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Biologically Prepared ZnO Nanoparticles for Effective Transparent Sunscreen Applications†

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Sunscreens are used to provide protection against adverse effects of ultraviolet (UV)B (290-320 nm) and UVA (320-400 nm) radiation. The nanosized ZnO with the features of large volume to area ratio, high ultraviolet absorption and long life-span has been widely used as catalyst, UV absorber in cosmetics and solar cell applications. ZnO belongs to a group of metal oxides, which is characterized by photo catalytic ability and photo-oxidizing capacity against chemical and biological species. Here ZnO nanoparticles have been prepared by using chemical reduction method. Characterization studies such as XRD gives information about crystalline structure and Ultraviolet-visible spectroscopy is used to calculate the absorption peak of the material and Fourier transform infrared spectroscopy describes local environment around ZnO nanoparticles. Photoluminescent activity of biocompatible polymer coated and uncoated ZnO nanoparticles was studied.

Key Words: ZnO naoparticles, Biological synthesis, Free radicals, Avocado fruit, Photoluminescence study.

INTRODUCTION

ZnO is a wide-band gap semiconductor of the II-VI semiconductor group which has some favourable properties that includes good transparency, high electron mobility, wide band gap, high excitation energy and strong room-temperature luminescence. These properties are being widely used in existing as well as emerging applications like solar cells, textiles, electronics, optoelectronics, liquid crystal displays, light emitting diodes, thin film transistors and in cosmetics like sunscreens[1-6]. In sunscreen applications, because of the ingredient of bulk ZnO, it leaves a whitish tint when applied to the skin, but when ZnO nanoparticle is used in sunscreen application due to its transparent nature, it doesn't leave any tint on the skin while applying.

In the present work, we have investigated first through chemical method and then through biological method by making three varying extracts using *Persea americana* (avocado fruit). Then we made a comparative study of chemically prepared and biologically prepared ZnO by the photoluminescence study. Compared to titanium dioxide (TiO_2), ZnO is considered to be a good ingredient in sunscreen applications because of its wide bandgap due to which they can block UVA rays[7] which are at the wavelength range of 320-400 nm. It has been a drawback that free radicals may be produced due to the inclusion of chemically prepared ZnO nanoparticles. The fruit or mesocarp of *P. americana* contains flavonoids and they are also a free radical scavengers. The coconut milk added to one of the extract to produce oil is also a free radical scavengers. Also, avocado fruit contains vitamins like B-6, C, E and K. Cocunut milk contains vitamins like B, C and E. The presence of vitamin C due to its antioxidant properties, makes it a vital molecule for skin health. So, this biologically prepared ZnO nanoparticle may help to overcome the drawback of free radical formation on sunscreen applications.

EXPERIMENTAL

0.45 M of aqueous solution of zinc nitrate dihydrate and 0.9 M of aqueous solution of sodium hydroxide are prepared. NaOH solution is heated at a temperature of *ca.* 55 ºC. Zinc nitrate dihydrate solution is added dropwise for *ca.* 40-50 min to the solution under high speed stirring. Zinc hydroxide and sodium nitrate will be formed and the beaker is seated at this condition for *ca.* 2 h. Finally a precipitate will be formed which is cleaned 2-3 times with deionized water and ethanol. The obtained nanoparticle is calcined at 500 ºC for about 3 h to obtain a pale yellowish fine powder.

Biological extracts: Avocado fruit (*ca.* 1) kg and one coconut was collected from the local market to prepare the biological extract.

Aqueous extract: Half of the mesocarp of one avocado fruit was taken and crushed to a fine paste using a blender.

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The paste is mixed with *ca.* 50 mL of distilled water. The mixture is then strained in muslin cloth to get *ca.* 40-45 mL of aqueous extract.

Oil extract: The mesocarp of two avocado fruits are taken and crushed to a fine paste using a blender. The endosperm of one coconut is grated and grinded with 150 mL of distilled water in a blender which is then strained to obtain the coconut milk. The paste is mixed with coconut milk and cooked for *ca.* 135 min at about medium temperature. Initially the mixture was of pale green colour and finally it was of dark brown colour. As it gets cooked, it starts to ooze out oil. The final cooked product is then strained in a muslin cloth to get avocado oil of *ca.* 30 mL.

Liquid extract: Half of the avocado mesocarp of one avocado fruit and one seed is crushed to paste using a blender. About 100 mL of distilled water is mixed with it and cooked at medium temperature for *ca.* 0.5 h. Then it is allowed to slightly cool down and strained in muslin cloth to obtain a thick liquid exract of *ca.* 55-60 mL.

Synthesis procedure

Synthesis with 2 mL aqueous extract (sample-a): 0.1 M of aqueous solution of $Zn(NO_3)_2{\cdot}2H_2O$ and 0.5 g of NaOH with 20 mL of distilled water has been used as starting materials to which 2 mL of aqueous extract has been added and kept under vigorous stirring. The pH value was noted to be 10 at the end of 1 h. After stirring for *ca.* 3 h, a light yellow precipitate was obtained finally.

Synthesis with 5 mL aqueous extract (sample-b): 0.5 M of aqueous solution of zinc nitrate dehydrate and 0.5 g of NaOH with 20 mL of distilled water are mixed with 5 mL of aqueous extract and kept for vigorous stirring for *ca.* 1.5 h. At the end of 1 h the pH value was 10. Finally, a yellow precipitate was obtained.

Synthesis with 5 mL oil extract (sample-c): 0.5 M of aqueous solution of zinc nitrate dehydrate and 0.5 g of NaOH with 20 mL of distilled water was initially take. 5 mL of avocado oil is added to the initial mixture and kept for vigorous stirring. After 1.5 h the pH value was 12. After 1 h and 45 min, the liquid was at bottom and foam was formed at the top on stirring, slowly the foam and liquid gets mixed up to form a fine cream at the end of 2.5 h. After 3 h, a thick precipitate of light green colour has been obtained.

Synthesis with liquid extract (sample-d): 0.5 M of aqueous solution of zinc nitrate dihydrate and 1.0 g of NaOH with 40 mL of distilled water are mixed initially. 10 mL of liquid extract is added to them, which is then kept for vigorous stirring, for *ca.* 2 h. Finally, a brown colour precipitate was obtained.

All the four samples are then transferred to the crucibles and calcined at 600 ºC for *ca.* 2 h. The calcined samples are crushed to fine powder and transferred to the micro centrifuge tubes.

RESULTS AND DISCUSSION

UV spectrophotometer: In sample A there was a strong light absorption ($\pi \rightarrow \pi^*$) at the wavelength of 220 nm and there is a weak light absorption ($n \rightarrow \pi^*$) near 370 nm. The energetically most favourable ($\pi \rightarrow \pi^*$) excitation has occurred from highest energy bonding π-orbital (HOMO) to the lowest energy bonding π-orbital (LUMO). When 2 mL of aqueous extract is taken (sample A) and when 5 mL of aqueous extract is taken (sample B), the strong absorption was found to be of same range whereas the light absorption range has increased as there is an increase in concentration of extract. With 5 mL of oil (sample C), strong absorption was at 212 nm and light absorption was at 371 nm and with 5 mL of liquid extract (sample D), there was only a strong absorption at 213 nm. With the chemically synthesized sample E strong absorption was at 379 nm.The intensity of absorption is comparatively high in biologically prepared samples to that of chemically prepared sample.

FTIR: The presence of functional groups in samples a,b,c and d are nearly same, with the change in transmittance percentage from one another. It shows that it has a C=X stretch region with multiple, sharp and medium peaks. There is a peak around 1600 cm^{-1} and several others at lower wave numbers. There are aromatic C-H peaks *ca.* 3000 cm^{-1}. In sample e, there is a change in spectrum pattern comparing to all other samples. In 1300-1000 cm^{-1}, C-O bonding occurs and a strong absorption is observed here. There was a multiple sharp and medium peaks in the region of 1600-1400 cm^{-1}, sharp and medium intensity peaks occur in the region of 2260-2210 cm^{-1}. There was also a very broad signal in the region of 3300-2500 cm^{-1}, centered near 3000 cm^{-1}.

XRD: In sample a the intensity of the peak at maximum was *ca.* 30 in the 2θ position. In sample b there are two successive maximum peaks one at the value of 2θ as 30 and another *ca.* 37. In sample c, 2θ values are nearly same as sample b, but there is a variation in the intensity height. In sample d, for the value of 2θ at 30, intensity is little less than other samples, the maximum intensity peak was *ca.* 37 for the sample e. The maximum intensity peaks were above 6000, above 2000, above 1000, above 3000 and above 10000 for the samples a,b,c and d, respectively.

Conclusion

The 'green' route for nanoparticle synthesis is of great interest due to eco-friendliness, economic prospects, feasibility and wide range of applications in nanomedicine, catalysis medicine, nano-optoelectronics, *etc*. The green ZnO nanoparticle is synthesized using avocado fruit (*Persea americana*) because avocado fruit acts as free radical scavenger. The main point of synthesizing ZnO nanoparticle is for the application of transparent sunscreen since avocado fruit is strong anticancer activity and it prevents cell damage.This green synthesis approach shows that the environmentally benign and renewable latex of Avocado fruit and coconut can be used as an effective stabilizing as well as reducing agent for the synthesis of zinc oxide nanoparticles. These results inspire further experiments based on temperature dependence photoluminiscence for better clarifications of the optical properties occur in ZnO nanoparticles. Cosmetic industries can bank upon this product in order to synthesize sunscreen lotions *etc*., which would be done in the immediate future.

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