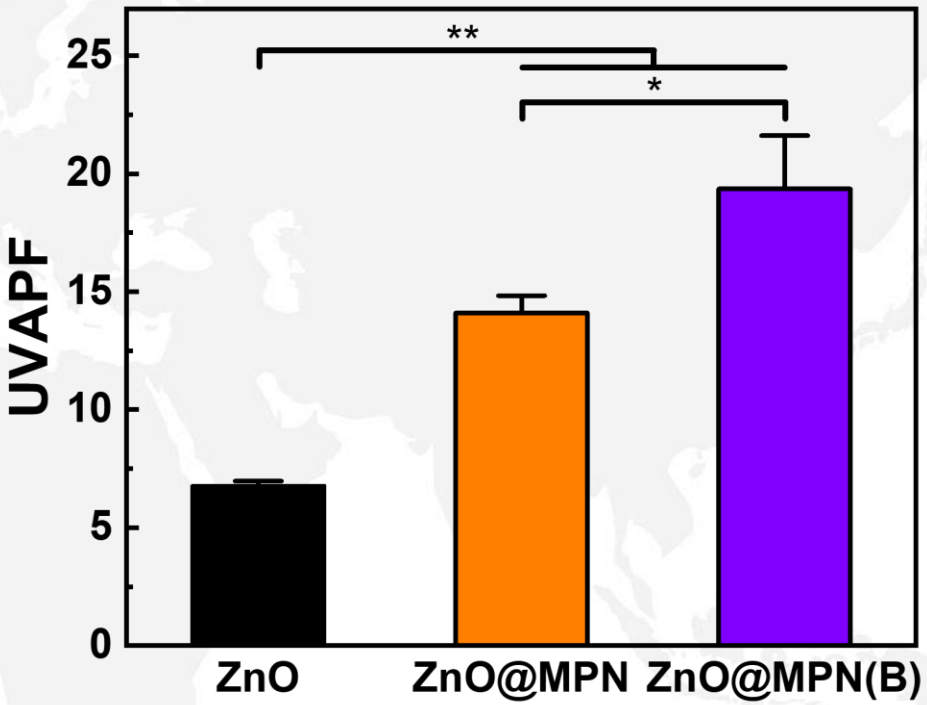


FT-IR spectra



Sunscreen Performance of ZnO@MPN and ZnO@MPN(B)

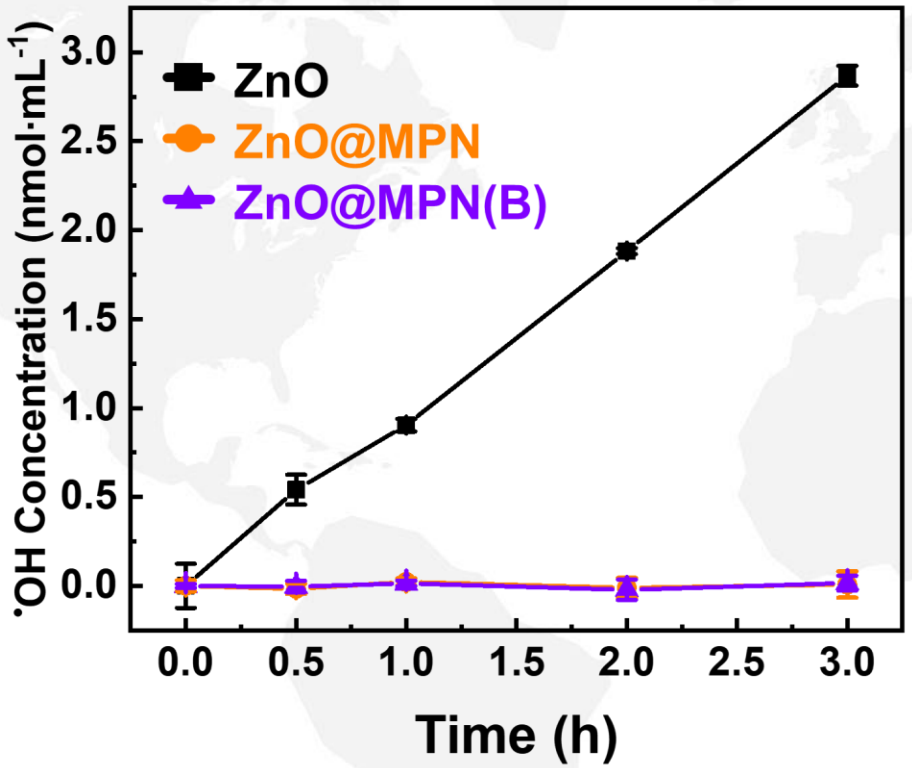




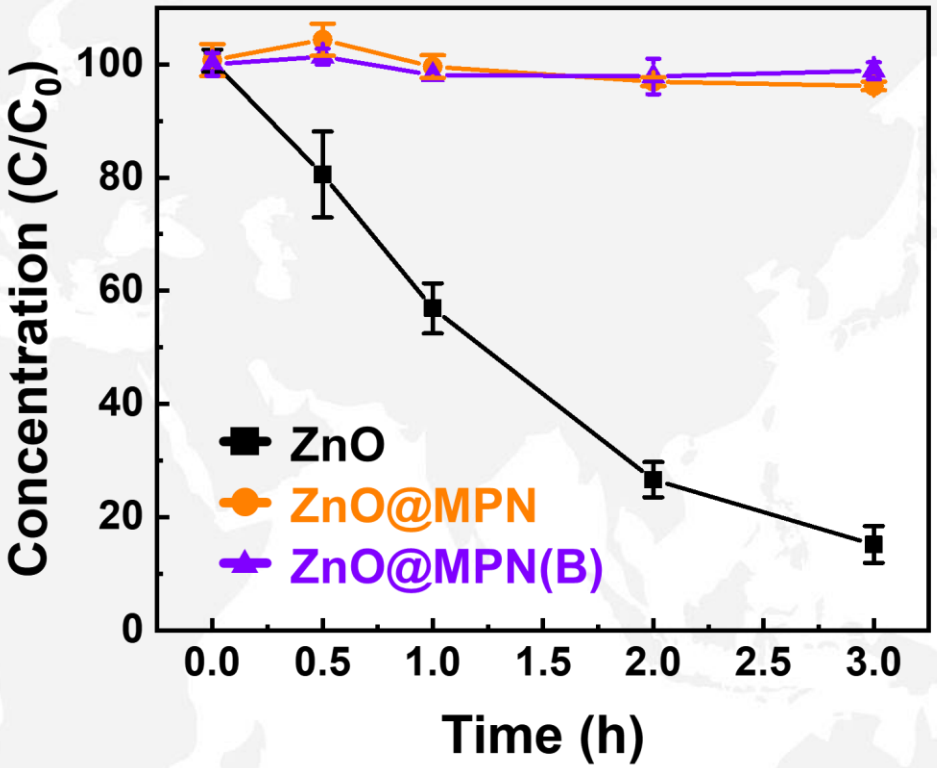
- 20 wt% dispersions of each ZnO, ZnO@MPN, and ZnO@MPN(B) particles in 1,3-BG.
- Statistical significance is denoted as *$p < 0.05$ and **$p < 0.0001$.

ROS Suppression of ZnO-MPN

Hydroxyl radical generation



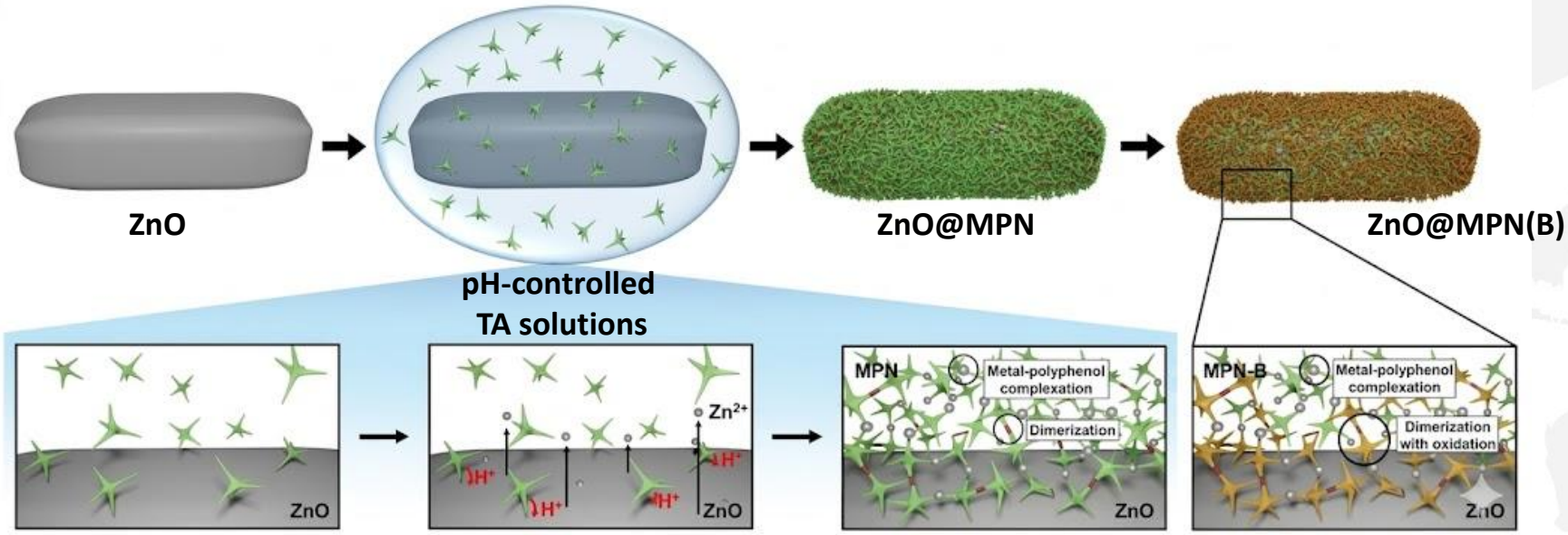
Degradation of organic UV filter



- Photo-induced ROS Suppression Assay*:* ZnO-PBS and terephthalic acid mixtures were irradiated under 1-sun.
- Organic UV Filter Degradation Assay: Ensulizole solution: ZnO solution (1:1), 1-sun irradiation.

Summary

1. We developed a simple one-pot MPN coating strategy for the rod-shaped ZnO.
2. Controlled oxidation was introduced to extend protection from the UV to the HEV region.
3. This resulted in improved performance and enhanced safety.



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Prof. Jongwon Shim

Sungkyunkwan University
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National Center for Cosmetics R&D
피부 기반기술 개발 사업단

Thank you!

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