In situ synthesis and characterizations of ZnO nanoparticles modified cotton fibre.

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Abstract

An attempt was made to obtain fabric made out of zinc oxide coating and cotton fibre with an improved performance towards heat and wet. A cheap, biodegradable, biocompatible biopolymer i.e. cotton fabric was modified with zinc oxide nanoparticles using a cheaper in-situ deposition process and checked for multifunctional properties such as photocatalytic purity and hydrophobicity. Ultrasonic impregnation of ZnO NPs into cotton fabric structure was performed homogeneous mixing, focusing on the concentration, shape and size of ZnO NPs. The surface morphology was characterized by scanning electron microscopy. Due to the presence of ZnO NPs great roughness was observed on the modified surface. Photocatalytic cleaning has been verified by putting a stain of turmeric or tea on the modified fiber and exposing it to sunlight. The hydrophobicity is analyzed by measuring the contact angle of the liquid, and the contact angles of the modified cotton is 125.50. XRD data shows the wurtzite structure of the coated ZnO nanoparticles and the improved crystallinity after modification.UV-Visible analysis proved the presence of ZnO NPs in cotton or cellulose structure and by TGA study the improved thermal stability of the modified fiber was confirmed.

Keywords: ZnO NP, hydrophobicity, SEM, XRD,UV-VIS, TGA.

I. INTRODUCTION

Cellulose is the most common and widely distributed biopolymer. Due to its abundance, biodegradability and special properties, cellulose is a very important renewable raw material that can be used to develop ecological, biocompatibility and functional materials prior to it's traditional and large-scale use in paper and cotton fabric manufacturing. Cellulose is widely used in membrane separation, pharmaceutical, cosmetic and food industries [1]. Although cellulose has good properties, it has some undesirable ones such as low tensile strength, high moisture regain, and low strength against microbial attack [2]. A no.of research has been carried out to in recent years to fulfil the shortcomings of cellulose through various processes such as grafting, blending, or blending. Zinc oxide nanoparticles have not only been artificially used for textile purposes, but also used for many other purposes with cellulose acetate and cotton fabrics to improve functional properties like food packaging, water treatment and cotton cloth [3-8].

In this work, cotton fabric was modified in situ using zinc oxide nanoparticles, and various changes in functional properties were observed. In-situ synthesis refers to the instant synthesis of fiber modification and nanoparticle

synthesis or mixing occur simultaneously. Use in-situ synthesis instead of traditional methods because it provides the best adhesion of zinc oxide particles to the fiber or film surface. The fiber modified according to the classic method is obtained by synthesizing the fiber and then coating it with nanoparticles, but using this method, the adherence of nanoparticle to the fiber surface is amazing . The in-situ synthesis method was used to ensure better adhesion between the surface and the particles, and the resulting film was characterized by UV-VIS,SEM,XRD and TGA analysis.

II. MATERIALS AND METHODS

2.1.Materials

The fiber cotton is brought from the local clothing store. Zinc acetate dihydrate, DMF(E-Merck), sodium hydroxide and ethyl alcohol were reagent grade chemicals and used as such.

2.2 Experimental Methods

2.2.1.Preparation of ZnO nanoparticles

10.97 g $Zn(CH_3COO)_2.2H_2O$ was dissolved in 50 ml ethanol for 30 minutes under a constant magnetic stirrer. Dissolve 40 g of NaOH in 100 ml of distilled water to make a 1 M solution. Then the NaOH solution was mixed with the zinc acetate solution. A white precipitate of ZnOH is formed. In order to obtain a uniform colloidal solution, the mixed solution is stirred on a magnetic stirrer at 250 rpm and 270°C for 3 hours, and then the solution mixture is allowed to stand until the precipitation is stable. Separated by decantation process. The resulting precipitate was washed twice with acetone and then washed three times with distilled water.Then the ZnOH precipitate was heated in a hot air oven at 970°C for about 4 hours to dehydrate the ZnOH powder into ZnO. Then the prepared ZnO nanoparticle sample was weighed on a digital balance, and the result was 4.11 g.

2.2.2.Modification of Cotton fiber with ZnO nanoparticles

Initially, a 0.04 M zinc acetate dihydrate solution was prepared by mixing 0.43 g weighed zinc acetate dihydrate using a digital balance and mixing the weighed zinc acetate with 50 ml distilled water. Then prepare a 0.04 M NaOH solution by dissolving 0.16 g NaOH in 100 ml. Then the two solutions were mixed under ultrasound for about 2 hours, and the pH of the solution was measured with a pH meter. It was found that the mixture had a pH of 6.22 at a normal temperature of 27°C. The cotton purchased from local clothing store was cut into 4 cm pieces, rinsed with ethanol, and then dried at room temperature. The dried cotton fibers are then immersed in the zinc oxide precursor solution for about 1 hour. Then, the fiber was dried in an oven at 80°C for about 3 hours to obtain ZnO-NPs/cotton fiber.

III.CHARACTERIZATIONS

3.1.Photocatalytic cleaning

For the detection of photo catalytic cleaning or self cleaning (in both air and water medium) of the zinc oxide modified textile (cotton) fiber is first stained with different type of stains like turmeric powder solution, tea or coffee separately by dipping the small piece of zinc oxide modified fiber in the stain solution or by adding one or two drops of the stain on the modified fiber. Then the untreated fiber was also stained with the same procedure such that both the fiber pieces are equally stained. Then both the fiber pieces are dried under the sunlight for several hours and with respect to time the colour intensities of the stains on both the zinc oxide treated and untreated fiber were compared.

3.2.Hydrophobicity

The hydrophobic property of the surface was analyzed by measuring the , WCA (water contact angle) by a goniometer (DGX Digidrop, France). Certain software like image j was used to measure the WCA of the desired

surface with high quality imaging of the water droplet dropped on the surface. Both the two fiber pieces i.e. the zinc oxide modified fiber/film and the untreated fiber/film were taken and placed on a plane surface by fixing all the four corners with pins. A dropper is fixed with a stand above the surface of the fiber/film (close to it)so that the height of the dropper will not change. Then the dropped was loaded with water and a drop of water was dropped from the dropper on both the two surfaces i.e. zinc oxide treated and untreated fibers separately from equal height with equal pressure. The images of both the droplets were captured with a 8 megapixel oppo camera instantly. Images were taken in 2 minutes interval for 6 minutes. These images of the drolets were then processed with the image j software using the tool drop analysis or angle measurement and hence the desired angle value was displayed and recorded.

3.3.UV-VIS Analysis

UV-Visible spectroscopic analysis of the modified cotton with ZnO NPs was carried out in a perkin Elmer Lambda 25 spectrophotometer in a range of 200 to 600 nm

3.4.SEM

The surface structure of the nanocomposites were viewed through Scanning Electron Microscope (JEOL 6510 LV, Japan).The membranes were rubbed with tissue paper and then dipped in liquid nitrogen for freezing before analysis.

3.5.XRD

X–Ray diffraction (XRD) of the modified and unmodified cottons and cellulose acetate film samples were carried out with PAN Analytical Xpert Pro Diffractometer with Co Kα radiation (30mA40kV).The range of diffraction was 5 to 800 with a scanning speed of 10 per minute

3.6.Thermal Analysis

The thermal analysis of the modified cotton fabric was performed by a Perkin Elmer simultaneous thermal analyzer (STA 6000) in a temperature range of 50 ^{0}C -600 ^{0}C in a heating rate of 10 ^{0}C per minute under nitrogen atmosphere and Indium is used as a reference material.

IV.RESULTS AND DISCUSSIONS

4.1.Photo catalytic cleaning

The zinc oxide modified cotton fibers are found to be effectively self-cleaning property against different organic stains like turmeric and tea stain on exposure to solar radiation. the turmeric stains are faded on 7 hours exposure to solar radiation while the tea stain took 14 hours of solar radiation exposure to get removed. This time duration is lesser than the time required for the turmeric and tea stain to get vanished on the untreated fiber under strong solar radiation which are 11hours and 25hours respectively under average humidity as mentioned in Table 1. The (self) cleaning property is found to be depended upon the atmospheric humidity condition. With increase in the humidity of atmosphere, the organic stains vanishes more easily within less time than a normal humid condition as shown in figure 1. This is due to the more frequent formation of the ROS utilizing the moisture present in air.

(a) **(b)** **(c)**

Figure -1: Photo catalytic cleaning of Cotton fiber modified ZnO NPs with turmeric and tea (a) at initial stage (b) at 7 hrs (c) at 14 hrs

The zinc oxide modified surfaces provide a slightly white background for the stains so that it is more visible that the unmodified fiber surfaces.

Table-1: Photo catalytic activity of ZnO NPs modified cotton fiber

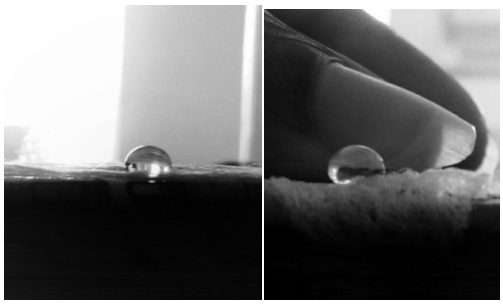
Stain Type	Types of Fiber	Time Required for Stain Removal (In Hours)
Tea	Untreated cotton fiber	25
Tea	ZnO NPs modified cotton fiber	14
Turmeric	Untreated cotton fiber	11
Turmeric	ZnONPs modified cotton fiber	07

4.2.Hydrophobicity analysis

The hydrophobicity of the Cellulose with ZnO nano particles were analyzed by measuring the contact angle by dropping water on the surfaces as shown in figure 2.The zinc oxide modified cotton fiber has shown hydrophobic property which is of less significant. This may be due to the photocatalytic activity of ZnO nano particles but compared to untreated one there is an increase in contact angle around 10^0 as evidenced from the results summarized in Table-2.

Table-2: Contact angle measurement data of ZnO modified CA films and ZnO NPs modified Cotton fibers.

Serial number	Types of films or fibers	Water contact angle (WCA) in degree
1	Untreated cotton fiber	118.7^0
2	ZnO NPs/Cotton fiber	128.5^0



(a) (b)

Figure-2: water droplets on (a)untreated cotton fiber (b) ZnO NPs modified Cotton fiber

4.3.SEM

Surface morphology of the cotton modified with ZnO NPs fiber was analyzed by SEM Figure 3(a) and (b) show the surface morphology of cotton and cotton modified with ZnO NPs. The ZnO material on the cotton fiber has a fairly narrow size distribution centered around 250 nm[9]. It is interesting to observe that the formation of the ZnO lying parallel to the direction of cotton fibre (Fig. 3b).

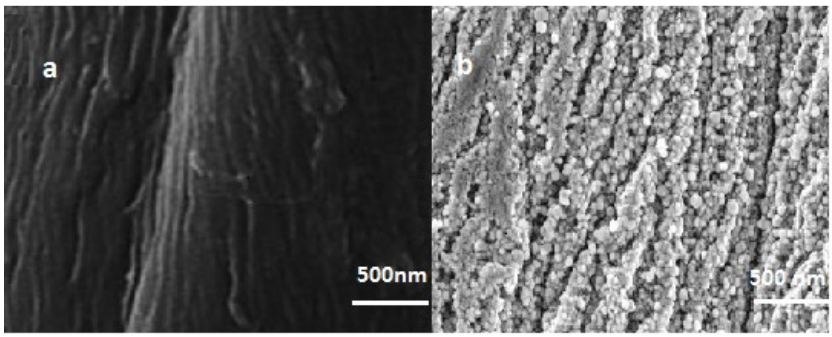


Figure -3: SEM images of (a) cotton fiber (b) cotton fiber treated with ZnO NPs

4.4. XRD

XRD pattern of ZnO nanoparticles modified cotton fabric is shown in Figure 4 . The diffractogram exhibits a broad peak at 2θ value of 21^0 for the regenerated cellulose. The nano sized ZnO particles are of wurtzite structure (hexagonal face, space group 250 P63mc showed characteristic peaks at 2θ value of 31.7^0 (100), 34.4^0(002), 36.2^0 (101), 47.5^0 (102), 56.6^0 (110), 62.8^0 (103), 67.9^0 (112) and 69.1^0 (201) . It is also clear that the crystallinity of ZnO NPs retained which has a major role of reducing hydrophilic nature of cellulose and cellulose acetate[9][10].

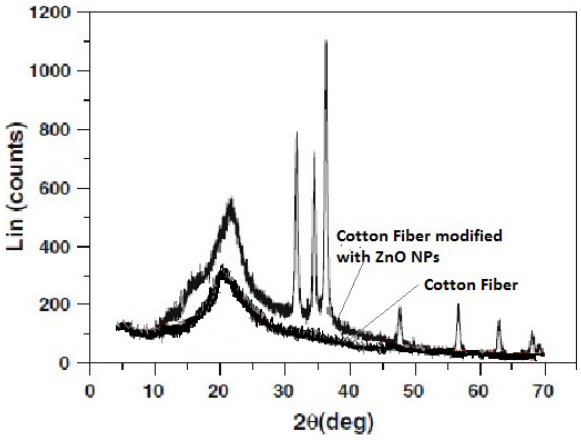


Fig-4: X-ray diffraction pattern of Cotton fiber and ZnO NPs modified with Cotton fiber.

4.5.UV-VIS Analysis

The modified cotton fibre with ZnO NPs showed an absorption band at 355 nm confirming the presence of ZnO in the fibre structure as shown in the recorded UV-VIS recorded spectrum (fig.5)

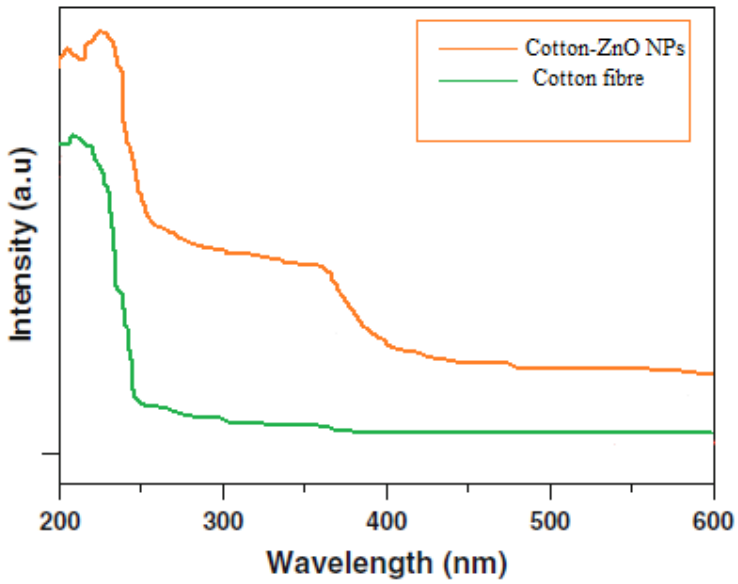


Figure-5: UV-VIS Spectra of (a)modified cotton fiber with ZnO NPs (b) cotton fiber

4.6.TGA

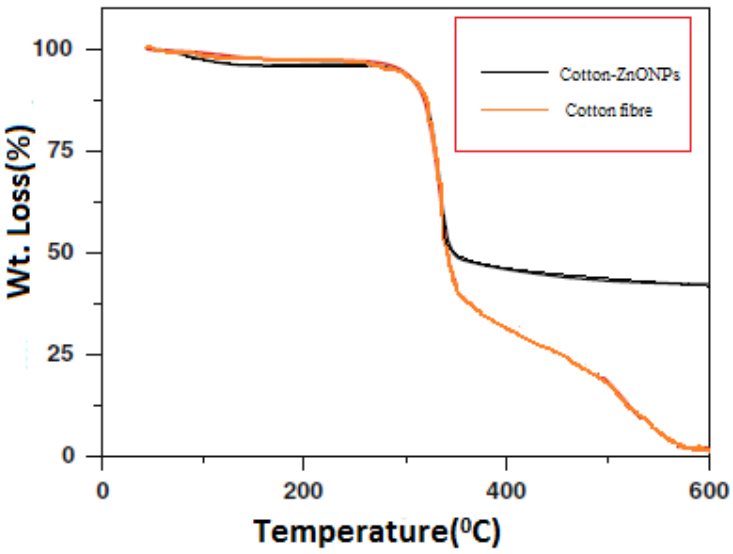


Figure-6: Thermal analysis of Cellulose fibre and Cotton-ZnO NPs

The thermal analysis of the modified cotton with and without ZnO NPs was shown in the figure 6.compared to pure cotton , the modified fiber showed 52% weight loss at 600 ^{0}C which is attributed to presence of ZnO NPs where as Pure cotton have two major weight loss at around 250 ^{0}C and 274 ^{0}C and around 3% residue remain upto 600 ^{0}C . So it is clear that thermal stability of the cotton has been increased after modification with ZnO NPs.

V.CONCLUSION

Cotton was fabric successfully modified with ZnO NPs. The fibre gained improved hydrophobicity.The by increasing water contact angle by 10^0.The surface structural analysis by SEM revealed the irregularity of the modified cotton fibers. XRD analysis was showed the presence of impurities and crystallinity in the modified structure of cotton fibre. The modified cotton also has excellent photo catalytic cleaning surface compared to unmodified one. UV-VIS Spectral analysis also revealed that presence of ZnO NPs in the structure of cotton fiber showing an absorption band at 355 nm.The thermal stability of the cotton was also enhanced after modification with the ZnO nanoparticles. So as the research result the modification improved the thermal stability but improvement in the hydrophobic property is not appreciable. Hence the future research demands more study on how to improve the hydrophobicity.The of the cotton material so as to prepare effective hydrophobic textiles materials out of cotton.

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