

ZnO Nanosheets Exhibiting High UV Blocking Efficiency for Effective Application in Sunscreen

DOJALISA SAHU^{1,✉}, NIHAR R. PANDA^{2,*✉} and DEBASRITA DASH^{1,✉}

¹School of Applied Sciences, Centurion University of Technology and Management, Khurda-752050, India

²School of Basic Sciences, Indian Institute of Technology Bhubaneswar, Khurda-752050, India

*Corresponding author: E-mail: nihar@iitbbs.ac.in

Received: 17 March 2020;

Accepted: 6 May 2020;

Published online: 27 June 2020;

AJC-19953

Zinc oxide (ZnO) nanopowder has been prepared by wet chemical method and tested for its effective UV blocking property coated on photosensitive paper/fabric samples. Zinc acetate dihydrate and ammonium hydroxide were adopted as synthesis precursors. Phase and crystallographic analysis of the samples have been carried out by X-ray diffraction (XRD) and show that ZnO sample belong to hexagonal wurtzite phase without any impurity. Surface morphology of ZnO samples studied by field emission scanning electron microscopy (FESEM) shows the formation of nanosheets with porous structure. These porous nanosheets have surface area varying from 5000–30000 nm² with thickness 10–15 nm. ZnO nanosheets on the photosensitive paper show UV absorbance around 300 nm as observed from the absorption spectrum. The reflectance spectrum of ZnO also shows its effectiveness in reflecting UV light in the region of 350–400 nm. The sun protection factors (SPF) and ultraviolet protection factors (UPF) calculated from the above studies are also encouraging implicating the use of ZnO in sunscreen. The above experiment is carried out by preparing a photosensitive layer similar to human skin. Similar experiment has also been carried out by treating ZnO nanosheets on fabric samples and studying its effectiveness for protection from UV rays.

Keywords: Zinc oxide, X-ray diffraction, Nanosheet, UV-Blocking, Sunscreen, Reflectance.

INTRODUCTION

The destruction of the ozone layer due to rapid growth in industrialization and population has resulted alarming menace to living beings (human/animal and plant) [1]. Depletion of ozone layer allows the ultraviolet (UV) radiation to fall on human skin which leads to number of health issues *e.g.*, DNA damage, skin irritation/etching, acne, aging, skin cancer and other severe skin problems. Exposure of skin cells to UV radiation triggers the emergence of free radicals which cause biological damage and carcinogenic effects [1–3]. So, there is a necessity of formulation of products that may help in shielding human skin from UV radiation [4]. This leads to the search for skin friendly materials which can accord protection from the adverse effects of UV rays [5–7]. The UV-absorbing materials must have some of the features like high photo-stability, transparency, UV-absorption coefficient and affordability. Various UV-absorbers have been already prepared with inorganic and organic components. But, due to lower stability of the organic components present in the material, inorganic absorbers are commonly used

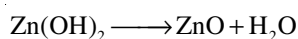
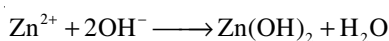
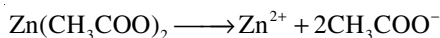
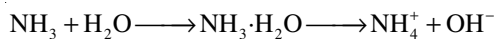
for better results due to their good scattering and reflecting properties [8]. Metal oxide semiconductor based inorganic UV absorbing materials demonstrate good heat-resistance and UV absorbance properties [9,10]. Nanoscale inorganic materials exhibit promising applications in this field as they offer good stability to protective coatings by absorbing the UV light [11]. Sun protection creams and textiles commonly use these types of materials to have protection against UV radiation. Harmful effects of UV-A (320–400 nm) and UV-B (290–320 nm) radiations are checked by these sunscreens. Further, textile industries apply these products to prepare UV protective fabrics for its sustainable use [12].

To absorb UV-radiation, the band gap of the materials must be comparable to the incident photon. So, nanomaterials of zinc oxide and titanium dioxide with higher band gaps are suitable for this purpose. These nanoparticles can eventually absorb/reflect/scatter UV-A and UV-B radiations providing safety attributes to the living cells [2]. Metal oxides such as: TiO₂ and CeO₂ have optical absorption in the range of 310–400 nm but the factors like noncoverage of whole UV range

and physical properties like coloration limits their application to a significant extent [9,13]. ZnO nanoparticles with novel characteristic attributes such as photoluminescence, photocatalysis, solar energy conversion and UV absorption are extensively studied for maximum implementation in consumer oriented products [14]. Unique electro-optical properties like transparency in the visible range and absorption in ultraviolet range are viable due to its wide band gap [15,16]. Due to high visible-light transparency and UV-light obstruction, ZnO can act as a good packaging material for UV white-LEDs [17,18]. Due to good photo and thermal stability, UV absorbents like ZnO is stable, non migratory within a matrix, impart improved properties and have longer service life as compared to other UV-protection candidates [14]. UV-blocking ability of nano ZnO significantly alters with size and morphology and after absorbing UV radiation, it transforms the energy into infrared light and dissipates as heat [19]. Oxidative damage to DNA molecules by free radicals evolved due to UV exposure can be avoided by application of ZnO nanoparticles on skin. This may be achieved by elevation in the UV-protection factor (UPF) by coating ZnO nanopowders [20-22]. The morphology of ZnO evolving out of various synthesis techniques plays very important role in determining its utilization as UV-radiation absorbers. The preparation of ZnO nanoparticles by various techniques such as sol-gel method [23,24], precipitation [25], hydro-thermal synthesis [26] and spray pyrolysis [26-28] have been reported. Among these methods, soft-solution route is one of the simple and fruitful techniques to prepare nano ZnO in variety of morphology. In this present work, ZnO nanopowder is prepared and coated on photosensitive paper and cotton fabric to study its UV blocking properties.

EXPERIMENTAL

For this experiment, zinc acetate dihydrate and NH_3 were taken directly without further purification. Zinc acetate dihydrate (0.1 M) was dissolved in 20 mL of distilled water and the resulting solution was stirred continuously and liquid ammonia was added dropwise to the above solution till a white precipitate was obtained. The pH of the solution was measured before and after the process of precipitation and found to be 8.7 and 10.5, respectively. The precipitate was collected through centrifugation and washed several times with water and acetone and collected. The prepared nanopowder was dried at 100 °C for 24 h overnight. The possible chemical reaction involved in the synthesis [29] is represented as follows:



Structural analysis of the samples was carried out using XRD by using a diffractometer (X' Pert Pro, M/s Panalytical). The morphology of the samples was studied by FESEM (M/s Zeiss). The UV absorbance was measured by UV-VIS spectrometer (M/s Shimadzu, Spec-1000). Photosensitive paper (cellu-

lose made) was prepared by coating a sheet of paper with a water-soluble, bluish-green compound called iron(III) hexacyanoferrate(III). A gel was prepared by 5 mL of glycerin mixed with 0.025 g of prepared nano ZnO by sono-chemical method. The paper was coated with this gel and exposed to sunlight for 20 min until the photo-sensitive paper turns pale blue. The paper was taken out from sunlight and allowed to soak water for about 2 min and dried later. Similarly, the absorption study was carried out by smearing prepared nano ZnO gel with bleached cotton fabric and exposed to solar light for 20 min to measure the absorbance and transmittance. The ultraviolet protection factors (UPF) and sun protection factors (SPF) were calculated from the experiment.

RESULTS AND DISCUSSION

Structural and morphological analysis: X-ray diffraction data of the prepared sample has been recorded using $\text{CuK}\alpha$ radiation (1.5418 Å). XRD pattern of the nanoparticles synthesized by wet-chemical method is displayed in Fig. 1. The peak positions are identified and indexed by comparing the standard JCPDS. It shows that the standard pattern of wurtzite ZnO is matched with the pattern recorded for the prepared sample. The XRD pattern of ZnO illustrated in Fig. 1 does not show any peak related to any impurity such as $\text{Zn}(\text{OH})_2$, $\text{Cu}(\text{OH})_2$, etc. This indicates the high purity of the product. However, the intensities of different peaks representing the growth of ZnO nanoparticles along different planes differ substantially. The highest intensity is obtained for the (100) peak indicating the growth of ZnO along this plane. The crystallographic parameters of ZnO have been calculated and the values (Table-1) are close to the standard crystallographic data obtained for Wurtzite ZnO.

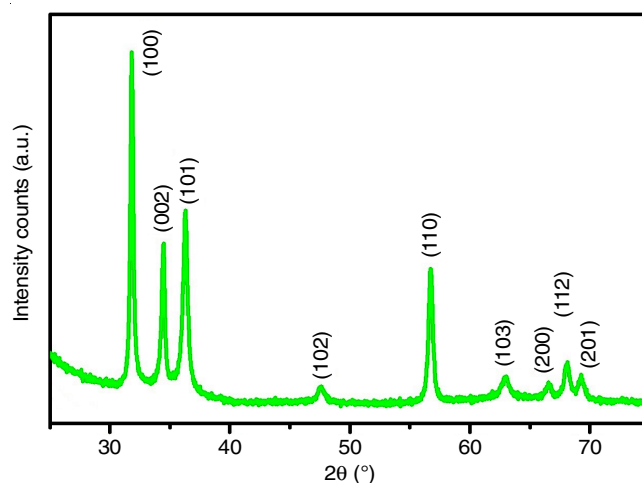


Fig. 1. X-ray diffraction spectrum of ZnO nanopowder

TABLE-1
CRYSTALLOGRAPHIC PARAMETERS OF ZnO NANOPOWDER

Crystallographic parameters (Å)	Value
a	3.689
c	5.974
u	0.377
Bond length	5.092

Surface morphology of ZnO nanopowder has been investigated by FESEM measurements and shows the formation of nanosheets of irregular shape (Fig. 2). The area of these nanosheets varies from 5000-30000 nm² with thickness ranging from 10-15 nm. These nanosheets are of high density and observed to have porous structure. Owing to higher surface area, these nanosheets are more favorable to show different optical properties like photoluminescence/UV absorbance/reflectance.

UV blocking studies: When UV light is irradiated on the photosensitive paper, a chemical reaction triggered. This results the change of water-soluble bluish-green coloured iron hexacyanoferrate(III) {Fe[Fe(CN)₆]} into water-insoluble Prussian blue coloured iron(III) hexacyanoferrate(II), Fe₄[Fe(CN)₆]₃. The water soluble portion washed away upon rinsing with water but the water-insoluble part remains intact on the paper. The light exposure time of the photosensitive paper and the intensity of the light source largely define the intensity of the Prussian blue. The above experiment of photosensitive paper works in sunny day. In this present study, ZnO nanopowder was taken for gel preparation for the coating of photosensitive paper and cotton fabric in order to give a better result and good adhesion. The prepared ZnO nanoparticle was smeared uniformly on

the photosensitive paper (Fig. 3a) and exposed to solar light for 20 min. The absorbance was recorded by the UV-VIS spectrophotometer to calculate the SPF factor. Fig. 3b shows the absorbance spectrum of ZnO coated on the photosensitive paper after exposing to sun light. The wavelength of the peak is found to be 299 nm. The above experiment is carried out to determine the sun protection factor for ZnO nanoparticles. ZnO is well known as an inorganic UV filter. There are some superior features of inorganic UV blockers such as non-toxic nature and chemical/thermal stability in higher temperature under UV irradiation as compared to organic counterparts for which these are suitably used. Sun blocking agents are the materials, which reflect and block the rays of sunlight. A mathematical equation has been proposed utilizing the data of the UV spectrophotometer to determine the SPF of synthesized nanoparticles which has been given in eqn. 1. As reported in literature, a standard sunscreen formulation contains 8% homosalate with SPF of 4 and any value greater than this is more effective [30].

$$SPF = CF \cdot \sum_{290}^{320} EE(\lambda) \cdot I(\lambda) \cdot ABS(\lambda) \quad (1)$$

where $EE(\lambda)$ is the erythemal effect spectrum; $I(\lambda)$ is the solar intensity spectrum; $ABS(\lambda)$ is the absorbance of sunscreen product; and CF is the correction factor (=10).

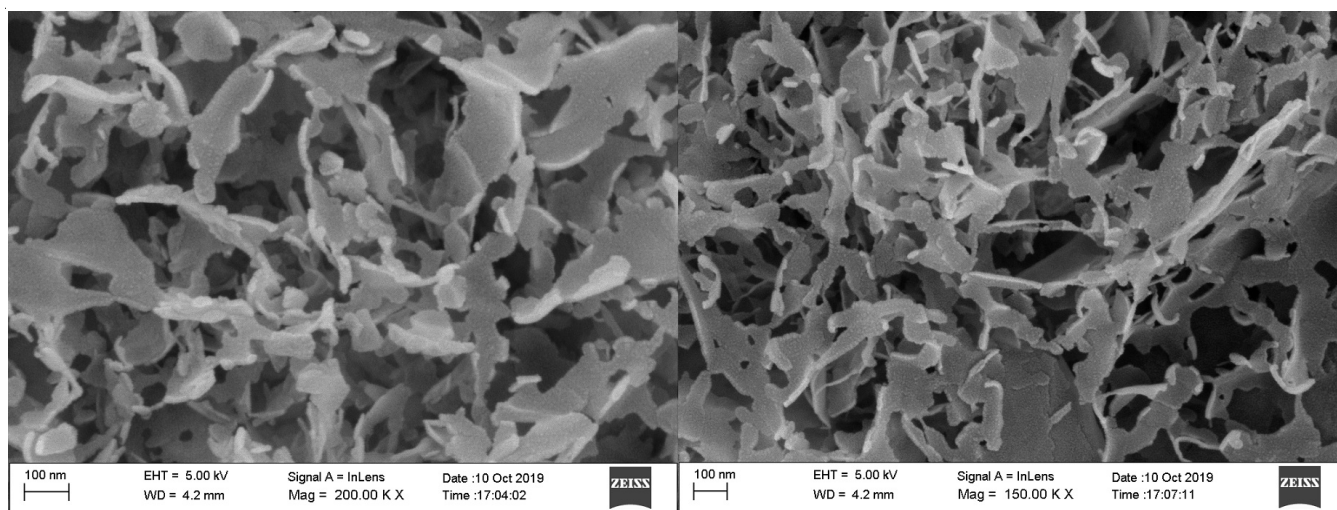


Fig. 2. FESEM images of ZnO

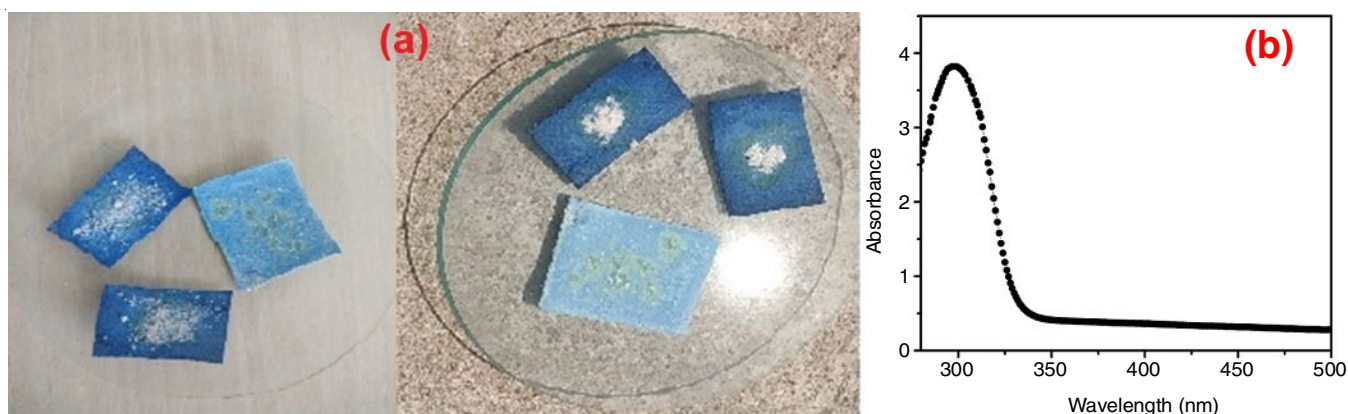


Fig. 3. (a) UV blocking experiment with photosensitive paper and (b) UV-VIS absorption spectrum of ZnO nanopowder on photosensitive paper

The product of $EE(\lambda)$ and $I(\lambda)$ is a constant and given in Table-2 [31,32]. The absorbance of ZnO nanoparticles is found to be 299 nm from the absorption spectra. Accordingly, the value of SPF is calculated using this data and found to be 28 ± 0.0054 . This result of SPF value falls on skin prototype-II (which burns easily but tan minimally) category [33]. The higher value of SPF indicates the more effective nature of the product in prevention of sunburn. It has been found that by increasing the concentration of coating in the photosensitive paper, the SPF value also increases. ZnO has many advantages over other UV-blockers as it possesses features like broader range of protection over long periods and non-whitening of skin. These UV-protecting properties of materials are based on the scattering and/or absorption of light. ZnO absorbs both UV-A and UV-B radiations and re-emit it as visible light in the form of fluorescence or heat. It protects the skin as it is applied on it by scattering, absorbing and reflecting the UV-radiation. ZnO nanoparticles used as a vital constituent of sunscreen formulations used in present days due to its better photoprotective attributes with minimized risk of skin irritation compared to other sunscreen agents.

TABLE-2
NORMALIZED PRODUCT FUNCTION
USED IN THE CALCULATION OF SPF

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

UV protective properties of ZnO are studied by measuring its reflectance and transmittance. Some pieces of cotton cloth/fabric was dipped in ZnO gel (prepared with glycerol) and exposed to solar light. The reflectance/transmittance spectra were recorded and studied. The reflectance spectra of ZnO nanoparticles coated on the cotton fabric has been illustrated in

Fig. 4a along with the reflectance spectra of uncoated cotton. It has been observed that cotton fabric coated with ZnO shows 21% of UV light reflection as compared to normal cotton. So, by treating ZnO nanoparticles on fabric materials may formulate good UV shielding dress materials with a better blocking efficiency. Ultraviolet protection factor is related to the reflectance and absorbance of UV radiation after falling on a material. This UPF factor has been calculated for our experiment which indicates the protection efficiency of ZnO nanoparticle over the cotton materials. The measure of UV light blocked by any fabric material may be explained in terms of the UPF value. The textile material will provide more UV protection if its UPF value is high. Fig. 4b depicts the transmittance spectrum of the fabrics treated with ZnO nanoparticles. The blank reference was air while conducting the experiment. The UPF is calculated using the data obtained from transmission spectra using the eqn. 2 [10,34-37]. The detailed experimental steps adopted have been shown in Fig. 5.

$$UPF = \frac{\int_{\lambda_1}^{\lambda_2} E(\lambda) \cdot S(\lambda) \cdot d\lambda}{\int_{\lambda_1}^{\lambda_2} E(\lambda) \cdot S(\lambda) \cdot T(\lambda) \cdot d\lambda}$$

where $E(\lambda)$ is the relative erythemal spectral effectiveness; $S(\lambda)$ is the solar spectral irradiance in $W m^{-2} nm^{-1}$; $T(\lambda)$ is the spectral transmission of the sample; and $d\lambda$ is the measure of wavelength (nm).

The National Oceanic and Atmospheric Administration database (NOAA) has been used to determine the values of $E(\lambda)$ and $S(\lambda)$. The UPF value has been found out for both UV-A (315-400 nm) and UV-B (295 and 315 nm) regions by extracting the percent of UV transmission data from the transmission spectra of the cotton samples. The value is found to be approximately 2.25, which falls in the range of standard value (according to UV STANDARD 801 for light woven cotton clothing). The UPF of cotton fabric samples coated with ZnO nanoparticles is higher than that of uncoated ones which shows the UV absorption capacity of ZnO nanoparticles on the surface

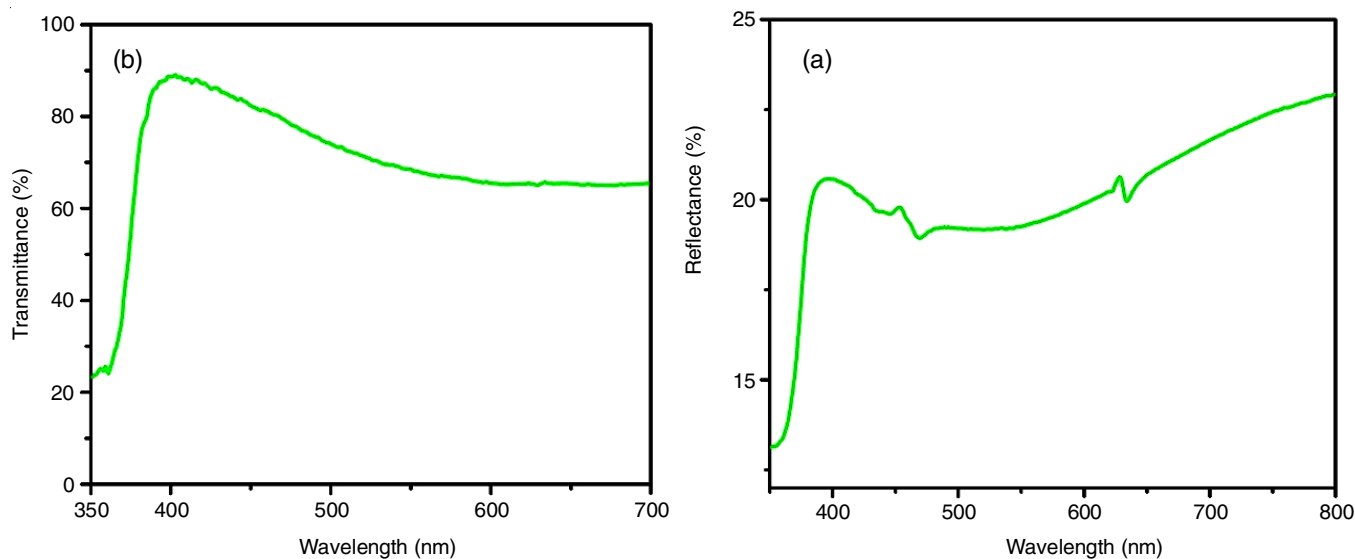


Fig. 4. (a) % Reflectance and (b) % transmittance of ZnO on photosensitive paper

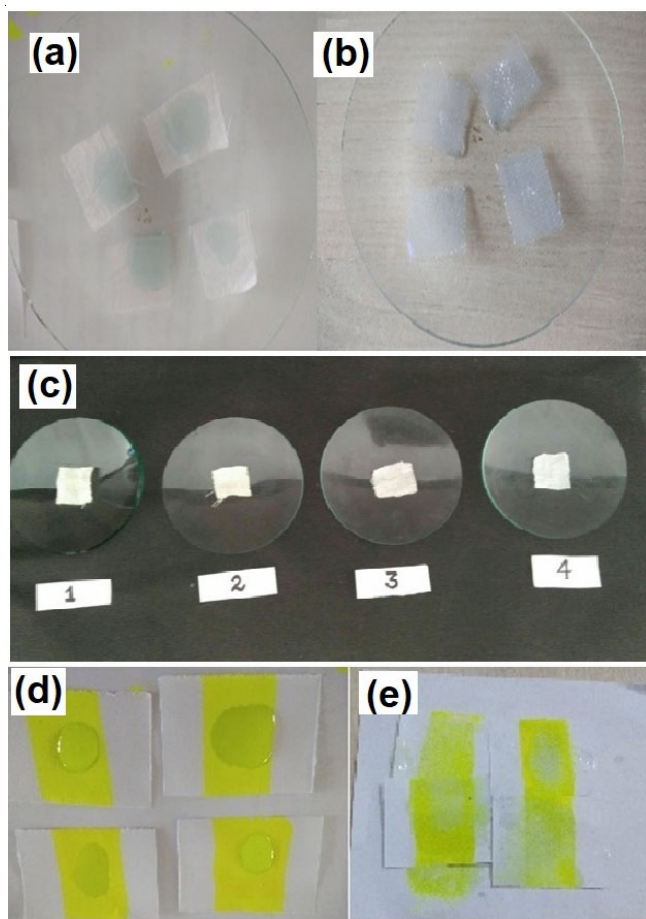


Fig. 5. (a-e) Different stages of experiment for evaluating the UV blocking efficiency of ZnO on cotton fabric

of the cotton fabric [30]. For this purpose, ZnO is preferentially used in nano-sized formulations which will provide higher durability and more intensive absorption/blocking of UV light [35,38-42].

Conclusion

The present study deals with the synthesis of novel ZnO nanoparticles by wet chemical route and its effective use as UV protective agents in sunscreen and textile materials. The nanoparticle property has been analyzed by measurement techniques like XRD, FESEM and UV-Vis spectrophotometry. The structural analysis of the samples enumerates the growth of ZnO along (100) as nanosheets with higher surface area. The UV protective property of ZnO has been studied by recording its absorbance/reflectance/transmittance by coating it on photosensitive paper and cotton fabric samples. ZnO nanoparticles exhibit excellent UV shielding and transparency properties in both the UV-A and UV-B region. The sun protection factor and UV protection factor are also evaluated by exposing the coated sample to direct and intense solar radiation. As per the result, it is verified that the prepared nanoparticles will be effective in preparation of sunscreen and UV-shielding fabric.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. A.F. Bais, R.M. Lucas, J.F. Bornman, C.E. Williamson, B. Sulzberger, A.T. Austin, S.R. Wilson, A.L. Andrad, G. Bernhard, R.L. McKenzie, P.J. Aucamp, S. Madronich, R.E. Neale, S. Yazar, A.R. Young, F.R. de Grujil, M. Norval, Y. Takizawa, P.W. Barnes, T.M. Robson, S.A. Robinson, C.L. Ballaré, S.D. Flint, P.J. Neale, S. Hylander, K.C. Rose, S.-Å. Wängberg, D.-P. Häder, R.C. Worrest, R.G. Zepp, N.D. Paul, R.M. Cory, K.R. Solomon, J. Longstreth, K.K. Pandey, H.H. Redhwi, A. Torikai and A.M. Heikkilä, *Photochem. Photobiol. Sci.*, **17**, 127 (2018); <https://doi.org/10.1039/C7PP90043K>
2. A. Wiesenthal, L. Hunter, S. Wang, J. Wickliffe and M. Wilkerson, *Int. J. Dermatol.*, **50**, 247 (2011); <https://doi.org/10.1111/j.1365-4632.2010.04815.x>
3. A. El-Shafei and A. Abou-Okeil, *Carbohydr. Polym.*, **83**, 920 (2011); <https://doi.org/10.1016/j.carbpol.2010.08.083>
4. P.G. Parejo, M. Zayat and D. Levy, *J. Mater. Chem.*, **16**, 2165 (2006); <https://doi.org/10.1039/b601577h>
5. P. Hayoz, W. Peter and D. Rogez, *Prog. Org. Coat.*, **48**, 297 (2003); [https://doi.org/10.1016/S0300-9440\(03\)00102-4](https://doi.org/10.1016/S0300-9440(03)00102-4)
6. A. Piegari and P. Polato, *J. Opt. A: Pure Appl. Opt.*, **5**, 152 (2003); <https://doi.org/10.1088/1464-4258/5/5/357>
7. J. Aarik, A. Aidla, A.A. Kiisler, T. Uustare and V. Sammelselg, *Thin Solid Films*, **305**, 270 (1997); [https://doi.org/10.1016/S0040-6090\(97\)00135-1](https://doi.org/10.1016/S0040-6090(97)00135-1)
8. F. Aloui, A. Ahajji, Y. Irmouli, B. George, B. Charrier and A. Merlin, *Appl. Surf. Sci.*, **253**, 3737 (2007); <https://doi.org/10.1016/j.apsusc.2006.08.029>
9. H. Cui, M. Zayat, P.G. Parejo and D. Levy, *Adv. Mater.*, **20**, 65 (2008); <https://doi.org/10.1002/adma.200701960>
10. M.S. Ghamsari, S. Alamdari, W. Han and H.-H. Park, *Int. J. Nanomed.*, **12**, 207 (2017); <https://doi.org/10.2147/IJN.S118637>
11. M. Thiruvengadam, G. Rajakumar and I.M. Chung, *3 Biotech.*, **8**, 74 (2018); <https://doi.org/10.1007/s13205-018-1104-7>
12. G. Reinert, F. Fuso, R. Hilfiker and E. Schmidt, *Text. Chem. Color.*, **29**, 36 (1997).
13. G. Broasca, G. Borcia, N. Dumitrascu and N. Vranceanu, *Appl. Surf. Sci.*, **279**, 272 (2013); <https://doi.org/10.1016/j.apsusc.2013.04.084>
14. N.R. Panda, D. Sahu and B.S. Acharya, *Curr. Appl. Phys.*, **15**, 389 (2015); <https://doi.org/10.1016/j.cap.2015.01.014>
15. O.S. Kushwaha, C.V. Avadhani and R.P. Singh, *Carbohydr. Polym.*, **123**, 164 (2015); <https://doi.org/10.1016/j.carbpol.2014.12.062>
16. M. Eita, L. Wagberg and M. Muhammed, *ACS Appl. Mater. Interfaces*, **4**, 2920 (2012); <https://doi.org/10.1021/am300243u>
17. A. Becheri, M. Dürr, P. Lo Nostro and P. Baglioni, *J. Nanopart. Res.*, **10**, 679 (2008); <https://doi.org/10.1007/s11051-007-9318-3>
18. Y.-Q. Li, S.-Y. Fu and Y.-W. Mai, *Polymer*, **47**, 2127 (2006); <https://doi.org/10.1016/j.polymer.2006.01.071>
19. Y.J. Lee, D.S. Ruby, D.W. Peters, B.B. McKenzie and J.W. Hsu, *Nano Lett.*, **8**, 1501 (2008); <https://doi.org/10.1021/nl080659j>
20. J.L. Ge, X.F. Zeng, X. Tao, X. Li, Z. Shen, J. Yun and J. Chen, *J. Appl. Polym. Sci.*, **118**, 1507 (2010); <https://doi.org/10.1002/app.32530>
21. C. Huang, F.S. Yang, H. Wang, H.J. Zhang and L.J. Zhang, *Text. Res.*, **27**, 12 (2006).
22. Y.B. Han, J.B. Han, S. Ding, D.J. Chen and Q.Q. Wang, *Opt. Express*, **13**, 9211 (2005); <https://doi.org/10.1364/OPEX.13.009211>
23. N.B. Hubbard, M.L. Culpepper and L.L. Howell, *Appl. Mech. Rev.*, **59**, 324 (2006); <https://doi.org/10.1115/1.2345371>
24. H.J. Lee, S.Y. Yeo and S.H. Jeong, *J. Mater. Sci.*, **38**, 2199 (2003); <https://doi.org/10.1023/A:1023736416361>

25. L. Wang and M. Muhammed, *J. Mater. Chem.*, **9**, 2871 (1999); <https://doi.org/10.1039/a907098b>
26. H.Y. Xu, H. Wang, Y.C. Zhang, W.L. He, M.K. Zhu, B. Wang and H. Yan, *Ceram. Int.*, **30**, 93 (2004); [https://doi.org/10.1016/S0272-8842\(03\)00069-5](https://doi.org/10.1016/S0272-8842(03)00069-5)
27. T. Tani, L. Mädler and S.E. Pratsinis, *J. Nanopart. Res.*, **4**, 337 (2002); <https://doi.org/10.1023/A:1021153419671>
28. L.H. Li, J.C. Deng, H.R. Deng, Z.L. Liu and L. Xin, *Carbohydr. Res.*, **345**, 994 (2010); <https://doi.org/10.1016/j.carres.2010.03.019>
29. D. Sahu, B.S. Acharya, B.P. Bag, Th. Basanta Singh and R.K. Gartia, *J. Lumin.*, **130**, 1371 (2010); <https://doi.org/10.1016/j.jlumin.2010.02.049>
30. J.S. Mansur, M.N.R. Breder, M.C.A. Mansur and R.D. Azulay, *An. Bras. Dermatol.*, **61**, 121 (1986).
31. R.M. Sayre, P.P. Agin, G.J. Levee and E. Marlowe, *Photochem. Photobiol.*, **29**, 559 (1979); <https://doi.org/10.1111/j.1751-1097.1979.tb07090.x>
32. C. Walters, A. Keeney, C.T. Wigal, C.R. Johnston and R.D. Cornelius, *J. Chem. Educ.*, **74**, 99 (1997); <https://doi.org/10.1021/ed074p99>
33. A.P. Fonseca and N. Rafaela, *Health Care Curr. Rev.*, **1**, 108 (2013); <https://doi.org/10.4172/2375-4273.1000108>
34. S. Kathirvelu, D. Souzaa and B. Dhurai, *Indian J. Fibre Text. Res.*, **34**, 267 (2009).
35. A.R.R. Abdel Ghani, W.A.R. Qorshi, A.F.A.H.A. Romyia and E.R.S. El-Sayd, *Int. Design J.*, **4**, 103 (2015).
36. T. Gambichler, A. Avermaete, A. Bader, P. Altmeyer and K. Hoffmann, *Br. J. Dermatol.*, **144**, 484 (2001); <https://doi.org/10.1046/j.1365-2133.2001.04072.x>
37. T. Gambichler, K.L. Hatch, A. Avermaete, P. Altmeyer and K. Hoffmann, *Photodermatol. Photoimmunol. Photomed.*, **18**, 29 (2002); <https://doi.org/10.1034/j.1600-0781.2002.180105.x>
38. D. Sahu, N.R. Panda, B.S. Acharya and A.K. Panda, *Opt. Mater.*, **36**, 1402 (2014); <https://doi.org/10.1016/j.optmat.2014.03.041>
39. N.R. Panda, B.S. Acharya, P. Nayak and B.P. Bag, *Ultrason. Sonochem.*, **21**, 582 (2014); <https://doi.org/10.1016/j.ultsonch.2013.08.007>
40. N.R. Panda, B.S. Acharya and P. Nayak, *Mater. Lett.*, **100**, 257 (2013); <https://doi.org/10.1016/j.matlet.2013.03.059>
41. D. Dash, N.R. Panda and D. Sahu, *Appl. Surf. Sci.*, **494**, 666 (2019); <https://doi.org/10.1016/j.apsusc.2019.07.089>
42. D. Sahu, N.R. Panda and B.S. Acharya, *Mater. Res. Express*, **4**, 114001 (2017); <https://doi.org/10.1088/2053-1591/aa9597>