Ultraviolet Protection Properties of Commercial Sunscreens and Sunscreens Containing Zno Nanorods

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Abstract. Zinc oxide nanorods were used as the main ultraviolet agent in the development of sunscreens. Four commercial sunscreens containing organic and inorganic UV agents were studied for their UV performances and SPF determinations. From FESEM and TEM micrographs of ZnO powder, the dominant structure was rod structure with width range 61-70 nm. Sunscreens containing different concentrations of ZnO nanorods were characterized using UV-Vis spectrophotometer and X-ray diffraction (XRD). The absorbance spectra for commercial sunscreens showed a good protection in range of UVB (280-320nm), while sunscreens containing 20-40% (weight percentage) of ZnO nanorods showed a greater UV absorbance in UVA and UVB (280-400 nm). The strong UVA absorbance of ZnO nanorod can offer extra UV protection for commercial sunscreens. The average crystallite sizes of the sunscreen samples calculated from the XRD spectra were in the range 45.27 to 47.36 nm. In vitro sun protection factor (SPF) method was carried out to determine the SPF value of sunscreen specimens. SPF values of sunscreens containing ZnO nanorods were 29.50 to 43.48, whereby these SPF values indicated more than 93% of UVB blocking capability. The SPF values found of commercial sunscreens were slightly different from the SPF values in the product labels. In conclusion, incorporation of ZnO nanorods into sunscreen can greatly enhanced the UV blocking performance of sunscreens.

1. Introduction
The destruction of ozone layer of the atmosphere led more ultraviolet to penetrate in the earth and causes health issues, such as sunburn, aging, skin reddening, acne allergies and even skin cancer [1]. The use of sunscreen is one of the most popular approach to protect skin against UV radiation. The introduction of zinc oxide nanoparticles (ZnO NPs) contributed to higher UV protection efficacy due to higher surface area to volume ratio and appear transparent to the skin surface compared to ZnO bulk particles [2]. Besides, they offer a broad spectrum protection besides very low of skin irritation and sensitization, inertness of the ingredients and low penetrate skin [3], [4]. Sun protection factor (SPF) is the universal parameter for describing the efficiency of sunscreen products, which can draws attention of consumers in terms of reduce UV-induced erythema [5]. It is measured by both in vivo [6] and in vitro SPF determination methods [7]. However, due to high cost and time consumption of in vivo methods, the SPF of sunscreens was determined by in vitro of ultraviolet spectrophotometry, which substitutes in the in-vivo method [7]–[9]. UV-vis spectroscopy was employed to measure absorbance at 290 to 320 nm and a SPF was calculated using the absorbance measured and Mansur mathematical equation [10].
In this study, sunscreen contained different concentrations of ZnO were prepared. Four commercial sunscreens from different brands and different values of SPF were purchased. We report the UV performances of sunscreen contained ZnO and commercial sunscreen. The determination of SPF value for both samples were determined using an in-vitro UV spectrophotometry method.

2. Experimental details
A commercial pharma grade ZnO powder was used in this work. The ZnO was synthesized using French process [11]. In this study, sunscreen creams were made from mineral oil and beeswax, while ZnO was used as the main UV agent. The sunscreens were produced with different weight percentage (wt %) of 5, 10, 15, 20, 25, 30, 35 and 40 of ZnO, respectively. Other than these higher concentrations were not produced because it will cause the texture of sunscreen to be more harder and appear white pigment on the skin [12]. Besides that, four different brands of commercially available sunscreens were purchased in the drugstore in Penang. Morphology and composition of the ZnO powder were characterized using field-emission scanning electron microscope (FESEM-EDS, model: JSM – 6460 LV) and Phillips CM12, transmission electron microscopy (TEM). The structural and crystallinity properties of sunscreen samples were characterised by X-ray diffraction (XRD, model: Panalytical X’pert Pro MRD PW3040). The absorption spectra sunscreen containing ZnO and commercial sunscreens were obtained from Varian Cary 5000 UV/Vis/NIR spectrophotometer.

Sun protection factor of sunscreen contained ZnO and commercial sunscreen, were measured using in vitro UV spectrophotometry method [9]. All sunscreen contained different concentration of ZnO and commercial sunscreen (1.0 ± 0.05 g) were weighed individually, transferred to 100 mL volumetric flask and diluted with 40% ethanol and 60% water solution. Followed by 5 minutes of ultrasonication, the solution was filtered through cotton filter and producing 10 mL filtered solution. A 5.0 mL of aliquot was transferred to 50 mL volumetric flask and diluted with volume 40% ethanol and 60% water solution. The absorbance spectra of aliquot prepared were obtained from 290-320 nm at 5 nm interval. The measurements were taken three times and the determination of SPF values by application of Mansur mathematical equation in Equation (1);

\[
SPF = CF \times \int_{290}^{320} EE(\lambda) \times I(\lambda) \times Abs(\lambda)
\]  

where \( EE \) is erythema effect spectrum; \( I \) is solar intensity spectrum; \( Abs \) is absorbance of sunscreen and \( CF \) is correction factor (=10). The absorbance spectra were expressed as mean ± SEM, then multiplied with the respective \( EE(\lambda) \times I(\lambda) \times Abs(\lambda) \) constants in Table 1. Their summation \( \sum_{290}^{320} EE(\lambda) \times I(\lambda) \times Abs(\lambda) \) were taken and multiply with the correction factor (10).

| Wavelength (nm) | \( EE \times I \) |
|-----------------|------------------|
| 290             | 0.0150           |
| 295             | 0.0817           |
| 300             | 0.2874           |
| 305             | 0.3278           |
| 310             | 0.1864           |
| 315             | 0.0839           |
| 320             | 0.0180           |

3. Results and discussion
From FESEM micrograph in Figure 1(a), several morphologies were identified in ZnO powder: rods, slabs, tripods and irregular-shaped particles. Among these structural morphologies, nanorods were dominant as observed in TEM image (shown in Figure 1(c)). The rod structures had width 61-70 nm (Figure 1(d)) was determined from TEM micrograph. The FESEM-EDS Figure 1(b) shows the
composition percentage of ZnO powder. The relative ratio of O: Zn in the atomic and weight percentages measurement were 0.74 and 0.18, respectively. This result shows content of oxygen atom was lower than zinc. The excess zinc could be attributed to intrinsic defects in crystalline ZnO including oxygen vacancies and zinc interstitials [13]. As a result, sunscreen contained ZnO nanorods as a main active UV filter. ZnO nanorods possess unique optical properties, where their absorption very high in UV regions that able to prevent UV rays from penetrating the skin [14].

XRD pattern of the sunscreen contained ZnO nanorods and commercial sunscreens are shown in Figure 2(a-b). The highest peaks including (100), (002) and (101) were selected for average size analysis. Figure 2(a) shows the higher the concentration of ZnO nanorods in the sunscreen, exhibited sharp and greater peak intensities. It clearly revealed that the ZnO nanorods diffraction peaks matched very well with the hexagonal wurtzite phase. Since the XRD do not have any additional peaks apart from the peaks characteristic for ZnO, suggesting that the formed product contained high-quality ZnO nanorods. The average particles size of the ZnO nanorods in the sunscreen were measured using Scherrer equation in the range of 45.27 to 47.36 nm, respectively. Figure 2(b) shows the presence of inorganic compounds such as ZnO. However, the percentages of these compound contained in the product were not labelled in the product labels; hence, it is difficult to determine their amount in the products. No peak indicated TiO₂ particles was found in the spectra of sunscreen A even though TiO₂ was label-printed to be one of the contents. Meanwhile, sunscreen B shows a very weak intensity of peak at 25.34° indicating the presence of TiO₂ particles found in the sunscreen. By contrast, the other two sunscreens showed high peak intensities allowing average of particles sizes to be calculated. Average zinc oxide particles sizes of 13 nm and 14 nm were found in sunscreen C and sunscreen D, respectively. The sharp intensity corresponding to TiO₂ particles in sunscreen D shows crystallite sizes below 20 nm. TiO₂ particles in the sunscreen might possessed anatase, rutile or brookite crystalline structures [3].

Figure 3(a-b) show the absorption spectra for the sunscreen contained different concentration of ZnO and commercial sunscreen. The observation of absorbance spectra shows higher concentration of ZnO, as main active UV filter offered higher protection over UVA (320-400 nm) and UVB (280-320 nm) regions. The highest absorption at ultraviolet region (376.3 nm) was achieved for sunscreen containing 40 wt% of ZnO nanorods. Commercially available sunscreen A, B, C and D contained both organic and inorganic UV filters and the percentages of these filters were not labelled in the packaging of the product. The absorbance spectra showed the same trend, which is exhibited good absorbance against UVB region and low absorbance approached UVA region. It was emphasized that the homemade ZnO sunscreens in this work offered much bigger protection in the UVA regions than other commercial sunscreens. With the nanorod shape, ZnO particles possessed very large surface-to-volume ratio that can offer much larger optical interaction in absorbing both UVA and UVB radiation. The absorbance spectrum of commercial sunscreen might be influenced by several factors affecting the action against UV rays such as combination of UV filters, concentration of sunscreen and type of emulsion [13-14].
Figure 1: (a) FESEM micrograph; (b) FESEM-EDS; (c) TEM image; (d) particle distributions of ZnO powder.

Figure 2: X-ray diffraction of (a) sunscreen contained ZnO nanorods and (b) commercial sunscreens.
Figure 3: Absorbance spectra of (a) sunscreen contained different concentration of ZnO; (b) commercial sunscreen.

SPF values of sunscreen contained different concentration of ZnO nanorods were determined and tabulated in Table 2, whereby the percentage amount of ZnO nanorods in the sunscreen played an important role in determining the sunscreen SPF. The higher the ZnO amount, the higher the SPF value of the sunscreen. SPF values of sunscreen containing 5 to 40 wt% of ZnO showed very good protection, where more than 93% of UVB blocking. SPF value of commercial sunscreens measured in this study showed sunscreen A and sunscreen B exhibited lower SPF than the SPF value in the product label. This observation was probably because of higher SPF values are more difficult to measure [17]. However, sunscreen C and D exhibited higher SPF value than their labelled SPF. These two sunscreens possessed ideal SPF value for adequate UV protection [18].

Table 2: In-vitro SPF value of sunscreens.

| Sunscreen contained ZnO | SPF value | Commercial sunscreen | SPF value |
|-------------------------|-----------|----------------------|-----------|
| Base cream (mineral oil and beeswax) | 11.51 | Sunscreen A (SPF60) | 51.04 |
| 5 wt% | 29.50 | Sunscreen B (SPF50) | 48.52 |
| 10 wt% | 36.06 | Sunscreen C (SPF30) | 42.48 |
| 15 wt% | 37.03 | Sunscreen D (SPF24) | 26.26 |
| 20 wt% | 40.37 | | |
| 25 wt% | 40.16 | | |
| 30 wt% | 42.40 | | |
| 35 wt% | 42.77 | | |
| 40 wt% | 43.48 | | |
4. Conclusion

ZnO nanorods as active ingredient showed excellent UVA and UVB absorbing performances in sunscreen. Sunscreen incorporated ZnO nanorods increased the SPF value and achieved greater UV protections. Commercial sunscreens exhibited various UV performances due to many chemical and physical compound in the formulations and mostly protects in UVB regions with little protection in the UVA region. SPF value of sunscreen must reflect their protection against UV rays and helps consumer to get adequate protections under the sun.

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