A Mini-Review on Recent Advances in Nanotechnology Applications with Reference to Cotton

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Dr. N. Vigneshwaran, Principal Scientist at ICAR-CIRCOT, Mumbai, India finished his Doctorate at Indian Institute of Technology, Delhi in 2005 in molecular biology towards fabrication of fiber optic-based biosensor. He initiated microbial synthesis of nanomaterials at ICAR-CIRCOT, Mumbai in 2005 and developed protocols for finishing of cotton by nano-silver and nano-zinc oxide to impart antibacterial and UV protection properties. The process of Nano-zinc oxide production was commercialized to a chemical company at Chennai, India in 2007. Later, he focused on energy-efficient nanocellulose production from cotton linters with a World Bank supported project (NAIP of ICAR). Dr Vigneswaran developed, a pilot plant for nanocellulose production. He successfully guided 2 scholars for Ph.D (Science) in Microbiology and 3 scholars are currently pursuing PhD under his guidance. Dr. Vigneshwaran received the NASI-SCOPUS Young Scientist Award for Agriculture in 2014; Young Scientist Award from Association of Microbiologists of India in 2018 and ICRA-Asia Young Scientist Medal in 2019.

Abstract

Nanotechnology is revolutionising the entire domain of scientific research resulting in unveiling of novel and unexpected products in the markets. The impacts of nanotechnology were felt earlier in the textile industry followed by pharma, electronics, energy, transportation, robotics, pulp and paper, food and health, as well as agriculture and allied sectors. As early as 1998, a company called Nanotex® was founded to replicate the natural water repellence of plant surfaces on the surfaces of textile materials. Today, the impact of nanotechnology is felt in all areas of cotton — breeding of cotton for targeted modifications, nano-fertigation, nano-pesticide applications, nano-sensors for precise farming, nano-clays and nano-hydrogels for soil improvement, nano-finishing of cotton textiles and production of nanocellulose from cotton fibres. This review focuses only on the application of nanotechnology on processing of cotton fibres/yarns/fabrics in the textile sector.

Nanotechnology

Nanotechnology refers to the manipulation of materials in the nano-size range for desired properties. The nano-size range mainly denotes 1 to 100 nanometres (nm) while a higher range is also included if the material is polymeric. The main concept is that the material should exhibit size-dependent properties in the defined size range. The size-dependent properties include surface area to volume ratio (SAR), surface plasmon resonance, quantum confinement effect, super conductivity, super para-magnetism, etc. Except SAR, other properties are also dependent on the composition of materials. Hence, based on the requirement, the specific material needs to be identified and produced in a nano-size range for specific applications. Followed by the selection of material, the methodology for conversion to the nano-form needs to be finalised. Two major approaches are available for the production of nanomaterials: The first is a top-down approach, in which the bigger particles are reduced in size to form nanomaterials; the second is a bottom-up approach, in which the atoms/ions are aggregated in controlled manner to produce nanoparticles. Both approaches have their own pros and cons. In the top-down approach, the process is simple, yield is very high and hence, easily scalable on an industrial scale; however, the quality of the product is low due to wide-size distribution. In the bottom-up approach, though a narrow size distribution of particles is obtained, the yield is very low and hence, scalability is very difficult.

Classification of Nanomaterials

Nanomaterials, based on their dimensions, are classified as 0D, 1D and 2D. The 0D includes nanoparticles in which all their three dimensions are restricted within the nano-size range. The 1D includes nanomaterials in which two dimensions are restricted within the nano-size range and the third may be of higher size; examples include nanotubes, nanorods and nanowires. The 2D includes nanomaterials having only one dimension restricted in nano-size range and the other two dimensions are of any size; examples include thin films and nano-layers. An entirely different class of nanomaterial is nanostructures, in which the object will be of macro-size and the features in that object shall fall in the nano-size range. A broad classification is given in Figure 1 is a modified version from an earlier reference (Gubala et al. 2018).

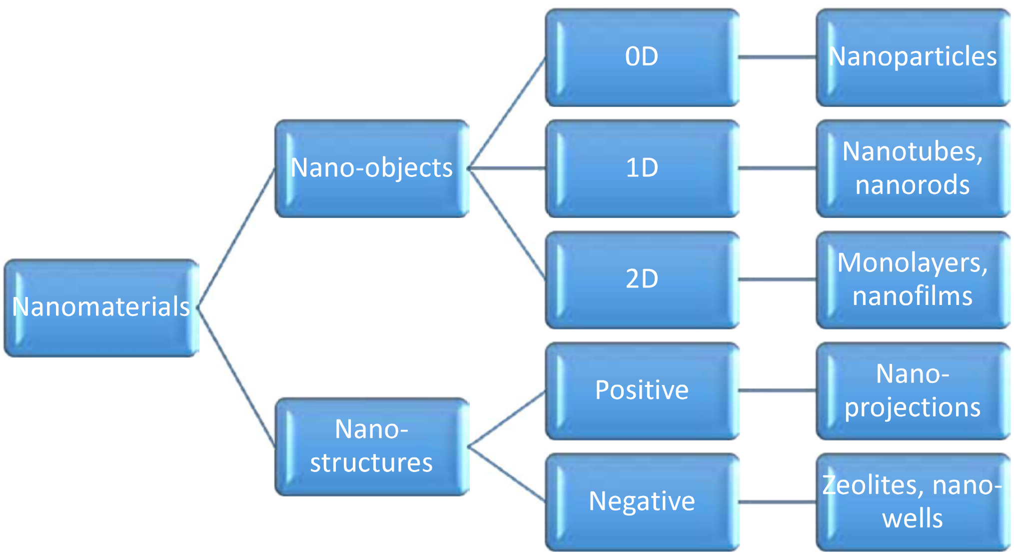

Figure 1. Classification of nanomaterials

Based on the source of formation, the nanomaterials are classified as naturally available, incidental/accidental and engineered nanomaterials. Another way of classifying nanomaterials is based on their chemical compositions — metals, metal oxides, ceramics, organic, polymeric and carbon nanomaterials. Based on multiple components of nanomaterials, they are also classified as core-shell, core-sheath, binary, tertiary, composites and hybrid nanomaterials.

Synthesis and characterisation of nanomaterials

Similar to synthesis, the characterisation of nanomaterials is also technically demanding and a tedious process. Since nanomaterials have very high surface energy, they tend to aggregate or agglomerate making it difficult to study their individual properties. Therefore, strategies are required to maintain the size of nanomaterials by avoiding the aggregation or agglomeration. Generally, stabilisers are used for this purpose and the principle involves imparting ionic charges on the surface of nanoparticles or coating with a polymer or both. The use of stabilisers also interferes with characterisation. The standardised size measurement techniques include DLS (dynamic light scattering) analysis, AFM (atomic force microscopy), SEM (scanning electronic microscopy) and TEM (transmission electron microscopy). The surface charges are measured by DLS and titrimetric techniques. BET (Brunauer–Emmett–Teller) analysis helps to measure the surface area and porosity of the nanomaterials. XRD analysis reveals the crystal size and crystallinity of nanomaterials. SAXS is used to measure the size, shape and internal structure of the nanomaterials. AFM is also used for analysing the mechanical and chemical properties of nanomaterials in addition to their size analysis. Apart from these specialised measurement techniques, routine physical and chemical measurement techniques are used to characterise nanomaterials.

Need for nanotechnology in cotton textiles

The impact of nanotechnology in cotton textiles started two decades ago with a promise to impart novel and efficient characteristics for cotton materials. Though cotton is the king of fibres, it has many drawbacks when compared to its synthetic counterparts. The major problems faced in cotton textiles include microbial attack and corresponding odour development, wrinkle development on usage, lack of hydrophobicity and UV transparency. These problems restrict the use of cotton in sportswear, medical textiles, agro-textiles and other technical textiles. Though many chemical and polymeric finishing agents are available to overcome a few of the above mentioned problems, they do have their own limitations. Nanomaterials are now being used to impart the desired functionalities to cotton.

Antimicrobial finish

Our research team at ICAR-CIRCOT in Mumbai developed a novel green process for the production of stable nano-silver stabilised by soluble starch (Vigneshwaran et al. 2006c) and also demonstrated an *in-situ* process for application of nano-silver on the surface of cotton to impart antibacterial activity (Vigneshwaran et al. 2007). The production process was considered as environmentally 'green' because harmful chemicals were avoided in the protocols and only green chemistry was used in the synthesis protocol. The major problem during the application is binding of the nanoparticles to the surface of cotton fibres since they do not have any affinity. A simple option could be the use of textile binders to assist cotton fibres to hold the nanoparticles, but the antibacterial efficiency gets affected. Latest research evaluates the use of carboxymethyl chitosan and l-cysteine to improve the surface affinity of cotton fabrics to nano-silver (Xu et al. 2019). The *in-situ* synthesis process helps to avoid the use of binders (Montazer et al. 2012; Vigneshwaran et al. 2007) but the nanoparticles located deep inside the cotton fibre may not participate in the antibacterial activity. Figure 2 shows the photos of cotton fabrics treated with nano-silver. The colour of the fabric is due to the surface plasmon resonance property of nano-silver. The mode of action of nano-silver is due to the release of silver ions and their binding with the essential proteins of microorganisms. Apart from nano-silver, nano-ZnO (Vigneshwaran et al. 2006b), nano-lignin (Juikar and Vigneshwaran 2017), nano-copper oxide (Bashiri Rezaie et al. 2018) and nano-chitosan (Hebeish et al. 2013) are also reported to show antibacterial properties on cotton textiles.

Figure 2. Cotton fabric treated with nano-silver (light brown above). The colour is due to the surface plasmon effect of nano-silver.

UV-resistant finish

Having a UV-resistant finish helps cotton fabrics restrict the entry of UV rays. Conventionally, various chemical finishing agents and dark-coloured dyes are used to restrict the entry of UV rays. With the developments in the use of nanomaterials, the requirement of pigments has drastically reduced without affecting their activity. Nano-ZnO and nano-titania are the well-demonstrated nanomaterials being used for UV-resistant finishes. Our research group worked on the production of nano-ZnO by reacting zinc nitrate with sodium hydroxide in the presence of soluble starch resulting in the nanoparticle size of 38 ± 3 nm (Vigneshwaran et al. 2006a). This nano-ZnO, after applying to the surface of cotton fabrics, imparted excellent antibacterial and UV-resistant properties. Figure 3 shows the scanning electron microscopic view of nano-ZnO deposited on the surface of cotton fibres. The UV-absorbing property is mainly due to the semi-conducting property of metal oxide nanoparticles like nano-ZnO and nano-titania. The band gap in these nanoparticles is sufficient enough to absorb the UV rays. Knitted cotton fabrics with nano-ZnO showed moderate to high ultraviolet protection factor (UPF), while 50+ UPF value was achieved in case of nano-titania (Paul et al. 2010). Also, this work reported that the rutile phase of titania was better than anatase phase in blocking UV rays. Another study demonstrated that the use of dumbbell-shaped nano-ZnO exhibits better UV-absorbing property after application on the surface of cotton fabrics (Wang et al. 2005). Ag/ZnO nanocomposite was applied on coloured cotton fabric to impart special properties such as self-cleaning, anti-bacterial, and UV-absorbing traits (Avazpour et al. 2017). Organic nanoparticles like nano-lignin can also impart UV-absorbing property to cotton textiles (Juikar and Vigneshwaran 2017).

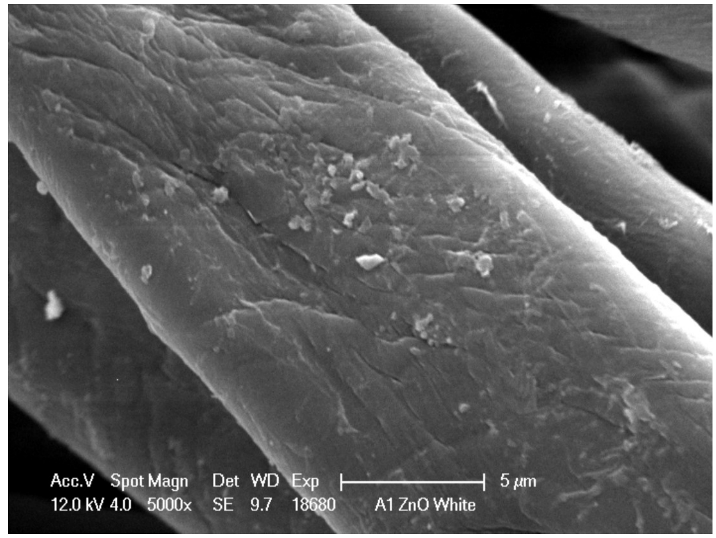

Figure 3. Scanning electron micrograph of cotton fibres impregnated with nano-ZnO

Self-cleaning property and Superhydrophobicity

Nano-titania in the size of range of 3 to 15 nm was found to impart self-cleaning properties to cotton by its photocatalytic activity to degrade methyl orange (Tan et al. 2013). The use of a stabiliser such as chitosan coated nano-titania for the nanomaterials, resulted in a reduction of self-cleaning properties from 96% to 89% due to the presence of organic coating (chitosan, in this case); however, it was compensated by its antibacterial activity (Goyal et al. 2016). The photocatalytic activity depends on the band gap of metal oxide nanoparticles which, generally fall in the UV-range. Hence, UV light is required for photocatalytic activity of nanoparticles. To overcome this issue, doped nanomaterials are being evaluated to have visible light induced photocatalytic activity. Nitrogen-doped nano-titania, synthesised by sol-gel route provides photocatalytic property without the requirement of UV radiations of high energy photons (Katoueizadeh et al. 2018). Apart from photocatalytic activity, self-cleaning property could be achieved by Lotus Effect® or superhydrophobicity. To obtain the superhydrophobic water repellent surfaces on cotton fabrics, silica nanoparticles coated with water-repellent agents are used. The water contact angle above 130° could be achieved using the combination of silica nanoparticles and water repellent agent (Bae et al. 2009). In this case, hydrophobicity was introduced by chemistry of the water-repellent agent and superhydrophobicity was achieved in combination with the effect produced by nano-architecture of the silica nanoparticles.

Flame-retardant finish

Environmental concerns of fluorinated and organophosphorus compounds result in exploration of different nano-based methodologies to impart flame retardancy to cotton textiles. The limiting oxygen index, which indicates the flame retardant property of a fabric, increased from 18.6 to 23 when the cotton fabrics were coated with sodium hypophosphite, maleic acid, triethanol amine and nano-titania (Lessan et al. 2011). Cotton functionalised with epoxy and carboxyl via grafting cotton with nano-emulsion consisting of glycidyl methacrylate and acrylic acid was treated for functional finishing by the traditional pad-dry-cure process and it resulted in excellent flame-retardant properties (Mohamed et al. 2014). Another research group explored the use of nano-titania on cotton fabrics in the presence of poly-carboxylic acid [1,2,3,4-butane tetracarboxylic acid (BTCA)] with sodium hypophosphite as catalyst and chitosan phosphate through conventional pad-dry-cure method; this expressed flame retardancy and antibacterial properties (El-Shafei et al. 2015).

Nanocellulose from cotton

Our research team at ICAR-CIRCOT is also working towards the development of a value-added product like nanocellulose from cotton linters and other cotton wastes. Nanocellulose is an amazing material with excellent mechanical properties while retaining its organic/biodegradable nature. The standard method used most commonly deploys sulfuric acid hydrolysis process to produce nanocellulose from any cellulosic biomass including cotton (Theivasanthi et al. 2018). The acidic hydrolysis process to extract nanocellulose (177 nm long and 12 nm wide, as measured by microscopy) from cotton increases the crystallinity index and the hydrophilicity and decreases their thermal stability (Morais et al. 2013). The by-products of cotton like cotton gin motes and cotton gin waste were also evaluated for production of nanocellulose having diameters < 10 nm and lengths of ca. 100–300 nm (Jordan et al. 2019). Novel eco-friendly processes for production of nanocellulose from cotton fibres were reported by our group in which cellulolytic fungus (Satyamurthy et al. 2011) and an anaerobic microbial consortium (Satyamurthy and Vigneshwaran 2013) were used to reduce the size of cellulosic particles. The primary advantage of microbial processes is their eco-friendliness, which eliminates the need for harmful chemicals, while yield and purity are the main bottlenecks to be solved. Transmission electron microscopic image of nanocellulose prepared at ICAR-CIRCOT by a chemo-mechanical process is shown in Figure 4 and the AFM image of nanocellulosic fibrils prepared by mechanical process is shown in Figure 5. ICAR-CIRCOT's unique nanocellulose pilot plant is producing nanocellulose from cotton fibres at a capacity of 10 kg per eight-hour shift and is being supplied to researchers and industries for product development.

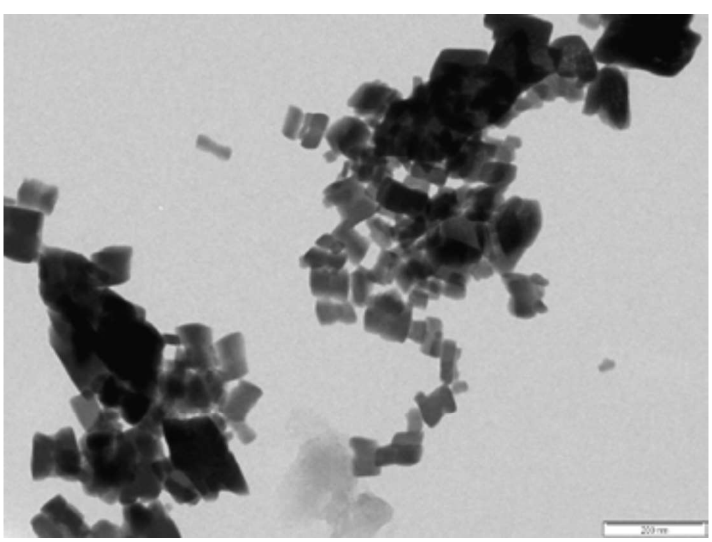

Figure 4. Transmission electron micrograph of nanocellulose nanoparticles produced from cotton linters.

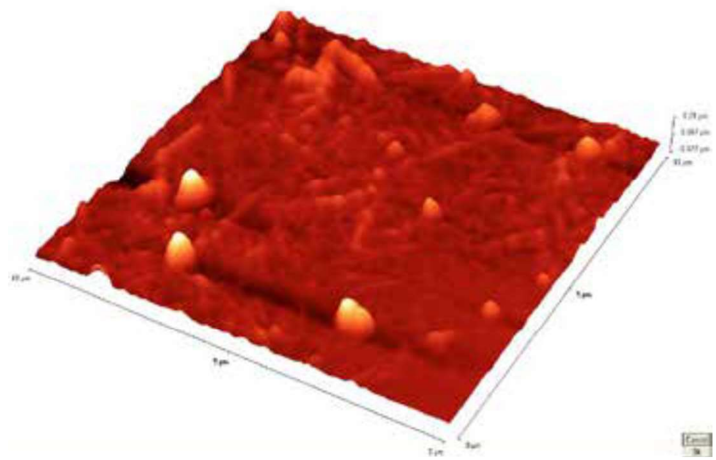

Figure 5. AFM image of cellulose nanofibres

Standards and safety

Standardisation in the field of nanotechnology is being handled by five international agencies: International Organization for Standardization (ISO), European Committee for Standardization (CEN), British Standards Institution (BSI), ASTM International and OECD Working Party on Manufactured Nanomaterials (WPMN). In addition, specific materials' standards are taken care by respective expert groups. For example, the ISO/TC 229 – Nanotechnologies expert group is being supported by TAPPI, a registered not-for-profit, international non-governmental organisation involved in the areas of pulp and paper technology for developing standards related to nanotechnology. Nanotechnology is an emergent and facilitating technology with the potential to create novel materials and products with various advantages in scientific and medical applications. The Division of Occupational Health and Safety of National Institute of Health has released the *Nanotechnology Safety and Health Program 2014* to help researchers and other stakeholders in the field of nanotechnology to familiarise themselves with safety precautions to be followed in the field of nanotechnology. Similarly, the National Institute for Occupational Safety and Health published a document titled '*Building a Safety Program to Protect the Nanotechnology Workforce: A Guide for Small to Medium-Sized Enterprises 2016*' for the benefit of people involved in nanotechnology-related enterprises. These documents are available free online and help in the research and development of nanomaterials.

Conclusions

Nanotechnology has begun to make its impact visible in the field of cotton textiles and cotton biomass utilisation. The established work force around the world is producing novel processes and products using nanotechnology for applications in cotton. Apart from solving the existing problems, nanotechnology also helps to evolve newer products and finishes in cotton textiles. With responsible use of nanotechnology, the cotton finishing and biomass value-addition sectors are bound to benefit from this revolution.

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References

Avazpour S, Karimi L, Zohoori S (2017) Simultaneous coloration and functional finishing of cotton fabric using Ag/ZnO nanocomposite Coloration Technology 133:423-430 doi:10.1111/cote.12296

Bae GY, Min BG, Jeong YG, Lee SC, Jang JH, Koo GH (2009) Superhydrophobicity of cotton fabrics treated with silica nanoparticles and water-repellent agent Journal of Colloid and Interface Science 337:170-175 doi:https://doi.org/10.1016/j.jcis.2009.04.066

Bashiri Rezaie A, Montazer M, Mahmoudi Rad M (2018) Environmentally friendly low cost approach for nano copper oxide functionalization of cotton designed for antibacterial and photocatalytic applications Journal of Cleaner Production 204:425-436 doi:https://doi.org/10.1016/j.jclepro.2018.08.337

El-Shafei A, ElShemy M, Abou-Okeil A (2015) Eco-friendly finishing agent for cotton fabrics to improve flame retardant and antibacterial properties Carbohydrate Polymers 118:83-90 doi:https://doi.org/10.1016/j.carbpol.2014.11.007

Goyal N, Rastogi D, Jassal M, Agrawal AK (2016) Chitosan as a potential stabilizing agent for titania nanoparticle dispersions for preparation of multifunctional cotton fabric Carbohydrate Polymers 154:167-175 doi:https://doi.org/10.1016/j.carbpol.2016.08.035

Gubala V et al. (2018) Engineered nanomaterials and human health: Part 1. Preparation, functionalization and characterization (IUPAC Technical Report) vol 90. doi:10.1515/pac-2017-0101

Hebeish A, Sharaf S, Farouk A (2013) Utilization of chitosan nanoparticles as a green finish in multifunctionalization of cotton textile International Journal of Biological Macromolecules 60:10-17 doi:https://doi.org/10.1016/j.ijbiomac.2013.04.078

Jordan JH, Easson MW, Dien B, Thompson S, Condon BD (2019) Extraction and characterization of nanocellulose crystals from cotton gin motes and cotton gin waste Cellulose 26:5959-5979 doi:10.1007/s10570-019-02533-7

Juikar SJ, Vigneshwaran N (2017) Microbial production of coconut fiber nanolignin for application onto cotton and linen fabrics to impart multifunctional properties Surfaces and Interfaces 9:147-153 doi:https://doi.org/10.1016/j.surfin.2017.09.006

Katoueizadeh E, Zebarjad SM, Janghorban K (2018) Synthesis and enhanced visible-light activity of N-doped TiO2 nano-additives applied over cotton textiles Journal of Materials Research and Technology 7:204-211 doi:https://doi.org/10.1016/j.jmrt.2017.05.011

Lessan F, Montazer M, Moghadam MB (2011) A novel durable flame-retardant cotton fabric using sodium hypophosphite, nano TiO2 and maleic acid Thermochimica Acta 520:48-54 doi:https://doi.org/10.1016/j.tca.2011.03.012

Mohamed AL, El-Sheikh MA, Waly AI (2014) Enhancement of flame retardancy and water repellency properties of cotton fabrics using silanol based nano composites Carbohydrate Polymers 102:727-737 doi:https://doi.org/10.1016/j.carbpol.2013.10.097

Montazer M, Alimohammadi F, Shamei A, Rahimi MK (2012) In situ synthesis of nano silver on cotton using Tollens' reagent Carbohydrate Polymers 87:1706-1712 doi:https://doi.org/10.1016/j.carbpol.2011.09.079

Morais JPS, Rosa MdF, de Souza Filho MdsM, Nascimento LD, do Nascimento DM, Cassales AR (2013) Extraction and characterization of nanocellulose structures from raw cotton linter Carbohydrate Polymers 91:229-235 doi:https://doi.org/10.1016/j.carbpol.2012.08.010

Paul R, Bautista L, De la Varga M, Botet JM, Casals E, Puntes V, Marsal F (2010) Nano-cotton Fabrics with High Ultraviolet Protection Textile Research Journal 80:454-462 doi:10.1177/0040517509342316

Satyamurthy P, Jain P, Balasubramanya RH, Vigneshwaran N (2011) Preparation and characterization of cellulose nanowhiskers from cotton fibres by controlled microbial hydrolysis Carbohydrate Polymers 83:122-129

Satyamurthy P, Vigneshwaran N (2013) A novel process for synthesis of spherical nanocellulose by controlled hydrolysis of microcrystalline cellulose using anaerobic microbial consortium Enzyme and microbial technology 52:20-25

Tan B, Gao B, Guo J, Guo X, Long M (2013) A comparison of TiO2 coated self-cleaning cotton by the sols from peptizing and hydrothermal routes Surface and Coatings Technology 232:26-32 doi:https://doi.org/10.1016/j.surfcoat.2013.04.048

Theivasanthi T, Anne Christma FL, Toyin AJ, Gopinath SCB, Ravichandran R (2018) Synthesis and characterization of cotton fiber-based nanocellulose International Journal of Biological Macromolecules 109:832-836 doi:https://doi.org/10.1016/j.ijbiomac.2017.11.054

Vigneshwaran N, Kathe A, Varadarajan P, Nachane R, Balasubramanya R (2007) Functional finishing of cotton fabrics using silver nanoparticles Journal of nanoscience and nanotechnology 7:1893-1897

Vigneshwaran N, Kumar S, Kathe A, Varadarajan P, Prasad V (2006a) Functional finishing of cotton fabrics using zinc oxide–soluble starch nanocomposites Nanotechnology 17:5087-5095

Vigneshwaran N, Kumar S, Kathe AA, Varadarajan PV, Prasad V (2006b) Functional finishing of cotton fabrics using zinc oxide–soluble starch nanocomposites Nanotechnology 17:5087-5095 doi:10.1088/0957-4484/17/20/008

Vigneshwaran N, Nachane R, Balasubramanya R, Varadarajan P (2006c) A novel one-pot 'green' synthesis of stable silver nanoparticles using soluble starch Carbohydrate research 341:2012-2018

Wang RH, Xin JH, Tao XM (2005) UV-Blocking Property of Dumbbell-Shaped ZnO Crystallites on Cotton Fabrics Inorganic Chemistry 44:3926-3930 doi:10.1021/ic0503176

Xu Q et al. (2019) Enhancing the surface affinity with silver nanoparticles for antibacterial cotton fabric by coating carboxymethyl chitosan and l-cysteine Applied Surface Science:143673 doi:https://doi.org/10.1016/j.apsusc.2019.143673