Zinc Stannate Nanostructure: Is It a New Class of Material for Multifunctional Cotton Textiles?

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ABSTRACT: This study demonstrates the synthesis of nano-zinc stannate and its application as a novel multifunctional finishing agent on cotton fabric. Nano-zinc stannate has been synthesized by the co-precipitation method, and the nanostructures produced have been characterized to investigate their morphology and microstructure by using scanning electron microscopy, transmission electron microscopy, and X-ray diffraction techniques. The synthesized nano-zinc stannate has been applied on cotton fabric and the multifunctional efficacies of the treated fabric, like UV resistance, antibacterial property, self-cleaning, as well as thermal stability, were analyzed. The as-synthesized zinc stannate-treated cotton fabric showed excellent efficiency in self-cleaning, antibacterial property, and flame-resistant action compared to the annealed nano-zinc stannate-treated cotton fabric. It was observed that the ultraviolet protection factor of the treated (annealed zinc stannate-treated) fabric shoot up more than 45 after treatment, and the same fabric showed more than 90% bacterial resistance against both Gram-positive and Gram-negative bacteria. Concerning thermal kinetics, the as-synthesized zinc stannate-treated fabric registered a 39% reduction in the peak heat release rate compared to the untreated cotton fabric, and it also showed catalyzed pyrolysis action and more amount of char mass (30−40% more compared to the control cotton) formation at higher temperature. The self-cleaning efficacy of the treated fabric has been examined against coffee stain and basic methylene blue dye. The treated fabric exhibited a good efficiency in cleaning of stain due to the free-radical scavenging behavior. Finally, it also has been proved that the integration of these nanostructure did not have any detrimental effect on the important physical properties (tensile strength, flexibility, and crease resistance) of the treated fabric.

1. INTRODUCTION

Textile finishing is the final step of textile chemical processing and is in great demand in the recent era as this is the area where highest value addition to textile substrate takes place. Various demanding value-added textile materials (with features like antimicrobial, UV-protective, fire-retardant, softened, crease proof, aroma textile, stiff fabric, odor proof textile, etc.) have been invented by researchers and launched into the market for customers. However, in most of the cases, a large quantity of synthetic chemicals have been explored for getting value-added property of textiles.1

Slowly at the dawn of the 21st century, issues like eco-friendly technology, sustainability, health hazards have grown so much that all of the consumers are slowly shifting their demands toward products that meet sustainability norms. Most of the synthetic chemicals explored in conventional finishing of fabric are slowly being banned due to their toxic and carcinogenic nature. As far as the conventional value addition of the textile material is concerned, wrinkle recovery, fire retardancy, softener finish, water repellency, etc. require a single synthetic chemical agent for each purpose. Therefore, especially in the current decade, reducing the process cost, consumption of larger quantity of chemicals, energy, time, etc. are the biggest challenges for industries as well as researchers. This leads to the necessity of the development of multifunctional finishing, which is defined as treating textile fabrics with two or more finishing agents in a combined bath and in a single step to impart multiple functional properties together. Multifunctional finishing therefore results in savings, in terms of energy, time, and water.2 Multifunctional finishing also implies using a single agent that can confer multiple functionalities in a fabric. This process makes the application easy and energy-efficient in terms of water and power saving. Moreover, the chemical consumption for different finishing approaches will decrease, resulting in a sustainable approach. However, the real challenge exists to develop such a material which would potentially possess the ability to render multifunctionalities in textile substrate.

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Adequate research with different technical approaches has been focused on developing such type of multifunctional agents starting from bio-macromolecules to inorganic metal oxides. Exploration of the bio-macromolecule-based technology and nanotechnology is the most popular and emerging research domain in the field of multifunctionality. Different waste bio-macromolecule-based extracts (banana pseudo-stem sap, coconut shell extract, pomegranate rind extract, etc.) have recently been explored by researchers for making natural-dyed, UV-protective, and fire-resistant textiles.3−8 Moreover, most of the treated fabrics also show antimicrobial efficacy against both Gram-positive and Gram-negative bacteria.9,10 However, the extraction process of natural dyes becomes very costly and time-consuming, high add-on to the fabric, and also application by mordant makes the process slightly more difficult. Therefore, nanotechnology uplifted in the research field and nanotechnology is an area of science that deals with matters having one or more dimension of less than 100 nm, and it is being used in many areas at the recent times, most likely in information technology, communication, paints, textiles, medicines, cosmetics, and many others. There has been a recent trend in the application of nanostructured materials in textile finishing. Nanotechnology promulgates special properties like antimicrobial, UV resistance, self-cleaning, nanoencapsulation of moisturizing agents, deodorizing, water or oil repellency, and many more to textile substrate.11−15

The nontoxicity and the chemical stability of UV blockers like TiO$_2$ and ZnO make them preferable over organic blockers.16 Antimicrobial properties are also demonstrated by imbuing various nanoparticles like nanosilver, ZnO, TiO$_2$, etc. into textile substrates. Nanoparticles of ZnO and TiO$_2$ are very effective in the UV region between 300 and 400 nm, which is mainly the UV A region and the UV B region. The maximum absorbance is mainly at 290−320 nm for TiO$_2$ and at 370−385 nm for ZnO.17,18 This is a drawback pertaining to the commercial UV blockers. TiO$_2$ nanoparticles have been well explored for UV-resistant and antibacterial finish, but yet there is no conclusive evidence of it having a fire-retardant property without any synergistic chemicals added. At the same time, ZnO has very low chemical stability and TiO$_2$ does not have a broad absorption range. Silver nanoparticles are also popular in the market in terms of only antibacterial efficacy. However, the application of silver nanoparticle is disadvantageous in terms of

Figure 1. (a) FE-SEM image of the as-synthesized ZnSnO$_3$. (b, c) TEM images at 80,000× magnification of the as-synthesized zinc stannate structures. (d, e) TEM images of annealed ZnSnO$_3$ and (f) EDX analysis of the as-synthesized ZnSnO$_3$. 

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harming the environment. Being a heavy metal, the existence of silver in the aquatic organisms may cause various genetic mutations, and later on, deposition in human body can also cause various health issues. The silver nanoparticle has been reported only in the field of antibacterial finishing; it does not possess any other properties like fire retardancy or UV resistance. Thus, we need to develop a nanoparticle of a metal oxide kind, which could provide protection from UV rays around 300−400 nm (i.e., it will cover both the UV A and B regions), be nontoxic so that its deposition on organisms does not cause any detrimental effect to the ecosystem, and act also as a finishing agent that can impart multifunctional properties like UV protection, fire resistance, antimicrobial, antistatic, self-cleaning, and others.

Zinc stannate nanostructure is a comparatively newly explored semiconducting metal oxide, which is similar to ZnO or TiO2 and with a band gap ranging from 3.8 to 4.1 eV (depending on the structure of zinc stannate), whereas ZnO and TiO2 have band gaps of 3.2−3.3 and 3.0−3.22 eV, respectively.18 Higher the band gap, more will be the absorbance of the UV rays when they will fall on these particles. This makes zinc stannate to cover a wider range of wavelength during the UV absorbance phenomenon. It is also known as zinc tin oxide, which has received more attention due to its good optical characteristics, high electron mobility, high electrical conductivity, and excellent stability compared to ZnO and SnO2.19 In addition, zinc stannate has been reported as a metal oxide which can be used as a fire retardant as well as an antimicrobial agent. Thus, application of zinc stannate on textile can be a very novel approach to discover it as a chemical agent that can endow a broad spectrum of multifinishes such as UV resistance, antibacterial, as well as fire-retardant behavior to textile substrates. The application in the nano form reduces the add-on percentage of the fabric to a large extent than the conventional finishes where for properties like fire retardancy, it requires at least 20−30% add-on. Zinc stannate nanostructure has been explored in various fields like gas sensing anode for lithium batteries, catalyst, fire retardant, antimicrobial, and most importantly as a dye destructor due to its photocatalytic effect (in textiles).20−24 However, there is no systematic study on the multifunctional efficacy of the same on textile substrate. Thus, the prime objective of this research context is to explore its functional effect to impart multiple protections of textile substrates against harmful UV rays, microorganisms, fire, and to make a self-cleaning fabric which can remove the stain by its own mechanism.

2. RESULTS AND DISCUSSION

2.1. Characterization of ZnSnO3 Nanostructures. Nanostructured zinc stannate has been synthesized according to the technical procedure mentioned in the Materials and Methodology of this manuscript. Thereafter, nano zinc stannate has been characterized by advanced technological tools for understanding its morphology, chemical composition, crystal structure, and particle size.

2.1.1. Field Emission Scanning Electron Microscopy (FE-SEM) and Transmission Electron Microscopy (TEM) Analyses. Confirmation of the morphology of the synthesized zinc stannate nanoparticles is an important parameter, and it has been analyzed by FE-SEM and TEM images. Higher-magnification images of FE-SEM showed the presence of cubelike structures. TEM images of same magnification (from different places of the sample) are represented in Figure 1b,c, which shows a clear view of the cubic-shaped zinc stannate nanoparticles, and the average dimension as analyzed from the ImageJ software is approximately 65 nm. The homogeneity of the shape is quite good as most of the visible images do not have large variation in the size of the cubes. A similar result has been found when the samples were annealed and its TEM images were analyzed. Figure 1d,e depicts the similar shape of the nanostructures, but the average dimension has been found to be reduced to 33 nm, which is quite possible after annealing.

2.1.2. Fourier Transform Infrared (FTIR) Spectrum Analysis. The FTIR analysis of both the samples (as-synthesized and annealed) revealed a significant change in the spectra of both the structures, depicted in Figure 2. The earlier structure showed the presence of bending vibration and stretching vibration modes of the −OH group at 3200 cm−1 in the structure of the as-synthesized zinc stannate. Thus, the as-synthesized structure can be depicted as ZnSn(OH)6 due to the presence of these surface OH groups. However, in case of the annealed one, there is no prominent peak at this range, which is one of the clear signatures of the dehydration, which has occurred by annealing. In addition, the bands observed at 778, 850, 1174, and ~2303 cm−1 due to the vibration of the M−OH or M−OH−M groups are also not present in the FTIR curve of the annealed one. The presence of a broad absorption peak from 530 to 591 cm−1 is mainly due to M−O−M that is the metal oxide bond of ZnO and SnO2, or Zn−O−Sn which do exist in the annealed sample. Thus, FTIR analysis clearly indicates the elimination of the −OH groups present at the surface of zinc stannate nanostructures during annealing.25

2.1.3. X-ray Diffraction (XRD) Analysis. The XRD pattern of the as-synthesized ZnSnO3 nanostructures is represented in Figure 3. The spectra pattern reveals that the structure of ZnSnO3 has proper peaks, which is matched with the JCPDS (No. 11-0274), confirming the cubic structure of ZnSnO3.26 No peak from other impurities, such as ZnO, other phases of ZnSnO3, etc., are detected by XRD analysis, and the results indicating that the products formed on the Zn substrate are...
pure face-centered cubic-ZnSnO$_3$. The XRD pattern showed many distinct peaks starting from 19.76 and the maximum intensity being at 22.84. The full width at half-maxima value was calculated to find the mean crystal size of the material. The Debye–Scherrer equation has been used to calculate the crystal size, and it has come around 27.32 nm. The annealed structure reveals that there is a shift in the maximum intensity of the peak to 33.96, but no match has been found with any JCPDS data. There is a significant decrease in crystal size to 2.89 nm. This may be due to the reduction in particle size due to annealing at high temperature.

**2.2. Characterization of Treated Fabric.** The SEM images of the control and the treated fabric are shown in Figure 4. The treated fabric showed the deposition of synthesized nanostructures on the cotton substrate. Some of the SEM images represented in Figure 4, showing agglomerated structure, may be due to a bigger cube size, but the higher-magnification picture reveals the presence of nanocubes on the surface of the cotton fibrils.

The FTIR characterization of the control and treated fabric is depicted in Figure 5. Concerning the control cotton fabric, a peak was observed at 3344 cm$^{-1}$ attributed to the O–H stretching for intramolecular bonding and another peak was observed at 3286 cm$^{-1}$ attributed to the O–H stretching for intermolecular bonding of hydrogen bonds present in the cellulosic structure. The peaks visible at 2921 and 2847 cm$^{-1}$ are assigned to the C–H asymmetric and symmetric stretching vibration, respectively. In the same curve, the peaks observed at 1740 and 1649 cm$^{-1}$ are mainly due to C═O stretching vibration and the O–H bending of adsorbed water in cotton structure, respectively. The peaks observed at 1364 and 1316 cm$^{-1}$ are the characteristic peaks for C–H bending in the cotton structure and for the rocking movement of CH$_2$ group, respectively.
For fabric treated with ZnSn(OH)$_6$, the bands observed at 778, 850, 1180, and $\sim2303$ cm$^{-1}$ may be correlated with the presence of M$^-$OH or M$^-$OH$^-$M groups, i.e., the metal hydroxide bond. The concerned FTIR curve also showed the bending vibration modes of surface $-\text{OH}$ groups at 3200 cm$^{-1}$, which may be associated with the presence of H-bonding with ZnSn(OH)$_6$ and the hydroxyl groups of cellulose due to a slight shift of the vibration of $-\text{OH}$. The FTIR curve for the fabric treated with annealed zinc stannate did not show the presence of M$^-$OH or M$^-$OH$^-$M groups on the substrate, whereas the intensity of the M$^-$O$^-$M or the Zn$^-$O$^-$Sn or ZnO or SnO$_2$ bonds got strengthened, which is visible at 530–591 cm$^{-1}$.

2.3. UV Absorbance and UV Protection Factor. The UV–visible spectroscopy of zinc stannate nanocubes reveals that mostly the absorbance range of this material lies between 280 and 310 nm with the maximum peak at 290.5 nm, as observed in Figure 6. The range of coverage at the maximum absorbance region is quite broad and, at the same time, this phenomenon is advantageous compared to ZnO and TiO$_2$ as it can cover the region of both UV-A and UV-B. Concerning the absorbance of annealed zinc stannate, the material did not show any major change in the nature of the curve, but there is a slight change in the maximum absorbance value. This may be attributed to the fact that there is a decrease in nanocubes’ size after annealing, which has also been supported by the TEM analysis, represented in Figure 1.

The UV protection factor (UPF) evaluation of the treated and untreated cotton fabric had a drastic difference in the results obtained. Details of the UPF values of the control and treated fabric are represented in Table 2 and also in Figure 7. Data represented in Table 1 reveal that there is an improvement of UPF value after incorporation of the zinc stannate nanocubes irrespective of as-synthesized and annealed form on the fabric. It is clear that zinc stannate can prevent the UV rays from coming in direct contact with the fabric which is done by absorption of the UV rays from the range of UV-A to UV-B approximately 290–400 nm.

Figure 5. FTIR images of treated and untreated cotton fabric.

Figure 6. UV–visible spectroscopy of the as-synthesized and annealed ZnSnO$_3$.

Figure 7. UPF results of treated and untreated cotton fabric in bar chart.

Table 1. UPF Results of Treated and Untreated Cotton Fabric

| sample details | add-on (%) | UPF (average of six readings) | CV (%) |
|----------------|------------|------------------------------|--------|
| control (C)    |            | 7.12                         | 2.14   |
| A$_1$          | 2          | 14.76                        | 3.15   |
| A$_2$          | 5          | 22.48                        | 2.58   |
| A$_3$          | 7          | 30.06                        | 6.42   |
| A$_4$          | 10         | 48.43                        | 4.37   |
| P$_1$          | 2          | 8.79                         | 2.85   |
| P$_2$          | 5          | 10.45                        | 4.10   |
| P$_3$          | 7          | 13.62                        | 3.00   |
| P$_4$          | 10         | 18.79                        | 3.84   |
testing results revealed that the treated samples of both P and O2 species by generation of holes due to its semiconductor nature. This may occur when this material is exposed to UV light or sunlight. The maximum reduction was showed by sample P4 which contained the highest add-on %. However, even a lower extent of add-on is good enough for achieving 90% bacterial reduction. Thus, the zinc stannate nanostructures have effectiveness to kill the bacteria and reduce the number of colonies built on the plate. The plates were checked after 24 h incubation at 37 °C. The antimicrobial results against E. coli were slightly lower than those against S. aureus, as the former has three layers in cell wall, which sometimes are difficult to penetrate or attack by even nanostructures. However, still the results are quite positive to say that zinc stannate acts as an effective antibacterial agent. The mechanism is mainly related to the photocatalytic activity of the material where it produces OH*, O2−, and HO2− free radicals which can disrupt the cell membrane as well as the cell wall of the bacteria which are made of phospholipids.30 Though the testing conditions, according to the AATCC 100 method, were kept in moist atmosphere and in the dark conditions for the inoculation of bacteria, the mechanism of antimicrobial effect is different in that scenario. The antibacterial activity in dark condition can be explained by the slow release of Zn2+, which comes from a very small dissolution of zinc stannate in the moist atmosphere only to disrupt the bacterial cell wall.31 The use of this fabric will mainly be a garment, so for that, the earlier-mentioned mechanism of free-radical formation will take place when it is exposed to sunlight.

### 2.5. Thermal Properties

#### 2.5.1. Thermogravimetric (TG) Analysis (TGA)

Thermal kinetics of the control and treated fabric have been measured by TG analysis (with the first derivative) and are represented in Figure 9. Control cotton fabric showed one sharp peak at around 380 °C, which may be due to the liberation of flammable gases (levoglucosan, pyroglicosan, etc.), and it has been assigned as the pyrolysis (depolymerization of cellulosic chain) temperature of the cellulosic polymer.32–34 In addition, it also shows one peak at around 480 °C, which may be assigned to the char oxidation from aromatic to the aliphatic form.4,35 On the contrary, the first derivative of the as-synthesized zinc stannate-treated cotton fabric showed two major peaks at 300 and 413 °C, which may be corroborated with the pyrolysis and with the char oxidation phenomena, respectively. It clearly shows that in the treated cotton fabric, the pyrolysis phenomenon has been catalyzed by 70–80 °C, and as a result, the extent of the flammable gas formation also has been reduced. On the other hand, annealed zinc stannate-treated cotton fabric shows only one sharp peak at around 340 °C, which is somehow more than the as-synthesized nano zinc stannate-treated cotton fabric but 40 °C less than the pyrolysis point of the control cotton fabric. Another observation from the TG curve is that the annealed zinc stannate-treated cotton sample retains 3–4% of char mass, which is almost equal to the char mass of the control cotton fabric. However, the as-synthesized treated cotton fabric showed 30% char mass retention at higher temperature. This high thermal stability behavior also can be correlated with the LOI value (26) and the burning rate of the treated fabric. All of the important data connected with the TG curve are represented in Table 2.

From the overall TG curves, it can be revealed that the zinc stannate treatment on the cotton fabric has enhanced the dehydration potential of cellulose polymer by catalyzing the pyrolysis phenomenon and more amount of char mass

| sample code | control (C) | A4 | P4 |
|-------------|-------------|----|----|
| temperature at 5% loss °C | 232 | 67.32 | 234 |
| temperature at 10% loss °C | 278 | 232 | 280 |
| major mass loss °C | 365 | 340 | 310 |

Table 2. Temperature at Different Weight Loss Percentage and Limiting Oxygen Index (LOI) of Samples A4, P4, and C

Figure 8. Percentage bacterial reduction of treated fabric of different add-on tested against both E. coli and S. aureus bacteria.
retention. However, the as-synthesized zinc stannate-treated sample is more stable compared to the annealed treated cotton fabric in terms of the pyrolysis behavior and, more importantly, a significant amount of char mass is retained at higher temperature.

2.5.2. Limiting Oxygen Index (LOI). The LOI tests were performed separately on treated fabric. The control fabric showed an LOI of 20.83, and the treated fabric A4 and P4 had a greater LOI value than the control one, 25.69 and 26.21, respectively. This means that it will have more oxygen content than the normal atmosphere for the fabric to burn, thus making it a flame-resistant textile.

2.5.3. Cone Calorimeter Test: Fire Retardancy. For further technical understanding corroborated with the thermal kinetics and also for the fortification of the TG results, forced combustion experiments of the control and the treated fabric have been performed. A cone calorimeter study of the untreated and the treated fabric has been carried out to understand the burning behavior of the samples. It is known that heat flux is directly related to the temperature of the flaming. The temperature of the calorimeter can be adjusted to generate different heat fluxes like 25, 35, 60, and 75 kW/m². The samples were tested at a heat flux level of 35 kW/m², as in the case of a developing fire, the heat flux level remains similar. Home furnishing textile materials have been standardized to be tested in a similar heat flux. The related data for this test are captured in Table 3. The analysis is depicted in Figure 10. It has been noticed from the cone calorimeter analysis that the control fabric was prone to catch fire quickly and the time to ignition (TTI) is around 13.8 s, whereas both the annealed and the as-synthesized fabric showed high time to ignition values of 61.9 and 28.8 s, respectively. It implies that zinc stannate present on the surface of the fabric has decreased the flow of heat, and as a result, the time to ignition (TTI) value is higher compared to the control fabric. After completion of the combustion process, the treated fabric showed intense white-colored ash material, whereas the control cotton fabric showed light gray color, netlike fragile char mass after combustion. It has been observed from the experimental values that the peak heat release rate (PHRR) of the treated (A4 and P4) fabric is reduced 30 and 45% compared to the control fabric, which may be due to the heat absorption by the insulating coating of nano zinc stannate. Likewise, the peak heat release rate and total heat release (THR) of the treated fabric were also found to be lowered and much lower (THR: 0.22) in the case of the as-synthesized zinc stannate-treated cotton fabric compared to the control cotton fabric (THR: 0.35). The concerned curves of the control and treated fabric are represented in Figure 10. The calorimetric analysis also determines the maximum average rate of heat emission (MARHE), which signifies the average energy value produced in a single combustion period. The maximum average rate of

![Figure 9. TGA and differential thermal analysis results of fabric sample A4 (annealed), P4 (as-synthesized), and control cotton.](image1)

### Table 3. Summary of Cone Calorimeter Data

| sample code | add-on (%) | heat flux (kW/m²) | PHRR a (kW/m²) | THR a (mJ/m²) | MARHE a (kW/m²) | time to ignition a (s) |
|-------------|------------|------------------|----------------|--------------|----------------|---------------------|
| control     | 35         | 84.8             | 0.35           | 14.58        | 13.80          |
| A4          | 10         | 35               | 63.0           | 1.61         | 14.90          | 61.90               |
| P4          | 10         | 35               | 52.54          | 0.22         | 9.89           | 28.80               |

aAverage value of three readings.
heat emission (MARHE) exhibited an almost 30% reduction in the case of the as-synthesized zinc stannate-treated cotton fabric compared to the control cotton fabric, as depicted in Figure 10. In summary, it can be concluded that the as-synthesized zinc stannate treatment has reduced heat release from the treated fabric during combustion. The high thermal stability of the as-synthesized zinc stannate-treated cotton fabric has also been reaffirmed by thermogravimetric analysis, which shows more mass retention of the same fabric at higher temperature compared to the control cotton fabric.

It has been observed from TG analysis that the zinc stannate treatment catalyzes the pyrolysis phenomenon and also assists to enhance the char formation. Thermal stability of the treated fabric also has been reflected by the LOI value (25 and 26) of the treated fabric. Moreover, forced combustion behavior reveals that the treated fabric shows lower heat release compared to the control cotton fabric. In fact, cubes of nano zinc stannate deposited on the cotton fabric surface absorb heat and accelerate the dehydration of cellulosic structure. It means that the treated fabric has been made nonconductive and fabric has been made fire resistant by condensed phase mechanism of fire resistant action. It also may be the fact that the concern zinc stannate treatment can form intumescent coating on the fabric surface, which resists the heat flow through the fabric. From both the TG analysis and forced combustion behavior, it has been confirmed that the as-synthesized zinc stannate-treated cotton fabric shows more thermal stability (in terms of char, pyrolysis action, heat release, rate of heat emission, etc.) compared to the annealed treated fabric. This phenomenon may be due to the fact that the surface energy of the annealed fabric is lower and also the nanocubes presented here are in the dehydrated form compared to the as-synthesized fabric. As a result, heat can easily get flow through the cotton fabric from one molecule to the next molecule of the fiber structure without obstacles, and as a result, it shows lower thermal effectiveness compared to the as-synthesized treated cotton fabric.

2.6. Self-Cleaning Efficiency. Self-cleaning is a phenomenon very common in most of the inorganic metal oxides. This is probable when the electrons present in the valance band of the material jumps to the conduction band only after exposure to UV rays and in turn releases CO₂ and H₂O with the formation of singlet oxygen which degrades the stain or dye that is attached on the treated fabric. The treated samples were tested for its self-cleaning effect by adding a small drop of coffee stain on the treated fabric and control cotton fabric, and then the samples were irradiated with UV light of intensity 1 W/m² in a closed chamber. The irradiation time was varied from 0, 8, and 20 h. It has been observed that as the irradiation time was increased, the coffee stain in the treated fabric vanished, whereas after 20 h, the stain is still visible in the control (a) sample, represented in Figure 11. The wavelength of the UV lamp lied between 300 and 350 nm. The self-cleaning effect of zinc stannate nanocubes also could be established by the dye degradation phenomenon.³⁹

Both the P₄ and C fabrics were dyed with methylene blue (commonly marketed as cationic dye) dye. The samples were exposed to daylight for 6, 12, and 24 h. The K/S values were calculated both for the control and preexposure and postexposure samples and are represented in Figure 12. There is a significant decrease in the K/S value for the P₄ sample, whereas in the control sample, the value is almost
constant. The percentage reduction in the K/S value is 83%. The tests for self-cleaning were only done on the as-synthesized zinc stannate-treated fabric. The presence of surface OH groups enhances the photocatalytic activity of the material by promoting the formation of OH\(^{-}\), which acts as an oxidizing agent and promotes degradation of the dyes or stains (organic molecules) that are available on the surface.\(^{40}\)

A detailed probable mechanism that lies behind the gradual scavenging mechanism of methylene blue dye by free radical is represented in Figure 13. From Figure 13, it has been observed that methylene blue is made by cumulating three benzene rings containing alternating double bond and single bond. Indeed, this structure acts as a chromophore for this dye. When light energy falls on the zinc stannate-treated cotton fabric surface, it generates free-radical OH\(^{\cdot}\) by the photocatalytic activity of zinc stannate. This free radical acts as an oxidizing agent and initially fragmented the collating benzene ring of the dye stain. The OH\(^{\cdot}\) free radical also reacts with the highly reactive sulfur group of the benzene ring of the dye by pie bond breakage mechanism and forms sulfinic acid (−SO\(_3\)H) in the further process of degradation. Finally, after further degradation, only the hydroxyl (−OH) has been observed outside the benzene ring, and in due course, it has been transferred to acid, water, and carbon dioxide. At the end of the radical scavenging process, dye destruction has occurred and the treated fabric looks cleaner like it was before the application of dye on it.\(^{41}\)

### 2.7. Physical Properties of Treated Fabric

The physical properties of the treated fabric (Table 4) were evaluated, in which the tensile strength retention was reported as 90–95% in the case of both warp and weft directions of the annealed treated fabric. The crease recovery angle (CRA) of the treated fabric showed almost no change in the angle; thus, there is no significant effect on the dimensional stability of the treated fabric. Also, there is a slight increase in bending length in both weft and warp directions, which may be due to the finishing treatment, which makes the fabric somewhat stiff when particles enter within the fiber structure.

#### Table 4. Physical Properties Like Tensile Strength Loss, Crease Recovery Angle, and Bending Length of Samples \(A_4\), \(P_4\), and \(C\)

| sample      | strength retain (\%)\(^{a}\) | CRA\(^{a}\) (W + F) | bending length (cm)\(^{a}\) |
|-------------|-----------------------------|-------------------|-----------------------------|
|             | warp | weft |                     | warp | weft                      |
| control (C) | 140  | 3    |                     | 4.04 | 3.92                      |
| sample \(P_4\) | 85.6 | 82.3 | 130                | 3.91 | 3.86                      |
| sample \(A_4\) | 92.3 | 90.7 | 137.5              |       |                           |

\(^{a}\)All of the results taken are average of 10 readings with CV % less than 5.

### 3. CONCLUSIONS

The synthesis method for zinc stannate has been optimized and a proper nanocube-like structure has been achieved with conclusive evidence by various characterization techniques. The crystal structure obtained has been found to be perovskite. The structural and morphological analysis of the annealed form of zinc stannate has also been elucidated in a systematic way. In addition of the synthesis details, in the present research work, zinc stannate has been demonstrated as a promising new class of nanomaterials to impart multifunctional properties to the textile substrates. The maximum UPF achieved on a cotton fabric was around 48, which is good enough to protect textiles against harmful UV rays. The UPF was high for the annealed zinc stannate-treated fabric, the main reason being very small cube size and the structure was free from −OH groups. On the contrary, the as-synthesized zinc stannate (before annealing) rendered very promising results for other properties like self-
cleaning, antibacterial, as well as thermal stability. The mechanisms of various functional properties of the nanostructures on textile substrates also have been established. However, finishing durability against washing is a big challenge in the field of nanotechnology, which needs to be addressed separately in a subsequent study. But obviously the developed functional fabrics could easily find their usages in various home textile-based products where washing is not very frequent. Such applications are always faced with various challenges while processing as we know all nanoformation techniques have not been yet fully scalable in terms of commercialization. The feasibility of the manufacturing process focused in this research work gives it an added advantage compared to other processes so that this method can be easily taken forward for industrial trials.

4. MATERIALS AND METHODOLOGY

4.1. Materials. 100% Cotton fabric of 100 g/m² with 60 ends per inch and 50 picks per inch has been used for the application of multifunctional finish. Zinc acetate dihydrate \([\text{Zn(CH}_3\text{COO)}_2]\) and potassium stannate \((\text{K}_2\text{SnO}_3)\) were acquired from Sigma-Aldrich Pvt. Ltd., Bengaluru, India. Deionized water has been used for the synthesis of zinc stannate nanostructures.

4.1.1. Synthesis of Zinc Stannate Nanostructure. In a typical experiment to manufacture zinc stannate nanostructures, 2.1949 g of zinc acetate \([\text{Zn(CH}_3\text{COO)}_2\cdot3\text{H}_2\text{O}]\) salt (10 mmol) was added to 100 mL of deionized water and the solution was stirred completely until it got dissolved. Another 10 mmol solution of potassium stannate trihydrate was made by dissolving 2.9894 g of \(\text{K}_2\text{SnO}_3\cdot3\text{H}_2\text{O}\) in 100 mL deionized water. This solution (100 mL) was added to the previously made zinc acetate solution keeping the molar ratio 1:1. Then, the solution was stirred vigorously in a magnetic stirrer and kept for 7 h. The temperature maintained was 40 °C in the reaction medium. After the reaction, the precipitates were collected by centrifugation and washed with deionized water several times to remove residual ions in the products. The final products were then dried in an oven at 80 °C for 2–3 h before characterization. This material collected is the as-synthesized zinc stannate. The synthesized zinc stannate was further calcinated at 600 °C for 3 h before application of both as-synthesized and calcinated one on textile substrate.

4.2. Integration of Synthesized ZnSnO₃ Nanostructure on Cotton Fabric. First, 5 and 10% (w/v) concentrations of zinc stannate nanostructures were prepared by ultrasonication at 60 °C. The fabric was dipped in it for 5 min and then padded. Padding mangle (RBE Engineering Pvt. Ltd., India) at a nip pressure of 0.2 kg/mm² and wet expression min and then padded. Padding mangle (RBE Engineering Pvt. Ltd., India) at a nip pressure of 0.2 kg/mm² and wet expression

4.2.1. Calculation of Add-on %. The fabric was dried completely and weighed after treatment in a weighing balance, and the untreated fabric was previously dried and weighed. The difference between the weight was calculated with respect to the original weight and multiplied by hundred to get the add-on percentage

\[
\text{add-on \%} = \left(\frac{W_2 - W_1}{W_1}\right) \times 100
\]

where \(W_1\) and \(W_2\) are the oven-dried weights of the control and treated samples, respectively. The reported results are an average of five readings.

The add-on % obtained (as mentioned in Table 5) after the treatment on the fabric are 2, 5, 7, and 10%, and they were conditioned according to the testing conditions before the treated fabric were tested for the properties mentioned.

The treated fabrics were coded by the name A (1–4) for the annealed zinc stannate-treated fabric and P (1–4) for as-synthesized zinc stannate.

4.3. Characterization of Zinc Stannate Nanostructures. 4.3.1. Scanning Electron Microscopy (SEM) and EDX Analyses. ZEISS scanning electron microscope (model: SEM Evo 50) was used to observe the morphology of the synthesized nanoparticles and also their distribution on fabric surface. This was also used to calculate the dimensions of the nanoparticles that are present. EDX analysis of the samples was carried out in a TM3000 table top microscope (Hitachi, Swift ED3000). EDX analysis was also done as a confirmatory test for the elemental analysis and the atomic weight content of the elements of the manufactured nanostructures.

4.3.2. Transmission Electron Microscopy (TEM). TEM was done to view the synthesized ZnSnO₃ nanostructures at a higher magnification level than SEM as the particle size was lower than 100 nm. JEOL JEM 1400 instrument with an acceleration voltage of 120 kV was used to record the images. In addition to it, selected area electron diffraction diagram was analyzed from the images received.

4.3.3. X-ray Diffraction (XRD). XRD (PANalytical odel: X’Pert PRO) was done to analyze the structure of the formed ZnSnO₃ crystals. As zinc stannate has two different structures, this structural confirmation is very important, as structural properties can change the application properties of the material. The X-ray diffractometer with Cu Ka, λ = 1.5406 Å as the source with 30 kV capacity was used for this analysis. 4.3.4. Fourier Transform Infrared (FTIR) Spectroscopy. FTIR was used mostly for identifying chemicals that are either organic or inorganic. The infrared absorption spectrum was used to identify the chemical bonds present in zinc stannate nanostructures. FTIR analysis has been performed by using PerkinElmer Spectrum BXFT-IR system. The range of wavelength measured was 450–4000 nm. The data were measured in transmission mode.

4.4. Characterization of Treated Fabric and Its Multifunctional Properties. 4.4.1. UV Absorbance and UPF. The evaluation of UV protection given by the fabric was done according to the AATCC test method 183 (AATCC 2005). It measures the transmittance or blocking of erythemal weighted UV radiation through fabrics by the use of an instrument called UV–visible spectrophotometer. A single wavelength beam is directed in the UV light (which is of measured quantity and perpendicular to the surface of the

| sample code | add-on % |
|-------------|---------|
| control (C) |         |
| A₁          | 2       |
| A₂          | 5       |
| A₃          | 7       |
| A₄          | 10      |
| P₁          | 2       |
| P₂          | 5       |
| P₃          | 7       |
| P₄          | 10      |

Table 5. Coding of Treated and Untreated Cotton Fabric
is denoted as weight with varying temperature and time. The test was carried out against Gram-positive (S. aureus) and Gram-negative (E. coli) bacteria. The percentage reduction of bacteria by the cotton fabric treated and untreated is denoted as R

\[ R = \frac{(B - A)}{B} \times 100 \]  

where “R” is the percentage reduction, “A” is the number of bacteria colonies formed on the control sample, and “B” is the number of bacteria colonies formed on the treated sample.

4.4.3. Dye Degradation. The control cotton fabric and ZnSnO₃-treated fabric were dipped in a methylene blue dye solution (1% on the weight of the fabric) for 15 min for proper staining. The samples were dried and conditioned after that and were exposed to daylight irradiation for 12 h. The color strength of the fabric was measured before and after the irradiation, which is the K/S value. This is also known as the color strength, which is expressed as the ratio of absorption and scattering coefficient

\[ K/S = \frac{(1 - R)^2}{2R} \]  

where R is the reflectance value of the methylene blue dye at its maximum absorbance.

4.4.4. Assessment of Degradation of Coffee Stain. A coffee solution was prepared in water to replicate the situation of a stain. The treated fabric was cut into 6.5 cm x 4.5 cm, and one drop of stain was spread on the treated fabric. All of the samples were irradiated with a UV lamp of the 354 nm wavelength interval (nm), and then the fabrics were tested for their physical properties.

4.4.5. Physical Properties Testing of Fabric. The physical properties of the control and the treated fabric were measured in terms of tensile strength (ASTM D 5035:2006) and crease recovery angle (AATCC 66:2008). Conditioning of the specimens was done keeping the fabric samples at a relative humidity (RH) of 65% and a temperature 26 ± 2 °C for 24 h, and then the fabrics were tested for their physical properties.

4.4.6. Thermal Properties. 4.4.6.1. Thermogravimetric Analysis (TGA). The TGA of the fabrics was done by thermogravimetric analyzer (METTLER TOLEDO TG-50/MTS). The tests were executed in air atmosphere at 2 mL/min at a heating rate of 20 °C/min and ranging from 50 to 700 °C. This test helps to develop knowledge about the degradation of fabric with varying temperature and time.

4.4.6.2. Limiting Oxygen Index (LOI). LOI test was performed on control and all treated samples. LOI values of the fabrics were determined by the amount of O₂ and N₂ present in the chamber to ignite the clamped material. The following equation was used to calculate this value

\[ \text{LOI} = \frac{\{[O_2]/([O_2] + [N_2]) \} \times 100} \]  

4.4.6.3. Cone Calorimeter Analysis. A sample specimen of “100 x 100” mm² control and the zinc stannate-treated cotton textile were tested according to procedure of ASTM standard: ISO 5660. The specimens were kept horizontally under the cone with a heat flux value of 35 kW/m². Conditioned samples (65% RH and 27 °C) were ignited to record the data according to ISO 5660-1. Machine was calibrated by methane gas and the spark igniter was used above the sample according to standard test method.

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**Notes**

The authors declare no competing financial interest.

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