Optimization of Sun Protection Factor from ZnO Nanoparticles and Heartwood of Thanaka

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Abstract

Sun protection factors (SPF) of zinc oxide (ZnO) nanoparticles mixed with heartwood of Myanmar thanaka were optimized by Ultraviolet-Visible (UV-Vis) spectroscopy and SPF values were calculated by using standard SPF formula. ZnO nanoparticles were prepared by low temperature solution method. The maximum absorption wavelength of as-synthesized ZnO nanoparticles was confirmed by UV-Vis spectroscopy. The structural properties of ZnO were characterized by X-ray diffraction (XRD) by preparing the ZnO/Si films which were annealing at different temperatures 400, 500 and 600 °C for 2 h. The functional groups of the samples were identified by Fourier transform infrared spectrophotometer (FT-IR). The antimicrobial activities of prepared samples were also performed for the purpose of using them in cosmetics. It was found out that SPF values of ZnO nanoparticles could be greatly enhanced when it was mixed with heartwood of thanaka powder and all prepared samples showed high antimicrobial activities.

1. Introduction

Thanaka is abundant in the central and upper parts of Myanmar including Mandalay, Magwe and Sagaing divisions. Thanaka tree is a medicinal plant. Myanmar people use thanaka as a cosmetic in their daily lives in order to prevent ultraviolet (UV) radiations. The wavelengths of electromagnetic spectrum of ultraviolet radiation (UVR) are between 100-400 nm which are shorter than that of visible light but longer than X-rays. UV spectra can be subdivided into a number of ranges such as UVA, UVB, UVC, near ultraviolet (NUV), middle ultraviolet (MUV) and far ultraviolet (FUV) respectively.

Depending on the wavelengths of UV rays, the types of UV spectra are defined. The wavelength of UVA is between 400-315 nm, UVB is between 315-280 nm and UVC is between 280-100 nm, NUV is between 400-300 nm, MUV is between 300-200 nm and FUV is between 200-100 nm respectively. While the UVA radiations are not absorbed by ozone layer, UVB radiations are mostly absorbed by ozone. UVC radiations are completely absorbed by ozone and atmosphere and thus they do not reach to the earth. Among them, both UVA and UVB can penetrate to the atmosphere and they have a potential to cause the premature skin aging, eye damage and skin cancers. The effects of the UVB are human skins reddening and sunburn of UVB tends to damage the skins more superficial epidermal layers. UVB plays the fatal issues in skin cancer and a contribution in tanning and photoaging.

Sunscreen such as sunblock, suntan lotion and sunburn cream block out the UV radiation since they have high sun protection factors (SPF). SPF is a measure of how well a sunscreen will protect skin from UVB rays but not from UVA rays. The protection level of sunscreen based on the SPF values are generally defined as maximum for SPF > 50, high for SPF 30-50, medium for 15-30, low for SPF 2-15. Besides, SPF 15 filters out approximately 93 percent, SPF 30 keeps out 97 percent and SPF 50 keeps out 98 percent of all incoming UVB rays. The Academy of Dermatology (AAD) recommends the sunscreen must be at least a SPF of 15+. There are numerous reports of cosmetics produced from various parts of trees and plants [1-3]. Sunscreens included in ZnO nanoparticles are widely applied in cosmetics because such small particles do not scatter light and are therefore they could be absorbed into the skin. This study was only focused on the blocking ability of UVB from ZnO nanoparticles and mixed ZnO nanoparticles and thanaka.

Therefore, the aims of the work are optimization of the SPF from ZnO nanoparticles, heartwood of thanaka and mixing samples from ZnO and thanaka in order to use them as facial and body lotions and masks in human skins. The objectives are to measure the absorbance of both ZnO and mixed samples by UV-Vis spectroscopy, to calculate the SPF values in the UVB wavelength ranges by using the standard formula [4] and to optimize their SPF results.

2. Materials and Method

2.1. Synthesis of ZnO Nanoparticles

ZnO precursor was prepared by dissolving zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$, 1 g) and ethanolamine ($NH_2CH_2CH_2OH$, 0.28 g) in 2-methoxyethanol ($CH_3OCH_2CH_2OH$, 10 mL) under vigorous stirring for 12 h in air [5].

2.2. Preparation of ZnO and Thanaka Samples

Six samples were prepared depending on the weights of ZnO solution, namely M_0, M_5, M_{10}, M_{15}, M_{20} and M_{25} respectively. Each 0, 5, 10, 15, 20 and 25 g of ZnO were used for six samples. Firstly, different weights of thanaka heartwood powder, 100, 95, 90, 85, 80, 75 g were weighted and they were separately transferred to 100 mL volumetric flasks. Then, different volumes of distilled water were added in them until to reach 100 mL volume. The flasks were continuously shaken by a rotary shaker for three days. The extraction was then filtered and collected. Finally, the filtrate of thanaka solution and ZnO solution were mixed and additionally stirred for 3 days. The final mixed solution was used to measure the absorbance by UV-Vis spectroscopy. SPF values for UVB wavelength ranges were calculated through their absorbance results and comparatively determined for all prepared samples.

2.3. Calculation of Sun Protection Factor

Table 1 shows the normalized product function used in the calculation of SPF [6]. The values of EE*I were predetermined according to this referenced paper.

The absorbance between the UVB wavelengths (290-320 nm) of each sample was firstly measured by UV method and the observed absorbance values at 5 nm intervals were secondly multiplied by EE (λ)*I(λ) values at each wavelength. They were finally summed and then multiplied by the correction factor (10). SPF values were calculated according to the standard formula shown in equation (1).

$$SPF = CF \times \sum_{290}^{320} \left[EE(\lambda) \times I(\lambda) \times Abs(\lambda) \right] \qquad (1)$$

EE (λ) = erythemal effect spectrum
I(λ) = solar intensity
Abs(λ) = absorbance
CF = correction factor

The values of EE*I are constant and predetermined.

Table 1. Normalized product function at UVB wavelength (290-320 nm) [6]

Wavelength (λ) nm	EE*I (normalized)
290	0.0150
295	0.0817
300	0.2874
305	0.3278
310	0.1864
315	0.0839
320	0.0180
Total	1

3. Results and Discussion

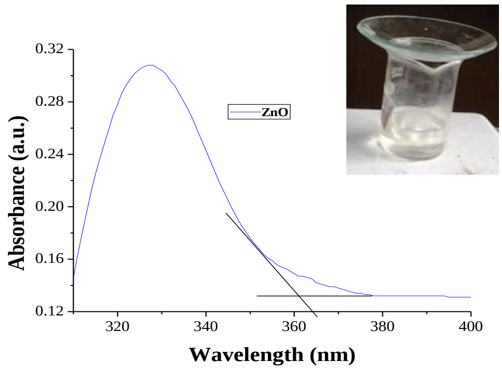


Figure 1. UV-Vis spectrum of as-synthesized ZnO nanoparticles. Insets shows as-synthesized ZnO nanoparticles solution

UV-Vis measurement is carried out in order to estimate the absorbance of samples. The formation of ZnO nanoparticles was monitored by Shimadzu UV-1800 UV-Vis spectrophotometer. As shown in figure 1, The maximum absorption wavelength was occurred around 327 nm. Thus, the synthesized product can be confirmed that ZnO due to well agreement with the report of Getie *et al.*, 2017 [7]. Besides, the band edge wavelength of ZnO estimating from the UV-Vis spectrum was found out to be 360 nm (3.44 eV). This result was totally agreed with the previous reports [8-10]. On the other hand, the bandgap of bulk ZnO at room temperature was 3.2 eV. Therefore, room temperature solution method could be successfully obtained well dispersed nano- size of ZnO particles dispersed in the solution which in turn advantage to mix with thanaka powder. The UV-Vis spectra of mixed samples were shown in figure 2. It was clearly seen that the absorbance of ZnO were greatly enhanced when they were mixed with thanaka heartwood.

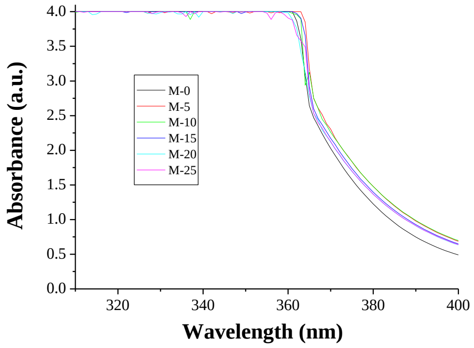


Figure 2. UV-Vis spectrum of ZnO mixed with thanaka

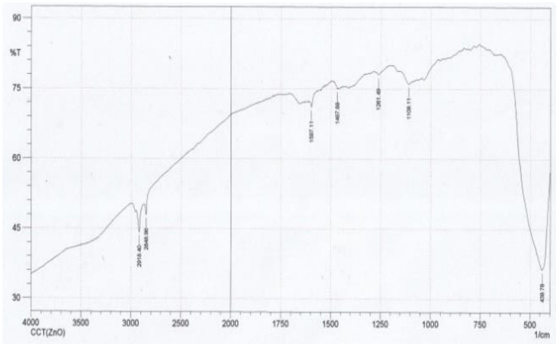


Figure 3. FT-IR spectrum of ZnO nanoparticles

The compound identification of ZnO was obtained by FT-IR 8400 Shimadzu spectrophotometer using a KBr pallet in the mid IR radiation range between 4000 cm^{-1} to 400 cm^{-1} with a resolution of 4.0 cm^{-1}. FT-IR spectrum of the ZnO nanoparticles annealing at 500 °C was shown in figure 3. The fundamental mode of vibration at 2918 cm^{-1} corresponds to C-H stretching vibration and at 2848 cm^{-1} is responsible to N-H stretching. The peak at 1467 cm^{-1} corresponds to C=O asymmetric and C=O stretching vibration. The frequency 1597 cm^{-1} corresponds to C=O symmetric stretching vibration. The peak at 1261 cm^{-1} indicated the saccharide structure and the band at 1109 cm^{-1} is due to the C-O stretching vibration. The sharp peak at 439 cm^{-1} indicates the stretching vibration of ZnO nanoparticles [11]. This result indicates the successful synthesis of ZnO nanoparticles by low temperature solution method.

XRD data was analyzed by RIGAKU-RINT 2000 X-ray Diffractometer. XRD spectra of ZnO/Si thin film shown in figure 4 confirmed that the crystalline phase of ZnO was hexagonal, the most stable form at ambient conditions, according to the standard library file (ICDD-PDF#89-0511). The strengths of the diffracted beams depending on the arrangement of atoms in each unit cell is the highest in a (101) plane for all samples annealing at 400, 500, 600 °C. The degree of structural order (crystallinity) of ZnO was also high due to the zinc and oxygen atoms are arranged in a regular and periodic manner. The crystallite size of ZnO was estimated by Debye Scherrer formula as follows.

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad (2)$$

Where,
λ = wavelength of the incident X-ray beam (1.54056 Å) for CuKα
K = constant equal to 0.89
β = FWHM (full width at half maximum) (degree)
θ = diffraction angle (degree)
D = crystallite size (nm)

The calculated crystallite sizes for the strongest diffraction peak for (101) plane were found out to be 24.63, 30.98 and 40.13 nm respectively for the samples annealing at 400, 500 and 600 °C. These results showed that crystallite sizes were depended on the annealing temperatures.

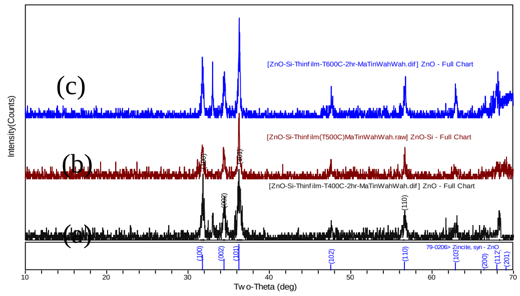


Figure 4. XRD spectra of ZnO/Si thin films annealing at (a) 400 (b) 500 and (c) 600 °C

Table 2 presents the absorbance of ZnO and its SPF determined by equation (1) at different wavelengths. The calculated SPF value of pure ZnO nanoparticles was obtained 2.8770. The graph depicted in figure 5 showed the comparative SPF values for various samples.

Table 2. Absorbance of ZnO at different normalized product function and at different UVB wavelength (290-320 nm)

Wavelength (λ) nm	Absorbance
290	0.743
295	0.533
300	0.38
305	0.231
310	0.188
315	0.134
320	0.099

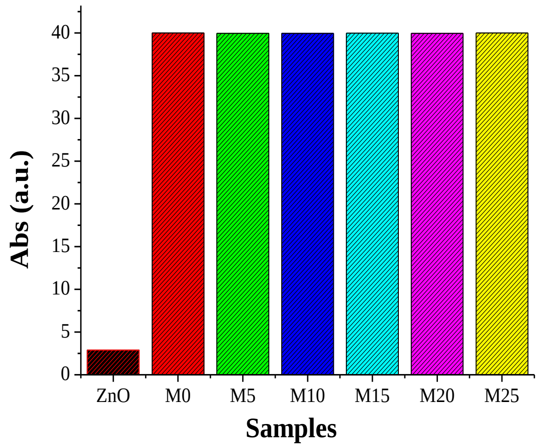


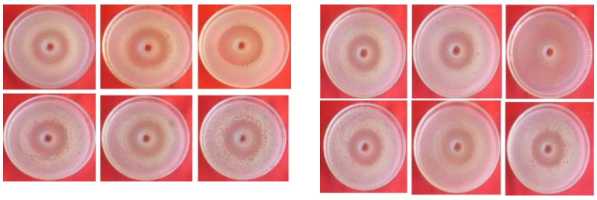
Figure 5. Comparative SPF graph illustrated from various samples

3.1. Antimicrobial Activity Performance

Table 3. Comparative inhibition zone against on six test organisms

	ZnO	ZnO + Thanaka
Test Organisms	**Inhibition Zones**	
Bacillus subtilis	42 mm (+++)	40 mm (+++)
Staphylococcus aureus	45mm (+++)	40mm (+++)
Pseudomonas aeruginosa	47 mm (+++)	50 mm (+++)
Bacillus pumalis	42 mm (+++)	40 mm (+++)
Candida albicans	41 mm (+++)	38 mm (+++)
Escherichia coli	42 mm (+++)	39 mm (+++)

Both pure ZnO nanoparticles and mixed samples showed strong antimicrobial activities against six test organisms including *Bacillus subtilis, Staphylococcus aureus, Pseudomonas aeruginosa, Bacillus pumalis, Candida albicans and Escherichia coli* respectively. Thus, they are very effective to apply as cosmetics due to their antimicrobial activities. Figure 6 showed the antimicrobial activities of ZnO and ZnO mixed with thanaka on six test organisms obtained from table 3.



(a) (b)

Figure 6. Antimicrobial activities of (a) ZnO nanoparticles and (b) ZnO nanoparticles mixed with thanaka

4. Conclusions

Low temperature solution method was very excellent technique for synthesis of ZnO nanoparticles. It was found that the sizes of ZnO nanoparticles precipitated in the synthesized solution were small enough to absorb the UVB radiation. The crystal phase investigated by XRD exhibited hexagonal system which was the most stable form in the ambient condition. As a result, ZnO nanoparticle advantages to mix with thanaka powder. The absorbance of ZnO nanoparticles measured by UV-Vis was additionally confirmed by FT-IR and XRD. All characterized results totally agreed that the previous investigation of nanoparticles were ZnO. The calculated SPF value of pure ZnO nanoparticles was found out to be 2.8770 and this value greatly increased to 40.00 when they were combined with thanaka. The antimicrobial activities of ZnO nanoparticles and mixed samples could strongly against the six test organisms. Therefore, all optimized samples were very useful, reliable and effective to use as a natural sunscreen due to their high SPF values.

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