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Low-Heavy-Metal ZnO to Address Stricter Heavy Metal Limit

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1. Introduction

Heavy metals in cosmetic products have long been a concern due to their potential adverse effects on human health. Prolonged exposure to heavy metals like lead (Pb), nickel (Ni), chromium (Cr), and mercury (Hg) through cosmetics can lead to a range of health issues, including skin irritation, allergic reactions, systemic toxicity, and even carcinogenic effects. For instance, lead exposure is linked to neurotoxicity and developmental harm, while nickel and chromium can cause immune disorders and DNA damage. Mercury, often found in skin-lightening products, poses risks such as kidney damage and neurological impairments. These metals can enter the body through dermal absorption and accumulate over time, exacerbating their toxic effects [1,2]. To mitigate these risks, regulatory bodies worldwide have established strict limits on heavy metal content in cosmetics. In the United States, the FDA recommends a lead limit of 10 ppm for cosmetics, while Washington State's newly enacted Toxic-Free Cosmetics Act (HB 1047) sets an even stricter threshold of 1 ppm for lead impurities in personal care products starting January 1, 2025. This law also restricts other harmful substances like poly- and perfluoroalkyl substances (PFAS), formaldehyde, and phthalates to ensure consumer safety [3]. Recognizing the challenges posed by these stringent regulations, particularly for raw materials prone to contamination, innovative solutions are essential. Zinc oxide (ZnO), a widely used ingredient in sunscreens and cosmetics, is one such material that has been optimized to meet these standards.

With the tightening regulations on heavy metals in cosmetic raw materials, the choice of ZnO manufacturing methods has become increasingly critical. The French process, which involves vaporizing and oxidizing pure zinc metal at temperatures above 1,000°C, is widely used for ZnO production due to its efficiency in producing high-purity products. However, it has significant limitations, including the inability to remove heavy metal impurities from raw materials. Similarly, the direct process, which reduces and oxidizes zinc ores using carbon, is cost-effective but transfers impurities from the raw materials directly into the final product, resulting in ZnO with lead (Pb) levels of 2–5 ppm [4]. These limitations make both processes less suitable for producing ultra-pure ZnO required for cosmetic applications. In contrast, the wet process offers a superior alternative for producing ZnO with low heavy metal content. This method relies on chemical precipitation reactions using zinc salt solutions, enabling multi-step purification. Additionally, the wet process allows precise control over particle size (50–150 nm) and surface area while minimizing environmental impact through wastewater recycling systems [5, 6]. These advantages make the wet process particularly

well-suited for producing ZnO that complies with stringent regulations such as Washington State's HB 1047 and the EU Cosmetics Regulation (EU No 1223/2009).

Here, we have developed ZnO with exceptionally low levels of heavy metals. ZnO was chosen due to the inherent risk of heavy metals in inorganic materials, as raw materials or during processing may introduce contaminants. Our ZnO features Pb levels below 1 ppm, nickel (Ni) below 2 ppm, and chromium (Cr) below 1 ppm, ensuring compliance with stringent safety standards while supporting the production of safer personal care products. This achievement was made possible through the use of the wet process manufacturing method including purification step using ammonium carbonate, which allows for better control over metal impurities. The ZnO was further optimized in terms of shape and size to serve as a suitable alternative to existing products. The prepared ZnO samples were then compared with other commercial ZnO samples to evaluate heavy metal content.

2. Materials and Methods

2.1 Synthesis of refined zinc oxide through removal process

The hydrothermal method was used to obtain rod-shaped ZnO with low heavy metal content. ZnCl₂ was first dissolved in distilled water. To synthesize the desired rod-shaped ZnO (ZnO 200), an alkaline solution was slowly added to the precursor under mild stirring, while the pH was carefully monitored and maintained at 7 through neutralization. The resulting Zn(OH)₂ precipitate was then leached using an aqueous ammonium carbonate solution to remove heavy metal contained in the Zn(OH)₂ [7-9]. The leaching solution was prepared by dissolving 2 M ammonium carbonate in water and gradually heating it under vigorous stirring. Subsequently, the ammonium carbonate solution was added to the Zn(OH)₂, and the mixture was stirred for one hour. During this time, gaseous ammonia was occasionally introduced to maintain the pH between 10 and 11 at a temperature of 50 °C. The purified Zn(OH)₂ was separated by filtration, and the resulting solid was washed three times with deionized water. Finally, the product was dried at 140 °C until completely dry. This process is illustrated in Fig. 1.

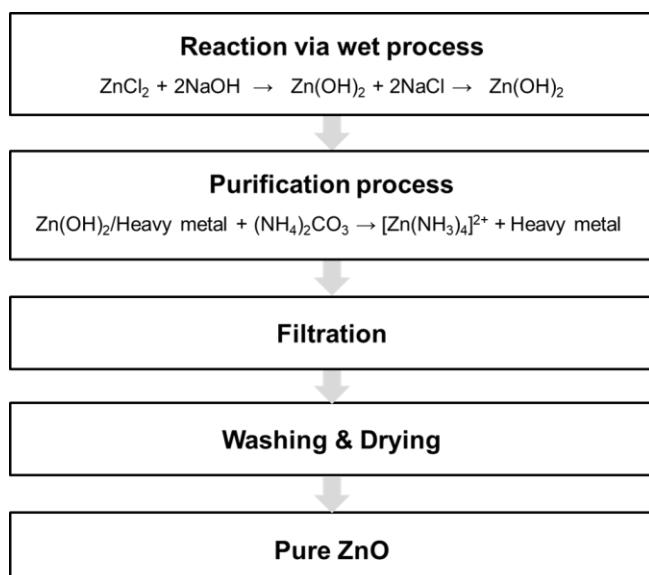


Figure 1. Schematic illustration of refined ZnO production via heavy metal removal

2.2.Characterization

To confirm the formation of a crystalline phase and to indentify impurities attributed to the ZnO 200, an X-ray diffraction (XRD) analysis of the samples was performed on the samples. XRD patterns were made at room temperature with a step size of 0.05° in the angular range of 20–80° in 2θ, using a D8 Advance Diffractometer (Bruker, Germany) with the copper Kα1 radiation ($\lambda = 1.5406 \text{ \AA}$). The surface morphology of the ZnO200 was analyzed using scanning electron microscopy (SEM) (Zwess, Germany). Heavy metal content of the ZnO200 was analyzed using ICP-MS (NexION 1000, PerkinElmer, USA) after microwave-assisted digestion of the samples with a mixture of nitric acid and hydrofluoric acid (7:3, v/v). Yellow index of ZnO powders was measured by color meter (ZE 6000, NIPPON DENSHOKU, Japan).

2.3 Hydrophobic coating on the rod-shaped ZnO200

After purification process, the hydrophobic coating agent, triethoxycaprylylsilane, was added into the solution, followed by filtration, washin, drying steps, which were carried out the same manner as described in Figure 1. The transparency of the coated ZnO samples were visually evaluated using the W/O suncare formulation (Table 1) applied to PMMA plate, and their white index was measured using chroma meter (Konica Minolta, Japan).

Table 1. Ingredients of the W/O suncare formulation

	Ingredient	Formula (w/w, %)		
		ZnONAS	ZnOAS	ZnO200AS
A	Coco-caprylate/caprate	11.0	11.0	11.0
	Carpylic/Capric Triglyceride	2.0	2.0	2.0
	Undecane & Tridecane	8.0	8.0	8.0
	Polyglyceryl-3 Polyricinoleate & Sorbitan Isostearate	5.0	5.0	5.0
	Silica & Cetyl alcohol	2.0	2.0	2.0
B	Zinc oxide & Triethoxycaprylylsilane	25		
	Zinc oxide & Triethoxycaprylylsilane		25	
C	Zinc oxide & Triethoxycaprylylsilane			25
	Water	38.0	38.0	38.0
	Glycerin	5.0	5.0	5.0
	Sodium chloride	1.0	1.0	1.0

3. Results

In contrast to organic UV filters, inorganic alternatives such as ZnO often exhibit limited spreadability and produce a visible white cast, particularly problematic on darker skin tones [10]. To address these limitations, we synthesized rod-shaped ZnO particles, ZnO200, with reduced agglomeration tendencies. The morphological characteristics of these particles were precisely controlled by adjusting the flow rate during the precipitation reaction. As demonstrated in Figure 1, the aspect ratio of ZnO particles exhibited a strong inverse

correlation with flow rate parameters. When the flow rate was reduced from 300 rpm to 100 rpm, the fluid dynamics transitioned toward laminar flow conditions, resulting in ZnO particles with significantly increased aspect ratios (from 1.5:1 to approximately 6:1). This morphological modification can be attributed to the preferential crystal growth along the c-axis under reduced shear stress conditions, as previously reported by Wang et al. [11].

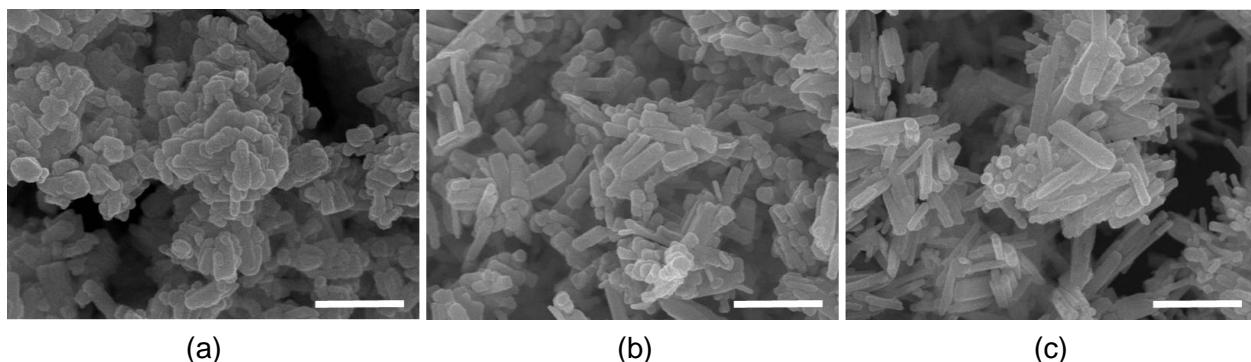


Figure 2. FE-SEM images of ZnO particles synthesized under different flow rates: (a) 300 rpm, (b) 200 rpm, (c) 100 rpm. Scale bar: 500 nm

Current regulatory limits on heavy metal impurities in cosmetics, as outlined in Table 1, are becoming increasingly stringent, exemplified by the Toxic-Free Cosmetics Act (HB 1047) which establishes a more restrictive threshold of 1 ppm for lead in personal care products effective January 1, 2025. In response to this regulatory trend toward stricter control of multiple heavy metals, this study investigated an ammonium carbonate-based purification process for removing heavy metal contaminants from the ZnO₂₀₀ particles, with particular focus on Pb, Cr, and Ni reduction. As demonstrated in Table 2, the concentration of ammonium carbonate emerged as the critical parameter influencing heavy metal removal efficiency. The results revealed that when the molar ratio of ZnO:NH₄CO₃ was increased to 1:2, Pb content was successfully reduced to below 1 ppm, meeting the forthcoming regulatory requirements. Additionally, even at the lower molar ratio of 1:1, the process effectively reduced Ni and Cr concentrations to maximum levels of 2 ppm and 1 ppm, respectively. This ammonium carbonate leaching approach demonstrates significant potential as an economical and efficient method for producing high-purity ZnO that complies with increasingly rigorous cosmetic safety standards.

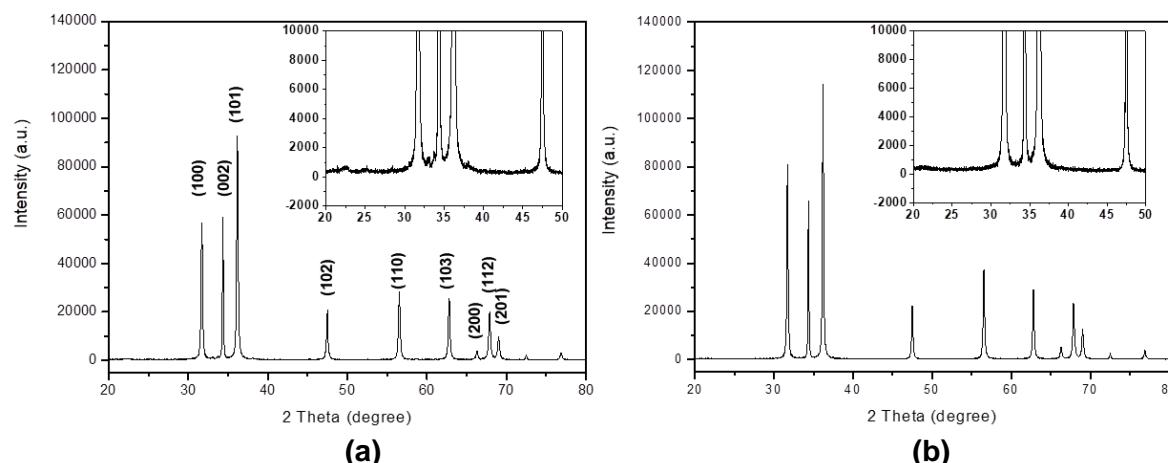
Table 1. Regulatory limits on heavy metal impurities in cosmetics

Heavy metals	Max. (ppm)			Remark
	US	EU (German)	Korea	
Pb	20	2	20	10 for lip care product (US)
Cd	-	0.1	5	
Hg	1	0.1	1	
As	3	0.5	10	
Cr	15	15	15	
Ni	-	10	10	

Table 2. Chemical composition of ZnO200 obtained through ammonium carbonate leaching

Mole ratio (ZnO: NH ₄ CO ₃)	Content (ppm)		
	Pb	Ni	Cr
1:0	2.234	0.298	0.822
1:1	1.175	0.122	0.498
1:2	0.362	0.132	0.478
1:3	0.024	0.108	0.498

The crystallinity and phase purity of both untreated and ammonium carbonate-treated ZnO200 powders were evaluated using XRD (Figure 3). Both samples displayed sharp diffraction peaks corresponding to the hexagonal wurtzite ZnO structure (JCPDS card No. 36-1451), confirming their high crystallinity and phase stability [12]. Notably, the XRD pattern of the unpurified ZnO200 powders (Inset graph in Figure 3a,) revealed additional peaks in attributable to impurities. In contrast, the unpurified ZnO200 powders (Inset graph in Figure 3b) exhibited only the characteristic ZnO peaks, with no detectable signals from impurity phases, indicating the successful removal of contaminants and the formation of a highly crystalline wurtzite structure. This result demonstrates that leaching low-grade ZnO in ammonium carbonate solution effectively eliminates heavy metal impurities.

**Figure 3.** XRD patterns of (a) unpurified ZnO200 and (b) purified ZnO200 powders.

In addition, we analyzed the heavy metal content (Pb, Ni, Cr) in commercial ZnO produced by the French process, finding concentrations of 5.393 ppm for Pb, 2.103 ppm for Ni, and 7.098 ppm for Cr. Furthermore, we compared the yellow index of the purified ZnO200 with that of the commercial ZnO produced by the French process. The purified ZnO200 exhibited a significantly lower yellow index, indicating improved optical quality. Although the French process is widely used for industrial ZnO production, it does not effectively remove heavy metal impurities during synthesis, often resulting in noticeable yellow discoloration due to residual contaminants and structural defects. In contrast, the ZnO200 purified in this study demonstrated enhanced color stability and a reduced yellow index, confirming its superior purity and quality compared to conventional commercial ZnO.

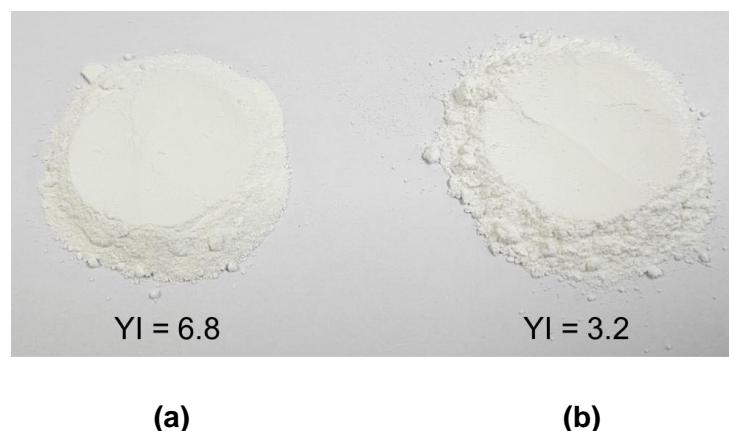


Figure 4. Comparison of the yellow index between (a) commercialized ZnO prepared by the French method and (b) purified ZnO200 powders

Transparency assessments were conducted by comparing the rod-shaped ZnO200AS particles with spherical ZnO particles of two distinct size distributions: nano-sized ZnO NAS (40 ± 10 nm) and larger ZnO AS (150 ± 15 nm). As shown in Figure 5, the white index (WI) measurements revealed that rod-shaped ZnO200AS exhibited excellent transparency with a WI value of 27.19, comparable to that of nano-sized spherical ZnO NAS (WI: 28.26). In contrast, the non-nano sized spherical ZnO AS demonstrated significantly higher whiteness (WI: 38.63), indicating greater visibility when applied to skin. These findings demonstrate that rod-shaped ZnO particles can achieve transparency levels similar to those of much smaller nano-sized particles while potentially avoiding the associated risks of nanoparticle penetration. The rod morphology appears to optimize both the optical properties and sensorial attributes of ZnO formulations, making them particularly suitable for cosmetic and dermatological applications where minimal white cast is desired.



Figure 5. Images of the ZnO W/O suncare formulation applied to PMMA plates and their white index value: (a) ZnONAS, (b) ZnOAS, (c) ZnO200AS. All the results were obtained from three replicate experiments

4. Discussion

The development of rod-shaped ZnO200 particles with controlled aspect ratios represents a significant advancement in addressing the cosmetic limitations of inorganic UV filters. The

inverse relationship between flow rate and aspect ratio observed in this study provides a straightforward, scalable method for tuning ZnO morphology without additional chemical modifiers. More importantly, the ammonium carbonate purification process demonstrated remarkable efficiency in heavy metal removal, with the optimal 1:2 (ZnO:NH₄CO₃) molar ratio achieving Pb levels below 1 ppm—a critical threshold for compliance with emerging regulations such as the Toxic-Free Cosmetics Act. This purification mechanism likely operates through selective complexation of heavy metals with ammonium carbonate followed by their separation from the ZnO matrix, while the preservation of rod morphology throughout the purification process indicates minimal surface etching or restructuring. The comparable white index values between rod-shaped ZnO200AS (WI: 27.19) and nano-sized ZnO NAS (WI: 28.26) suggest that aspect ratio manipulation can achieve the transparency benefits of nanoparticles without reducing particle dimensions below potentially concerning thresholds. This represents a promising alternative approach to the ongoing safety debates surrounding nanoparticle use in topical formulations, particularly considering the maintained crystallinity and phase purity confirmed by XRD analysis.

5. Conclusion

This study successfully developed a comprehensive approach to engineering ZnO particles for cosmetic applications through controlled morphology and targeted purification. By manipulating flow rate during precipitation, we produced rod-shaped ZnO200 particles with aspect ratios up to 6:1, while subsequent ammonium carbonate leaching efficiently reduced heavy metal impurities below regulatory thresholds (Pb <1 ppm, Ni <2 ppm, Cr <1 ppm). The optimized ZnO200AS particles demonstrated transparency comparable to nano-sized ZnO but without the potential risks associated with nanoparticle penetration. The preservation of crystalline integrity and morphological features throughout the purification process further validates the practical applicability of this method. These findings offer a scalable solution to the persistent challenges of white cast and regulatory compliance in inorganic UV filters, potentially expanding the acceptability of ZnO-based sunscreens across diverse skin tones. Future research could explore further optimization of the rod aspect ratio for specific formulation requirements and investigate the photostability and dispersion behavior of these particles in various cosmetic bases to enhance their commercial viability.

6. Acknowledgments

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7. References

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