International Journal of Pharmaceutics 434 (2012) 366–374

Contents lists available at SciVerse ScienceDirect

International Journal of Pharmaceutics

journal homepage: www.elsevier.com/locate/ijpharm

Pharmaceutical Nanotechnology

Antibacterial effect of novel synthesized sulfated β-cyclodextrin crosslinked cotton fabric and its improved antibacterial activities with ZnO, TiO_2 and Ag nanoparticles coating

S. Selvam[a], R. Rajiv Gandhi[a], J. Suresh[a], S. Gowri[a], S. Ravikumar[b], M. Sundrarajan[a,*]

[a] Advanced Green Chemistry Lab, Department of Industrial Chemistry, School of Chemistry, Alagappa University, Karaikudi 630 003, Tamilnadu, India
[b] Department of Oceanography and Coastal Area Studies, School of Marine Science, Alagappa University, Thondi Campus, Thondi 623409, Tamil Nadu, India

ARTICLE INFO

Article history:
Received 25 January 2012
Received in revised form 5 April 2012
Accepted 25 April 2012
Available online 3 May 2012

Keywords:
Sulfonation
Pad-dry-cure
β-Cyclodextrin
Crosslinking
Antibacterial activity
Nanoparticles

ABSTRACT

Sulfated β-cyclodextrin was synthesized from sulfonation of β-cyclodextrin and sulfated polymer was crosslinked with cotton fabric using ethylenediaminetetraacetic acid as crosslinker. ZnO, TiO_2 and Ag nanoparticles were prepared and characterized by XRD, UV, DLS, SEM and PSA. The prepared nanoparticles were coated on crosslinked cotton fabric. The crosslinking and nanoparticles coating effects of cotton fabrics were studied by FTIR and SEM analysis. The antibacterial test was done against gram positive Staphylococcus aureus and gram negative *Escherichia coli* bacterium.

1. Introduction

Nanoparticles treated fabrics have some functional behaviors including antibacterial activity, UV-protection, self-cleaning etc. These properties increased in the modified fabrics by eco-friendly polymer modifications like chitosan and β-cyclodextrin. These types of textile materials are needed in the increasingly demanding human society with environmental safety (Kitkulnumchai et al., 2008; Abidi et al., 2009; Sorapong et al., 2006). In increasing population load, the consumption of cotton fabrics is also increased. So, the applications of cotton fabrics increased day by day. The improved qualities and functionalities of cotton fabrics are necessary for kid's cloths, inner wears, medical bandage cloths (Teli and Shrish kumar, 2007). The structural modified cellulose fabric is possible and this type of fabric has some interesting properties. Our recent report deals with such type of modification that is β-cyclodextrin modified cotton fabric with thymol for antibacterial activity (Rukmani and Sundrarajan, 2011) and PVP modification of cotton fabric and its improved antibacterial activity was tested with ZnO nanoparticles coating (Selvam and Sundrarajan, 2012).

β-Cyclodextrin is a water soluble carbohydrate polymer containing seven glucose units linked by glucosidic bonds like a shallow truncated cone shape. It has a hydrophobic cavity and a hydrophilic exterior. The structural modified β-cyclodextrin has increased reactivity by sulfonic acid groups (Biwer et al., 2002; Biswas and Biswas, 2005; Martin and Valle, 2004). The β-cyclodextrin polymer has been covalently fixed on cotton fabric by a polycondensation reaction at controlled conditions. The β-cyclodextrin modification on cotton fibers occurred through the formation of a crosslinking between hydroxyl groups of cotton and β-cyclodextrin polymer (Pipatchanchai and Srikulkit, 2007). The β-cyclodextrin polymer solution has the ability to anchor on cotton fabrics through gelation process in order to impart new surface property of cotton. The suitable technical condition of forming stable β-cyclodextrin solution has been reported. The β-cyclodextrins are able to form inclusion complexes with other guest components (Sorapong et al., 2006).

The introduction of sulfonic acid groups (—SO_3H) on polymer surfaces has been found for important biomedical applications. It has been shown that the expansion on polymeric materials is improved if the surface of the polymer contains sulfonic acid groups (Loftsson and Duchene, 2007). Pharmaceutical applications of cyclodextrins have been mainly described. The use of cyclodextrins in textile processes has been studied by some researchers (Loftsson and Marcus Brewster, 2010; Buschmann et al., 2001; Cireli and Yurdakul, 2006).

A hot water treatment could transform the morphology of the ZnO nanoparticles on the surface of cotton fabric from sphere and rod to needle shape through a recrystallization process Ostrovsky

* Corresponding author. Tel.: +91 94444 96151; fax: +91 04565 225202.
E-mail address: sundrarajan@yahoo.com (M. Sundrarajan).

0378-5173/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ijpharm.2012.04.069

et al. (2010). Though hot water treatment could not significantly increase the amount of ZnO on the surface of cotton fabric, longer treatment time and high treatment temperature can make the needle-shaped ZnO nanorods have smaller diameter and better crystalline perfection (Cai et al., 2010; Mao et al., 2009). Hence modified polymer surface is required for increasing the nanoparticles deposition by suitable modification.

Cotton fabrics coated with TiO_2 nanoparticles have been successfully developed by dipping the fabrics in to TiO_2 sol–gel, which was synthesized by a simple and effective method at ambient atmosphere. TiO_2-coated cotton fabrics have notable and stable self-cleaning functions as demonstrated by their photocatalytic degradation of bactericidal activities. TiO_2 coating not only prevented the formation of a bio-film of adsorbed bacteria but also destroyed the bacteria cell (Wu et al., 2009).

The zinc oxide, titanium dioxide and silver nanoparticles are successfully prepared by the chemical and sol–gel methods (Stanier et al., 2001). These nanoparticles have great promise as antimicrobial agents. Applications of nanoparticles based on these findings may lead to valuable discoveries in various fields such as medical devices and antimicrobial systems (Kim et al., 2007). Nanoparticles with mean sizes of 20–45 nm were successfully prepared using the sol–gel method and also we have reported the TiO_2 nanoparticles preparation (Lkhagvajav et al., 2011; Sundrarajan and Gowri, 2011). The work is aimed at the antibacterial activity of sulfated β-cyclodextrin (sb-cd) crosslinked with cotton and to study the improved antibacterial activity using ZnO, TiO_2 and Ag nanoparticles coating.

2. Materials and methods

2.1. Materials used

The polymer β-cyclodextrin was purchased from HiMedia chemicals and sulfuric acid, calcium carbonate, sodium carbonate, ethylenediaminetetraacetic acid (EDTA), starch, zinc nitrate, glucose and silver nitrate were purchased from Merck products. Titanium isopropoxide (98%) was supplied by Acros Organics. Cotton fabric was used as a bleached knitted fabric purchased from Textile Industry, Tirupur.

2.2. Preparation of sulfated β-cyclodextrin (sb-cd)

β-Cyclodextrin (10 g) was mixed with 3 ml of 90% of sulfuric acid at 0–5 °C temperature maintained for 2 h in an ice bath. The superfluous sulfuric acid was then counteracted with 1 N calcium carbonate solution. After filtering, 95 wt% of alcohol was added into the filtrate, and the mixed solution was kept overnight at 0–5 °C. The pH of the sedimentation was adjusted to 7 using acetic acid. The sulfated β-cyclodextrin (sb-cd) sedimentation was obtained after adding a great amount of alcohol (Yang, 2009). Then the sulfated β-cyclodextrin powder was dried in a vacuum oven at 110 °C for 15 min.

2.3. Synthesis of sb-cd crosslinked cotton fabric

The prepared sulfated β-cyclodextrin (sb-cd) (5 wt%) was dissolved in water and 90% of wet pickup. Bleached 30 cm × 25 cm of cotton fabric was immersed into sb-cd solution with 5 g/l EDTA for crosslinking (Ghoul et al., 2003). The treated cotton fabric was padded continuously for 15 min on two bowel padding mangle. Then the fabric was cured at 120 °C for 3 min. The schematic representation of sb-cd preparation and crosslinking reaction is exhibited in Fig. 1.

2.4. Preparation of ZnO nanoparticles

The ZnO nanoparticles were prepared by thermolysis method (Perelshtein et al., 2009). About 7.43 g of zinc nitrate was dissolved by magnetic stirring (JSGW 13162) with 200 ml of 2% starch solution. The soluble starch was acted as a stabilizing agent. Then 0.2 mole of sodium hydroxide was added drop by drop as precursor to this solution. The mixture was stirred for 2 h and the temperature was maintained from 60 °C to 70 °C. After stirring the precipitate was filtered. This precipitate was washed three times with distilled

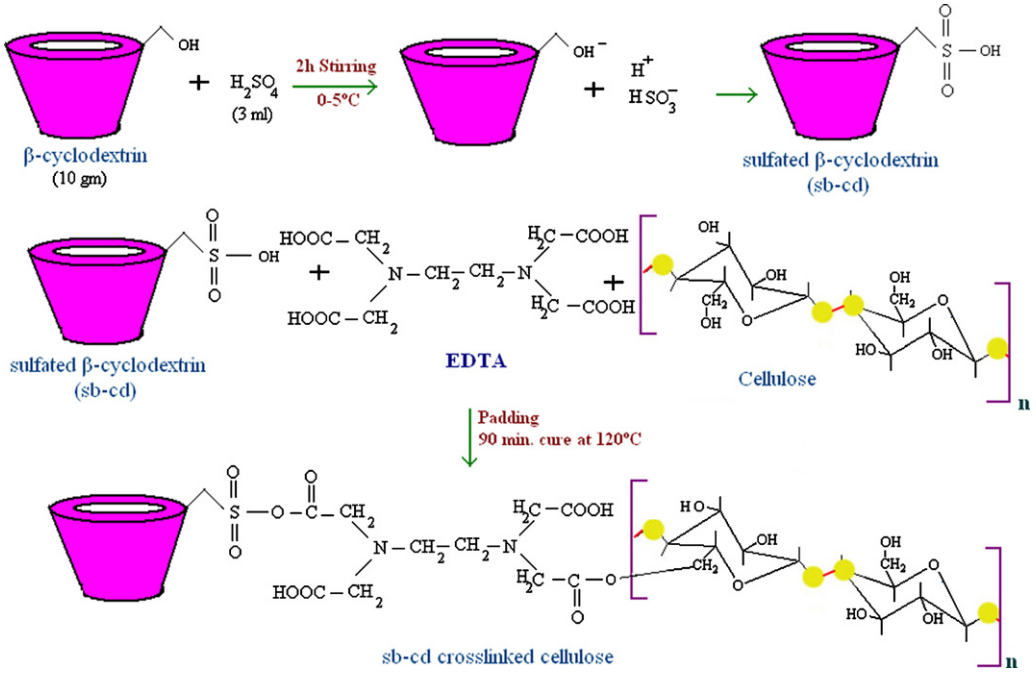

Fig. 1. Schematic representation of sb-cd crosslinking of cotton fabric.

water. After washing the nanoparticles were dried at 80 °C for 12 h and then ZnO nanoparticles were obtained.

2.5. Preparation of TiO_2 nanoparticles

Titanium isopropoxide (6 ml) was mixed with 2 ml of 10% acetic acid with continuous stirring using JSGW 13162 magnetic stirrer (Vives and Meunier, 2008). After 5 min, 56 ml of ethanol was added drop wise with continuous stirring. Then pH of the solution was adjusted to 1–2 by adding 2 ml of con. HCl. The mixture was magnetically stirred well for 45 min. The obtained sol–gel TiO_2 was used for treating of cotton fabric.

2.6. Preparation of silver nanoparticles

The silver nanoparticles were prepared by chemical method (Chudasama et al., 2010). About 20 ml of 0.1 m $AgNO_3$ solution was taken in a dark conical flash and 5 g of glucose was added to this solution. This mixture was stirred using magnetic stirrer (JSGW 13162) with 2000 rpm for 30 min. Then, 50 ml of 0.1 m Na_2CO_3 solution was added drop wise to the silver nitrate solution and stirred for 45 min. The obtained silver nanoparticles were dried and characterized.

2.7. Coating of cotton fabrics with nanoparticles

The prepared nanoparticles were coated by Pad-dry-curve method (Kim et al., 2010). 10 cm × 5 cm of untreated and sb-cd crosslinked cotton fabrics were wet pickup using nonionic wetting agent. These samples were immersed in nanoparticles colloidal solutions separately. Then these fabric samples were padded continuously for 15 min in a two bowl padding mangle. After completion of padding these fabrics were cured at 120 °C for 3 min. Then the unfixed nanoparticles were removed by washing with sodiumlaurylsulfate solution. Finally these fabrics were completely washed 10 times with water and then dried.

2.8. Antibacterial test

The antibacterial activities of modified and unmodified fabrics were done by the reduction of colony forming units (CFU) of *Staphylococcus aureus* and *Escherichia coli* bacterium (AATC Test Method (100–1999); Li et al., 2006; Cao and Sun, 2009). The cell culture was done in Marine Bio-technology Lab, Alagappa University Thondi campus. The initial concentration of *S. aureus* is 12×10^5 CFU mL^{-1} and *E. coli* concentration is 6×10^5 CFU mL^{-1}. The percentage reduction of colony forming unit (CFU) was calculated by the following Eq. (1):

$$\text{Reduction in CFU}\,(\%) = \frac{C - A}{C} \times 100\% \quad (1)$$

where, C and A are the bacterial colonies of the untreated cotton fabric and the treated cotton fabrics respectively.

3. Results and discussion

3.1. FTIR studies

The FTIR spectra were measured by transmission mode using Perkin Elmer IR SPECTRUM ASCII PEDS 1.60 instrument with KBr pellets. The —OH stretching absorption displayed a typical broad peak from 3557 cm^{-1} to 3247 cm^{-1}(Fig. 2a). It indicates that the compound has many numbers of hydroxyl groups in β-cyclodextrin. The peak from 2932 cm^{-1} to 2119 cm^{-1} represented the —CH_2 groups. Although it has —CH_2 groups in their structure, the peaks are corresponding to the asymmetric stretching modes.

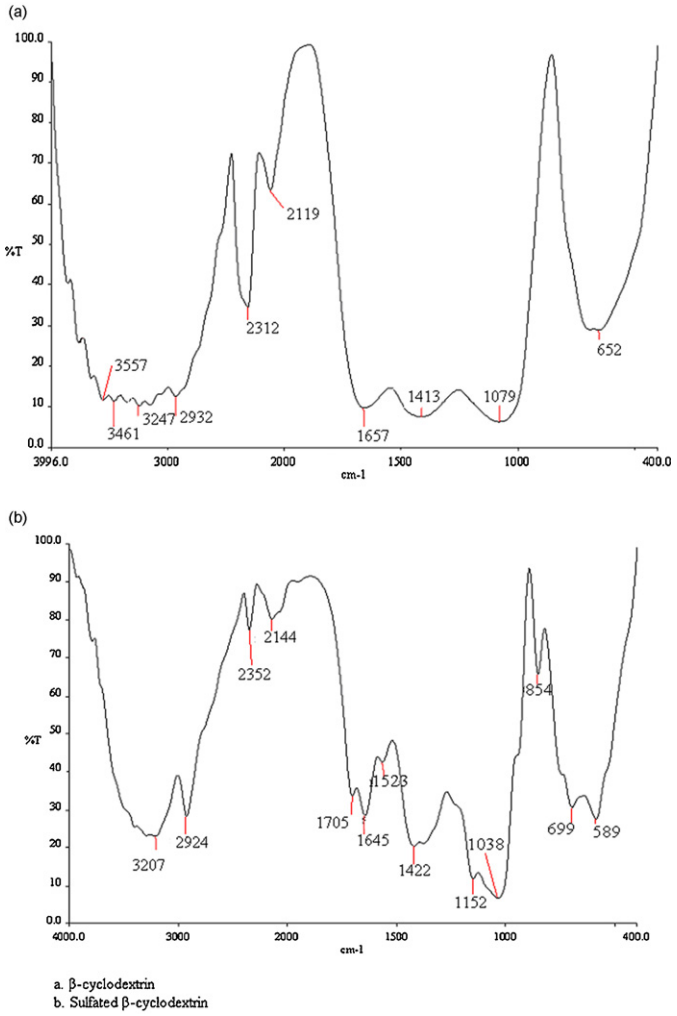

Fig. 2. FTIR spectra of β-cyclodextrin and sulfated β-cyclodextrin.

The stretching vibration of C—O—C bond has been identified at 1413 cm^{-1} and 1079 cm^{-1}. It is the evidence for glucose linkages in β-cyclodextrin structure. The Fig. 2b expresses the FTIR spectrum of sulfated β-cyclodextrin (sb-cd). A broad peak at 3207 cm^{-1} indicates the —OH stretching and it exhibits the available free hydroxyl groups in sb-cd. The peak values from 2924 cm^{-1} to 2144 cm^{-1} exhibited the —CH_2 asymmetric stretching. The S—O stretching absorption peak is exhibited at 699 cm^{-1}. The asymmetric and symmetric stretching of —SO_3 groups from sb-cd showed in the range from 1152 cm^{-1} to 699 cm^{-1}. It is the evidence that the sulfonic acid reacted on the β-cyclodextrin and the primary hydroxyl groups may involve sulfonation reaction.

The FTIR spectrum of pure cotton fabric is exhibited in Fig. 3a. The peak 3418 cm^{-1} corresponds —OH stretching and also the —CH_2 stretching corresponds to region at 2894 cm^{-1}. It is the evidence of hydroxyl groups presented in cotton fabric. The peaks exhibited at 1110 cm^{-1} and 1049 cm^{-1} due to the C—O—C stretching. The FTIR spectrum of sb-cd crosslinked cotton fabric is shown in Fig. 3b. The —OH stretching of alcoholic groups indicates at peak 3269 cm^{-1}. A peak at 2906 cm^{-1} corresponds to —CH_2 stretching and the peak at 1111 cm^{-1} represents S—O stretching. This S—O starching is the evidence for crosslinking of sb-cd with cotton fabric. This stretching of C—N bond of EDTA confirms by peaks at 1285 cm^{-1} and 1349 cm^{-1}. It is the evidence that the EDTA has crosslinked between sb-cd and cotton fabric. These FTIR results showed that the sb-cd has crosslinked with cotton fabric by EDTA crosslinker.

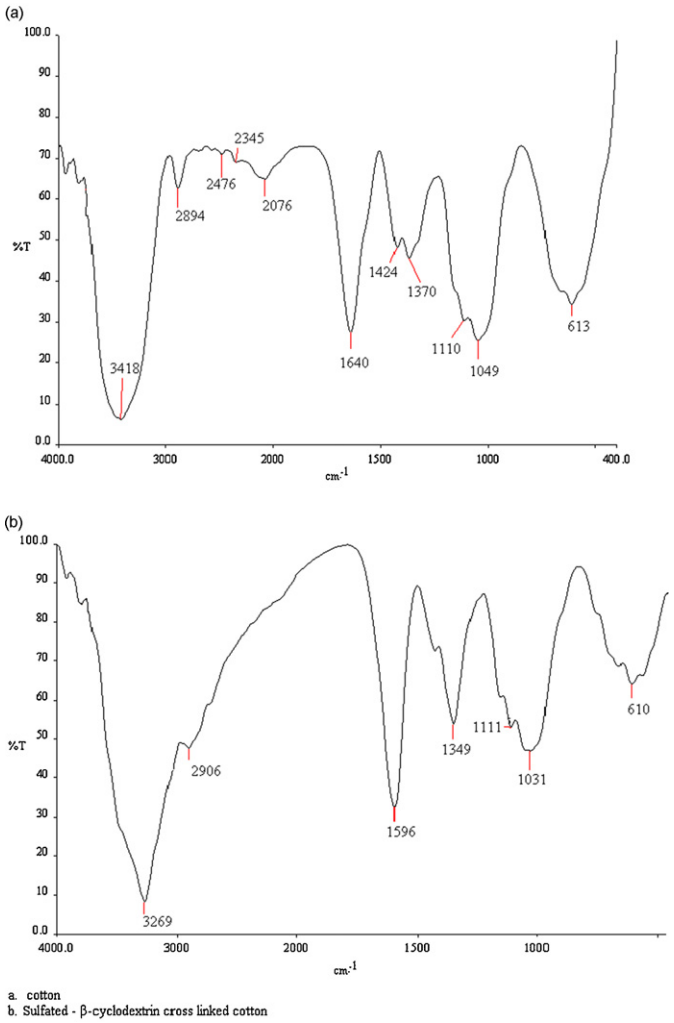

Fig. 3. FTIR spectra of untreated cotton and sb-cd crosslinked cotton.

3.2. XRD pattern of prepared nanoparticles

The crystalline and average particle size of prepared nanoparticles was analyzed by XRD pattern using XPERT PRO diffractometer. The average crystal size was calculated from Debye–Scherer in Eq. (2).

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (2)$$

where, K is the shape factor, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle (Scherrer, 1918; Patterson, 1939; Piga et al., 2008; Bashkorov et al., 2011).

From Fig. 4a, the peaks at $2\theta = 36^\circ$, 38°, 43°, 54° and 70° of ZnO nanoparticles are corresponding to (0 0 2), (1 0 0), (1 0 2), (1 0 1) and (1 0 3) in lattice (JCPDS No. 87-0713). Hexagonal structure of ZnO was confirmed by the (1 0 2) crystalline peak (Wu et al., 2010) and the average crystal size of synthesized ZnO nanoparticle is 37 nm. The Fig. 4b explained XRD Pattern of TiO_2 nanoparticles. The peaks at $2\theta = 25^\circ$, 38°, 48°, 55° and 70° correspond to the TiO_2 nanoparticles with (1 0 1), (0 0 4), (2 0 0), (2 1 1) and (2 2 0) lattice (JCPDS No. 84-1286). From the sharp peaks, it is obvious that the obtained TiO_2 nanocrystals have high crystallinity and it is confirmed by the (1 0 1) crystalline peak (Kasetsart et al., 2008, Thamaphat et al., 2008) and the average particle size is 19 nm. The sharp XRD peak corresponds to Ag (1 1 1), (2 0 0) and (2 2 0) lattice with peaks at $2\theta = 25^\circ$, 36° and 63° (Fig. 4c). The face centered cubic structure (Zheng et al., 2006; Zhang et al., 2001) is confirmed by (1 1 1) crystalline peak of Ag nanoparticles (JCPDS File No. 4-0783) and the average crystal size is 18 nm.

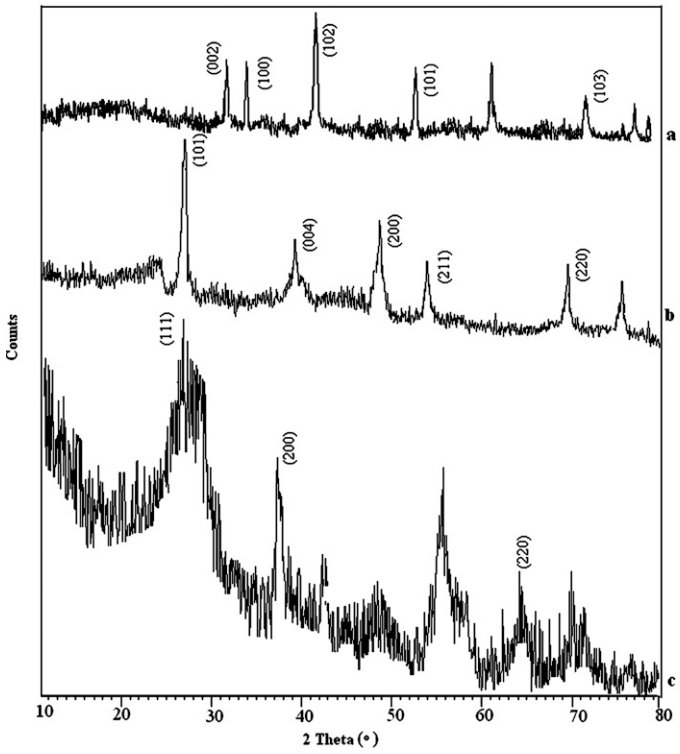

Fig. 4. XRD pattern of (a) ZnO, (b) TiO_2 and (c) Ag nanoparticles.

3.3. UV–vis and DLS studies of nanoparticles dispersions

The prepared ZnO nanoparticles were first dispersed in water and then the UV–vis optical absorption characteristics of the ZnO nanoparticles. The UV–vis spectrum carried out using JASCO UV–Vis. 530 spectrophotometer. Fig. 5a1 showed the excitonic absorption peak is observed due to the ZnO nanoparticles at 236 nm. The surface plasmon resonance (SPR) absorption spectrum of colloidal solution has a peak centered at 365 nm. This peak is the characteristic of ZnO formation while confinement in nano scale is proved by blue shift (Agnieszka Dybowska et al., 2011). Dynamic light scattering (DLS) result of zinc oxide nanoparticles exhibits the size distributions starting from 20 to 70 nm with average size of 35 nm (Fig. 5a2). Relatively good symmetry of size distribution diagrams in DLS analysis illustrates uniformity of the formed nanoparticles. The data clearly show broadening of size distribution and increase of average particles size distribution (Ashkarrana et al., 2009).

Fig. 5b1 shows the ultraviolet–visible (UV–vis) optical absorption spectrum of the obtained colloid solutions. A significant increase in the absorption at wavelengths starting at 400 nm is observed. Further investigation reveals that the absorbance value in the edge region can well be determined by the optical absorption edge expression of the semiconductor with direct band gap: The blue shift indicated the nanosizes of prepared TiO_2 nanoparticles (Chowdhury and Sharon Walker, 2012). The DLS result showed the particles distribution of TiO_2 nanoparticles with average particle size of 20 nm ranges (Fig. 5b2).

Silver nanoparticles suspension exhibits typical peaks due to the surface plasmon resonance (SPR), which results from collective oscillations of their conduction band electrons in response to

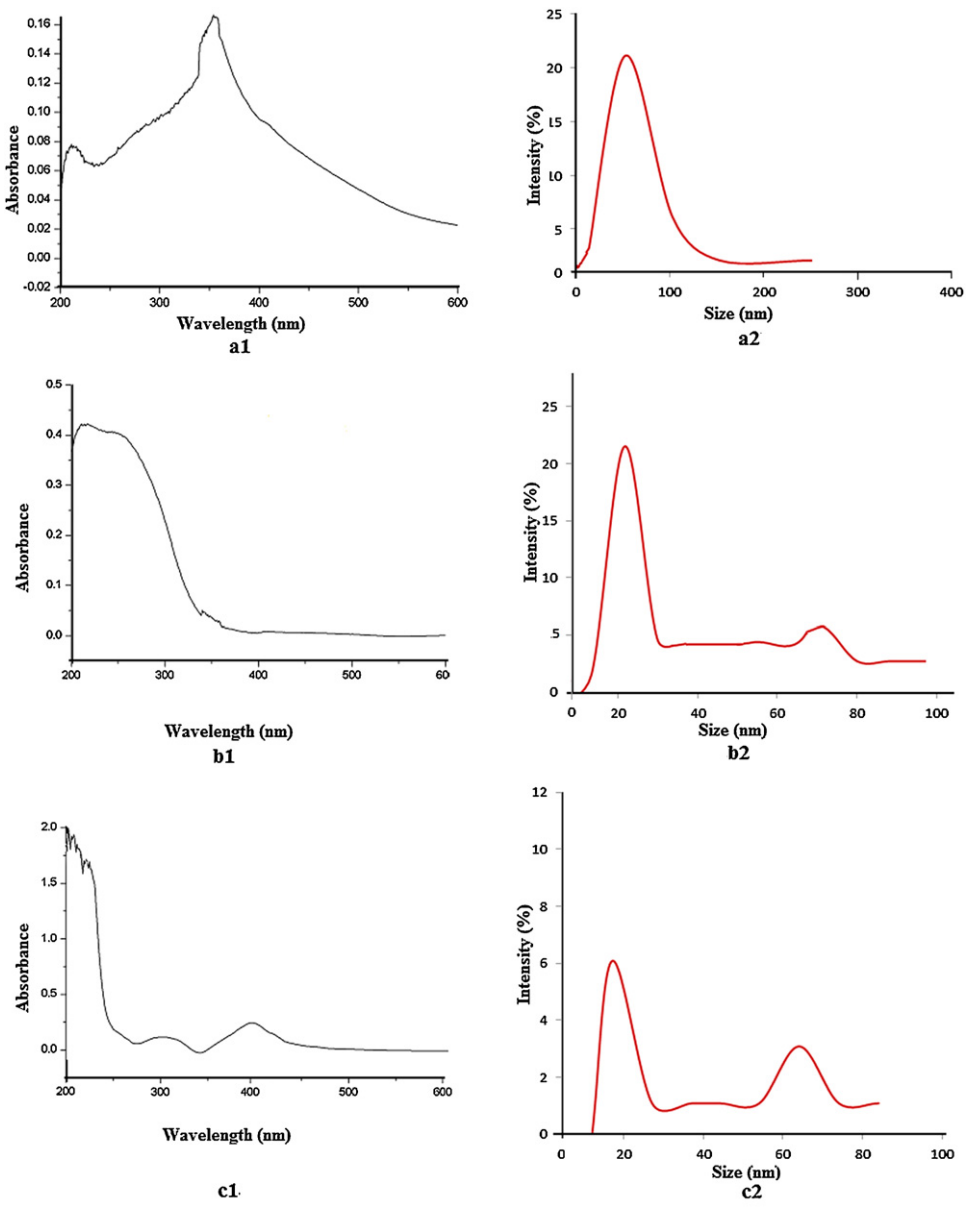

Fig. 5. UV–vis and DLS studies of nanoparticles dispersions.

electro-magnetic waves. Under the UV region, sliver nanoparticles give a characteristic absorbance band due to the excitation mode of the surface plasmon, which is dependent on the size of nanoparticles. These SPR bands undergo red-shift or blue-shift depending on the quantum size effects. Consequently, absorbance peaks can be used as tools to predict particle size and stability. Smaller silver nanoparticles will have an absorbance maximum around 400 nm, which increases with size and disappears when particle size falls outside nano dimensions. It is apparent that the dipole maximum rapidly shifts to longer wavelengths as the particle size increases beyond 70 nm (450 nm spectral maximum) revealing the peak at about 420 nm. The observed spectral shift results from the "spreading" of the particle's surface charge over a larger surface area so that the surrounding medium better compensates the restoring force thus slowing the electron oscillations (Maqusood Ahamed et al., 2011; Mahl et al., 2011). Our results showed that the maximum absorbance of synthesized nanoparticle was at 402 nm (Fig. 5c1) and with smaller sized particles predominating. The dynamic light scattering permits the determination of the particle size distribution from dispersed particles. It relies on Brownian motion which is monitored by Rayleigh scattering from dispersed particles. As Fig. 5c2 shows, the method gives reasonable size distribution data for the silver nanoparticles and the majority of particle size from 16 to 25 nm.

3.4. Surface morphology and particle size analysis of prepared nanoparticles

The surface morphology was studied by JEOL USA JSM-6390 Scanning Electron Microscope (SEM) and the average particle size was analyzed by Nanotract Particle Sized Analyzer (PSA). From the prepared ZnO it is visibly judged that the particle is in nanostructure and it has on track to produce but still maintained at a regular shape of hexagonal structure (Fig. 6a1). The ZnO nanoparticles have particle size appearing at 40 nm. Maximum of ZnO nanoparticles have 200 nm ranges (Fig. 6a2). The grain boundaries are clearly observed in the SEM micrographs of the TiO_2 nanoparticles (Fig. 6b1). It was revealed that the spherical morphology was a specification of the prepared powder under acidic solution of pH 2 and it is difficult to exactly measure the size of the primary spherical particles

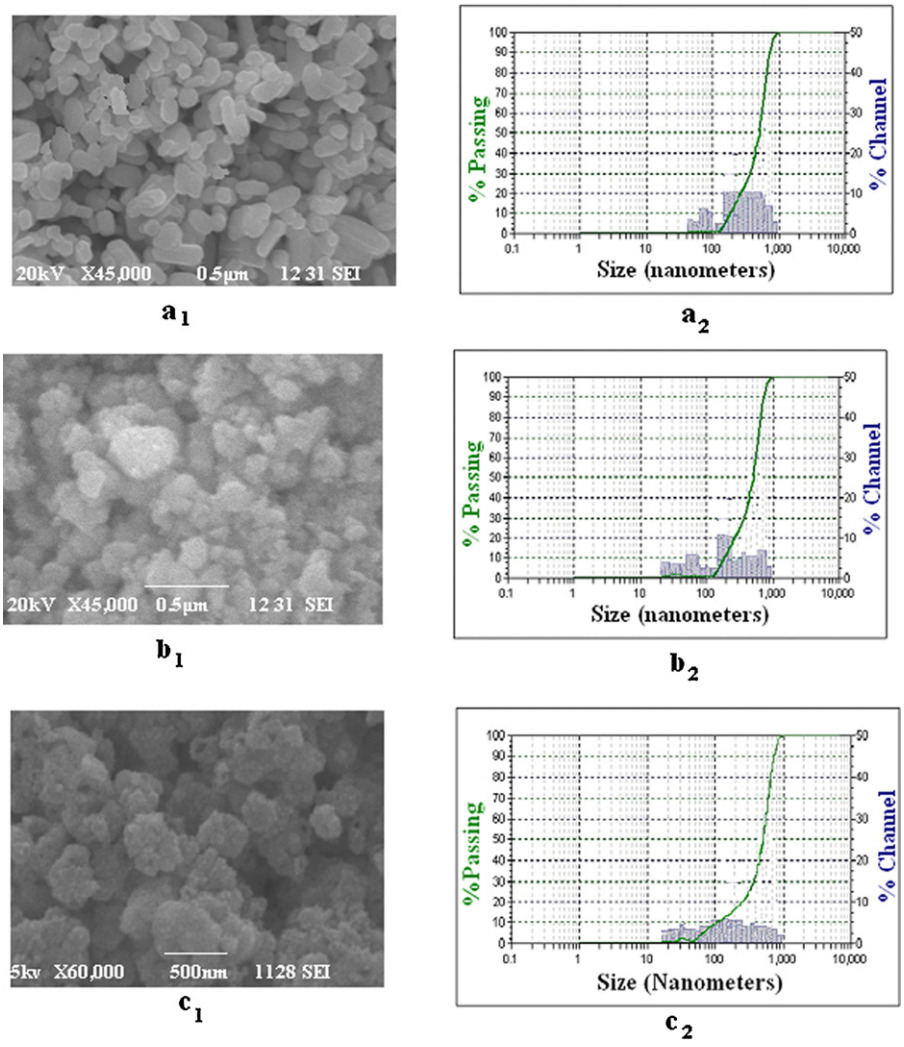

Fig. 6. SEM and PSA images of (a) ZnO, (b) TiO_2 and (c) Ag nanoparticles.

accurately. From the micrograph, its diameter estimated the ranges from 20 to 200 nm (Fig. 6b2). The Fig. 6c1 exhibited the appeared agglomerated spherical in nature of prepared silver nanoparticles and the PSA reports exhibited silver nanoparticles size ranges starts from 20 to 500 nm (Fig. 6c2).

3.5. Surface morphology studies of untreated and treated fabrics

From Fig. 7a1, the untreated cotton fabric surface has a clean, ribbon like structure and no deposition on its surface (Fig. 7a2). In sb-cd crosslinked fabric surface exhibited swelling nature (Fig. 7b1) and it is due to the crosslinking of sb-cd. The crosslinked sb-cd polymer is visually identified from Fig. 7b2. The ZnO nanoparticles coated fabric deposited on fabric surface (Fig. 7c1) and the needle shaped ZnO nanoparticles are clearly shown at higher magnification (Fig. 7c2).

The TiO_2 nanoparticle coated cotton fabric showed uninformed surface (Fig. 7d1) and the deposition also is clearly viewed at higher magnification (Fig. 7d2). Fig. 6e1 shows more swelling nature of fibers and a layer formation on fabric surface at higher

Table 1
Antibacterial activity test of the untreated and treated cotton fabrics against *S. aureus* and *E. coli*.

Sample	*S. aureus*				*E. coli*			
	10 min %R	15 min %R	20 min %R	30 min %R	10 min %R	15 min %R	20 min %R	30 min %R
Control	0	0	0	0	0	0	0	0
Cotton	0	2	2	2	0	0	0	0
sb-cd + cotton	40	64	77	85	38	61	70	78
ZnO + cotton	33	61	80	86	21	44	60	87
TiO_2 + cotton	23	41	58	76	27	53	76	87
Ag + cotton	43	71	83	rc	45	56	67	85
sb-cd + ZnO + cotton	87	92	99	100[a]	79	91	97	100*
sb-cd + TiO_2 + cotton	59	80	84	90	50	77	81	85
sb-cd + Ag + cotton	78	82	90	92	59	89	96	99

%R = bacterial reduction viability.
[a] Very good antibacterial activity.

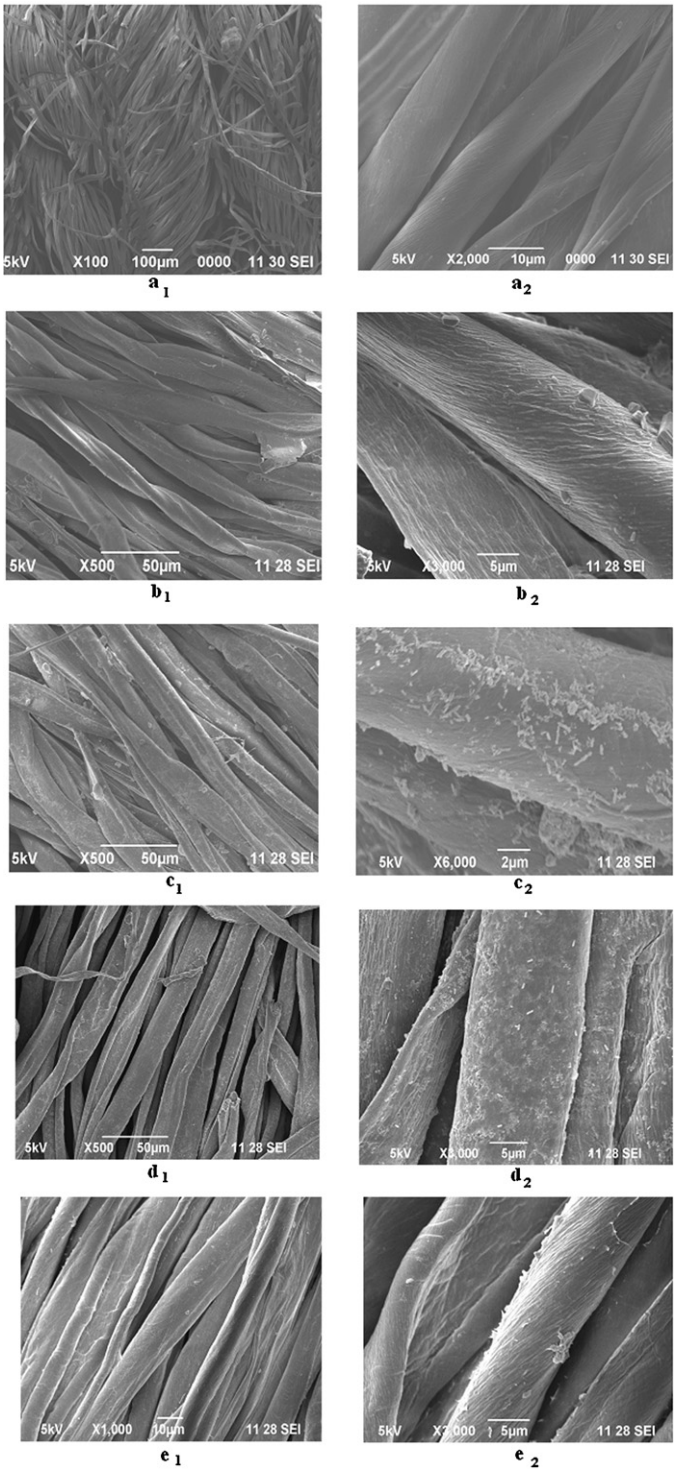

Fig. 7. SEM images of (a) untreated, (b) sb-cd crosslinked, (c) ZnO, (d) TiO_2 and (e) Ag nanoparticles coated fabric.

magnification (Fig. 7e2). It is formed by the Ag nanoparticles coating. These SEM studies proved that the coated nanoparticles deposited on the sb-cd crosslinked cotton. The sb-cd crosslinking was creating uninformed surface structure of cotton fiber. Subsequently a higher amount of nanoparticles can be absorbed on the surface scales. Therefore smaller particles could penetrate into the fiber structure (Rahal et al., 2011). The nanoparticles coated fabrics have been identified visually at three different depositions.

3.6. Antibacterial activity of untreated and treated fabrics

Table 1 shows the antibacterial activity of gram positive bacteria (*S. aureus*) and gram negative bacteria (*E. coli*) for untreated and treated fabrics. The antibacterial activity was determined by colony forming units (CFU) with time intervals. The untreated cotton fabric has no antibacterial effect. But sb-cd crosslinked fabric exhibited maximum of 85% of reduction for *S. aureus* and 78% of reduction for *E. coli*. It is due to the fact that untreated fabric does not have any antibacterial agent in its structure or surface. But the sb-cd polymers have the sulfur and nitrogen unit; it acts as an antibacterial agent. The untreated nanoparticles coated cotton fabric also performed as antibacterial agent. This activity increased in the sb-cd crosslinked nanoparticles coated fabrics. The sb-cd crosslinked ZnO nanoparticles coated fabric performed 100% of antibacterial activity for *S. aureus* and *E. coli* at 30 min. The sb-cd treated fabric TiO_2 nanoparticle coated fabrics showed 90% and 85% for *S. aureus* and *E. coli* respectively. The sb-cd treated fabric Ag nanoparticle coated fabrics exhibited 92% for *S. aureus* and 99% for *E. coli*. The effect of antibacterial activity of fabrics increases with crosslinked and nanoparticles coatings. The sulfonated polymers inhibit the in vitro growth of bacteria and N-sulfonated compounds act as a microbial inhibition compound. The ZnO and Ag nanoparticles performed better antibacterial reports than TiO_2 nanoparticles.

The ZnO nanoparticles have been measured to possess probable biological applications as efficient antimicrobial agents, drug carriers, bioimaging probes and possessing cytotoxic behavior for the treatment of cancer (Hanely et al., 2009; Ostrovsky et al., 2009). Being a semiconducting material, the band gap between conduction and valence electrons plays a vital role in the generation of ROS, which brings about conformational changes and oxidant injury to the surface of the membrane of the microorganism (Sharma et al., 2010). The ZnO nanoparticles, which have positive zeta potential, easily ruptures the cell membrane of *E. coli* (gram negative) on contact and releases Zn^{2+} ions, which causes lysosomal and mitochondrial damage. Finally, it is leading to the death of bacterial cells (Huang et al., 2008; Sharma et al., 2011). The antibacterial activity of TiO_2 is also related to ROS production. Particularly hydroxyl-free radicals and peroxide were produced under UV irradiation via oxidative and reductive pathways. A strong absorbance of UV renders activation of TiO_2 under solar irradiation, and significantly enhances solar disinfection (Zielinska et al., 2010).

The Ag nanoparticles also inhibit the growth of bacterium. So this type of fabric performed good antibacterial activity. Ag nanoparticles are binded to the bacterial cell wall and cell membrane from the interaction with the thiol groups of bacterial proteins leading to their subsequent inactivation. That is the loss of biochemical competence and without damage the cell. The small size of silver nanoparticles gives improved antibacterial effects due to the increase in their surface area for interaction with the microorganisms, as well as potentially enhanced oxidation–solvation and uptake rates across cell membranes into the cytosol to disrupt intracellular protein thiol groups (Feng et al., 2000; Panáček et al., 2006; Kulthong et al., 2010).

3.7. Cost vs performance analysis

Cost vs antibacterial performance studies of nanoparticles and modified fabrics are shown in Fig. 8. The production cost of three nanoparticles, ZnO exhibits lower cost than other TiO_2 and Ag nanoparticles production cost. The antimicrobial activity of Ag nanoparticles for *S. aureus* showed high cost but the production cost was higher than ZnO nanoparticles. But in the combination of sb-cd nanoparticles modified fabric showed good antibacterial activity for ZnO nanoparticles with low cost production (Fig. 8a). And also in antibacterial property for *E. coli*, ZnO with sb-cd crosslinked fabric

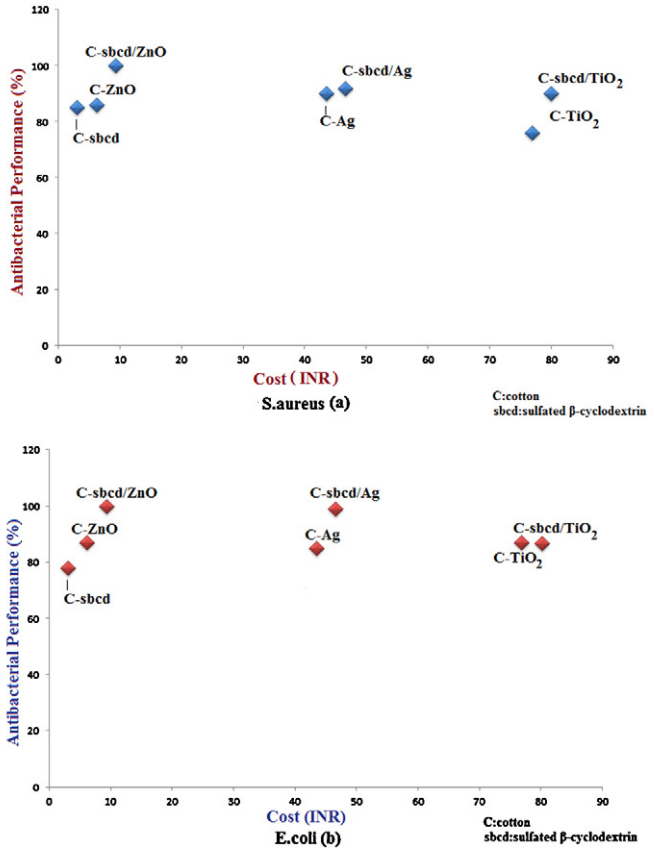

Fig. 8. Cost vs performance analysis.

exhibited low cost (Fig. 8b). In overall system, the ZnO nanoparticles performed very well with low cost. Though the Ag and TiO_2 nanoparticles exhibited good antibacterial activity, these nanoparticles production cost is expensive. This costing and performance analysis guide provides guidance to associations to determine the cost structure of their products and services.

4. Conclusion

The sb-cd crosslinking on cotton fabric has successfully prepared and also the nanoparticles were coated on this fabric by pad-dry-cure method. The sb-cd crosslinking properties were studied by FTIR and SEM studies. UV–vis and DLS studies proved the average particle size of the nanoparticles. The coated nanoparticles are clearly shown in the SEM images. The antibacterial activities were studied using bacteria *E. coli* and *S. aureus* The sb-cd with ZnO nanoparticles coated fabrics performed strong antimicrobial activity against both *S. aureus* and *E. coli* with low production cost. From this study we have concluded that sb-cd crosslinked ZnO nanoparticles coated fabric act as best antibacterial agent. This type of cellulose fabric may be suitable for kid's wears, medicinal bandages etc.

Acknowledgments

The authors acknowledge the financial support of DST-SERC/FT Major Research Project from Department of Science and Technology, New Delhi and Prof. & Head, Department of Physics, Alagappa University, Karaikudi for the XRD facilities.

References

AATCC Test Method 100–1999, 2002. Assessment of antibacterial finishes on textile materials. In: American Association of Textile Chemists and Colorists Technical Manual. AATCC, Research Triangle Park, NC.
Abidi, N., Cabrales, L., Hequet, E., 2009. Functionalization of a cotton fabric surface with titania nanosols: applications for self-cleaning and UV-protection properties. Applied Materials Interfaces 1, 2141–2146.
Agnieszka Dybowska, D., Croteau, M.-N., Superb Misra, K., Berhanu, D., Samuel Luoma, N., Christian, P., O'Brien, P., Jones, E.V., 2011. Synthesis of isotopically modified ZnO nanoparticles and their potential as nanotoxicity tracers. Environ. Pollut. 159, 266–273.
Ashkarrana, A.A., Iraji zada, A., Mahdavi, S.M., Ahadiana, M.M., 2009. ZnO nanoparticles prepared by electrical arc discharge method in water. Mater. Chem. Phys. 118, 6–8.
Bashkorov, S.A., Gremenok, V.F., Ivanov, V.A., 2011. Physical properties of SnS thin films fabricated by hot wall deposition. Surf. Interface Thin Films 45, 765–769.
Biswas, N.P., Biswas, A.K., 2005. Evaluation of some leaf dusts as grain protectant against rice weevil *Sitophilus oryzae*. Environ. Ecol. 23, 485–488.
Biwer, A., Antranikian, G., Heinzle, E., 2002. Enzymatic production of cyclodextrins. Appl. Microbiol. Biotechnol. 59, 609–617.
Buschmann, H.J., Knittel, D., Schollmeyer, E., 2001. New textile applications of cyclodextrins. J. Incl. Phenom. Macrocycl. Chem. 40, 169–172.
Cai, Z., Xu, B., Wang, W., Ge, F., 2010. Preparation of superhydrophobic cotton fabrics based on SiO_2 nanoparticles and ZnO nanorod arrays with subsequent hydrophobic modification. Surf. Coat. Technol. 204, 1556–1561.
Cao, Z., Sun, Y., 2009. Polymeric N-halamine latex emulsions for use in antimicrobial paints. Appl. Mater. Interfaces 1, 494–504.
Chowdhury, I., Sharon Walker, L., 2012. Deposition mechanisms of TiO_2 nanoparticles in a parallel plate system. J. Colloid Interface Sci. 369, 16–22.
Chudasama, B., Anjana Vala, K., Andhariya, N., Mehta, R.V., Upadhyay, R.V., 2010. Highly bacterial resistant silver nanoparticles: synthesis and antibacterial activities. J. Nanopart. Res. 12, 1677–1685.
Cireli, A., Yurdakul, B., 2006. Application of cyclodextrin to the textile dyeing and washing processes. J. Appl. Polym. Sci. 100, 208–218.
Feng, Q.L., Wu, J., Chen, G.Q., Cui, F.Z., Kim, T.N., Kim, J.O., 2000. A mechanistic study of the antibacterial effect of silver ions on *Escherichia coli* and Staphylococcus. J. Biomed. Res. 52, 662–668.
Ghoul, M., Bacquet, M., Crini, G., Morcellet, M., 2003. Novel sorbents based on silica coated with polyethylenimine and crosslinked with poly(carboxylic acid): preparation and characterization. J. Appl. Polym. Sci. 90, 799–805.
Hanely, C., Thurber, A., Hanna, C., Punnose, A., Zhang, J., Wingett, D.G., 2009. The influences of cell type and ZnO nanoparticle size on immune cell cytotoxity and cytokine induction. Nanoscale Res. Lett. 4, 1409–1420.
Kim, J.S., Kuk, E., Yu, K.N., Kim, J.H., Park, S.J., Lee, H.J., Kim, S.H., Park, Y.K., Park, Y.H., Hwang, C.Y., Kim, Y.K., Lee, Y.S., Jeong, D.H., Cho, M.H., 2007. Antimicrobial effects of silver nanoparticles. Nanomed.: Nanotechnol. Biol. Med. 3, 95–101.
Kim, S.S., Park, J.E., Lee, J., 2010. Properties and antimicrobial efficacy of cellulose fiber coated with silver nanoparticles and 3-mercaptopropyltrimethoxysilane (3-MPTMS). J. Appl. Polym. Sci. 119, 2261–2267.
Kitkulnumchai, Y., Ajavakom, A., Sukwattanasinitt, M., 2008. Treatment of oxidized cellulose fabric with chitosan and its surface activity towards anionic reactive dyes. Cellulose 15, 599–608.
Kulthong, K., Srisung, S., Boonpavanitchakul, K., Kangwansupamonkon, W., Maniratanachote, R., 2010. Determination of silver nanoparticle release from antibacterial fabrics into artificial sweat. Particle Fibre Toxicol. 7, 1–9.
Li, Y., Leung, P., Yao, L., Song, Q.W., Newton, E., 2006. Antimicrobial effect of surgical masks coated with nanoparticles. J. Hosp. Infect. 62, 58–63.
Lkhagvajav, N., Yaşa, I., Çelik, E., Koizhaiganova, M., Sari, Ö., 2011. Antimicrobial activity of colloidal silver nanoparticles Prepared by sol–gel method. Digest J. Nanomater. Biostruct. 6, 149–154.
Loftsson, T., Duchene, D., 2007. Cyclodextrins and their pharmaceutical applications. Int. J. Pharm. 329, 1–11.
Loftsson, T., Marcus Brewster, E., 2010. Pharmaceutical applications of cyclodextrins: basic science and product development. J. Pharm. Pharmacol. 62, 1601–1621.
Mahl, D., Diendorf, J., Meyer-Zaika, W., Epple, M., 2011. Possibilities and limitations of different analytical methods for the size determination of a bimodal dispersion of metallic nanoparticles. Colloids Surf. A: Physicochem. Eng. Aspects 377, 386–392.
Mao, Z., Shi, Q., Zhang, L., 2009. The formation and UV-blocking property of needle-shaped ZnO nanorod on cotton fabric. Thin Solid Films 517, 2681–2686.
Maqusood Ahamed, Majeed Khan, M.A., Siddiqui, M.K.J., Mohamad AlSalhi, S., Salman Alrokayan, A., 2011. Green synthesis, characterization and evaluation of biocompatibility of silver nanoparticles. Physica E 43, 1266–1271.
Martin, E.M., Valle, D., 2004. Cyclodextrins and their uses: a review. Process Biochem. 39, 1033–1046.
Ostrovsky, S., Kazimirsky, G., Gedanken, A., Brodie, C., 2010. Selective cytotoxic effect of ZnO nanoparticles on glioma cells. Nano Research 2, 882–890.
Panáček, A., Kvítek, L., Prucek, R., Kolář, M., Večeřová, R., Pizúrova, N., Sharma, V.K., Nevìčna, T., Zbořil, R., 2006. Silver colloid nanoparticles: synthesis, characterization and their antibacterial activity. J. Phys. Chem. B 110, 16248–16253.
Patterson, A., 1939. The Scherrer formula for X-ray particle size determination. Phys. Rev. Lett. 56, 978–982.
Perelshtein, I., Applerot, G., Perkas, N., Wehrschetz-Sigl, E., Hasmann, A., Guebitz, G.M., Gedanken, 2009. Appl. Mater. Interfaces 1, 361–366.

Piga, G., Malgosa, A., Thompson, T.J.U., Enzo, S., 2008. A new calibration of the XRD technique for the study of archaeological burned human remains. J. Archaeol. Sci. 35 (8), 2171–2178.
Pipatchanchai, T., Srikulkit, K., 2007. J. Sol–Gel Sci. Technol. 44, 119–123.
Rahal, R., Pigot, T., Foix, D., Lacombe, S., 2011. Photocatalytic efficiency and self-cleaning properties under visible light of cotton fabrics coated with sensitized TiO_2. Appl. Catal. B: Environ. 104, 361–372.
Rukmani, A., Sundrarajan, M., 2011. Inclusion of antibacterial agent thymol on β-cyclodextrin-grafted organic cotton. J. Ind. Textil., http://dx.doi.org/10.1177/1528083711430244.
Scherrer, P., 1918. Göttinger Nachrichten Gesell. 2, 98.
Selvam, S., Sundrarajan, M., 2012. Functionalization of cotton fabric with PVP/ZnO nanoparticles for improved reactive dyeability and antibacterial activity. Carbohydr. Polym. 87, 1419–1424.
Sharma, D., Rajput, J., Kaith, B.S., Kaur, M., Sharma, S., 2010. Synthesis of ZnO nanoparticles and study of their antibacterial and antifungal properties. Thin Solid 519, 1224–1229.
Sharma, D., Sharma, S., Kaith, B.S., Rajput, J., Kaur, M., 2011. Synthesis of ZnO nanoparticles using surfactant free in-air and microwave method. Appl. Surf. Sci. 257, 9661–9672.
Sorapong, J., Ruangsri, W., Surasak, W., Peter, G., Orn Anong, A., Wimol, N., 2006. Comparative study of lack dye adsorption on cotton fiber surface modified synthetic and natural polymers. Dyes Pigments 71, 188–193.
Stanier, C.A., Connell, M.J.O., Anderson, H.L., Clegg, W., 2001. Synthesis of fluorescent stilbene and tolan rotaxanes by Suzuki coupling. Chem. Commun. 5, 493–494.
Sundrarajan, M., Gowri, S., 2011. Green synthesis of titanium dioxide nanoparticles by *nyctanthes arbor-tristis* leaves extract. Chalcogenide Lett. 8, 447–451.
Teli, M.D., Shrish kumar, G.V.N., 2007. Functional Textiles and Apparels. J. Textil. Assoc. 68 (1), 21–30.
Thamaphat, K., Limsuwan, P., Ngotawornchai, B., 2008. Phase characterization of TiO_2 powder by XRD and TEM. Nat. Sci. 42, 357–361.
Vives, S., Meunier, C., 2008. Influence of the synthesis route on sol–gel SiO_2–TiO_2 (1:1) xerogels and powders. Ceram. Int. 34, 37–44.
Wu, D., Long, M., Zhou, J., Cai, W., Zhu, X., Chen, C., Wu, Y., 2009. Synthesis and characterization of self-cleaning cotton fabrics modified by TiO_2 through a facile approach. Surf. Coat. Technol. 203, 3728–3733.
Wu, D., Huang, Z., Yin, G., Yao, Y., Liao, X., Han, D., Huang, X., Gu, J., 2010. Preparation, structure and properties of Mn-doped ZnO rod arrays. Cryst. Eng. Commun. 12, 192–198.
Yang, T., 2009. Poly (vinyl alcohol)/sulfated β-cyclodextrin for direct methanol fuel cell applications. Int. J. Hydrogen Energy 34, 6924–6971.
Zhang, Z., Zhang, L., Wang, S., Chen, W., Lei, Y., 2001. A convenient route to polyacrylonitrile/silver nanoparticle composite by simultaneous polymerization–reduction approach. Polymer 42, 8315–8318.
Zheng, M., Wang, Z.-s., Zhu, Y.-w., 2006. Preparation of silver nanoparticles via template under ultrasonic. Trans. Nonferrous Met. Soc. China 16, 1348–1352.
Zielinska, A., Kowalska, A.E., Sobczak, J.W., Lack, I., Gazd, M., Ohtanie, B., Hupka, J., Zaleska, A., 2010. Silver-doped TiO_2 prepared by microemulsion method: Surface properties, bio- and photoactivity. Sep. Purif. Technol. 72, 309–318.