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Synthesis of Titanium dioxide Nanoparticles and Application on Nylon fabric using Layer by Layer technique for Antimicrobial Property

R. D. Kale* and Chet Ram Meena

Department of Fibres and Textile processing Technology, ICT, Mumbai 400019, India

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ABSTRACT

Nanotechnology is all about making products from very small constituents, components or subsystems to gain greatly enhanced material properties and functionality. In this work, Titanium dioxide (TiO_2) nanoparticles were produced using two different reacting mediums by Sol-gel method which were subsequently applied by layer by layer (LBL) technique on Nylon 6,6 fabric for imparting antimicrobial activity. The effectiveness of the treatment was assessed after washing treatment to check its durability. Transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to characterize the nanoparticles, their shape and size.

Keywords: TiO_2 Nanoparticles, Nylon 66, Layer-by-Layer Technique (LBL), Polyelectrolytes, Polyelectrolytes Multilayers (PEM), Antimicrobial Activity.

INTRODUCTION

In the last two decades different means of modification of synthetic fibres have been thoroughly explored. The increasing expectancy for smart materials in daily life has of late sharply influenced research in the area of modification. Technologies that involve engineering to convert inexpensive materials into valuable finished goods have become more important in the present scenario [1].

Functionalisation of textile polymers has been practiced by different techniques to confer new properties on to the fibre so as to enable their application in fields other than textile industry. The functionalities of fibres like anti-static, anti-bacterial, anti-odour, soil-resistance, biocompatibility etc. are function of fiber surface properties independent of characteristics of the fiber bulk. Development of processes for imparting these functionalities to the textile substrates is of prime importance [2].

Nanotechnology can provide high durability for fabrics, because Nano particles have a large surface area to volume ratio and high surface energy, thus presenting better affinity for fabrics and leading to an increase in durability of the function. In addition, a coating of Nano particles on fabrics will not affect their breathability or hand feel. It is concerned with materials whose structures exhibit significantly novel and improved physical, chemical and biological properties and functionality due to their nanoscale size [3].

There are two approaches to the synthesis of nanomaterials and the fabrication of nanostructures viz. top-down (attrition and milling) and bottom-up (sol-gel and precipitation) [4]. The intrinsic properties of metal nanoparticles are mainly determined by size, shape, composition, crystallinity and morphology. Nano finishing is concerned with positive control and processing technologies in the sub nano meter range [5]. Coating is a common technique used to apply nano-particles onto textiles. The coating compositions that can modify the surface of textiles are usually composed of nano-particles, a surfactant, ingredients and a carrier medium [6]. Several methods can apply coating onto fabrics, including spraying, transfer printing, washing, rinsing and padding, of which padding is the most commonly used [7].

Comfort and protection are two very important aspects of textiles today. Basically, with a view to protect the wearer and the textile substrate itself, antimicrobial finish is applied to textile materials. Antibacterial protection (additives) inhibits the growth of bacteria and allergens [8].

Today many research groups in physics, chemistry and biology are working on fabricating multicomposite films by LBL assembly that may lead to prototypes of devices like in optics, bio-sensing, separation membranes and technical textile applications [9] and antimicrobial activity [10]. Polymer thin film can be deposited directly onto textile fabrics by following LBL deposition technique to produce PEM [11]. The PEM method has opened the way for easy preparation of truly nano-composite textiles containing a wide range of molecules and nanoparticles allowing the preparation of new technical fibers [12].

MATERIALS AND METHODS

Substrate
Nylon 66 knitted fabrics was supplied by Piyush Trading, Mumbai, India.

Chemicals
Tetraisopropyl orthotitanate (TIPT) was purchased from Merck, Germany. Methanol, Ethanol Absolute AR (99.9%), Hydrogen Peroxide, n-hexane of AR grade were purchased from SD-fine Chemicals Ltd, Mumbai. Polyethylene Imine (PEI) of molecular weight 5430gm was supplied by BASF, Mumbai and Polyacrylic acid (PAA) having molecular weight 10154gm was sourced from Nixon Chemicals, Taloja, Navi Mumbai, India.

Nutrient Broth M 002, Nutrient agar M 001 and Agar-agar Type 1(all microbiology grades) were purchased from Himedia Lab. Ltd., Mumbai. *Staphylococcus aureus* (NCTC 3750 grade) and *Escherichia coli* (AATCC-10148 grade) were obtained from Haffkins Research Institute, Parel, Mumbai. All the cultures were maintained on nutrient's agar medium by periodic sub culturing.

Scouring of Knitted Nylon Fabric
Scouring of the nylon was carried out with 2gm/lit non-ionic detergent, Auxipon NP at boil for 45 min to remove the spinning oil and dirt. After scouring, fabric was washed with water and dried in air.

Synthesis and Characterisation of Nano Titanium dioxide (TiO_2)
Synthesis of TiO_2 nano particle was done by Sol-Gel technique by following two different methods.

Method I
In this method, 2.84ml TIPT was dissolved in a mixture of 0.5ml methanol and 5ml ethanol with molar ratio (1 : 1 : 10) and refluxed at 60ºC for 6 hours. 30 ml of distilled water was added drop wise into the above hot solution at 60ºC under continuous stirring condition. The precipitate was isolated by filtration and washed 2-3 times with hot water. White precipitate formed was dried at 130°C for 12 hrs in oven. This powder is then subjected to calcinations at 550°C for 10hrs in muffle furnace. The white crystalline powder of Nano TiO_2 was obtained at the end of the process [13].

Method II
1.02ml of hydrogen peroxide was taken in a round neck flask, into which 2.84ml of TIPT under stirring was added at 5°C for 1 hour. The initial pH of Hydrogen peroxide solutions was adjusted to 9 by NH_4OH. Yellow gel was observed indicating the formation of peroxide complex of Titanium. To this 10 of ml n-hexane and 0.05gm agar-agar was added. White precipitate formed was then filtered and washed first by distilled water and then ethanol. It was dried at 50°C for 12 hour in oven and then calcined at 550°C for 10 hour in muffle furnace to get the white crystalline powder of Nano TiO_2 [13].

Characterization of Nano TiO_2

Surface morphology of TiO_2 was characterized using SEM JEOL JSM 6380LA, JEOL ltd. Japan. XRD patterns were obtained by using XRD machine Miniflex, Rigaku, Japan. TEM was used to characterize the nanoparticles shape, size as well as electron diffraction pattern using TEM PHILIPS, Model: CM200S.

PEM Formation

Two polyelectrolyte solutions were prepared. The first solution containing 0.1 % PEI was prepared, followed by addition of 1 M HNO_3 to lower its pH to 7. Second solution containing 0.1 % PAA was prepared, by adjusting the pH to 5 using 1 M HNO_3 [14]. Addition of Nano TiO_2 to the PEI solution was always done just prior to the self-assembly procedure.

The PEM were obtained by first dipping the nylon fabric strip in a PEI solution having Nano TiO_2 for two minutes followed by rinsing in distilled water for 2 minutes for rinsing. The fabric is then dipped into the PAA solution for 2minutes and after that dipped into the distilled water for 2 minutes. The cycle is repeated till the required number of PEM is obtained. Following the deposition of required number of PEM, fabric strips were dried in air. In this study the number of PEM were varied to 1, 5, 11, and 25. The concentration of Nano TiO_2 in the PEI was also varied from 0.05, 0.1, and 0.2gpl.

Antimicrobial Testing

The antimicrobial efficacy of a compound will vary as per its presence in solution or on the textile substrate. Quantitative assessment of antimicrobial activity exhibited on knitted nylon 66 was carried out by AATCC Test 100-2004 (AATCC 2007) and the colony-forming units (CFUs) was enumerated using Lapiz Colony Counter (Medica Instrument Mfg.Co., Mumbai, India). The swatches were introduced in the 100 ml nutrient broth inoculated with the *S.aureus & E.coli* microbe and incubated at 37^{o}C for 24hour. Microbial inhibition was determined by the reduction in number of bacterial colonies formed with respect to the untreated control sample using following equations [15].

$$R = \frac{B - A}{B} \times 100$$

where:
R = percent reduction in bacteria
A = CFU for treated test specimen swatches in the jar incubated for 24h contact period,
B = CFU for untreated control test specimen swatches in the jar immediately after inoculation (at “0 hrs” contact time).

Durability

The durability of PEM was assessed by ISO 105-C014:1989 method for 15 washing cycles.

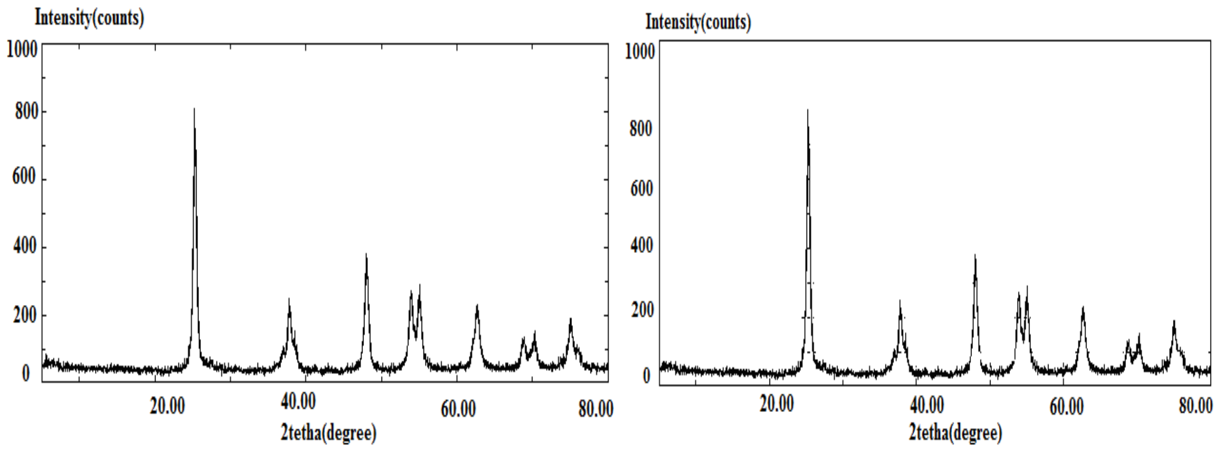
RESULTS AND DISCUSSION

Characterization of Nano TiO_2 Particles

X-Ray Diffraction Analysis

Powder XRD was used for crystal phase identification and estimation of the crystallite size of anatase phase present. The XRD intensities of anatase (101) peak and rutile (110) were analyzed. The percentage of rutile in the samples can be estimated from the respective integrated XRD. The amorphous anatase and anatase-rutile transitions depend strongly on the method of preparation, the nature of the precursor and calcination conditions.

Figure 1 represents the XRD pattern of nano TiO_2 synthesized by method I and method II. In the first method Nano TiO_2 particles are prepared from the organic precursors has more ability to form a product of high crystallinity than the second method where TiO_2 particles are generated from mineral precursors such as titanium peroxide [13].



(A) **(B)**

Figure 1: XRD peaks of Nano TiO_2 A) Method I; B) Method II

TEM Analysis

Figure 2 shows the TEM images of nano TiO_2 synthesized by method I and method II. In both the methods TiO_2 powder appears aggregated and range of the particle size is between 40-60nm for method I and method II. The electron diffraction of Nano TiO_2 is clearly visible as three diffraction rings. The brightest ring is closest to the centre [13].

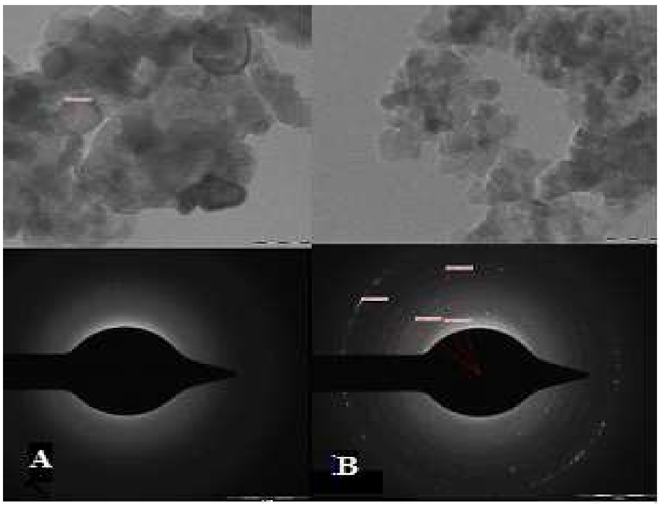


Figure 2: TEM image with Electron diffraction pattern of Nano TiO_2 by (A) Method I (B) Method II

Antimicrobial Activity

The functionalisation of textile polymers can be achieved by using LBL technique by adding the active component such as Nano particles into one of the polyelectrolyte solution. Nylon being an amphoteric fibre has both carboxyl and amine end groups. PEI and PAA used for this study have amine and acidic group respectively in its structure, is capable of forming ionic bonds with Nylon as well as with each other. Because of this reason the PEM that is built onto the Nylon is strongly attached to the fibre.

In this study nano TiO_2 particles which are obtained by different methods is added into the PEI solution so that it gets entrapped into the PEM as the number of layers is built up onto the Nylon Fabric.

Figure 3 and Figure 4 shows the results of antimicrobial activity of Nylon Fabric V/s Number of layers deposited and concentration of nano TiO_2, synthesized by Method I.

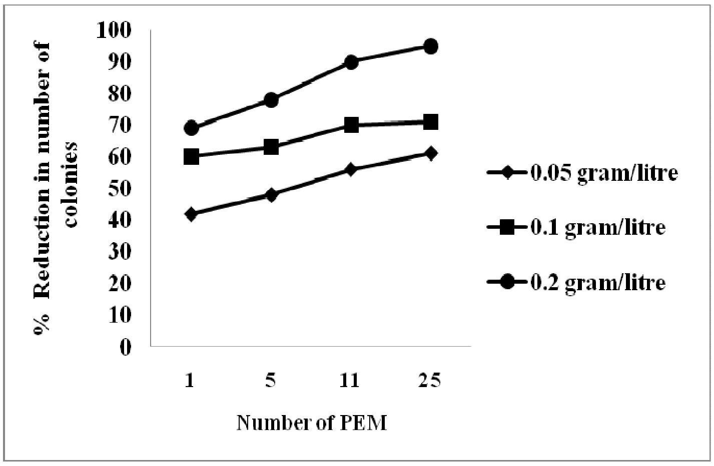


Figure 3: Relation between concentration of nano TiO_2, synthesized by Method I and number of PEM on % reduction in number of *S.Aureus* colonies on Nylon fabric

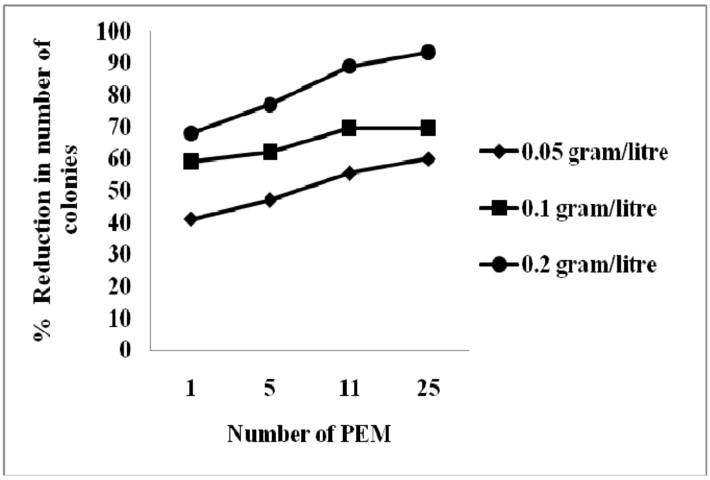


Figure 4: Relation between concentration of nano TiO_2, synthesized by Method I and number of PEM on % reduction in number of *E. coli* colonies on Nylon fabric

The % reduction in number of colonies of *S. Aureus* for TiO_2, synthesized by Method I increases from 1st PEM to 25th PEM and same trend is observed in case of *E.coli*. As the concentration of TiO_2 is increased from 0.05 gram/liter to 0.1 gram/liter and finally to 0.2 gram/liter the % reduction in number of colonies increases from 61% to 71% to 95% respectively for the 25th layer. Results of the antimicrobial activity for the Nano TiO_2 synthesized by method II are shown graphically in Figure 5 and Figure 6.

Exactly same pattern is observed for TiO_2, synthesized by Method II where the % reduction in no of colonies of *S.Aureus* and *E. coli* increases from 1st PEM and 25th PEM. As the concentration TiO_2 is increased from 0.05 gram/liter to 0.2 gram/liter, there is an increase in % reduction in number of colonies.

Thus if we increase the concentration of nano particles in the polyelectrolyte solution the desired effect can be obtained at less number of layers thereby saving time and chemicals. The reason for this antimicrobial activity is because of the presence of nano TiO_2 on the fabric which is a very efficient antimicrobial compound. Also as the number PEM goes on increasing from 1st PEM to 25th PEM there is further improvement in antimicrobial activity because as no of layers are built up, there is a proportionate increase in the concentration of TiO_2 onto the fabric.

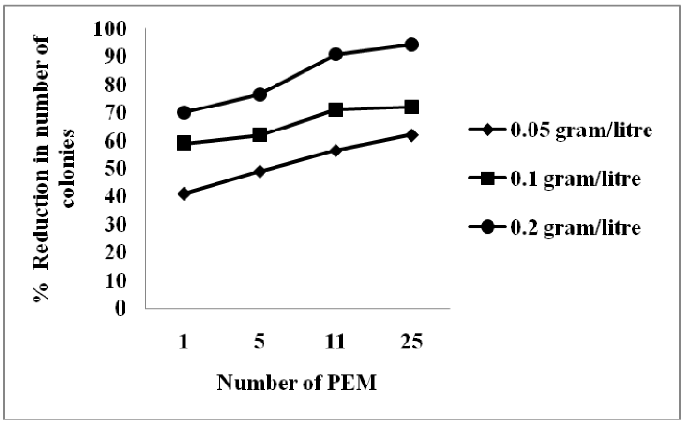


Figure 5: Relation between concentration of nano TiO_2, synthesized by Method II and number of PEM on % reduction in number of *S.Aureus* colonies on Nylon fabric

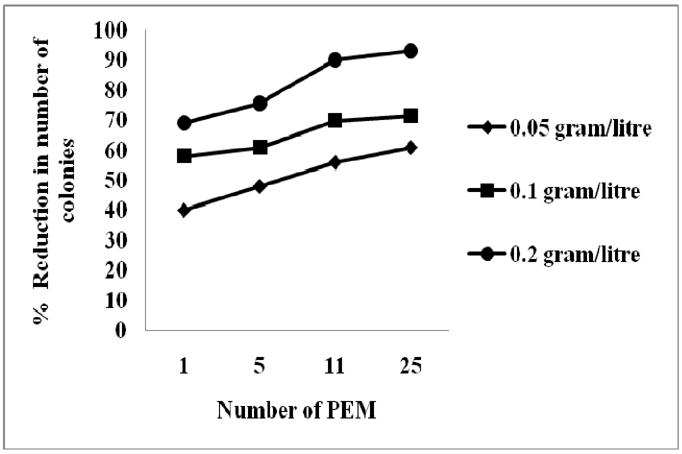


Figure 6: Relation between concentration of nano TiO_2, synthesized by Method II and number of PEM on % reduction in number of *E. coli* colonies on Nylon fabric

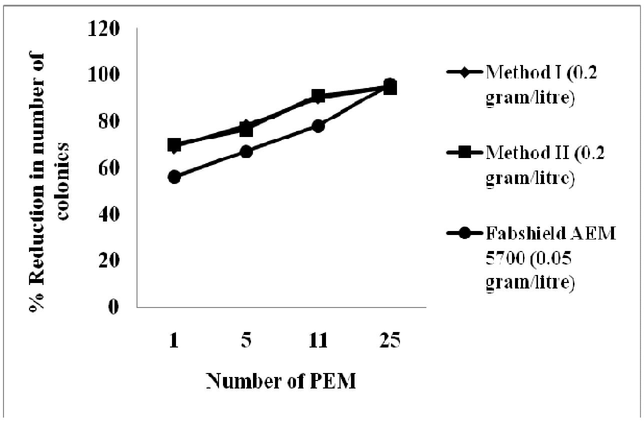


Figure 7: Comparison of nanoTiO_2 (0.2 gram/litre), synthesized by Method I, Method II & Fabshield AEM 5700 (0.05gm/litre) and Number of PEM on % reduction in number of *S.aureus* colonies on Nylon fabric

In order to compare the efficiency of NanoTiO_2, that is synthesized in this laboratory with the Fabshield AEM 5700, a commercial antimicrobial sample based on silver is also tested for comparison, using 0.05 gram/liter concentration to assess the efficacy of nano TiO_2 particles synthesized by us against *S.aureus* The results are shown in Figure 7 and compared against 0.2 gpl of nano TiO_2 synthesized method I & II. One can note that the nano TiO_2 synthesized either by method I or II has better antibacterial property than the commercial products.

The washing durability of nano TiO_2 deposited was also evaluated and the results are given in Figure 8. It can be noted that there is a negligible drop in antimicrobial activity from 1^{st} PEM to 25^{th} PEM. This proves that the TiO_2 particles deposited on the fabric were strongly bonded to the fabric.

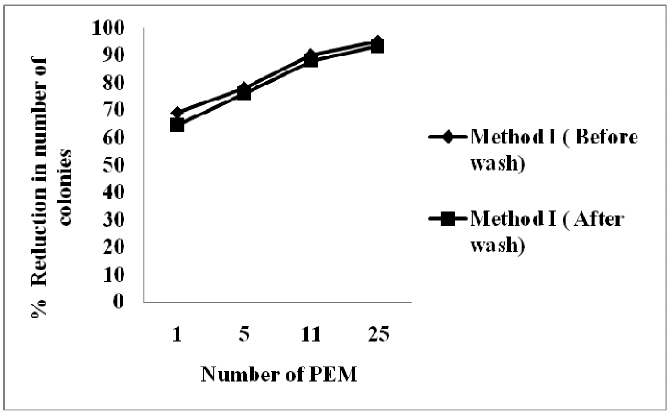


Figure 8: Effect of washing treatment on nano TiO_2 (0.2 gram/litre), synthesized by Method I after fifteen wash and Number of PEM on % Reduction in number of *S.Aureus* colonies on Nylon Fabric

The presence of nano TiO_2 particles on the fabric can be seen in the SEM pictures of unwashed and washed Nylon fabric as shown in Figure 9. We can see the presence of Nano particles on the washed samples and this explains the fact that even after washing, nano particles are firmly bound to the fabric and hence shows antimicrobial activity.

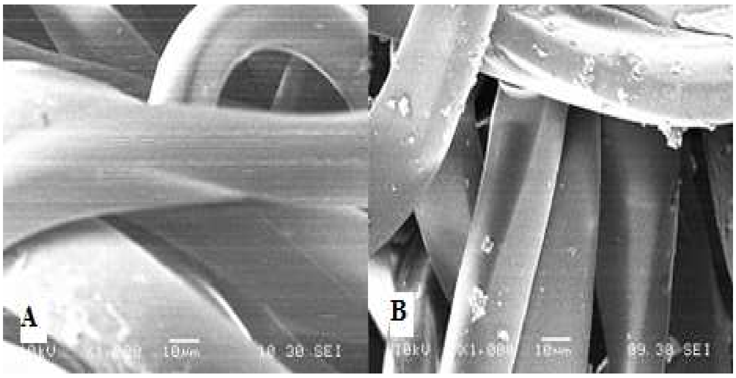


Figure 9: SEM image of nylon surface treated with Nano TiO_2 (A) untreated (B) Method II (after washing)

From above discussion it is clear that nano TiO_2 synthesized either by method I or II show more or less same antimicrobial property.

CONCLUSION

Nano TiO_2 synthesized by two different methods show more or less same antimicrobial property. The efficiency of antimicrobial activity increases with increase in the concentration of nano particles and the number of PEM deposited on the fibre surface. By taking the higher concentration of nano particles number of PEM required to get the desired level of antimicrobial property can be reduced. The effectiveness of the antimicrobial activity is comparable with that of the commercial antimicrobial product available in market.

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