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Research Article

SYNTHESIS AND APPLICATION OF ZINC OXIDE NANOPARTICLES ON NYLON FABRIC BY LAYER BY LAYER TECHNIQUE AS ANTIMICROBIAL PROPERTY

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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, Zinc oxide nanoparticles were synthesised by two different methods (sol-gel and precipitation), which were subsequently applied by layer by layer (LBL) technique on nylon 66 fabric for imparting antimicrobial activity to it. The effectiveness of the treatment was assessed after washing treatment to check its durability. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) were used to characterize the nanoparticles composition, their shape and size. ZnO nanoparticles synthesised by us in the laboratory were found to be comparable with commercial grade nano ZnO with respect to nano meter size and antimicrobial efficiency.

Key Words: *ZnO Nano particles, Nylon 66, Layer-by-layer techniques, Polyelectrolytes multilayers (PEM), Antimicrobial property*

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 (Desai and Singh, 2004).
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-odor, 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 (Chhaparwal, 2005).
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, 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 nanoscaled size (Ratner and Ratner, 2002). 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 (Russell, 2002). 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 (Cramer, Ponomarenko, Laurent and Burckett, 2003). Several methods can apply coating onto fabrics, including spraying, transfer printing, washing, rinsing and padding. Of these methods, padding is the most commonly used **(**Ward, 2003).
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 such bacteria and allergens (Aravin, 2008).

Today many research groups in physics, chemistry or biology are working on fabricating multicomposite films by LBL assembly that may lead to prototypes of devices like in optics, bio-sensing, separation membranes, technical textile (Hinestroza, Hyde and Rusa, 2005) and antimicrobial property (Dai and Bruening, 2002). Polymer thin film can be deposited directly onto textile fabrics by following Layer-by-Layer (LBL) deposition technique to produce Polyelectrolyte Multilayers (PEM) (Decher, 2007). The PEM method has opened the way for the easy preparation of truly nano-composite textiles containing a wide range of molecules and nanoparticles allowing the preparation of new technical fibers (Dubas, Kumlangdudsana and Potiyaraj, 2006).

MATERIALS AND METHODS

Substrate

Nylon 6 6 knitted fabric was supplied by Piyush Trading, Mumbai, India

Chemicals

Zinc Acetate dihydrate, Oxalic acid dihydrate, Ethanol Absolute AR (99.9%) AR grade were purchased from SD-fine chemicals Ltd, Mumbai. Ethandiol was procured from Loba Chemicals, Mumbai. Nano Zinc oxide was purchased from Sigma - Aldrich, Germany. Commercial antimicrobial agent Fabshield AEM 5700 was supplied by Rossari Biotech Pvt. 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.

Nutrient Broth, M 002, Nutrient agar M 001 and Agar-agar, Type 1(all Microbiology grade) 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 fabric 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 Zinc Oxide (ZnO)

The Nano ZnO particles were synthesized by the following two methods.

Sol-gel Technique (Method I)

In this method, zinc acetate dehydrate salt (10.98 g) was taken in a beaker and dissolved in ethanol (300 mL) at 60°C in about 30 min. In the second beaker oxalic acid dihydrate (12.6 g) was dissolved in ethanol (200 mL) at 50°C. This oxalic acid solution was then added slowly under continuous stirring to the warm ethanolic solution of zinc acetate. A thick white gel formed, which was kept for drying at 80°C for 20 h. The white powder was calcined at 600°C for 2hr in a muffle furnance to yield ZnO nanoparticles (Kanade, Kale, Aiyer and Das, 2006).

Precipitation Method (Method II)

In second method, ethandiol was used instead of ethanol with the procedure remaining same. Around 85-90% enthandiol was recovered using distillation at boiling temperature in order to improve the economy of the process. The reaction scheme can be represented as follows (Alessio, Maximilian and Pierandrea, 2008).

Formation of Zinc Oxalate

$Zn(CH_3COO)_2.2H_2O + H_2C_2O_4.2H_2O \rightarrow ZnC_2O_4.2H_2O + 2CH_3COOH + 2H_2O$

Calcination of Zinc Oxalate

$ZnC_2O_4.2H_20 + 1/2O_2 \rightarrow ZnO + 2CO_2 + 2H_2O$

Characterization of Nano ZnO

Surface morphology of ZnO was characterized using SEM JEOL JSM 6380LA, JEOL ltd. Japan. XRD patterns were obtained by using XRD machine Miniflex, Rigaku, Japan. Transmission electron Microscope (TEM) was used to characterize the nanoparticles shape, size, Electron Diffraction Pattern by 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 1M HNO3 to lower its pH to 7. Second solutions containing 0.1 % PAA was prepared, followed by pH adjustment to 5 using 1M HNO_3 (Jamine, Grulan, John and Albert, 2005). Addition of nano ZnO to the PEI solution was always done just prior to beginning the self-assembly procedure.

The PEM were obtained by first dipping the fabric strip in a PEI solution having Nano ZnO for two minutes followed by rinsing in distilled water for 2 minutes. 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 numbers of PEM are 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 ZnO 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 (American association of Textile and Colourist, 2007).

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

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

Figure 1 and Figure 2 shows the X-ray diffraction patterns of Nano ZnO prepared by method I and method II. No peaks due to impurity were observed, which suggests that high purity ZnO was obtained. In addition, the peak was widened implying that the particle size is very small. The peaks assigned to diffractions from various planes correspond to hexagonal close packed structure of zinc oxide (Kanade, Kale, Aiyer and Das, 2006).

The particle size and electron diffraction(ED) pattern determined from TEM are shown in Figure 3. It shows regular and spherical like morphology for nano ZnO prepared by both the methods. The ZnO powder appears aggregated with the particle size range of 20-40nm and 20-50nm for method I and II respectively.

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.

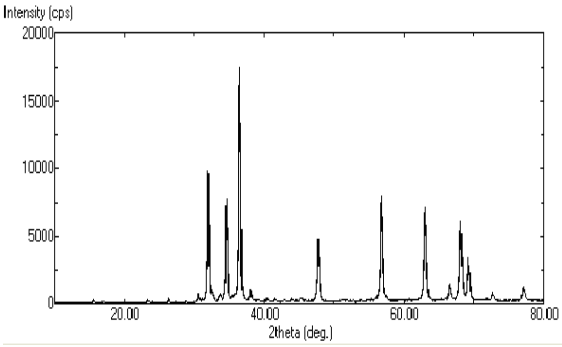

Fig. 1: XRD peaks of nano ZnO by method I

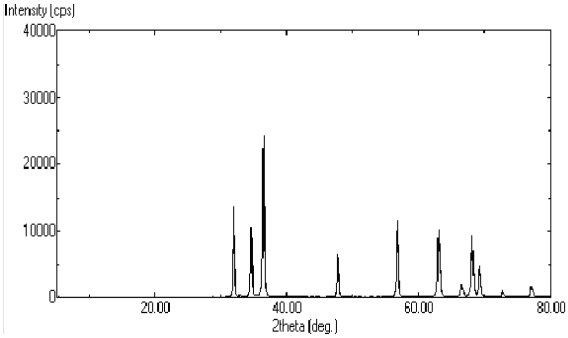

Fig. 2: XRD peaks of nano ZnO by method II

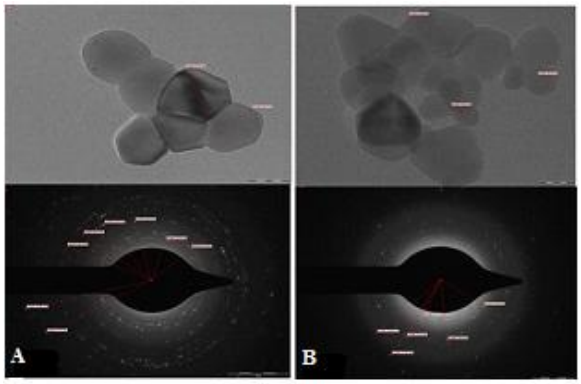

Fig. 3: TEM image with Electron diffraction(ED) pattern of Nano ZnO by (A) Method I (B)Method II

Nylon being an amphoteric fiber 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 surface is strongly attached to the fibre.

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

Figure 4 and figure 5 shows the results of antimicrobial activity of Nylon Fabric V/s Number of PEM deposited and concentration of nano ZnO, synthesized by Method I.

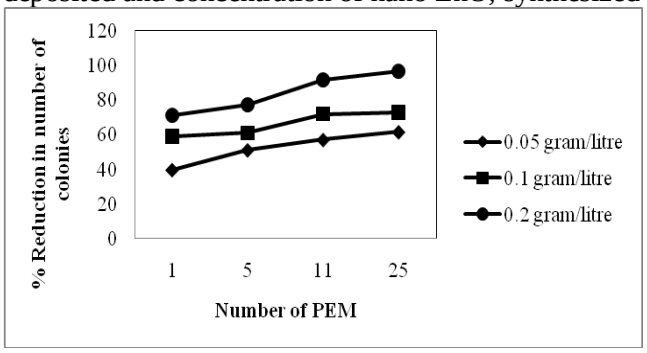

Fig. 4: Relation between concentration of Nano ZnO, synthesized by Method I and Number of PEM on % reduction in number of *S.aureus* colonies on Nylon Fabric

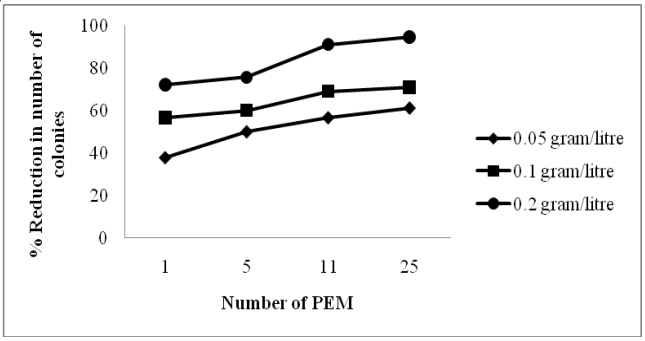

Fig. 5: Relation between concentration of Nano ZnO, synthesized by Method I and Number of PEM on % reduction in number of *E.coli* colonies on Nylon Fabric

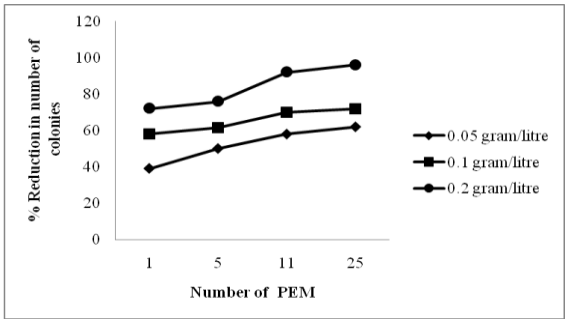

Fig. 6: Relation between concentration of Nano ZnO, synthesized by Method II and Number of PEM on % reduction in number of *S.aureus* colonies on Nylon Fabric

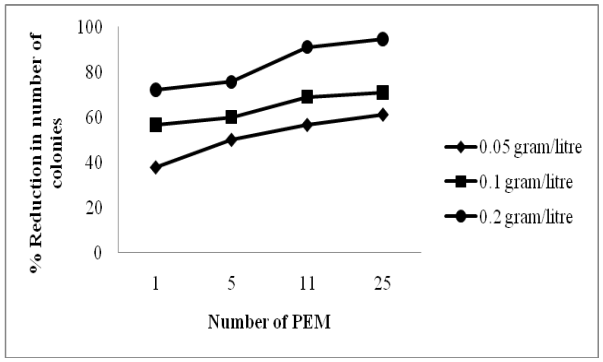

Fig. 7: Relation between concentration of Nano ZnO, synthesized by Method II and Number of PEM on % reduction in number of *E. coli* colonies on Nylon Fabric

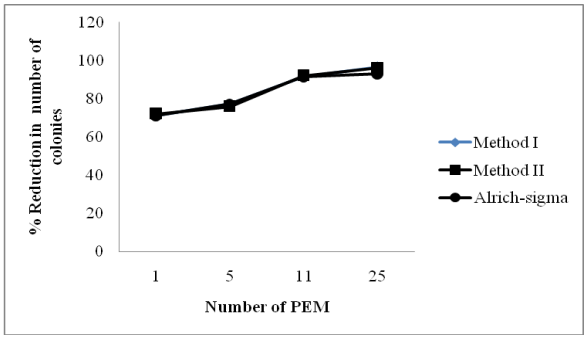

Fig. 8: Comparison of nano ZnO (0.2 gram/litre), synthesized by Method I, Method II & Aldrich- sigma and Number of PEM on % reduction in number of *S.aureus* colonies on Nylon Fabric

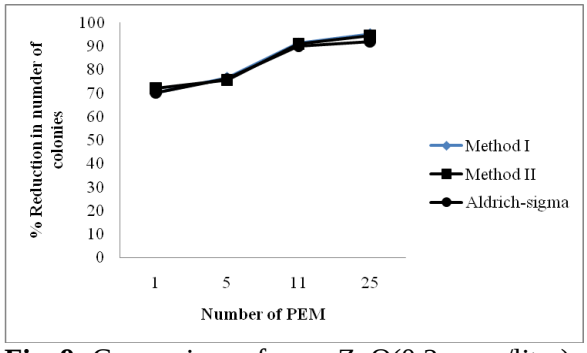

Fig. 9: Comparison of nano ZnO(0.2 gram/litre), synthesized by Method I, Method II & Aldrich- sigma and Number of PEM on % reduction in number of *E. coli* colonies on Nylon Fabric

One can find that the % reduction in number of colonies goes on progressively increasing from for 1st PEM to for 25th PEM in case of *S.aureus* and same trend is observed in case of *E. coli* also.

It is also observed that as the concentration of ZnO is increased from 0.05 gram/Litre to 0.2 gram/liter the antimicrobial activity enhanced further for both *S.aureus* and *E.coli*. This point is further accentuated by the fact that in case of 0.2 gram/liter of concentration, for the 1st PEM itself, for *S.aureus* the % reduction in number of colonies (71%) is greater than for 25th PEM of 0.05 gram/liter concentration (61.5%). Thus if we increase the concentration of Nano particles in the polyelectrolyte solution the desired effect can be obtained at less number PEM thereby saving the time. The same observation is made in case of antimicrobial activity against *E.coli*.

The reason for this antimicrobial activity is because of the presence of nano ZnO on the fabric which is a very efficient antimicrobial compound. Also as the number PEM goes on increasing from 1 to 25 there is further improvement in antimicrobial activity because as no of layers are built up, there is a proportionate increase in the concentration of ZnO on the fabric. Also when the concentration of ZnO added into the PEI solution was increased from 0.05 to 0.1 to 0.2 gram/litre the amount of nano ZnO that gets deposited onto the fabric increases and this result in the enhanced antimicrobial activity for the less number of PEM. Results of the antimicrobial activity for the Nano ZnO synthesized by method II are shown graphically in Figure 6 and Figure 7.

Here also the % reduction in number colonies increased as the number of PEM are increased and also when concentration of nano ZnO was increased in the polyelectrolyte bath for both the organism studied. The same argument that is explained earlier holds true for these results as well.

In order to compare the efficiency of Nano ZnO that is synthesized in this laboratory with the nano particles that is commercially available, the same experiments were carried out with nano ZnO supplied by Aldrich-sigma in Figure 8 and Figure 9. Again the same trend in results is noted when nano ZnO particles from Aldrich-sigma were used. The curves for all the three samples are overlapped indicating that the nanoparticles synthesized by method I and II displayed same level of antimicrobial activity as the one sourced from Aldrich-sigma.

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 ZnO particles synthesized by us against *S.aureus* The results are shown in Figure 10 and compared against 0.2 gpl of nano ZnO synthesized method I & II.

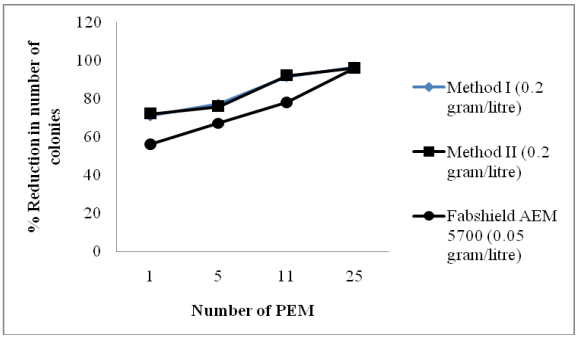

Fig. 10: Comparison of nano ZnO (0.2 gram/litre), synthesized by Method I, Method II & Fabshield AEM 5700(0.05gm/litre) and Number of PEM on % Reduction in number of *S.aureus* colonies on Nylon Fabric

Here again all the three curves are indistinguishable thus proving that nano ZnO synthesized by us are comparable with the commercial products.

It would be interesting to see whether the nano particles deposited via LBL technique are fast to washing. To assess their durability Nylon fabric activated by nano ZnO particles, synthesized by method II were subjected to 1, 5 and 15 cycles of washing and then again evaluated for their antimicrobial performance against *S. aureus.*

Results are presented in the Table 1. From the Table it can be seen that % reduction in no of colonies has marginally dropped due to washing effect. It is 96% for unwashed sample, 92% after 1st washing cycle, 84.5% after 5th washing cycle and 69% after 15 washing cycle. The SEM pictures of unwashed and washed Nylon fabric after wash are shown in Figure 11. We can still 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.

Conclusion

Nano ZnO synthesized by method I and II 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

Table 1: Effect of washing on Nano ZnO synthesized by Method and number of PEM on antimicrobial activity of Nylon Fabric against *S.aureus*

Number of Layers	Concentration of nano ZnO, 0.2 gram/liter											
	Method II			After 1 wash			After 5 wash			After 15 wash		
	Number of Colonies after		% Reduction in Number of Colonies	Number of Colonies after		% Reduction in Number of Colonies	Number of Colonies after		% Reduction in Number of Colonies	Number of Colonies after		% Reduction in Number of Colonies
	0 hr	24 hrs		0 hrs	24 hrs		0 hr	24 hrs		0 hr	24 hrs	
#Control	789	1485	--	796	1480	--	801	1460	--	789	1485	--
1	89	25	72	102	33	68	125	45	64	157	77	51
5	72	18	76	86	25	71.5	96	30	69.5	124	59	52.5
11	49	4	92	59	7	89	69	13	82	101	36	65
25	20	1	96	39	4	92	55	9	84.5	63	20	69

#Control = Nylon fabric treated with only PEM (up to 25 layers)

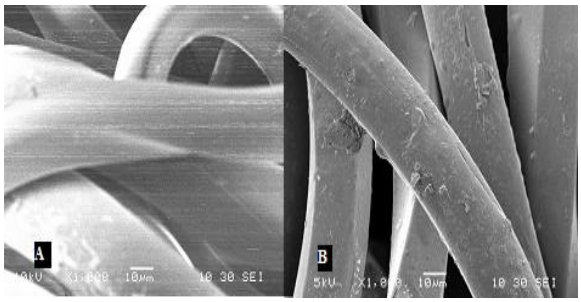

Fig. 11: SEM image of nylon surface treated with Nano ZnO (A) untreated (B) Method II (after washing)

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 commercial nano ZnO and commercial antimicrobial product available in the market.

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