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Original Article

Characterization of titanium dioxide and zinc oxide nanoparticles in sunscreen powder by comparing different measurement methods

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ABSTRACT

Numerous consumer products, such as cosmetics, contain nanoparticles (NPs) of titanium dioxide (TiO_2) or zinc oxide (ZnO); however, this raises questions concerning the safety of such additives. Most of these products do not indicate whether the product includes NPs. In this study, we characterized metal oxide NPs according to size, shape, and composition as well as their aggregation/agglomeration characteristics. In order to comprehend quickly the characterization of metal oxide NPs, we employed single particle inductively coupled plasma (SP-ICPMS) to help quantify the size of metal oxide NPs; then, we use transmission electron microscopy (TEM) to corroborate the results. The crystal size and structure was measured by X-ray diffraction (XRD), there are two crystal phase of TiO_2 NPs in sunscreen powder showed in XRD. However, SP-ICPMS proved highly effective in determining the size of NPs, the results of which remarkably good agreement with the TEM measurements. Pre-treatment included a conventional copper grid (requiring sample dilution) to evaluate the size, shape and composition of primary particles or plastic embedding (without the need for sample dilution) to evaluate the aggregate/aggregation of native NOAAs. The proposed method is an effective and fast approach to the characterization of oxide NPs in cosmetic sunscreen powder. These findings outline an alternative approach to the analysis of NPs in powder-form matrix.

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1. Introduction

Nanotechnology is widely used in cosmetic products, such as sunscreen and sunscreen powder. A lack of product labeling pertaining to nano-particles (NPs) means that consumers have no idea whether they are being exposed to nanomaterials. A large number of cosmetics that include NPs are high value-added items; however, they enjoy a time to market shorter than that of pharmaceuticals, which must undergo clinical evaluations [1].

According to the International Cooperation on Cosmetic Regulations (ICCR) [2], TiO_2 and ZnO NPs are used as inorganic UV filters in numerous personal care products. Metal oxide NPs are commonly used in sunscreen to provide broad-spectrum UV blocking without sacrificing transparency. NPs are a viable alternative to chemical UV filters, which pose the possibility of adverse health effects [3,4]. Furthermore, products that use NPs provide better texture, spread ability, and UV protection [5]. Nonetheless, NPs may also pose a threat to human health as well as the environment.

Under regulation (EC) No 1223/2009, the European parliament mandated the labeling of cosmetics that include NPs, starting on 11 July 2013 [6]. Commercial products containing nanomaterials must be registered at least six months prior to being released on the market. This labeling must include the name of the chemicals involved (IUPAC) as well as the size, physicochemical information, and toxicity. This has underlined the need for analytical methods with which to detect and characterize the nanomaterials used in cosmetics. The technical report from International Organization for Standardization (ISO) underlined the importance of physicochemical characterization in identifying such materials prior to toxicological testing. Particle size/particle size distribution, aggregation/agglomeration state, shape, surface area, composition, surface chemistry, surface charge, and solubility/dispersibility were listed as the physicochemical parameters [7]. The US FDA also emphasized the physicochemical properties and aggregation/agglomeration of nanoparticles in final cosmetic products [8]. It would be preferable to assess NPs in an unmodified state in order to prevent analytical artefacts associated with changes in the viscosity, aggregation/agglomeration, or the pH of the final products. The complexity and opacity of sunscreen formulations may also encumber efforts at characterization.

We previously investigated TiO_2 and ZnO NPs in liquid form (sprays, lotions, and creams) using XRD and TEM techniques [9–11]. To both observe sizing characterization and counting inorganic NPs more efficiently, single particle inductively coupled plasma-mass spectrometry (SP-ICPMS) is widely use in nano technology these few years. Thus, the aim of this study was investigated the feasibility of using XRD, SP-ICPMS, and TEM to analyze NPs in products in powdered form. No previous study has sought to characterize TiO_2 and ZnO NPs in sunscreen powder. First at all, the crystal phase was showed in XRD result. Then, we used SP-ICPMS which can quick and efficient know the mean size and size distribution of TiO_2 and ZnO NPs in sunscreen powder. In addition, the characterization of particle size, particle size distribution, shape, and aggregation/agglomeration were analysed by TEM to make sure the data of SP-ICPMS. Our results provide a valuable reference to guide the further application of NPs in a variety of cosmetic products.

2. Materials and methods

2.1. *Sunscreen powder samples and standard nanoparticle controls*

This study examined nine commercial sunscreen powders containing TiO_2 and/or ZnO, none of which provide any size-related information on the labels. Four of the samples contained only TiO_2 NPs and five contained a combination of TiO_2 and ZnO NPs, as shown in Table 1 All of these sunscreen products are available without prescription in Taiwan. Two products were made in the USA, seven products were made in Japan, and one product was made in Taiwan. We also purchased from Alfa Aesar (USA) standard TiO_2 powder that includes anatase and rutile crystals for the analysis of crystal structure. Standard solutions of ZnO NPs (76 nm) purchased from Sigma–Aldrich (USA) were also used for the analysis of crystal structure. We used NIST standard reference material (SRM) 1898 (mixed-phase nanocrystalline TiO_2) in powder form as a size control to verify the measurement methods. This SRM consisted of anatase and rutile crystals with an average size of 19 ± 2 nm and 37 ± 6 nm, as measured using XRD. The characteristic reflection patterns were 200 for anatase and 111 for rutile.

2.2. *X-ray diffraction*

XRD patterns were obtained from the samples at room temperature using a PaNalytical Pro X'pert Pro XRD (Netherlands), equipped with Cu Kα radiation ($\lambda = 1.54051$ Å). Prior to the measurement, we used NIST standard reference material 1976b consisting of a sintered alumina disc for XRD calibration with respect to instrumental broadening against all 2θ angles to eliminate variability in intensity measurements. Unmodified sunscreen samples and NIST SRM 1898 were placed in a metal holder and flattened gently using a glass coverslip. All samples were processed under the same operating

Table 1 – Summary of commercial sunscreen powder samples tested in this investigation.

Product No.	Origin	Ingredients		SPF
		TiO_2	ZnO	
1	USA	15.35%	–[b]	35
2	Japan	13.84%	4.43%	26
3	Japan	?[a]	3.35%	35
4	Taiwan	13.52%	5%	23
5	Japan	13.99%	–[b]	20
6	Japan	?[a]	4%	16
7	Japan	13.01%	4.99%	21
8	Japan	12.47%	–[b]	20
9	USA	9.5	–[b]	20

[a] Indicates inclusion of ingredient.
[b] Indicates that the substance is not present.

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