

**Doctoral Dissertation (Shinshu University)**

**Functional Modification of Bamboo Pulp  
Fabric Based on Nano Ag and ZnO  
Particles**

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# **Chapter 1**

## **General introduction**

## **Chapter 1: General introduction**

### **1.1 Synthesis and applications of hyperbranched polymers**

#### **1.1.1 Hyperbranched polymer-background**

Hyperbranched polymers belong to a class of highly branched macromolecules with three-dimensional called dendritic polymers.[1, 2] During the last 20 years, scientists, especially polymer chemists, have introduced a new philosophy of ‘dendritic macromolecules’ and prepared globular and spherical molecules in addition to the more conventional linear ones(Fig. 1).[3-10] Both dendrimer and hyperbranched polymer molecules are composed of repeating units emanating from a central core. The difference between dendritic polymers and hyperbranched polymers is that dendrimers which have completely branched star-like topologies while hyperbranched polymers which have imperfectly branched or irregular structure. Number of chemical bonds through the core of dendrimer can be connected to the external parts of the molecule, the layers through the core of linear units (single monomers or linear chains) are attached to the core and each of these arms is terminated with the multifunctional branched unit. A dendrimer is formed by units attached to the molecule perfectly[11, 12] Otherwisethe absence of any of these units in the molecule will result in a hyperbranched polymer structure.

Over the past decades, hyperbranched polymers have received much attention due to their unique chemical and physical properties as well as their potential applications in coatings, additives, drug and gene delivery, macromolecular building blocks, nanotechnology, and supramolecular science.

In comparison, synthesizing dendrimers is cost-intensive and time-consuming. Hyperbranched polymers can be prepared in one step manner without special protection, deprotection and purification. Despite its structure imperfection, hyperbranched polymers possess the similar properties to dendrimers, such as abundant reactive terminal groups, low viscosity, high reactivity, excellent solubility and dispersion.[13]

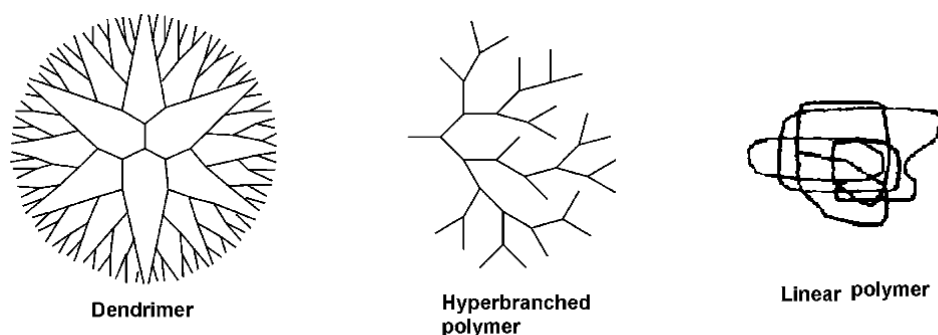


Figure 1 Molecular structure of dendrimer (a) hyperbranched polymer (b) and linear polymer(c)

### 1.1.2 History of hyperbranched polymers

In 1952 Paul Flory's wrote a famous book Principles of Polymer Chemistry, he indicated an alternative scheme for polymer synthesis.[14] He theorized about synthesizing condensation polymers from multifunctional monomers. Due to their highly branched structure the polymers were predicted to have a broad molecular weight distribution and to be non-entangled and non-crystalline. As they would provide materials with poor mechanical strength, Flory did not feel it was worth pursuing this research at that times.

A little more than 30 years later, the first papers on synthesis of dendritic polymers emerged (dendron, Greek for "tree") and revealed properties nobody could have foreseen. The dendritic polymers turned out to have a number of very unique and different properties compared to their linear analogs; for instance, at high enough molecular weight they were found to be globular. [5, 15]In contrast to linear polymers, the dendritic macromolecules behaved more like molecular micelles.

The initial research works on dendritic polymers were focused on the preparation of perfect monodisperse dendrimers. These well-defined macromolecules have very interesting material properties, but the synthesis is often time-consuming and elaborate. For use as engineering materials they are far too complicated and costly to produce. This was soon realized by researchers at DuPont Experimental Station, from which several publications emerged in the early 1990s.[16-18] Kim and Webster were working on dendritic polymers as rheology control agents and as spherical multifunctional

initiators. It was necessary to obtain the material rapidly and in large quantities. This forced them to develop a route for a one-step synthesis of dendritic polyphenylenes.[19] These polymers were polydisperse, and had defects in the form of built-in linear segments but they were highly branched dendritic molecules. Kim and Webster named them Hyperbranched Polymers. Ever since, a wide variety of hyperbranched polymers have been presented in the literature and some of them will be further described.

The synthesis of hyperbranched polymers can often be simplified compared to that of dendrimers as it does not require the use of protection/deprotection steps. This is due to the fact that hyperbranched polymers are allowed to contain some linearly incorporated AxB monomers. The most common synthesis route follows a one-pot procedure where AxB monomers are condensed in the presence of a catalyst. Another method using a core molecule and an AxB monomer has also been described.

The lower cost of synthesizing hyperbranched polymers allows them to be produced on a large scale, giving them an advantage over dendrimers in applications involving large amounts of material, although the properties of hyperbranched polymers are intermediate between those of dendrimers and linear polymers.[20]

### **1.1.3 Synthesis of hyperbranched polymers**

The synthesis of hyperbranched polymers can be divided into two major categories. The first category contains techniques of the single-monomer methodology (SMM), in which hyperbranched macromolecules are synthesized by polymerization of an AB<sub>x</sub>, AB\* or a latent AB<sub>x</sub> monomer. The second category contains examples of the double-monomer methodology (DMM) in which direct polymerization of two types of monomers or a monomer pair generates hyperbranched polymers. In SMM, the polymerization of an AB<sub>n</sub> or latent AB<sub>n</sub> monomer leads to hyperbranched macromolecules. [2] SMM consists of at least four components: (1) polycondensation of AB<sub>n</sub> monomers; (2) self-condensing vinyl polymerization; (3) self-condensing ring-opening polymerization; (4) proton-transfer polymerization.

#### **(1) polycondensation of AB<sub>n</sub> monomers**

The propagation reactions applied for the self-polycondensation of AB type monomers are potentially useful for the synthesis of hyperbranched polymers from



AB<sub>x</sub> type monomers. Some kinds of hyperbranched polymers including hyperbranched polyphenylenes[17-19], polyethers,[21-24] polyesters,[25-35] polyamides,[36-40] polycarbonates,[41, 42] and poly(etherketone)s[43-45] can be prepared by one-step self-polycondensation reactions of AB<sub>x</sub> type monomers, as shown in fig 2. AB<sub>2</sub> type monomers are often used as starting materials because of the easy preparation of the monomer, while AB<sub>3</sub>, AB<sub>4</sub> and AB<sub>6</sub> monomers have been reported as monomers for hyperbranched polyesters and polysiloxanes.[13, 46]

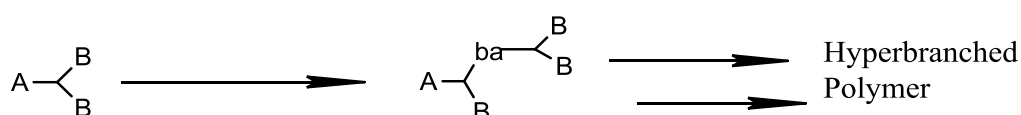


Figure 2 Scheme of the polycondensation of AB<sub>n</sub> monomers

## (2) Self-condensing vinyl polymerization

The second strategy to prepare hyperbranched polymers is termed self-condensing vinyl polymerization (SCVP) defined by Fréchet in 1995.[47, 48] The applicable monomer denoted by AB\* contains an initiating moiety in addition to a double bond. The initiating moiety is activated, and then, reacted with a double bond to form a covalent bond and a new active site on the second carbon atom of the double bond, as shown in Fig 3.

The number of activation sites increases proportionally to the propagation reaction in SCVP whereas two functional groups are always consumed during the self-polycondensation of AB\* monomers.[49] SCVP does exhibit some disadvantages. For example, side reactions may lead to gelation and the molecular weight distribution is usually very broad. In order to avoid crosslinking, living/controlled polymerizations such as atom transfer radical polymerization (ATRP) and group transfer polymerization (GTP) are combined in SCVP. SCVP of styrenes, methacrylates and acrylates through radical, cationic or group transfer polymerizations have all been reported.[50-54]

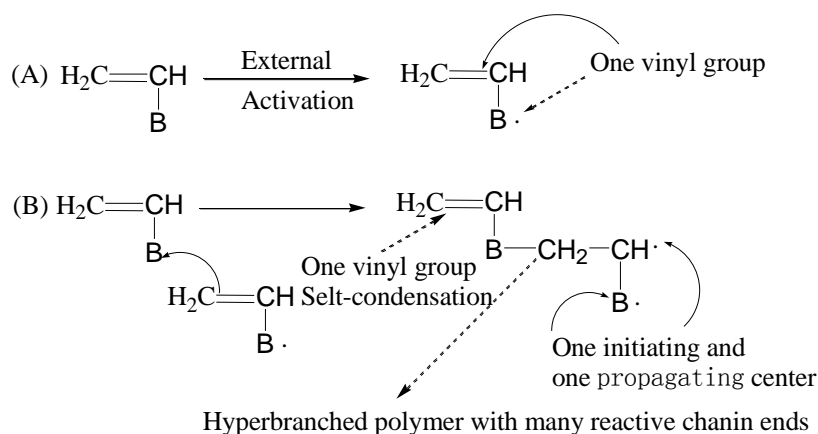


Figure 3 Scheme of the self-condensing vinyl polymerization

### (3) Self-condensing ring-opening polymerization

This method was first reported by Suzuki et al. in 1992[55] and involved the reaction of latent  $\text{AB}^*$  monomers that did not feature branching units—the branch points are generated by propagation during the reaction. The polymerization is initiated by the addition of proper initiators to generate active sites, which may allow for control over the molecular weight and molecular weight distribution of the resulting polymers. Ring-opening polymerizations of cyclic carbamates, epoxides, oxetane, and lactones have all been reported in literature.[56-59]

### (4) Proton-transfer polymerization

Finally, hyperbranched polyesters with epoxy or hydroxyl end groups and hyperbranched polysiloxanes were synthesized through proton transfer polymerization (Fig 4). The polymerization of  $\text{H-AB}_2$  monomer (1) is initiated by the addition of a catalytic amount of initiator such as hydroxide ion, that abstracts a proton affording the reactive nucleophile (2). Coupling of (2) with another monomer unit affords dimer (3) in which latent reactivity is now carried by one of the original B groups. This process is akin to that found in numerous conventional addition and ring-opening polymerizations. In this case, however, the active dimer (3) does not propagate directly but instead undergoes a thermodynamically driven proton exchange with another monomer (1) to produce nucleophile (2) and neutral dimer (4). Subsequent nucleophilic additions and proton transfers afford a polymeric product. Given the multiplicity of eactive B species in each growing molecule that contains a single H-A group, the

polymerization proceeds with branching, affording the desired hyperbranched structure. The feature of this polymerization is that each propagation step involves a proton transfer for the activation of the nucleophile used in epoxide opening.[60, 61]

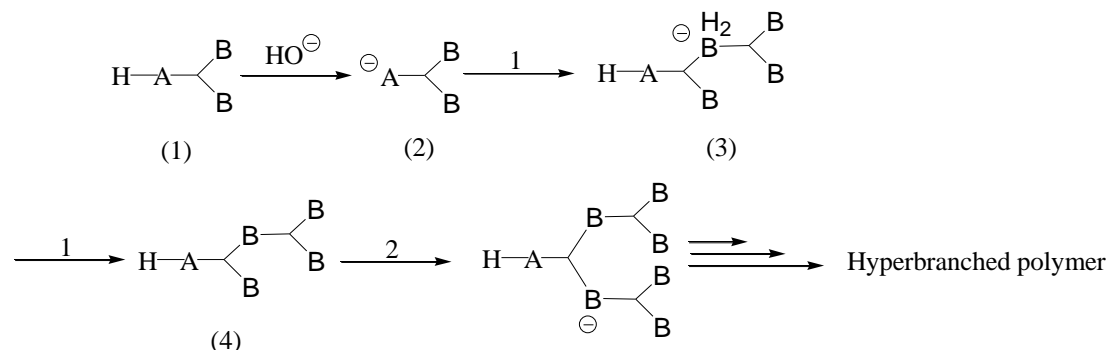


Figure 4 The illustration of proton-transfer polymerization

Double-monomer methodology (DMM) can be classified into two main subclasses based on the selected monomer pairs and different reaction pathways. (1) ‘ $\text{A}_2 + \text{B}_3$ ’ methodology has been applied to synthesize three main polymer architectures including polyamides, polycarbonates and polyureas.[58, 62] (2) Couple-monomer methodology (CMM), which is the combination of the basic SMM and ‘ $\text{A}_2 + \text{B}_3$ ’, is used to prepare many types of hyperbranched polymers such as poly(sulfone amine)s, poly(ester amine)s, poly(urea urethane)s.[63, 64]

#### 1.1.4 The properties of hyperbranched polymers

Hyperbranched polymers have special properties and it has many industrial applications. One of the most interesting properties of hyperbranched polymers is their low viscosity characteristics in comparison to linear analogues. The viscosities of hyperbranched polymers, both in solution and in the molten state, have been found to be considerably lower when compared to their linear analogues. Hyperbranched macromolecules in solution reach a maximum of intrinsic viscosity as a function of molecular weight as their shape changes from an extended to a more compact globular structure, especially at high molecular weights. In addition, for linear polymers, the melt viscosity increases linearly up to a critical molar mass where the viscosity drastically increases as a consequence of the entanglement of polymer chains. However, this phenomenon is not observed for dendrimers or hyperbranched polymers, which indicates that minimal entanglement of the branched chains occurs.

Other interesting characteristics of hyperbranched polymers are their conformation and degree of branching. X-ray and small-angle neutron scattering experiments show that dendrimers have spherical conformations, whilst hyperbranched polymers have globular structures. The degree of branching is reflected in the flexibility of the branching components contained within the architecture as well as the intrinsic viscosity of the polymer. Polymers with a higher degree of branching have lower viscosity. This affects the polymer's relative solubility in various media.

Besides, hyperbranched polymers have high chemical reactivity and enhanced solubility when compared to their linear analogues. They also exhibit enhanced compatibility with other polymers as has been demonstrated by blending studies. Hyperbranched materials also have outstanding mechanical properties such as initial modulus, tensile strength and compressive moduli, which reflect the compact highly branched structures.

### **1.1.5 Application of hyperbranched polymers**

Due to their unique properties and easy synthesis, hyperbranched polymers have a wide range of potential applications.

#### **(1) Synthesis of nanomaterials**

Hyperbranched polymers and their substitutes can be used as nanomaterials for host-guest encapsulation and the fabrication of organic-inorganic hybrids, and even directly used as nanoreactors for some reactions. Dendrimers and hyperbranched polymers are particularly well-suited for hosting nanoparticles for the following reasons[65]: (1) the hyperbranched polymers templates themselves are of fairly uniform composition and structure, and therefore they yield well-defined nanoparticle replicas;[66-68] (2) the nanoparticles are stabilized by encapsulation within the hyperbranched polymers, and therefore they do not agglomerate;[69, 70] (3) the encapsulated nanoparticles are confined primarily by steric effects, and therefore a substantial fraction of their surface is unpassivated and available to participate in catalytic reactions;[71] (4) the hyperbranched polymers branches can be used as selective gates to control access of small molecules (substrates) to the encapsulated (catalytic) nanoparticles;[65] (5) the terminal groups on the hyperbranched polymers periphery can be tailored to control

solubility of the hybrid nanocomposite and used as handles for facilitating linking to surfaces and other polymers.[72, 73]

## (2) Surface Modification

Corrosion of metal surfaces is a serious problem worldwide. It has been demonstrated that even rather thin organic layers can passivate and block electrochemical reactions on metal surfaces [74]. Bergbreiter et al. have demonstrated that hydrophobic, fluorinated, hyperbranched poly (acrylic acid) films can block these unwanted electrochemical reactions.[75-77] This technique proved to be useful for obtaining thick and homogeneous films. The acid groups were accessible to modifications. Fluorination of these films gave surfaces that were analyzed with cyclic voltammetry and a.c.-impedance measurements. These studies showed that the barrier to redox reactions was greatly improved.

## (3) Coating

Hyperbranched polymers have been used as the base for various coating resins, such as powder coatings, high solid coatings, flame retardant coatings and barrier coatings for flexible packaging, depending on their high solubility, low viscosity and abundant functional groups. [78-80] Ranby and Shi also studied hyperbranched methacrylated polyesters and their use in photopolymerizations of films and fiber-reinforced polymer composites. The resins were found to have low viscosities and higher curing rates than those of corresponding linear unsaturated polyesters.[81, 82]

## (4) Medicine

An important application of polymers in medicine is in advanced drug-delivery systems. The conventional micelle drug delivery systems based on the linear amphiphilic copolymers suffer from instability in vivo because the concentration of the copolymer is diluted in the bloodstream and micelles tend to disassemble once the concentration falls below the critical micelle concentration. Amphiphilic copolymers with dendritic or hyperbranched structure have been developed to solve the problem as the good stability and well-defined globular structure of dendritic and hyperbranched polymers. [83] Kolhe et al. studied that the ability of dendrimer to form complex or encapsulate drug molecules was explored using ibuprofen as model drug, with PAMAM

dendrimers and hyperbranched Polyol. They found that dendrimers may be able to carry the complexed drug inside cells efficiently. Hyperbranched Polyol appears to encapsulate approximately 24 drug molecules.[84]

#### (5) Application in textile industry

In recent years, Hyper branched polymers also has recently been of great interest in textile processing.

Due to the unique structure of dendrimers and hyperbranched polymer, a large number of end groups, which are often reactive and many branching points that highly branched molecules of dendrimers and hyperbranched polymer can be used as a host for the encapsulation or composite of guest dye molecules to achieve phase transfer dye. The phase transfer, including the dye transfer to the organic solution from the aqueous solution, fibers, or supercritical CO<sub>2</sub>. PP does not accept dyes, owing to its non-polar structure as well as its high crystallinity, resulting from the high stereo-regularity of the PP. The dyeability of PP with CI. Disperse Blue 56 can be markedly enhanced through the incorporation of hyperbranched macromolecules such as the Hybrance PS2550 (hyperbranched polyester-amide) into PP prior to fiber spinning.[85]

S. Burkinshaw et al. reported that cotton fabric which had been pretreated with a dendrimer displayed markedly enhanced colour strength with reactive dyes, even when dyeing had been carried out in the absence of both electrolyte and alkali.[86]

Zhang et al. has synthesized an amino-terminated hyperbranched polymer (HBP-NH<sub>2</sub>), characterized by a three-dimensional structure and a large number of amino groups (1°, 2°, and 3° amines). The pretreatment of cotton with the HBP-NH<sub>2</sub> can enhance the dyeability of the cotton fabric with reactive dyes.[87] Also nano-silver colloidal solution was papered in one step by mixing AgNO<sub>3</sub> aqueous solution and HBP-NH<sub>2</sub> aqueous solution under vigorous stirring, and subsequently to finish cotton fabric with the nano-silver colloidal solution by using an impregnation method to provide the cotton fabric with antibacterial properties.[88]

## 1.2 Nanocomposites for multifunctional finishing of textiles

Nanotechnology is an emerging interdisciplinary technology that has been booming

in many areas during the recent decade, including materials science, mechanics, electronics, optics, medicine, plastics, energy, electronics, and aerospace. Its profound societal impact has been considered as the huge momentum to usher in a second industrial revolution.

The fundamentals of nanotechnology lie in the fact that properties of substances dramatically change when their size is reduced to the nanometer range. When a bulk material is divided into small size particles with one or more dimension (length, width, or thickness) in the nanometer range or even smaller, the individual particles exhibit unexpected properties, different from those of the bulk material. It is known that atoms and molecules possess totally different behaviors than those of bulk materials; while the properties of the former are described by quantum mechanics, the properties of the latter are governed by classic mechanics. Between these two distinct domains, the nanometer range is a murky threshold for the transition of a material's behavior. For example, a gold particle of 1 nm across shows red color. Moreover, a small amount of nanosize species can interfere with matrix polymer that is usually in the similar size range, bringing up the performance of resultant system to an unprecedented level. These are the reasons why nanotechnology has attracted large amounts of federal funding, research activity and media attention.

The textile industry has already impacted by nanotechnology. Research involving nanotechnology to improve performances or to create unprecedented functions of textile materials are flourishing. (Fig 5) These research endeavors are mainly focused on using nanosize substances and generating nanostructures during manufacturing and finishing processes.[89]

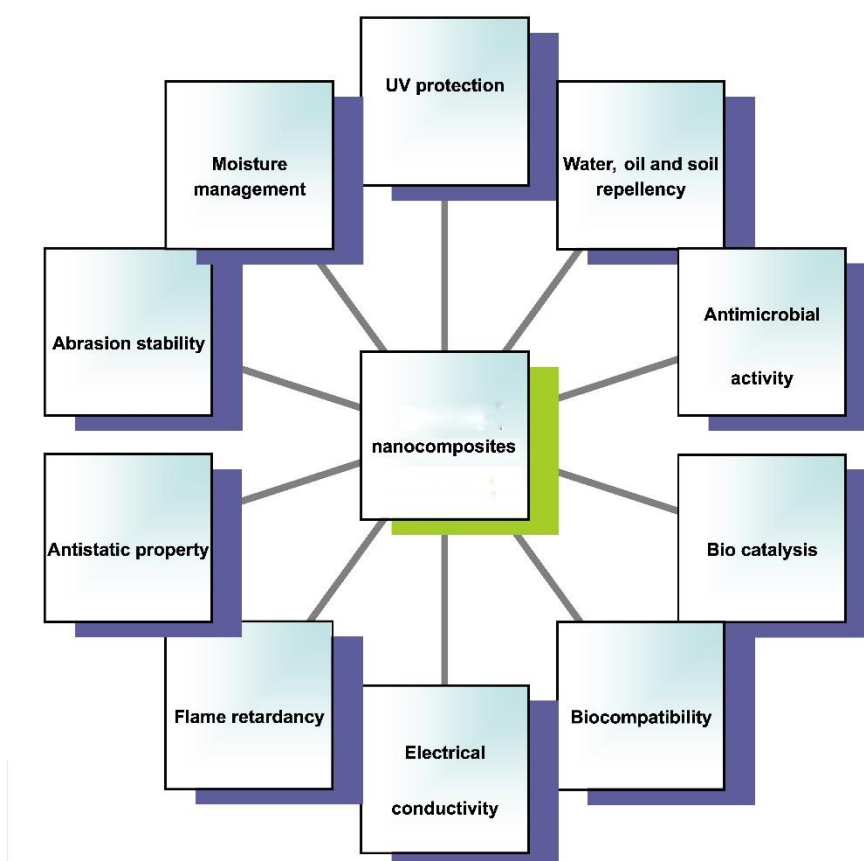


Figure 5 Possibilities of textile functionalization using polymer nanocomposites

By changing the surface structure of textiles by nanoparticles, several diverse textile functionalities can be obtained for profitable exploitation of functional textiles in special applications. Out of the many possible applications of nanoparticles for functional properties other than surface properties, some of the most successful ones are antimicrobial, UV protection, flame retardancy and conductivity properties of textiles.

### 1.2.1 Self-cleaning textile finishes using nanoparticles

The field of self-cleaning coatings is divided into two categories: hydrophobic and hydrophilic. These two types of coating both clean themselves through the action of water, the former by rolling droplets and the latter by sheeting water that carries away dirt. Hydrophilic coatings, however, have an additional property: they can chemically break down adsorbed dirt in sunlight.

The self-cleaning action of hydrophobic coatings stems from their high water



contact angles; water on these surfaces forms almost spherical droplets that readily roll away carrying dust and dirt with them. Dirty water falling onto the hydrophobic coating is removed before it can evaporate. Several techniques for the hydrophobic surfaces fishing of textile using nanoparticles has been reported. [90]Liu et al reported that artificial lotus leaf structures were fabricated on cotton substrates via the controlled assembly of carbon nanotubes onto the surface of cotton substrates. The treated fabric has a super-hydrophobic properties—water contact angles greater than 150 °.[91]

The second class of self-cleaning is that they are hydrophilic rather than hydrophobic, and do not rely solely on the flow of water to wash away dirt. These coatings chemically break down dirt when exposed to light, a process known as ‘photocatalysis’. Hydrophilic coatings have parallels with photosynthesis, using sunlight to drive chemistry.

TiO<sub>2</sub> have been coated on textiles with the purpose of inducing self-cleaning effects under daylight irradiation. Uddin et al. reported that Au/TiO<sub>2</sub> cotton nanocomposite textile was prepared at low temperature (~100 °C) by sol–gel and photodeposition process designed for practical applications, the produced composite cotton fibers display high potential and commercial importance for visible light self-cleaning properties.[92]. Several metal oxides nanoparticles including TiO<sub>2</sub>, WO<sub>3</sub>, ZrO<sub>2</sub>, ZnO and CdS have been studied for its self-cleaning properties.

### **1.2.2 Nanoparticles in antimicrobial finishing of textiles**

Many heavy metals nanoparticles are toxic to microbes at very low concentrations either in the free state or in compounds. They kill microbes by binding to intracellular proteins and inactivating them.[93] For instance, silver is referred as an antiseptic and disinfectant. Bacterial cells are constantly exposed to stressful situations and an ability to resist these stresses is essential for their survival. The powerful antimicrobial activity of silver is known to be effective against nearly 650 types of bacteria. In literature, silver is reported to be skin friendly and does not cause skin irritation[94].

Nanoparticles with silver nanoparticles are supposed to improve the properties of textiles. Silver nanoparticles deposited on textile surfaces can be used to make smart functional textiles, which have great potential for application as antibacterial materials.

Various techniques have been explored to attach silver to textile materials. For preparation of antimicrobial fabrics suitable for sterilization of air, cellulose was grafted with acrylic acid and treated with silver nitrate to bind the silver ions to the -COOH group of graft copolymer.[95]

Among silver nanoparticles, ZnO nanoparticles also have been found to be effective against antimicrobial. Li and colleagues have investigated the durability of antibacterial activity of nano-ZnO functionalized cotton fabric to sweat. [96] A negative surface charge has been deduced for ZnO nanoparticles and illumination can increase antibacterial performance compared to normal conditions.

### **1.2.3 Nanoparticles for UV protection of textiles**

To impart UV protection, several nanoparticles can be applied on textile material. The most common nanoparticles used are ZnO, TiO<sub>2</sub>, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. They provide a protection benefit by reflecting, scattering or absorbing harmful UV. Due to the minute size of the particles, the light scattering predominates at approximately 1/10 of the wavelength of the scattered light. Hence, for UV radiation to be scattered between 200-400 nm, the optimum particle size required is about 20-40 nm. The UV-blocking treatment for cotton fabrics consists of forming a thin layer of TiO<sub>2</sub> on the surface of the treated cotton fabric, which has been found to give a very high UV protection to fabrics. ZnO has a relatively high absorption band starting at 385 nm and extending with the far UV. [97] In addition to its excellent UV-absorption characteristics, ZnO has several other advantages, it does not migrate, not degraded by absorbed light and in many cases may improve mechanical, optical and electrical properties of the bulk polymer.

### **1.2.4 Nanoparticles in conductive fibers and fabrics**

Conductivity in textiles can be imparted by the application of nanoparticles. By adding conductive nanoparticles to the polymer system, it is possible to develop coating materials for conductive polyester, polyamide and acrylics. Conductive inks are alternatives for conductive coatings to specific areas of fabric or garments. Another area of application of ZnO is antistatic finishing agent in textiles. Alessio et al. [98] used ZnO nanoparticles to prepare the nanometer antistatic finishing agent, which was

applied to treat cotton and polyester fabrics and then the antistatic performance of the treated textile was evaluated through the charge density ZnO with amphoteric surface.

By adding nanoparticles such as graphite, carbon, silver, nickel and gold to conventional printing inks, conductive patterns can be directly printed on traditional fabrics. Recently, expanded graphite/polymer electrically-conductive nanocomposites have attracted great interest [99]. Expanded graphite particles have been combined with polymers such as polystyrene, polyethylene, PMMA and polypropylene to prepare electrically-conductive nanocomposites.[100] They have shown various interesting properties that can be expected to be different from those of the polymers or the inorganic particles themselves.

The application of nanoparticles in the field of textiles is gaining importance because of the current explosion of interest in nanoscience and nanotechnology. The main thrusts in nanoparticles applications in textiles will be to: enhance the functional properties and performance of existing materials, produce textiles with combined functional properties and increase the safe use of nanoparticles in technical textiles.

### **1.3 Regenerated bamboo fiber**

With the growing demand for more comfortable and environmentally friendly products, efforts in research and development activities in the textile industry have focused on the utilisation of renewable and biodegradable resources as well as environmentally sound manufacturing processes in textiles.[101, 102] In this respect, a new kind of regenerated fibers, which are an alternative to conventional ones, and cotton have gained importance in apparel and home textile manufacturing. The most commonly known novel type of regenerated fiber is lyocell, which is produced from wood pulp by a viscose like process but with a less hazardous environmental impact, as the compound (NMMO: N-methylmorpholine N-oxide) used in the lyocell manufacturing process for dissolving cellulose is organic and can be almost 99.5% recycled [103, 104].

One of the latest developments in new fiber researches is the use of bamboo fiber in various textile products that has been used in construction materials, furniture,

decorating items and high performance composite materials for years. Regenerated bamboo fiber is obtained from the bamboo plant which is abundant resource in nature. At present, there are two ways to utilize bamboo in the textile industry. One is to produce natural fiber from bamboo by chemical and physical treatment (this material is called bamboo fiber). Since a single bamboo fiber is 2 mm in length, it is usually in the form of a fiber bundle. The other method is to spin the regenerated fiber after the bamboo is retted into bamboo pulp (this material is called bamboo pulp fiber). Since the latter has a similar processing method to viscose, the structures and the properties of bamboo pulp fiber could be predicted well.[105]

There are some advantages to the development of bamboo fiber for textiles. First, bamboo fibers are an environmental friendly fiber extracted from bamboo, which is renewable, fast growing, degradable, and does not occupy cultivated land. Next, the exploitation of the abundant bamboo resources can be of significant economic benefit in hilly areas. In addition, the bamboo fiber can make up for the lack of natural textile fiber available and it may replace partial need for synthetic fibers used in garments and furniture fabric. Moreover, bamboo and the bamboo fibers are very competitive in price. Also the fiber is naturally smooth and very soft can be worn directly next to the skin. For these reasons, once the conception of the bamboo fibers appeared, it has drawn increasing attention from many international organizations and countries. Bamboo plant possesses anti-UV properties and antimicrobial function. Generally, bamboo pulp fiber has lost the antibacterial property resulting from the treatment with alkali in the processing.

#### **1.4 The purpose, method and significance for our research**

Bamboo pulp fibers are an environmental friendly fiber extracted from bamboo, which is renewable, fast growing, degradable, also bamboo pulp fiber possesses desirable comfort properties such as good moisture absorption and permeability, excellent dyeing and finishing abilities; Due to the unique chemical and physical properties, hyperbranched polymers can be directly used as nanoreactors for synthesis nanomaterials. The purpose of this paper is to synthesize water-soluble multi-amide

compound hyperbranched polymer RSD and HSDA, and then nano Ag and ZnO particles solution were synthesized by RSD and HSDA under hydrothermal condition. In order to improve the UV protection and antimicrobial properties of bamboo pulp fabric, the synthesized Ag and ZnO particles were applied to treat the fabric. Contents and significance of this dissertation are as follows:

(1) In chapter 2, Multi-amide compound hyperbranched polymer RSD was successfully prepared. RSD was applied as a stabilizer and a reductant to synthesis silver colloid nanoparticles with controllable sizes. Furthermore, in-situ synthesis method of silver nanoparticles on the bamboo pulp fabrics was developed. The nano silver-treated bamboo pulp fabrics have good antibacterial property against Gram-negative bacteria (*Escherichia coli*) and Gram-positive bacteria (*Staphylococcus aureus*), the treated fabric has excellent laundering durability.

(3) In chapter 3, bamboo pulp fabric was immersed in  $\text{Zn}(\text{NO}_3)_2$  and multi-amide compound (RSD) mixing solution under hydrothermal condition. In the process RSD which has numerous amino groups and three-dimensional structure was applied to entrap ZnO particles onto bamboo pulp fabric. When covered with ZnO particles, bamboo pulp fabric showed good UV protection properties.

(4) In chapter 4 and 5, new hyperbranched polymer HSDA was synthesized from the modified of RSD. In order to enhance the stability and decrease the size of ZnO particles, HSDA was used to synthesize ZnO nanoparticles. The synthesized ZnO nanoparticles showed good antibacterial activities against Gram-negative bacteria (*Escherichia coli*) and Gram-positive bacteria (*Staphylococcus aureus*). When bamboo pulp fabric was treated by ZnO nanoparticles, it showed ultraviolet protective properties and good antibacterial property against Gram-negative bacteria (*Escherichia coli*) and Gram-positive bacteria (*Staphylococcus aureus*).

(5) Hyperbranched polymer was applied to the functional modification of cellulose fiber. On one hand the research broaden the application fields of hyperbranched polymer, on the other hand the research provide a new train of thought for the functional modification of cellulose fiber.

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## **Chapter 2**

# **Synthesis of silver nanoparticles and antibacterial property of bamboo pulp fabrics finished by silver nanoparticles**

## **Chapter 2: Synthesis of silver nanoparticles and antibacterial property of bamboo pulp fabrics finished by silver nanoparticles**

A one-step simple synthesis of silver colloid nanoparticles with controllable sizes is presented. In this synthesis, multi-amide compound (RSD) was applied as a stabilizer and a reductant. The formation of silver colloid nanoparticles was characterized by Dynamic Light Scattering (DLS), Transmission Electron Microscopy (TEM), UV/Visible Absorption Spectrophotometry and X-ray Diffraction (XRD) measurements. Both particle size and the UV absorption are strongly dependent on the initial  $\text{AgNO}_3$  concentrations. The silver colloid nanoparticles, prepared with 0.35 g/l  $\text{AgNO}_3$  aqueous solution in the presences of 2g/l RSD, showed good antibacterial activities against Gram-negative bacteria (*Escherichia coli*) and Gram-positive bacteria (*Staphylococcus aureus*). A very low concentration of nano-silver (as low as 3.0  $\mu\text{g/ml}$  Ag) also gave excellent antibacterial performance. Furthermore, in-situ synthesis method of silver nanoparticles on the bamboo pulp fabrics was developed. The examined results confirmed that the in-situ synthesized silver nanoparticles were evenly distributed on the surface of fibers. The nanosilver-treated bamboo pulp fabrics were laundered 0, 5, 10, 20 times and still resist the exceptional antibacterial property. When the treated fabrics were washed 20 times, the antibacterial rate is more than 98.89% for *S. aureus* and 98.46% for *E.coli*. The excellent laundering durability may attribute to the tight binding between silver nanoparticles and bamboo pulp fibers through the in-situ synthesis. This method provides an economic method to enhance the antibacterial capability of bamboo pulp fabrics with a good resistance to washings.

### **2.1 Introduction**

Bamboo pulp fiber is made from cellulose of bamboo in the form of dissolving pulp, and then it is turned into something like viscose fiber via spinning. As a new cellulose-based material, bamboo pulp fiber has been growing in popularity because it

has many unique properties and can be easily obtained from nature[1, 2]. Bamboo grows to its mature size in only 6-8 months, whereas wood takes about 10 years. In terms of properties bamboo pulp fiber is light and strong, has excellent wicking properties. The fiber is also naturally smooth and very soft. Bamboo plant possesses anti-UV properties and antimicrobial function. Generally, bamboo pulp fiber has lost the antibacterial property laid inherently in bamboo resulting from the treatment with alkali in the processing[3, 4] .

The antibacterial activity of silver has been well known for many years. Even at a very low concentration, silver-ions are still effective against bacteria in water systems. Contrary to bactericide effects of ionic silver, the antimicrobial activity of silver particles is influenced by the dimensions of the particles. The smaller the particles, the greater antimicrobial effect[5, 6]. Nano-silver particles are generally smaller than 100 nm and contain 20-15,000 silver atoms. At nanoscale, silver exhibits remarkably unusual physical, chemical and biological properties, which also include remarkable antibacterial activity[7]. Due to its strong antibacterial activity, nano-silver particles in solution or on appropriate supporting substrates are currently used in various fields such as medicine [8-16], textile fabrics[17-20], coating materials and water treatment[21], etc.

Because of such wide range of applications, numerous synthetic methods have been developed. The most common synthesis of silver nanoparticles is the chemical reduction of a silver salt solution by a reducing agent such as sodium borohydride ( $\text{NaBH}_4$ ), formaldehyde, sodium citrate, hydrazine, ascorbic acid, glucose, and solvents like N, N-dimethylformamide (DMF), ethylene glycol, etc. In addition,  $\gamma$ -ray or UV irradiation was also utilized as an alternative to reduce the silver cations[22-24]. In these works, controlling the generation of the nano-silver particles are always difficult and steps are tedious. Many studies are focused on finding a simple and convenient method for preparing silver colloidal nanoparticles.

Due to the unique chemical and physical properties, dendrimers and hyperbranched polymers have received much attention over the past two decades and

have been applied to coatings, additives, drug and gene delivery, macromolecular building blocks, nanotechnology and supramolecular science [25, 26]. Esumi, et. al. prepared nanoparticles of gold, platinum, and silver by reduction of their metal salts with NaBH<sub>4</sub> in the presence of poly(amidoamine) dendrimers[27, 28]. However, the preparation of dendrimer is generally tedious because of various protection, deprotection and purification steps. Hyperbranched polymers can be synthesized by one-step polycondensation.

The purpose of the present work is to synthesize Multi-amide compound (RSD) from methylacrylate and diethylene triamine by melt polycondensation and prepare silver colloid nanoparticles (Ag NPS) in the presence of the RSD. In this synthesis, the RSD captured silver ions from the AgNO<sub>3</sub> aqueous solutions and abundant amino groups (1 °, 2 °, and 3 ° amines) reduced silver ions to silver nanoparticles as a highly effective self-reducing agent. In addition, the RSD acted as a stabilizer by preventing nanoparticles from agglomerating. The formation of silver colloid nanoparticles was characterized by Dynamic light scattering (DLS), TEM, UV/Visible absorption spectrophotometry and XRD measurements. The antibacterial activities of the prepared silver colloid nanoparticles against Gram-negative bacteria (*Escherichia coli*) and Gram-positive bacteria (*Staphylococcus aureus*) were also studied. Furthermore, in-situ formation of silver nanoparticles on the bamboo pulp fabric was carried out. The antibacterial property and wash ability of bamboo pulp fabrics was studied

## **2.2 Experiment**

### **2.2.1 Materials**

Diethylenetriamine, methyl acrylate, Silver nitrate (AgNO<sub>3</sub>) and sodium sulfide (Na<sub>2</sub>S) were purchased from Sinopharm Chemical Reagent Co. Ltd. (China) and of analytical grade. *Staphylococcus aureus* (*S. aureus*, ATCC 6538) and *Escherichia coli* (*E. coli*, ATCC 8099) were obtained from College of Life Science, Soochow University (China). Nutrient broth and nutrient agar were purchased from Scas Ecoscience Technology Inc. (China). Bamboo pulp fabric was purchased from Tanzhuzhuang bamboo fiber in Anji, Zhejiang, China, which was bleached and scoured, the density of

the fabric is 138g/m<sup>2</sup> and a thickness of 0.29mm.

### 2.2.2 Synthesis of RSD

RSD (Fig.1) was synthesized as reported. Diethylene triamine (52 ml, 0.5 mol) was added in a 250 ml three-neck round-bottomed glass flask equipped with a constant-voltage dropping funnel, a thermometer and a nitrogen inlet tube. The reaction mixture was stirred with a heat-up magnetic agitator and cooled with an ice bath, while the solution of methyl acrylate (43 ml, 0.5 mol) in methanol (100 ml) was added dropwise into the flask. Then the mixture was removed from the ice bath and left stirring for a further 4 h at room temperature. The light yellow AB<sub>2</sub> type monomer was synthesized and then the mixture was transferred to an eggplant-shaped flask for an automatic rotary vacuum evaporator. After removing the methanol under low pressure, the temperature was raised to 150 °C using an oil bath, and left for 4 h until the yellowish viscous multi-amide compound (RSD) was obtained.

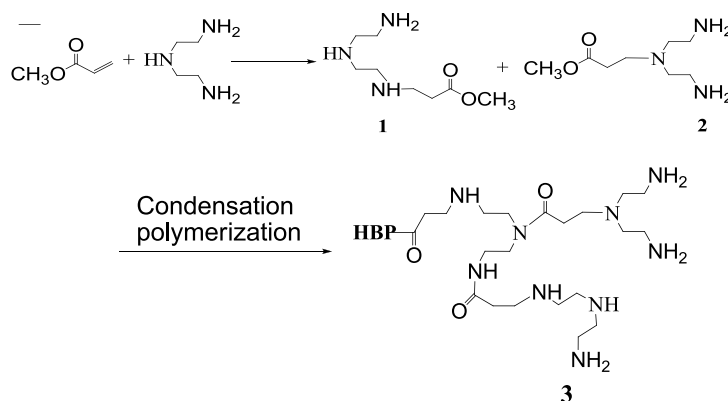


Figure 1 Schematic representation of the synthesis of RSD

### 2.2.3 Synthesis of silver nanoparticles

Silver nitrate (AgNO<sub>3</sub>) and the RSD were dissolved in deionized water, separately. Then AgNO<sub>3</sub> aqueous solution was added dropwise into RSD aqueous solution under vigorous stirring. The initial concentrations of the reaction components were 0.28, 0.35, and 0.56 g/l for AgNO<sub>3</sub> and 2 g/l for the RSD, respectively. Then the reaction mixture was kept stirring at room temperature until the reduction of Ag<sup>+</sup> to Ag<sup>0</sup> was completed and brown silver colloid nanoparticles was formed. The completion of the reduction of

$\text{Ag}^+$  to  $\text{Ag}^0$  was determined by using a procedure described by Aymonier et al.[29] When residual  $\text{Ag}^+$  ions were present in the solution, a black precipitate was observed. In addition, the course of the reduction of silver ions was continuously monitored by UV-visible spectroscopy, and the reaction was allowed to proceed until the amplitude of the absorption spectrum reached a plateau. The result silver colloids were stored in a brown-glass container.

When the initial concentration of the  $\text{AgNO}_3$  aqueous solution increased to 0.56 g/l, some particle aggregates were observed visually in silver colloid and some dark silver powders were precipitated from the colloidal solution after about 1 week. The precipitated silver powders were centrifuged, washed with methanol and dried in the air for XRD measurement.

#### **2.2.4 Characterization of silver nanoparticles**

The average values of the silver nanoparticle size and polydispersity, defined as a relative width of the size distribution, were determined by a DLS method using a HPPS 5001 grain-size analyzer (Malvern England). TEM micrographs were obtained by using an FEI Company (USA) Tecnai G220 transmission electron microscope operating at 300 Kv accelerating voltage. UV-vis absorption spectra were recorded on a UV-3010 spectrophotometer (Shimadzu, Japan). The XRD patterns of the silver nanoparticles were taken in the  $2\theta$  range of  $20-80^\circ$  at a scanning rate of  $2^\circ/\text{min}$  using Cu  $K\alpha$  radiation with a model D/max3c X-ray detector diffraction system (Japan).

#### **2.2.5 Antibacterial test of silver nanoparticles**

The antimicrobial activity of the prepared silver nanoparticles was tested by studying the growth kinetics of *S. aureus* and *E. coli*. This was done by measuring the optical density of the microbial culture at 546 nm after 0-24 h of incubation[30]. Optical density was measured using an ultraviolet-visible (UV-vis) spectrophotometer (751MC; Shanghai Analytical Instruments, China).

In addition, the effect of the silver nanoparticles' concentration on antimicrobial activity was tested by measuring the optical density of the microbial culture at 546 nm after 6 h of incubation.



### 2.2.6 Preparation of nanosilver treated bamboo pulp fabric

The bamboo pulp fabric was immersed in the solution which was mixed by AgNO<sub>3</sub> and RSD at their respective concentration with the process of dipping and rolling twice times, subsequently steamed 30 minutes. After that, the fabrics were washed by the demonized water and dried at ambient temperature to produce the finished bamboo pulp fabric.

### 2.2.7 Test methods for silver-treated bamboo pulp fabric

Whiteness of the fabrics was determined using a WSD-5 Full-automatic Whiteness Meter (Shanghai Jingshen Scientific Instrument Limited Company). Ag content in the silver-treated bamboo pulp fabrics was measured using a Vista MPX Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) (Varian, USA). The procedure was as follows: a sample (100 mg) was cut into small pieces and immersed in a 10 ml solution of HNO<sub>3</sub> (65%). After it dissolved, 90 ml of deionized water was used to dilute it. Then, 1 ml of the diluted solution was drawn to measure the concentration of Zn<sup>2+</sup>. The ZnO content in the fabric was calculated by equation (1)

$$w_{t(ZnO)}(\%) = \frac{C_{Zn^{2+}} \times 0.1 \times 81.39}{65.39} \quad (1)$$

Where,  $C_{Zn^{2+}}$  is the concentration of Zn<sup>2+</sup> in the solution, 0.1(L) is the total volume of the solution and 81.39 and 65.39 are the molar mass of ZnO and Zn, respectively. Model S-570 scanning electron microscope (SEM) was used to observe the particles size and morphology of silver nanoparticles on the surface of bamboo pulp fiber.

The antimicrobial activity of silver-treated bamboo pulp fabrics was tested against E. coli and S. aureus by using a shaking flask method according to FZ/T 73023-2006 (China). This method is specially designed for specimens treated with nonreleasing antibacterial agents under dynamic contact conditions. 0.75g sample fabric, cut into small pieces in a size around 0.5×0.5 cm<sup>2</sup>, was dipped into a flask containing 70 ml of 0.3 mM PBS (monopotassium phosphate, pH≈7.2) culture solution with a cell concentration of 1×10<sup>5</sup> cfu/ml-4×10<sup>5</sup> cfu/ml. The flask was then shaken at 150 rpm on a rotary shaker at 24 °C for 18 h. From each incubated sample, 1 ml of solution was

taken, diluted and distributed onto an agar plate. All plates were incubated at 37 °C for 24 h and the colonies formed were counted. The percentage reduction was determined as equation (2):

$$\text{Reduction in cfu (\%)} = \frac{C-A}{C} \times 100 \quad (2)$$

Where, C and A are the bacterial colonies of the bamboo pulp fabrics and the nano silver-treated bamboo pulp fabrics, respectively.

To evaluate the durability of the silver-treated bamboo pulp fabrics against repeated launderings, the AATCC Test Method 61-1996 was applied. An AATCC standard wash machine (Atlas Launder-Ometer) and detergent (AATCC Standard Detergent WOB) were used. Samples were cut into 5 × 15 cm<sup>2</sup> swatches and put into a stainless steel container with 150 ml of 0.15% (w/v) WOB detergent solution and 50 steel balls (0.25 in. in diameter) at 49 °C for various washing time to simulate 5, 10, and 20 wash cycles of home/commercial launderings.

## **2.3 Results and discussion**

### **2.3.1 Preparation of nano-silver colloidal solution**

Nano-silver colloidal solution was prepared by mixing AgNO<sub>3</sub> aqueous solution and RSD aqueous solution under vigorous stirring at room temperature. The formation of silver colloid nanoparticles was characterized by DLS, TEM and UV-vis Absorption Spectrophotometry. To prepare silver colloid nanoparticles, the AgNO<sub>3</sub> aqueous solution was dropwise added into the RSD aqueous solution under vigorous stirring at room temperature. As the stirring time went on, the colorless and transparent solution gradually changed into a light yellow solution, and subsequently the light yellow solution gradually changed into brown colloid. After 24 h stirring, the resulting silver colloid was stored in a brown-glass container. 0.1 g/l Na<sub>2</sub>S aqueous solution was applied to confirm that all silver cations (Ag<sup>+</sup>) had been changed to elemental silver (Ag<sup>0</sup>).

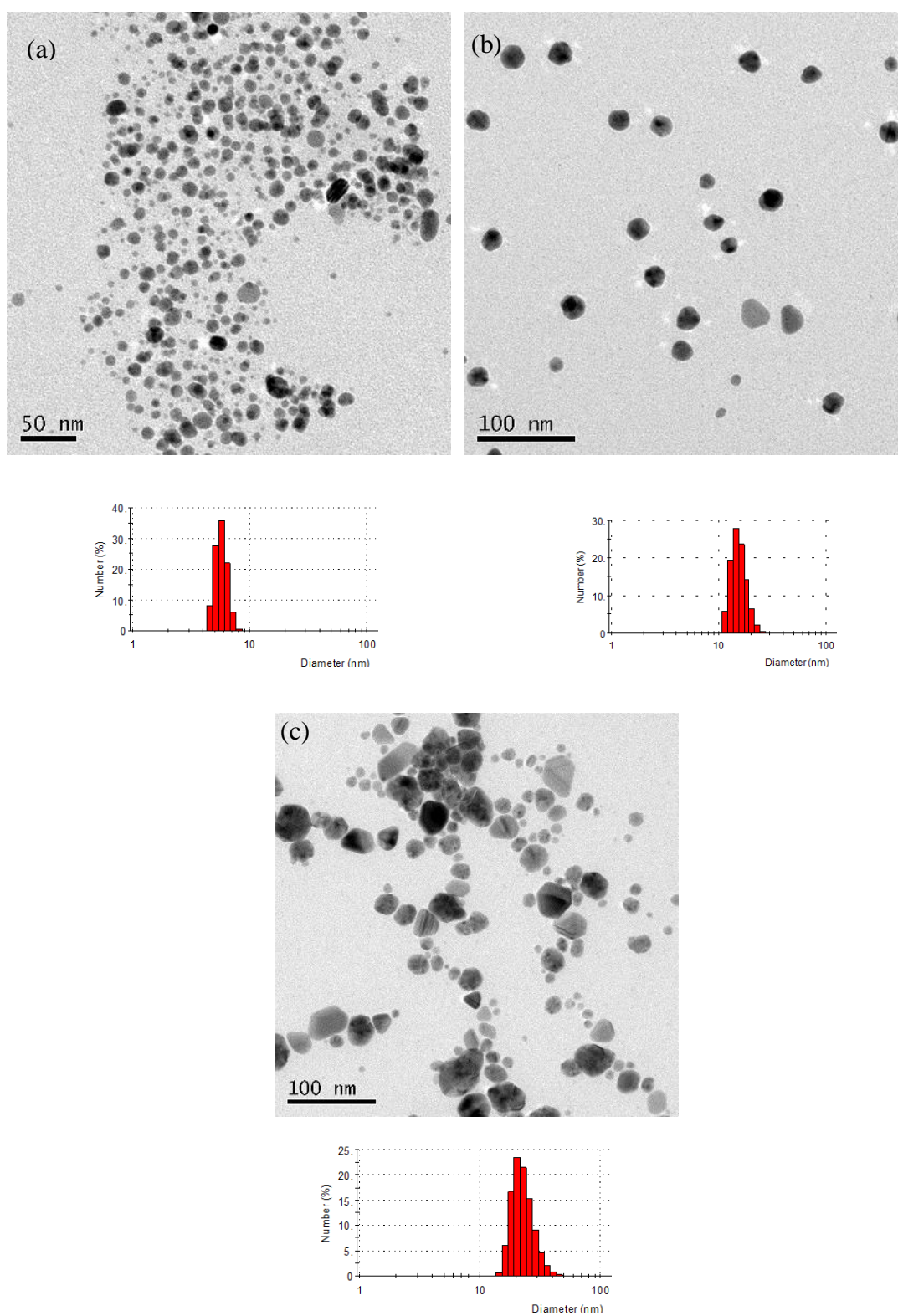


Figure 2 TEM images and the corresponding histograms of silver colloid nanoparticles prepared with different initial  $\text{AgNO}_3$  concentrations (a) 0.28 g/l, (b) 0.35 g/l, (c) 0.56 g/l. [RSD]=2.0 g/l.

The average silver nanoparticle size, the polydispersity and the stability of the silver colloid nanoparticles are strongly affected by the initial  $\text{AgNO}_3$  concentrations in the RSD aqueous solution. Figure 2 shows the TEM images and the corresponding histograms of three samples prepared with three different initial  $\text{AgNO}_3$  concentrations. Upon increasing the initial  $\text{AgNO}_3$  concentration from 0.28 g/l to 0.56 g/l, the mean particle size increased from 5.9 nm to 30.1 nm, meanwhile, the size distribution was also increased. The average silver nanoparticle sizes determined with DLS are in accord with the results in TEM.

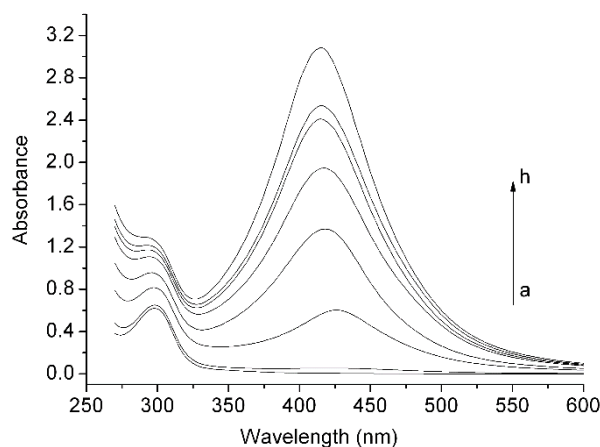


Figure 3 UV-vis spectra of the silver colloid nanoparticles at different time points: (a) 0 h; (b) 1 h; (c) 6 h; (d) 12 h; (e) 24 h; (f) 48 h; (g) 1 week; (h) 2 week.  $[\text{AgNO}_3]=0.17$  g/l,  $[\text{RSD}]=2.0$  g/l.

The characteristic absorption spectra are the important properties of silver nanoparticles, and the UV-vis spectral researches are a good way for characterization of the formation and growth of silver nanocrystals. Therefore, UV-vis spectra was applied to characterize the formation of silver colloid nanoparticles. Figure 3 shows the UV-vis spectra of the silver colloid nanoparticles recorded at time intervals during the preparing process. At the start time when the  $\text{AgNO}_3$  aqueous solution was mixed with the RSD aqueous solution, there was only one characteristic peak observed at 298 nm due to the pure RSD[31]. As the stirring time went on, a new characteristic absorption of spherical silver nanoparticles appeared at 408 nm. This confirms the nanocrystalline character of the silver particles[32], and the low degree of their polydispersity.

Further, Figure 3 shows the height of the absorption peak of the silver colloid

nanoparticles increased and the absorption spectrum narrowed with the time. As explained by Zhang et al. [33] and Petit et al. [34], when the silver particles diameter is less than 52 nm, an increase in particle size will result in narrowing of the absorption spectrum and increasing of the height of the absorption peak. So the changes in the UV-vis spectra of the silver colloid nanoparticles indicated that small silver nanoparticles were formed at the initial stage of the reaction and the small silver nanoparticles could collide with each other to produce larger, more stable particles with the time.

The effect of initial  $\text{AgNO}_3$  concentration on the stability of the resulting silver colloid nanoparticles was also investigated. The silver colloids prepared with initial  $\text{AgNO}_3$  concentration lower than 0.35 g/l showed good stability even after storing 2 months. However, when the concentration of the  $\text{AgNO}_3$  aqueous solution increased to 0.48 g/l, some particle aggregates were clearly observed in silver colloids and some dark silver powders were precipitated from the colloidal solution after it was kept for about 1 week. The precipitated silver powders in the silver colloid were centrifuged, washed with methanol and dried in the air for XRD measurement. The result is shown in Figure 4. It clearly shows the (111), (200), (220), and (311) planes of the silver nanoparticles. According to the Scherrer formula, the crystalline size of silver nanoparticles is about 26.7 nm, which agrees well with the TEM and DLS results.

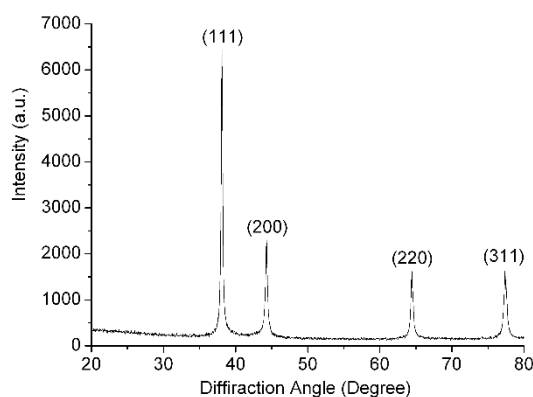


Figure 4 XRD spectrum of resulting silver nanoparticles.

$\text{Na}_2\text{S}$  determination, UV-vis spectra, TEM and DLS of the resulting silver nanoparticles indicated that silver ions ( $\text{Ag}^+$ ) had been reduced to form silver nanoparticles ( $\text{Ag}^0$ ) in RSD aqueous solution. It is worth noting that, in the synthesis, silver nanoparticles were prepared without adding extra reductants. The reduction of

silver ions were carried out by amino groups of RSD. It was reported that the amino groups could be oxidized in the aqueous phase as alkylamine, PEI, complexes with metal ions[35-37], indicating that the amino groups of RSD play a similar role in the reduction of silver ions in the present case. When the  $\text{AgNO}_3$  aqueous solution was dropped into the RSD aqueous solution under vigorous stirring at room temperature,  $\text{Ag}^+$  was complexed with RSD and then reduced in-situ to form silver colloid nanoparticles.

In addition, RSD plays an important role as a stabilizing agent in preventing nanoparticles from agglomerating. In silver colloids, we believe that there is a large amount of RSD adsorbed on the silver nanoparticle surface due to the effect of the positive charges in RSD. Therefore, silver nanoparticles agglomeration can be prevented.

The silver colloid nanoparticles prepared with initial  $\text{AgNO}_3$  concentration of 0.35 g/l in 2 g/l RSD aqueous solution was selected to evaluate their antimicrobial activity. The growth kinetics of *S. aureus* and *E. coli* were studied in the presence of the silver nanoparticles (Figure 5). It can be seen that microbial growth is significantly inhibited in the presence of 3.0  $\mu\text{g/ml}$  silver nanoparticles. In addition, the effect of concentration of the silver nanoparticles on antimicrobial activity was studied spectrophotometrically against *S. aureus* and *E. coli*. The results are shown in Figure 6. In each case, there was significant inhibition of microbes even at the minimum concentration (1  $\mu\text{g/ml}$ ) used. No significant increase in antimicrobial activity was observed beyond 3  $\mu\text{g/ml}$ , which appears to be the maximum concentration that should be used.

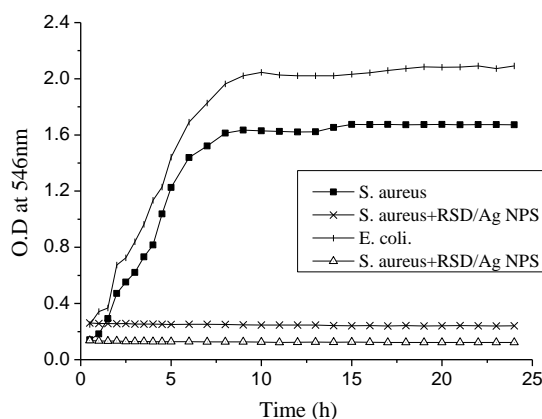


Figure 5 Growth kinetics of *S. aureus* and *E. coli* in the presence of silver

nanoparticles (concentration of silver nanoparticles: 3.0  $\mu\text{g/ml}$  )

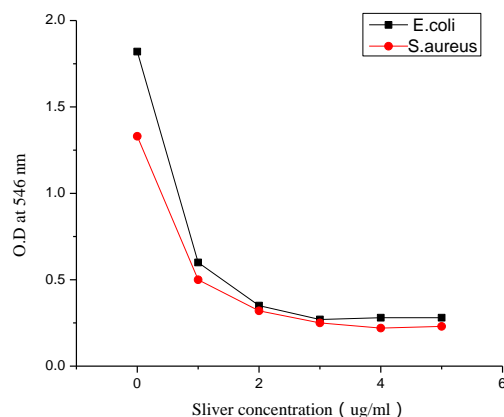


Figure 6 Effect of concentration on antimicrobial activity of the silver nanoparticles against *S. aureus* and *E. coli*

### 2.3.2 Characterization of in-situ synthesized silver nanoparticles on bamboo pulp fabric

After the in-situ reaction on the surface of bamboo pulp fabrics has completed, the dried fabrics show bright yellow visually. We can measure the absorbed value of the treated bamboo pulp fabrics, and then receive the absorption spectrum graphs.

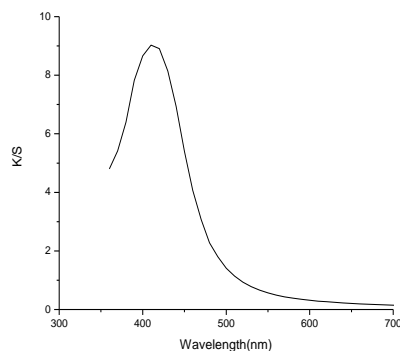


Figure 7 The spectra of treated bamboo pulp fabrics

As shown in Figure 7, the obvious absorption peak between 400nm and 420nm wavelength appeared in curves, which was consistent with the absorption peak of nano-silver solution. Thus we can deduce that there are nano-silver particles on the surface of silver-treated bamboo pulp fabrics.

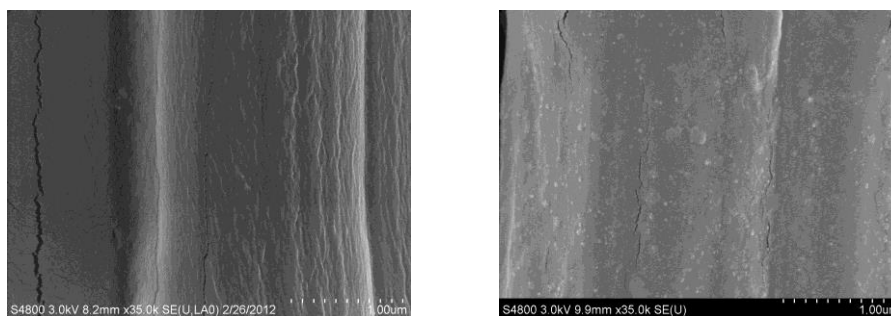


Figure 8 SEM images of surface of the bamboo pulp fiber(a) bamboo pulp fiber (b) nano silver-treated bamboo pulp fiber

The surface morphology of the original bamboo pulp fabric and the silver-treated bamboo pulp fabric can be seen in Figure 8. The images in Figure 8 show an obvious difference between the original bamboo pulp fabrics and the silver-treated sample. Many silver nanoparticles can be found after the bamboo pulp fabric was finished with 50mg/l silver nitrate solution, RSD mixed solution and silver nanoparticles were well dispersed on bamboo pulp fabrics' surface. Fig.7 together with Fig.8 completely confirmed that the silver exist in the form of nano silver particles on the surface of the finishing bamboo pulp fabric.

Generally the nano silver particles are considered as the good antimicrobial agent on the bamboo pulp fabrics. To study the antimicrobial activities of silver nanoparticle-treated bamboo pulp fabric, the *E. coli* and *S. aureus* were selected to perform the antibacterial experiments.

### 2.3.3 Antibacterial property of silver-treated bamboo pulp fabrics

Table 1 lists the whiteness index (WI), weight increase and inhibition rates to *E. coli* and *S. aureus*, which are measured from the silver nanoparticle-treated bamboo pulp fabrics by using 0.4g/l RSD solution with 0.0034g/l, 0.0105g/l, 0.017g/l, 0.034g/l and 0.068g/l  $\text{AgNO}_3$  solution respectively. The samples are denoted accordingly as a, b, c, d and e. As a reference, the whiteness of the original fabric is 91.50. As we can see in table 1, the finished bamboo pulp fabrics have the excellent antibacterial rate to *E. coli* and *S. aureus*, which are more than 99%. When the silver content of bamboo pulp fabrics increases from 97.25mg/kg to 147.38mg/kg, the antibacterial rate has no significant change, but the WI changed a little. Therefore, the silver nanoparticle-



treated bamboo pulp fabrics show an excellent antibacterial property and satisfied whiteness as the  $\text{AgNO}_3$  concentration of solution is shown in Table 1.

Table 1 The WI, the content silver, the antibacterial rate of nano-silver treated fabric

Sample Characterization	a	b	c	d	e
WI	87.50	86.18	84.37	83.26	82.22
mg/kg	97.25	102.69	126.48	139.82	147.38
<i>S. aureus</i> rate (%)	99.99	99.78	99.88	99.86	99.99
<i>E. coli</i> rate (%)	99.35	99.47	99.92	99.88	99.98

One of the most important features of nanosilver-treated bamboo pulp fabrics is its durability against repeated washings. To study the washing durability, the nano silver-treated bamboo pulp fabrics were laundered 0, 5, 10, 20 and 50 times with the detergents respectively in Table 2. The silver content of 97.25 mg/kg on the finished bamboo pulp fabric was selected to conduct the washing test. With the washing times increased, the silver content slightly decreased from 97.25 mg/kg to 89.72 mg/kg, while the corresponding whiteness increased. It is surprising that antibacterial rate is still more than 97.43% to *S. aureus* and 99.86% to *E. coli* after 20 washings.

Table 2 The WI, the content silver, the antibacterial rate of different washing times

Washing times Characterization	0	5	10	20
WI	87.50	87.62	88.03	88.21
mg/kg	97.25	94.36	91.95	89.72
<i>S. aureus</i> rate (%)	99.99	98.49	99.49	98.89
<i>E. coli</i> rate (%)	99.35	99.96	98.35	98.46

The excellent laundering durability of the silver nanoparticle-treated bamboo pulp fabrics may be caused as the following reasons. Some imino groups of the RSD form the silver ammonia complex with silver nanoparticles in Figure 9, which are easily

penetrating into the amorphous zone of bamboo pulp fibers. Secondly, bamboo pulp is cellulose fiber, which have a large number of hydroxyls on the surface. The van der Waals force between molecules, as well as hydrogen bond, will enhance the bonding between silver particle and bamboo pulp fabrics. [38]

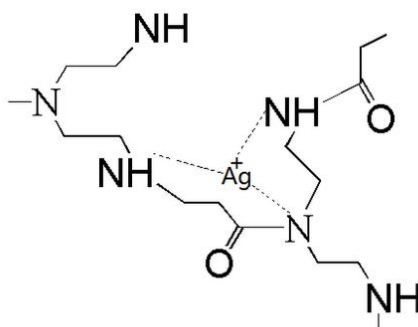


Figure 9 Schematic description of the silver ammonia

## 2.4 Conclusions

A one-step simple synthesis of silver colloid nanoparticles by mixing  $\text{AgNO}_3$  aqueous solution and RSD aqueous solution under vigorous stirring was reported. The synthetic process was carried out in aqueous solution and at room temperature, making the method versatile and environmentally friendly. The syntheses performed at various initial  $\text{AgNO}_3$  concentrations in RSD aqueous solution produced silver colloid nanoparticles having average sizes from 3 to 30 nm and narrow size distributions. The silver colloids prepared with initial  $\text{AgNO}_3$  concentration lower than 0.35 g/l showed good stability even after storing 2 months. The silver colloid nanoparticles prepared with initial  $\text{AgNO}_3$  concentration 0.35 g/l in 2 g/l RSD aqueous solution showed high antibacterial activities against *S. aureus* and *E. coli*. The maximum concentration that should be used was 3.0  $\mu\text{g/ml}$  to give good antibacterial performance.

Bamboo pulp fabric was treated by the multi-amine compound (RSD) and silver nitrate mixed solution by in-situ method. The surface morphology, the whiteness, silver content, antibacterial activity and washing durability of the silver-treated fabrics were determined. The experiment of antibacterial rate test showed that the finished fabrics had excellent antibacterial and wash-resisting property. Amazingly, even though

washed 20 times, the antibacterial rate of the finished bamboo pulp fabric still remained more than 98%, while the whiteness and the structure was less affected.

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# **Chapter 3**

## **In-situ growth of ZnO particles on bamboo pulp fabric and its anti-UV property**

### **Chapter 3: In-situ growth of ZnO particles on bamboo pulp fabric and its anti-UV property**

This research presents a simple way to enhance the anti-UV property of bamboo pulp fabric through in situ synthesis of ZnO particles on the fabric. Bamboo pulp fabric was treated in  $\text{Zn}(\text{NO}_3)_2$  and RSD mixing solution under hydrothermal condition, then the ZnO particles were deposited on the surface of bamboo pulp fabric by in-situ method. In this synthesis RSD was applied as a stabilizer, reactant and dispersant agent, the reaction mechanism was investigated. The ZnO particles were characterized by TEM, XRD and ultraviolet/visible light spectrophotometer. The anti-UV property of Bamboo Pulp Fabric was characterized by measuring its UPF. The results indicated that the diameter of ZnO is about 150nm, the length is about 600nm. The Bamboo Pulp Fabric treated with ZnO particles showed good anti-UV property and its UPF can reach to 83.59. After washing for 20 times, it can also keep good anti-UV property.

#### **3.1 Introduction**

In recent years, nature fiber has recently been of great interest due to its several advantages. Compared to the synthetic fibers, the nature fibers are available in abundance and easy to obtain. In addition, they are renewable resources and environmentally friendly. Bamboo is commonly used in conventional applications such as furniture, construction, paper industry. It is an abundant natural resource in most of the tropical countries, and its overall mechanical properties are comparable to those of wood [1-3]. Recently, bamboo pulp has been utilized in preparing fiber in some Asia countries, as it possesses desirable comfort properties such as good moisture absorption and permeability, excellent dyeing and finishing abilities [4-7]. Currently bamboo fibers are used in apparels including undergarments, sports textiles, t-shirts and socks. It has been reported that the bamboo fiber has the anti-UV properties that are inherited from the bamboo plant itself [8-9]. However, few literatures in this area could be found and

the research need for additional inquiry. In this study, we investigated the anti-UV property of untreated and ZnO particles treated bamboo pulp fabric.

ZnO is one of the important promising materials in many application such as UV-shielding, piezoelectric devices, electrodes for gas sensors, solar cells due to its optoelectronic and electrochemical properties, wide band gap (3.37 eV) and large exciton binding energy 60 meV [10-11]. ZnO is similar to TiO<sub>2</sub>, which can shield ultraviolet (200 ~ 400nm) through its reflection and retraction to the light [12]. But ZnO has better ultraviolet shielding properties, and a cheaper price.

ZnO particles are treated on fabric mainly through the composite spin-fling process or finishing method. For one thing, ZnO particles powder should be firstly prepared for both methods with the complex procedure, high consumed energy and cost. Meanwhile, most of zinc oxide particles are firmly embedded in the fiber during filature process or enwrapped by binder in coating method, both of which make ZnO hardly expose on the surface and cannot fully contact with the oxygen and water [13]. To eliminate the problems, it becomes hot spot for in-situ growth of ZnO particles on the surface of the fabric and providing the fabric with special function. Recently, Z Mao et al treated cotton fabric with nano ZnO through hydrothermal method to enhance UV-protective property. [14] R Wang et al grew nano ZnO crystallites on cotton fabrics to achieve excellent UV-blocking property by two-step approach, room-temperature zero-gel ZnO seeded growth process to grow hexagonal arrays of oriented ZnO nanorodson flexible cotton fabric substrate. [15] Here we report a simple one-step method for synthesis ZnO particles on bamboo pulp fabric by in-situ method to obtain anti-UV bamboo pulp fabric.

In our previous studies, multi-amide compound (RSD), was synthesized (As shown in fig.1). We prepare nano-silver colloidal solution in one step, and subsequently to finish cotton and silk fabric with the nano-silver colloidal solution. RSD served as a binder to impart and fix the silver nanoparticles on the bamboo pulp fabric to provide durability antimicrobial properties. In this study we finished the bamboo pulp fabric with the mixing Zn (NO<sub>3</sub>)<sub>2</sub> and RSD solution using an impregnation method under hydrothermal condition, then we obtained the ZnO growth bamboo pulp fabric in one



step by in-situ method. In this process, RSD served as a reactant, dispersant and complexing agent.

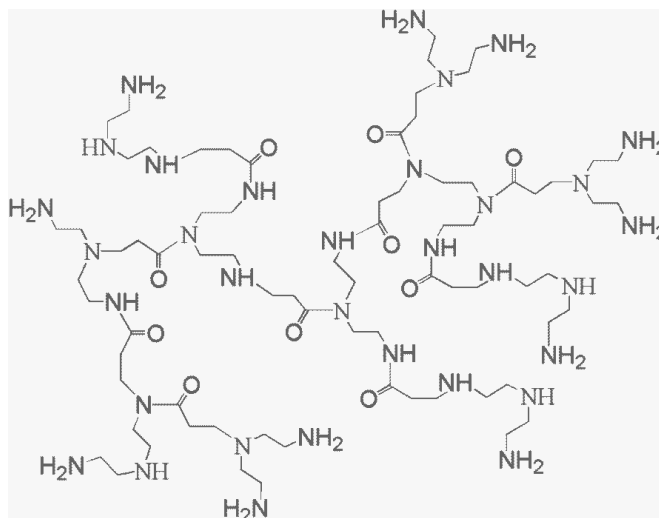


Figure 1 Schematic description of the RSD's molecule structure

## 3.2 Experiment

### 3.2.1 Materials

Bamboo and RSD was obtained as described in section 2.2.2. Zinc nitrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) were purchased from Sinopharm Chemical Reagent, China, as analytical reagents and employed without further purification.

### 3.2.2 Synthesis of ZnO dispersions in aqueous solution

ZnO dispersions solution was prepared in one step by mixing  $\text{Zn}(\text{NO}_3)_2$  aqueous solution and RSD aqueous solution under vigorous stirring at 100 °C. The initial concentrations of the reaction components were an equimolar (0.01M) aqueous solution of  $\text{Zn}(\text{NO}_3)_2$  and 2g/l RSD in this study. As the stirring time went on, the colorless and transparent solution gradually changed into a milky solution. After 10 min stirring, the resulting ZnO dispersions solution was stored in a glass container.

### 3.2.3 Fabric finishing process

An equimolar (0.01M) aqueous solution of  $\text{Zn}(\text{NO}_3)_2$  and 2g/L RSD were prepared in a beaker. The bamboo pulp fabric was immersed in the solution, the bath ratio is 1:50. The beaker was then sealed and held in the 60 °C water bath for 40min

with constant stirring. The temperature of water bath temperature rise at 2°C/ min till 100°C. After immersing for 2h at 100 °C water bath, the fabric washed with deionized water several times to remove unfixed materials. The resulting bamboo pulp fabric was dried in drying oven at 100 °C for 2 min, 130°C for 3min.

### 3.2.3 Ultraviolet protection factor (UPF) of the fabric

Ultraviolet Protection Factor (UPF) is the scientific term used to indicate the amount of UV protection provided to skin by fabric. UPF is defined as the ratio of the average effective UV irradiance calculated for unprotected skin to the average UV irradiance calculated for skin protected by the test fabric. The higher the value, the longer a person can stay in the sun until the area of skin under the fabric becomes red. An effective UVR dose (ED) for unprotected skin is calculated by convolving the incident solar spectral power distribution with the relative spectral effectiveness function and summing over the wavelength range 290–400 nm. The calculation is repeated with the spectral transmission of the fabric as an additional weighting to get the effective dose (ED<sub>m</sub>) for the skin when it is protected. The UPF is defined as the ratio of ED to ED<sub>m</sub> and calculated as follows

$$UPF = \frac{ED}{ED_m} = \frac{\sum_{\lambda=290}^{\lambda=400} [S_{\lambda} A_{\lambda} \Delta_{\lambda}]}{\sum_{\lambda=290}^{\lambda=400} [S_{\lambda} A_{\lambda} \Delta_{\lambda} T_{\lambda}]} \quad (1)$$

Where  $S_{\lambda}$  is the source spectrum ( $Wm^2 nm^{-1}$ ),  $T_{\lambda}$  is the transmittance,  $A_{\lambda}$  is the action action spectrum for measured response and  $\Delta_{\lambda}$  is the bandwidth in nm. Since the relative erythral spectral effectiveness is higher in the UV B region compared to the UVA region, the UPF values depend primarily on the transmission in the UV B region.

The UPF (Ultraviolet Protection Factor) of the bamoo pulp fabric were measured using a labsphere UV-100F Ultraviolet Transmission Analyzer. Fabrics with a UPF value in the range less than 15 (<15), between 15 and 50, and more than 50 (>50) are generally classified as nonrateable, good, and excellent UV blocking properties for fabrics [19-20].

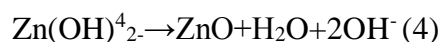
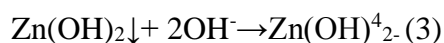
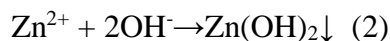
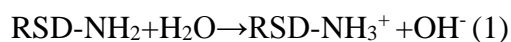
### 3.2.4 Characterization of ZnO particles

TEM micrographs, UV-vis absorption spectra and XRD patterns of the ZnO nanoparticles were taken as describe in section 2.2.4.

## 3.3 Results and discussion

### 3.3.1 Mechanism

In this study, ZnO dispersions were synthesized in Zn (NO<sub>3</sub>)<sub>2</sub> and RSD aqueous solution. The main chemical process is supposed as follows:



The RSD aqueous solution was alkaline when it was dissolved in deionized water due to the protonation of amino groups. In alkaline conditions zinc nitrate may convert into Zn (OH)<sub>2</sub> colloids which is shown in reaction 1 and 2. According to the reaction 3, part of the Zn (OH)<sub>2</sub> colloids dissolves into Zn(OH)<sub>4</sub><sup>2-</sup> during the hydrothermal process[9,21]. ZnO spontaneously from the solution of Zn(OH)<sub>4</sub><sup>2-</sup> to multinuclei aggregates. When the concentration of Zn<sup>2+</sup> and OH<sup>-</sup> reaches the supersaturation degree of ZnO, ZnO can evolve to complete.

### 3.3.2 Characterization of ZnO particles

The formation of ZnO colloid particles was characterized by XRD UV/Visible Absorption Spectrophotometry and TEM. ZnO dispersions solution was prepared in one step by mixing Zn(NO<sub>3</sub>)<sub>2</sub> aqueous solution and RSD aqueous solution under vigorous stirring at 100 °C. The initial concentrations of the reaction components were an equimolar (0.01M) aqueous solution of Zn(NO<sub>3</sub>)<sub>2</sub> and 2g/l RSD in this study. As the stirring time went on, the colorless and transparent solution gradually changed into a

milky solution. After 10 min stirring, the resulting ZnO dispersions solution was stored in a glass container. The formation of ZnO colloid particles was characterized by XRD analysis and UV/Visible Absorption Spectrophotometry.

RSD dispersions were diluted to 0.5g / L, the concentration of ZnO dispersion were determined by the UV spectrophotometry at 200-450nm, and the reference solution was 0.5g/L RSD aqueous solution. Fig.2 shows the UV-vis spectra of the prepared ZnO colloid particles. When the  $\text{Zn}(\text{NO}_3)_2$  and RSD mixing aqueous solution were boiled. A characteristic absorption of ZnO particles appeared at 362nm. This confirms the crystalline character of the result ZnO particle [22-23].

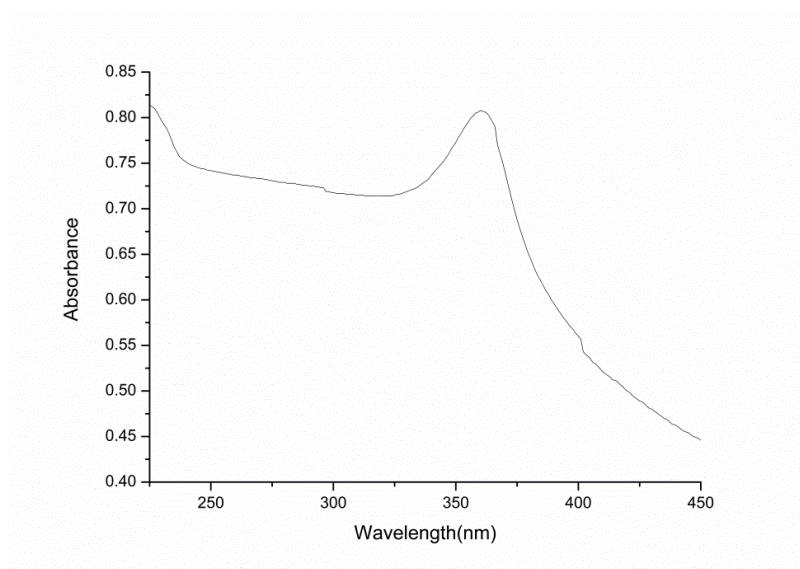


Figure 2 The absorbance spectra of ZnO particles

The precipitated ZnO powders in the ZnO dispersions were centrifuged, washed with methanol and dried in the air for XRD measurement. Fig.3 shows the XRD pattern of the ZnO particles. All diffraction peaks are indexed as typical hexagonal wurtzite ZnO structure with lattice constants  $a = 3.249 \text{ \AA}$  and  $c = 5.206 \text{ \AA}$  (JCPDS 36-1451) [11,24]. No diffraction peaks from other impurity phases are found, confirming that the products are pure ZnO. This indicated that the boiling water treatment helped completely transform  $\text{Zn}(\text{OH})_2$  crystallites into ZnO crystallites on the surface of bamboo Pulp fabric and make the ZnO crystallites a better crystalline perfection.

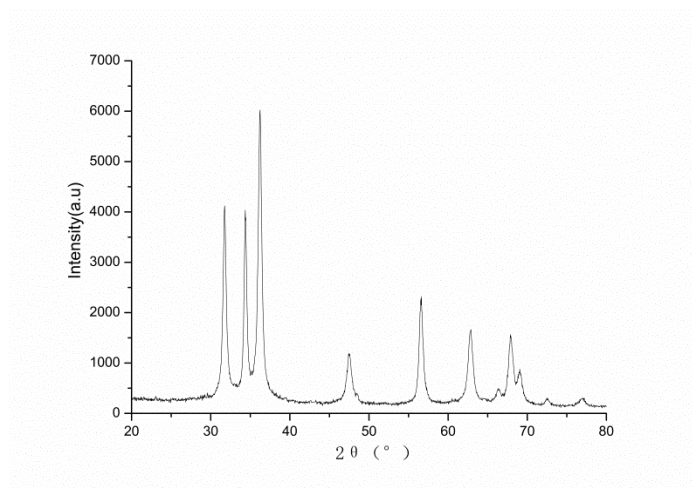


Figure 3 XRD patterns of ZnO particles

The morphology of the ZnO particles in aqueous solution was confirmed by TEM analysis. Fig. 4 shows a typical TEM pattern of rod-like ZnO particles with the diameter of 150 nm and length of 600 nm.

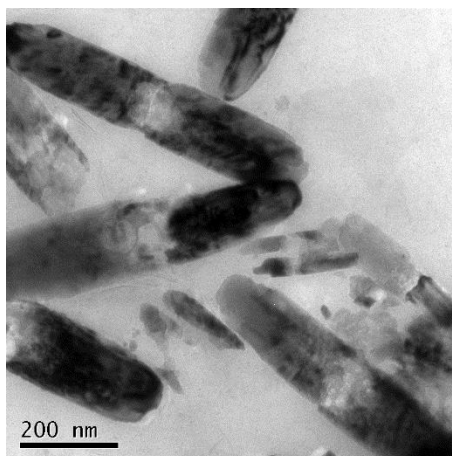


Figure 4. Tem image of ZnO nanoparticles

However, the synthesized ZnO particles is a little big (length > 100 nm) and if the ZnO particles solution was non-intrusively placed for more than 24 hours, the sediments would be appeared in the solutions. Due to the dispersion of ZnO particles is not very good, the ZnO particles tend to agglomeration in the solution. This has been confirmed by the TEM micrographs. Therefore, we will attempt the in-situ synthesis of ZnO nanoparticles directly on the bamboo pulp fabric, which may form a stronger binding between ZnO particles and fibers

### 3.3.3 Morphology observation and EDS analysis

SEM were used to observe the morphology of the fiber and ZnO particles. Fig. 5a shows the SEM image of the original bamboo pulp fiber. It can be seen that the bamboo pulp fiber is made up of fibrils which is arranged along the length of the fiber basically. There are full of grooves between fibrils in the longitudinal fiber surface and apertures along the length of the fibrils, and its morphology is straight stripes with a smooth, sleek shape. Fig. 5b demonstrates the SEM photographs of the ZnO particles treated bamboo pulp fibers by in-situ method. Compared with the untreated it is clear to see that the bamboo pulp fibers were covered with a uniform and dense ZnO particles. The obtained ZnO particles were well-crystallized. In the synthetic process, it indicated that RSD has been adsorbed to bamboo pulp fabric and ZnO particles have been fixed on the bamboo pulp fabric.

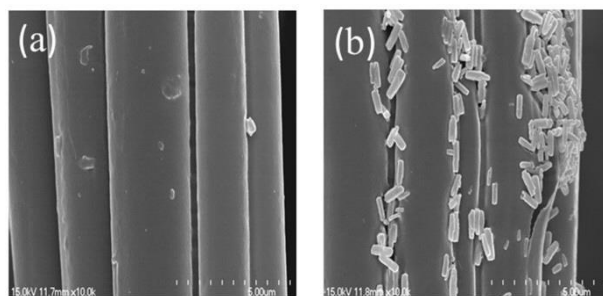


Figure 5 SEM images of (a) original bamboo pulp fiber, (b) ZnO grown bamboo pulp fibers.

To determine the composition of the treated bamboo pulp fabric, chemical elements of ZnO particles treated bamboo pulp fabric was characterized by EDS. The result can be seen in Fig. 6 and Table 1. Fig. 6 gives a typical EDS image recorded on the ZnO covered bamboo pulp fabric. There were three main elements (carbon, zinc, and oxygen) in the bamboo pulp fabric. The content of the three elements were shown in tab 1. From tab 1 we can see that the content of Zn is about 10%. No other elements were detected, confirming that the particles are primarily ZnO.

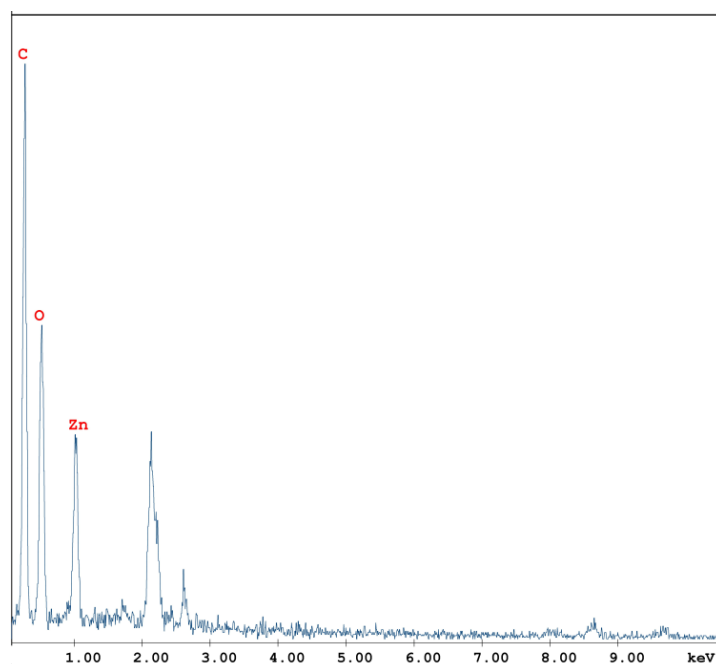


Figure 6 EDS analysis of the ZnO particles growth bamboo pulp fabric.

Table 1 The element on the ZnO bamboo pulp

Element	Wt%	$\lambda t\%$	K-Ration
C K	60.40	71.42	0.2629
Zn L	9.88	2.12	0.081572
O K	29.73	26.46	0.0672
Total	100.00	100.00	

### 3.3.4 UV transmittance and washability of bamboo fabric

UPF is defined as the ratio of the average effective UV irradiance calculated for unprotected skin to the average UV irradiance calculated for skin protected by the fabric. The UV-blocking activity of the fabric can be directly evaluated by measuring its UPF.

The UPF of ZnO coated bamboo pulp fabric are shown in Fig.7. Initial investigations regarding the UV protective property of untreated fabric and RSD treated fabric showed that the fabric afforded poor protection against ultraviolet radiation. An UPF value < 15 indicates no protection against transmission of UV radiation through fabric and onto skin. The ZnO particles coated bamboo pulp fabric has low UV transmission in UVB region (250 to 315 nm) and part of UVA region (315 to 370 nm) due to the UV absorption of ZnO and the UPF of ZnO coated fabric is 83.59, which is

considered as good UV blocking property. The effect of washing on UV protection of nano ZnO coated cotton fabric was studied. The experiments show that that the UPF value of the fabric reduced after washing. After 20 washes, the UPF reduces from 83.59 to 60.57, which is still considered good UV protection

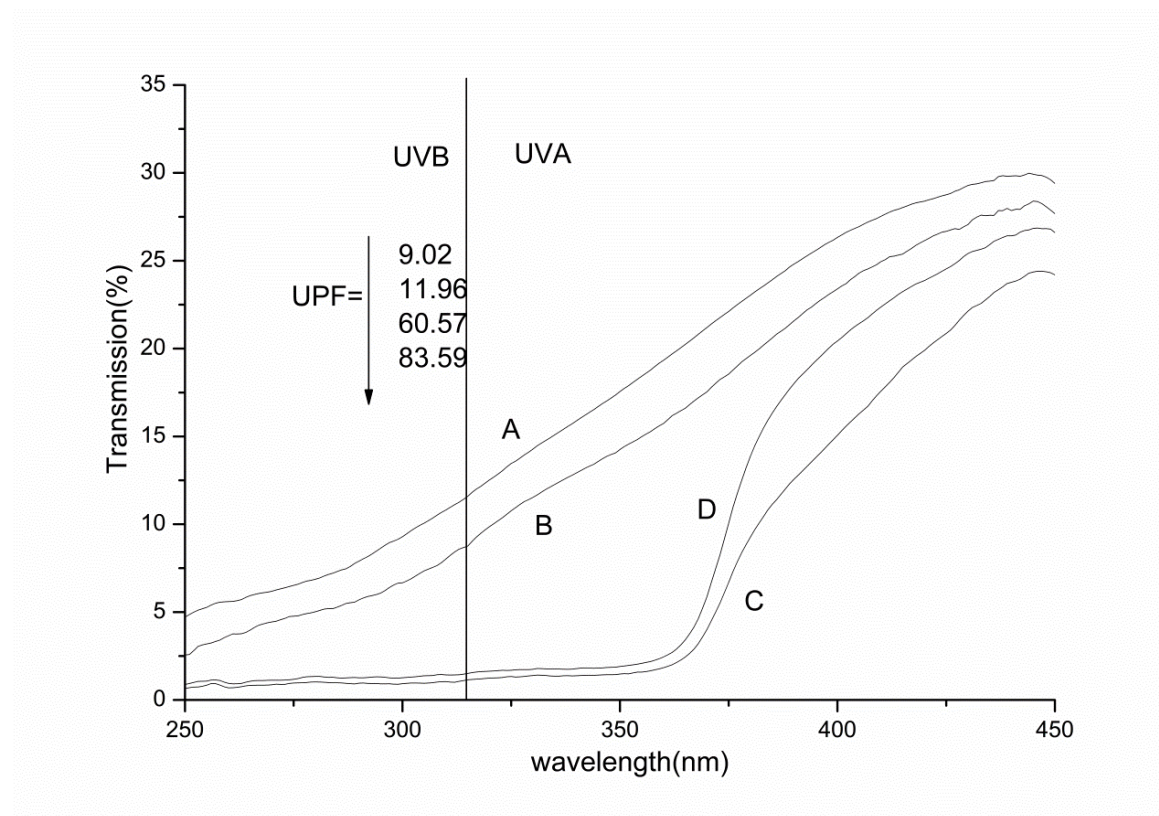


Figure 7. UV transmittances of original bamboo pulp fabric sample and ZnO particles covered bamboo pulp fabric (A) original sample (B) bamboo pulp fabric treated by RSD (C) ZnO particles coated bamboo pulp fabric (D) ZnO particles coated fabric washing for 20 times

### 3.4 Conclusions

In order to enhance the binding between ZnO particles and fibers, in-situ synthesis of ZnO nanoparticles directly on the bamboo pulp fabric was selected. The processes are versatile and environmentally friendly. ZnO dispersions were prepared in one step by mixing  $\text{Zn}(\text{NO}_3)_2$  and RSD aqueous solution under hydrothermal condition. During the synthetic process, RSD served as a reactant, dispersant and complexing agent.

In the finishing process, RSD served as a binder to impart and fix the ZnO particles on the bamboo pulp fabric. All the results of UV-vis, XRD, SEM and TEM



determination confirmed that the ZnO particles were synthesized and the ZnO particles were deposited on the bamboo pulp fabric. The anti-UV property of untreated fabric is very weak, Bamboo pulp fabric treated with ZnO particles provided high UV protection property with UPF 83.59 (more than 50) and good washing fastness.

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## **Chapter 4**

### **Preparation and characterization of ZnO nanoparticles/HSDA hybrid and study of their antibacterial activities**

## **Chapter 4: Preparation and Characterization of ZnO nanoparticles/HSDA hybrid and study of their Antibacterial Activities**

In our previous work, hyperbranched polyamide RSD with tertiary and secondary amine as well as a variety of free active surface primary amino groups was synthesized and used as template to fabricate ZnO particles. To further enhance the stability and decrease the size of ZnO particles, new hyperbranched polymers, HSDA-I and HSDA-II, were synthesized from the modified of hyperbranched polymer (RSD). FTIR and TGA showed that HSDA were synthesized and they had good thermal properties. ZnO nanoparticles colloidal solution was prepared in one step by mixing  $\text{Zn}(\text{NO}_3)_2$  and HSDA aqueous solution under hydrothermal condition. The results of TEM and UV-vis spectra indicated that ZnO nanoparticles had been formed in colloidal solution and ZnO nanoparticles synthesized by HSDA-II have a small size and better dispersibility. The ZnO colloid nanoparticles, prepared with 0.74 g/l  $\text{Zn}(\text{NO}_3)_2$  aqueous solution in the presences of 2 g/l HSDA-II, showed good antibacterial activities against Gram-negative bacteria (*Escherichia coli*) and Gram-positive bacteria (*Staphylococcus aureus*). A very low concentration of ZnO nanoparticles (as low as 5.0  $\mu\text{g/ml}$  Ag) also gave excellent antibacterial performance.

### **4.1 Introduction**

Nanoscale materials are defined as substances with at least one critical dimension less than 100 nm. In recent years, nanomaterial has attracted intensive attention from the industrial circle and academia. [1-3] Physical, chemical and electrical properties of the materials could be changed once the materials are prepared in the nano particulate forms.[4, 5] As one of the promising materials, ZnO nanoparticles exhibit excellent electrical, optical, and chemical properties with broad range of applications as semiconductors, in optical devices, piezoelectric devices, surface acoustic wave devices, sensors, transparent electrodes, solar cells etc.[6-8] Also it has been demonstrated that ZnO powders and nanoparticles exhibit antimicrobial activity against *Escherichia coli* and *Staphylococcus aureus*. [9-11] Extensive work on synthesis of ZnO nanoparticles

and nanostructures using physical and wet chemical methods has been reported since last decade, with regards to controlling the morphology and properties based on the applications.[12-14]

Nanoparticles are easily agglomerated in aqueous solutions due to the high surface energy, synthesizing nanoparticles in aqueous solutions with long stability and dispersity still remain a challenge. Traditionally, in preparing nanoparticles in aqueous solutions some polymeric materials such as poly (vinylpyrrolidone) (PVP), poly (ethylene glycol) (PEG), and some surfactants were used as stabilizers to prevent nanoparticles agglomeration and precipitation, which may impose some problems in applications. [15-19]In this concern, much attention has been focused on controlling the size, shape and stability of nanoparticles via surfactants and polymer templates, such as dendrimers and hyperbranched polymers.[20-24]

In our previous work, hyperbranched polyamide RSD with tertiary and secondary amine as well as a variety of free active surface primary amino groups was synthesized and used as template to fabricate ZnO particles.[25, 26] The ZnO nanoparticles have yet to aggregate to larger particles after formation. This may attribute to the formation of ZnO particles outside RSD. Masses of primary amine groups outside RSD can capture ZnO particles, which nevertheless are liable to drop off owing to the short branches of RSD. That's why it has poor stability. To solve the problem, the proportion of raw materials employed to prepare RSD was modified to synthesize HSDA with interior sealed-in "nanocages" with fewer primary amino and long chain structure at the peripheral. ZnO particles formed from HSDA behaved less size and more steadily. Also this work is concerned about the antibacterial behavior of synthesized ZnO nanoparticles aqueous solution against *Escherichia coli* and *Staphylococcus aureus*.

## **4.2 Experiment**

### **4.2.1 Materials**

Diethylenetriamine, tetraethylenepentamine, methyl acrylate, zinc nitrate and dodecanoic acid were purchased from Sigma-Aldrich. All chemicals were used as received without any further purification or treatment. Bamboo pulp fabrics were

purchased from Tanzhuzhuang, China. *Staphylococcus aureus* (ATCC 6538) and *Escherichia coli* (ATCC8099) were obtained from College of Life Science, Soochow University (China). Nutrient broth and nutrient agar were purchased from Scas Ecoscience Technology Inc.

#### **4.2.2 Synthesis of HSDA**

##### **Synthesis of HSDA-I**

HSDA-I (Fig.1) was synthesized. Diethylene triamine (52 ml, 0.5 mol) was added in a 250 ml three-neck round-bottomed glass flask equipped with a constant-voltage dropping funnel, a thermometer and a nitrogen inlet tube. The reaction mixture was stirred with a heat-up magnetic agitator and cooled with an ice bath, while the solution of methyl acrylate (43 ml, 0.5 mol) in methanol (100 ml) was added dropwise into the flask. Then the mixture was removed from the ice bath and left stirring for a further 4 h at room temperature. The light yellow AB<sub>2</sub> type monomer was synthesised and then the mixture was transferred to an eggplant-shaped flask for an automatic rotary vacuum evaporator. After removing the methanol under low pressure, the temperature was raised to 150 °C using an oil bath, and left for 4 h until the yellowish viscid scale aminoterminated hyperbranched polymer was obtained. Then 2g dodecanoic acid in methanol (100 ml) was added dropwise into 20g aminoterminated hyperbranched, the mixture was stirring for 4h at 60 °C. After removing the methanol under low pressure, the yellow viscid HSDA-I was obtained.

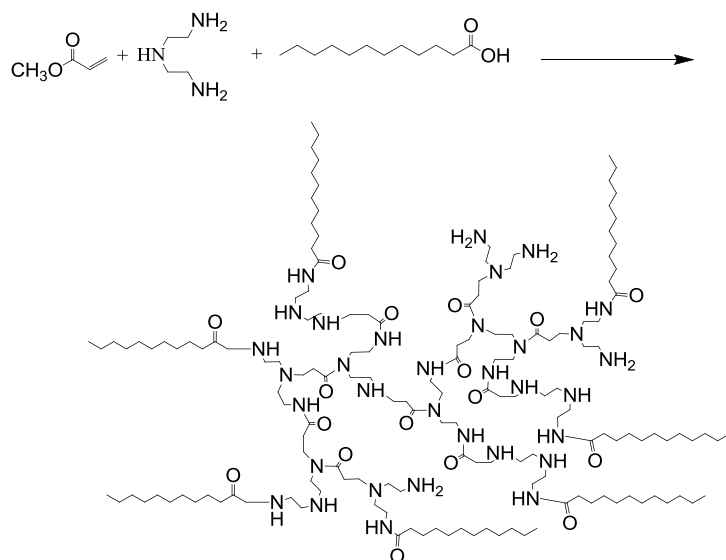


Figure 1 Schematic representation of the synthesis of HSDA-I

#### Synthesis of HSDA-II

HSDA-II (Fig.2) was synthesized through modification on the method of synthesis of hyperbranched polymer RSD. Tetraethylenepentamine (94 ml, 0.5 mol) was added in a 250 ml three-neck round-bottomed glass flask equipped with nitrogen gas protection and magnetic stirring. The reaction mixture was stirred with a heat-up magnetic agitator and cooled with an ice bath, while the solution of methyl acrylate (43 ml, 0.5 mol) in methanol (100 ml) was added dropwise into the flask. Then the mixture was removed from the ice bath and left stirring for a further 4 h at room temperature. The mixture was transferred to an eggplant-shaped flask for an automatic rotary vacuum evaporator, the temperature was raised to 150 °C using an oil bath, and left for 4 h until the yellowish viscid scale hyperbranched polymer was obtained. Then 2g dodecanoic acid in methanol (100 ml) was added dropwise into 20g hyperbranched polymer, the



mixture was stirring for 4h at 60 °C. After removing the methanol under low pressure, the yellow viscid HSDA-II was obtained.

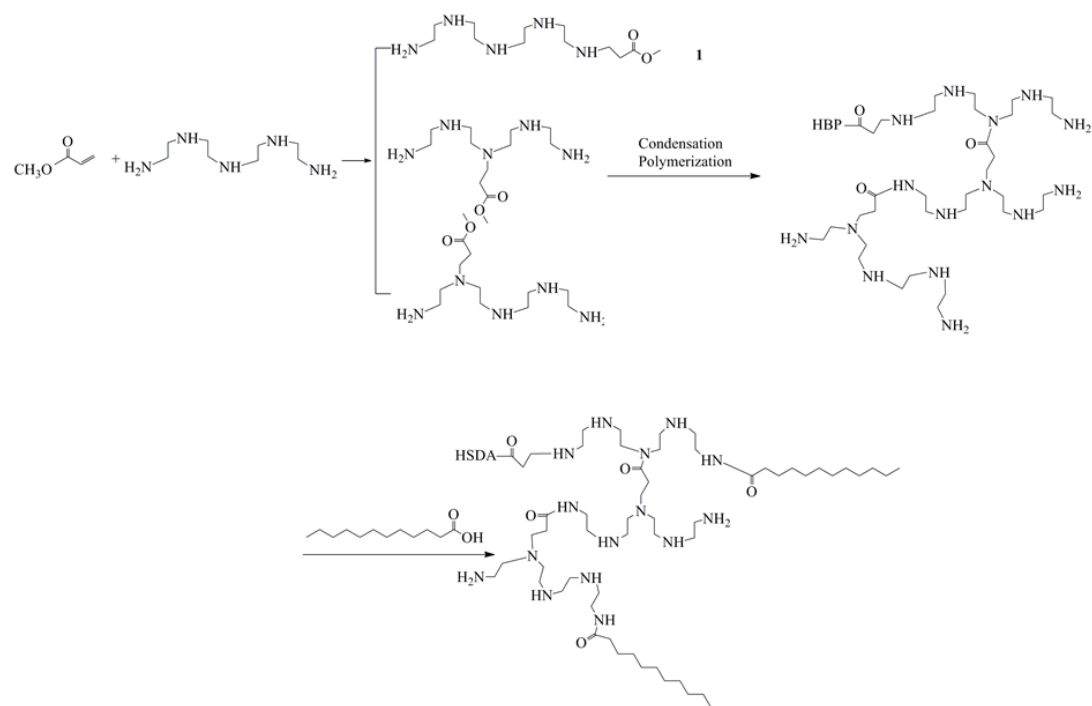


Figure 2 Schematic representation of the synthesis of HSDA-II

#### 4.2.3 Preparation of ZnO Nanoparticles Dispersion

Zn(NO<sub>3</sub>)<sub>2</sub> and HSDA solutions were prepared separately. The concentration of HSDA solution is 2g/L and the concentration of Zn(NO<sub>3</sub>)<sub>2</sub> is 0.1 mol/L. Then Zn(NO<sub>3</sub>)<sub>2</sub> solution (0.1 mol/L) was added in a dropwise manner into 2g/L HSDA solution and stirred constantly at room temperature. The mixture was then heated till it boils for 2 minute and then the solution turned white in color. Deionized water was added to maintain the mixing solution is 50ml during the process.

#### 4.2.4 Characterization of HSDA and ZnO nanoparticles

Infrared spectra of the HSDA-I and t HSDA-II were recorded on a Nicolet 5700

FT-IR spectrophotometer using a KBr disk (Nicolet, USA). The thermo gravimetric analysis (TGA) was carried out on a Diamond DSC (Perkin-Elmer, USA) under a constant nitrogen flow of 20 ml/min from 40 to 500°C at a heating rate of 10°C/min. UV-vis XRD and TEM was performed as described in section 2.2.4. The sample for XRD measurements was prepared in a high concentration of ZnO and HSDA-II to form big ZnO particles. Those particles were centrifuged and vacuum dry for two days.

#### 4.2.5 Antibacterial test of ZnO nanoparticles

The antimicrobial activity of the prepared ZnO nanoparticles was tested by studying the growth kinetics of *S. aureus* and *E. coli*. The method is shown in section 2.2.5.

### 4.3 Results and discussion

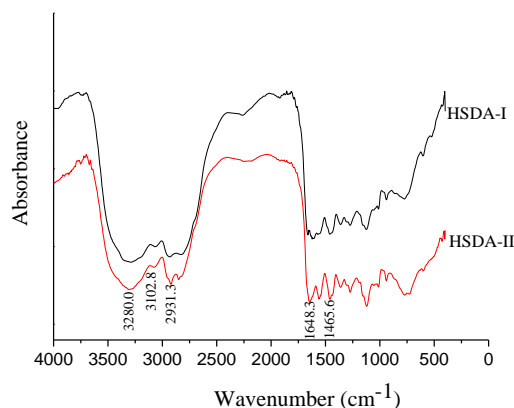


Figure 3 FT-IR spectrum of the HSDA

In order to confirm the polymerisation process, we conducted infrared spectral studies. FT-IR spectra of the HSDA-I and HSDA-II are shown in Fig.3. It was found that HSDA-I and HSDA-II have the similar structures and the absorptions at 1465.6 cm, 3280 cm corresponding to the  $\text{-CH}_2\text{-}$  bend and the N-H stretch of the primary amino groups and the imino groups respectively. The absorption at 1643.9 cm is characteristic of the  $\text{C=O}$  stretch in amide bonds ( $\text{-CONH-}$ ). It was concluded that the HSDA had successfully synthesized by melt polycondensation and that there were abundant imino groups and terminal primary amino groups in HSDA.[25]

Figure 4 shows TGA curves for HSDA-I and HSDA-II. The data are shown in Table 1. In the TGA curves weight loss of the HSDA-I occurred at about 258.7°C and weight loss of the HSDA-II occurred at 255.3°C. It indicated that the both HSDA-I and HSDA-

II exhibits a higher thermal stability.

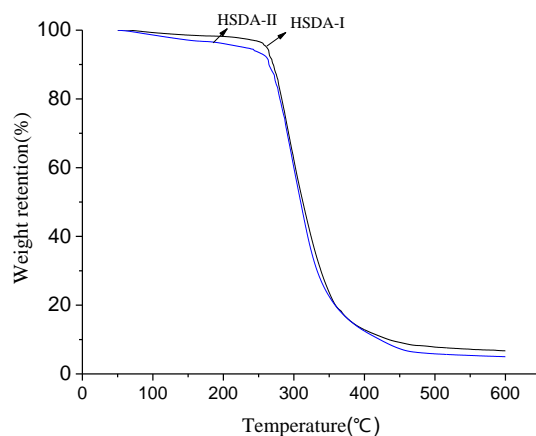


Figure 4 TGA for the HSDA

Table 1 Weight loss temperature of HSDA

Sample	HSDA-I	HSDA-II
Initial temperatures of weight lose °C	258.7	255.3

The pH value of HSDA (shown in table 2) aqueous solution is about 11 at the concentration of 2 g/L. After  $\text{Zn}(\text{NO}_3)_2$  aqueous solution was added dropwise into the alkaline HSDA solution, ZnO nanoparticles were synthesized [27, 28]. The principle was shown in section 3.3.1. After reaction, the pH value of ZnO nanoparticles/HSDA hybrid solution is about 7 which means  $\text{OH}^-$  was exhausted accordingly.

Table 2 PH value of HSDA solution

sample	HSDA-I	HSDA-II
pH	11.20	11.38

The formation of ZnO NPs can be verified by UV-visible spectrophotometer. Fig. 5 depicts the UV-visible absorption spectra of HSDA aqueous solution and the prepared ZnO Nanoparticles/HSDA hybrid solution. Both HSDA-I and HSDA-II aqueous solution has only one absorption peak at 299 nm. After reaction with zinc nitrate, another absorption peak at 370 nm appears in addition to the preceding one, which

demonstrates the generation of ZnO nanoparticiles.[29] Concurrently, the solution turned from transparent to semitransparent ivory. Subsequently, the ZnO NPs were further observed by TEM. Figs. 6(a) and (b) show the TEM images. The ZnO nanoparticles with small size generated in aqueous medium may be attributed to the adsorption of HSDA on ZnO nanoparticles which prevented the nanoparticles to grow to bigger ones. Due to the presence of HSDA, which can adsorb on the surface of ZnO nanoparticles and alter the relative growth rate in different crystallographic planes resulting in the formation of anisotropic ZnO nanoparticles. Primary amine groups outside HSDA can capture ZnO nanoparticles. Owing to the long chain out of HSDA-1 and HSDA-2, the captured ZnO nanoparticles would be hard to drop off. As HSDA-II has a large molecular weight and long branches, the HSDA-II generated ZnO nanoparticles (Fig.6(b)) has a small size and highly dispersed.

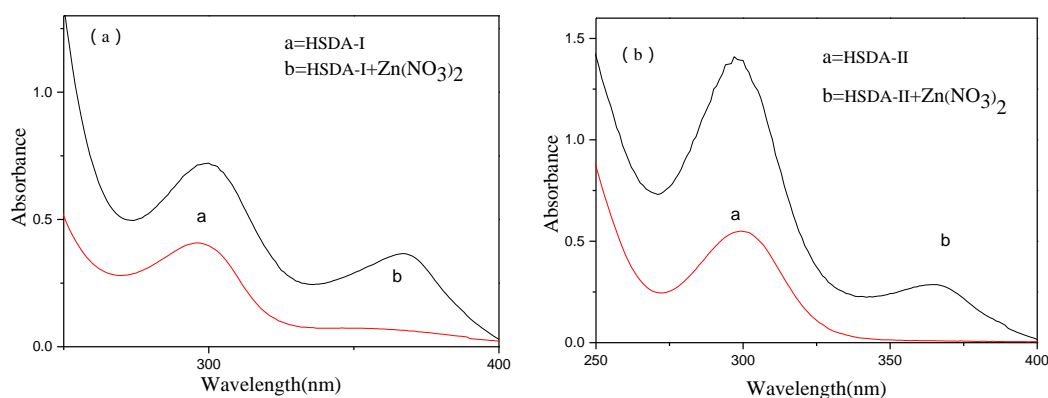


Figure 5 UV-visible absorption spectra of HSDA-I aqueous solution and ZnO nanoparticles/HSDA-I hybrid solution (a) and UV-visible absorption spectra of HSDA-II aqueous solution and ZnO nanoparticles/HSDA-II hybrid solution (b)

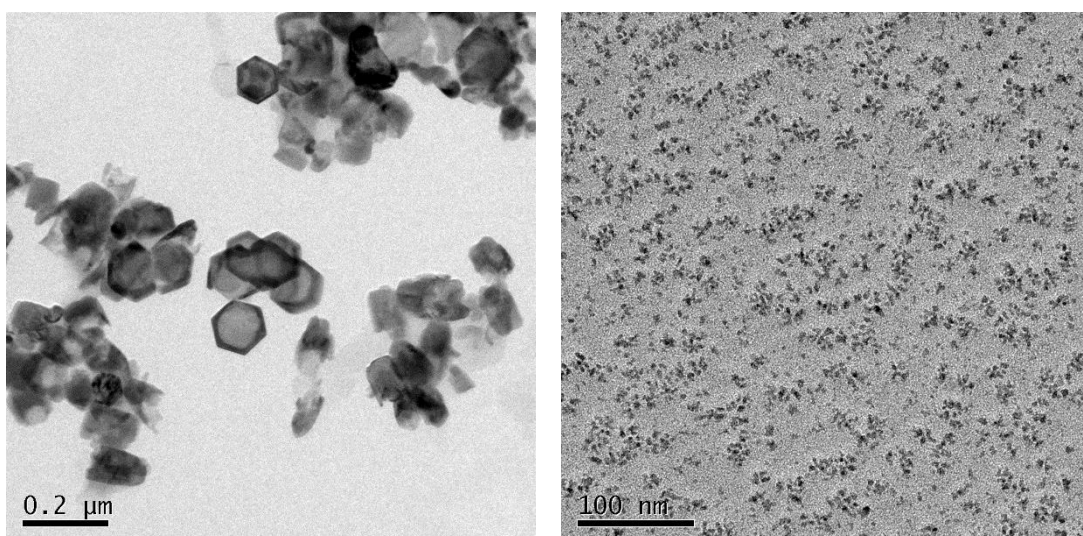


Figure 6 TEM images of ZnO nanoparticles (a)ZnO/ HSDA-I (b)ZnO/HSDA-II

The XRD pattern confirmed the wurtzite structure of ZnO NPs. As shown in Fig.7, all the peaks could be indexed to the planes of wurtzite ZnO and well agreed with JCPDS data (36-1451).[30] Interestingly, no additional peaks corresponding to other impurities were detected in the pattern, which implies the obtained ZnO NPs are purely crystalline in aqueous solution.

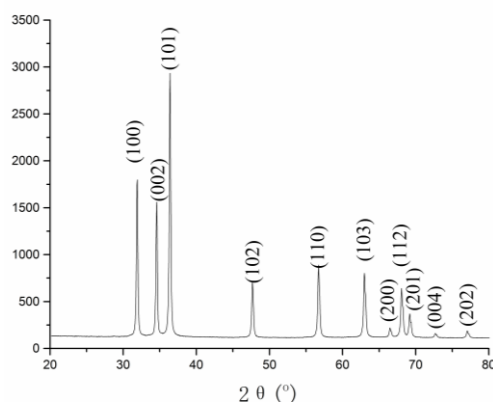


Figure 7 XRD patterns of ZnO particles

Yamamoto et.al reported that the antibacterial activity of ZnO nanoparticles depends on the size, the smaller the size, the better the antibacterial activity is[31]. According to the characterization results above, ZnO nanoparticles synthesized by HSDA-II have small size (only 10 nm). The antimicrobial tests of ZnO nanoparticles synthesized by HSDA-II were carried out. The ZnO colloid nanoparticles were prepared by adding  $\text{Zn}(\text{NO}_3)_2$  with an initial concentration of 0.74 g/l into the HSDA aqueous solution with an initial concentration of 2 g/l. The growth kinetics of *S. aureus* and *E. coli* were

studied in the presence of the ZnO nanoparticles (Fig. 8). It can be seen that microbial growth is significantly inhibited in the presence of 5.0 ug/ml ZnO nanoparticles. In addition, the effect of concentration of the ZnO nanoparticles on antimicrobial activity was studied spectrophotometrically against *S. aureus* and *E. coli*. The results are shown in Figure 9. In each case, there was significant inhibition of microbes even at the minimum concentration (1  $\mu\text{g/ml}$ ) used. No significant increase in antimicrobial activity was observed beyond 5  $\mu\text{g/ml}$ , which appears to be the maximum concentration that should be used.

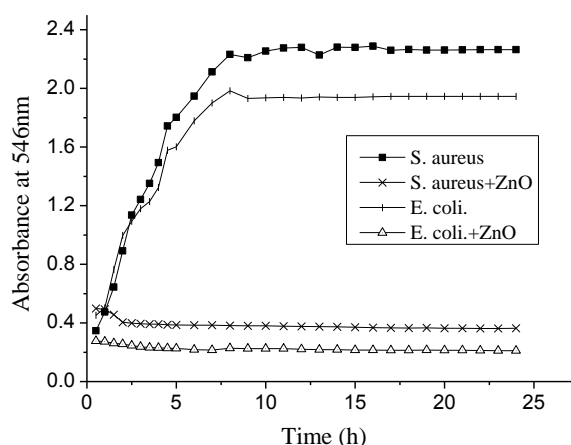


Figure 8 Effect of concentration on antimicrobial activity of the ZnO nanoparticles against *S.aureus* nanoparticles(concentration 5.0  $\mu\text{g/ml}$ ) and *E. coli*

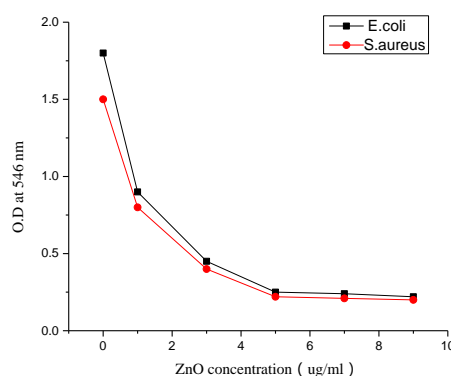


Figure 9 Growth kinetics of *S. aureus* and *E. coli* in the presence of ZnO

#### 4.4 Conclusions

New multi-amide compound hyperbranched polymers, HSDA-I and HSDA-II, were

successfully synthesized from the modified of hyperbranched polymer (RSD). FTIR and TGA showed that HSDA were synthesized and they had good thermal properties. ZnO nanoparticles were easily obtained in one-step by mixing  $\text{Zn}(\text{NO}_3)_2$  and HSDA aqueous solution under hydrothermal condition. The results of TEM and UV-vis Spectra indicated that ZnO nanoparticles had been formed in colloidal solution Compared to HSDA-I, HSDA-II has a large molecular weight and long branches, and ZnO nanoparticles synthesized by HSDA-II has a small size and highly dispersed.

The ZnO colloid nanoparticles, prepared with 0.74 g/l  $\text{Zn}(\text{NO}_3)_2$  aqueous solution in the presences of 2 g/l HSDA-II, showed good antibacterial activities against Gram-negative bacteria (*Escherichia coli*) and Gram-positive bacteria (*Staphylococcus aureus*). A very low concentration of ZnO nanoparticles (as low as 5.0  $\mu\text{g/ml}$  Ag) also gave excellent antibacterial performance.

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## **Chapter 5**

**Application of ZnO nanoparticles to  
enhance the antimicrobial activity  
and ultraviolet protective property of  
bamboo pulp fabric**

## **Chapter 5: Application of ZnO nanoparticles/HSDA hybrid to enhance the antimicrobial activity and ultraviolet protective property of bamboo pulp fabric**

This research presents generic strategy to fabricate functional textile through synthesis of ZnO nanoparticles on the fabric with smart polymeric molecules by in-situ synthesis and immersion method. Bamboo pulp fabric and Multi-amide compound HSDA were chosen for this study. HSDA which has numerous amino groups and three-dimensional structure was applied to entrap ZnO nanoparticles onto bamboo pulp fabric. The mechanism of the reaction process was investigated. The UV/Visible absorption spectrophotometry indicated that ZnO nanoparticles colloidal have been formed in the mixed solution. For in-situ synthesis of ZnO nanoparticles on bamboo pulp fabric, the results of scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) techniques confirmed that ZnO nanoparticles have been fixed and well dispersed on bamboo pulp fabric.

Also synthesis of ZnO nanoparticles on bamboo pulp fabric with HSDA by immersion method was studied. The ultraviolet (UV) protective properties and antibacterial activities of the ZnO nanoparticles treated fabrics were measured. The treated bamboo pulp fabrics were characterized by SEM and X-ray spectroscopy (EDS). The results indicated that the Bamboo Pulp Fabric treated with ZnO nanoparticles showed good anti-UV property and its UPF can reach to 90.38. Washing for 20 times, it can also keep good anti-UV properties. The ZnO nanoparticles treated fabric showed 99.91 % bacterial reduction of *Staphylococcus aureus* and 99.97 % bacterial reduction of *Escherichia coli*. The fabric was maintained at over 98.93 % reduction level even after being exposed to 20 consecutive home laundering conditions.

### **5.1 Introduction**

ZnO has been considered as promising semiconductors as it has wide band gap of 3.37 eV, large exciton energy of 60 meV. It is expected that the ZnO nanomaterial will be widely applied in nanoascer, solar battery, photo detectors, gas sensors, piezoelectric

devices, etc.[1-3] However, designing and modifying fabrics by ZnO nanoparticles for high protection against UV radiation, antibacterial and deodorant has attracted considerable interests in recent year. ZnO nanoparticles coating on textiles mainly through the composite spin-flying process or finishing method, such as preparation of ZnO nanoparticles polymer solutions before spinning, layer-by-layer deposition, method of immersion, supercritical carbon dioxide method and sol-gel coating. Recently, Li et al. reported that cotton fabric coating with ZnO nanoparticles could emit 82% more infrared than untreated cotton fabric[4]. Mao et al. treated cotton fabric with ZnO nanoparticles to enhance anti-UV property through hydrothermal method[5]. Li et al. reported that the cotton fabric have antibacterial performances when treated with ZnO nanoparticles [6].

Due to the unique chemical and physical properties, hyperbranched polymers have been received much attention over past years[7]. They have been widely applied to coatings, additives, drug, supra molecular science and nanotechnology. Hyperbranched polymers and their substitutes with higher generations taking a spherical shape can be used as nanomaterials for host-guest encapsulation and the fabrication of organic-inorganic hybrids, also can encapsulate metal complexes, nanoparticles.[8, 9] F Zhang et al. synthesized an amino terminated hyperbranched polymer (HBP-NH<sub>2</sub>). [10] It was utilized to control the synthesis of Ag nanoparticles, also served as a binder to impart and fix the silver nanoparticles on the cotton fabric to provide antimicrobial properties.

In our previous study, Multi-amide compound HSDA-II, characterized by a three-dimensional structure and a large number of imino groups and terminal primary amino groups, was synthesized (As shown in Fig.1)[11]. In order to give the fabric multiple functions, this research used the Multi-amide compound (HSDA) to prepare ZnO nanoparticles and fixed it on the fabric. A new cellulose-based material, bamboo pulp fabric was chosen as the substrate for this research as it naturally smooth and round. In this process, HSDA served acts as a reactant and capture agent to fix the ZnO nanoparticles on bamboo pulp fabric.

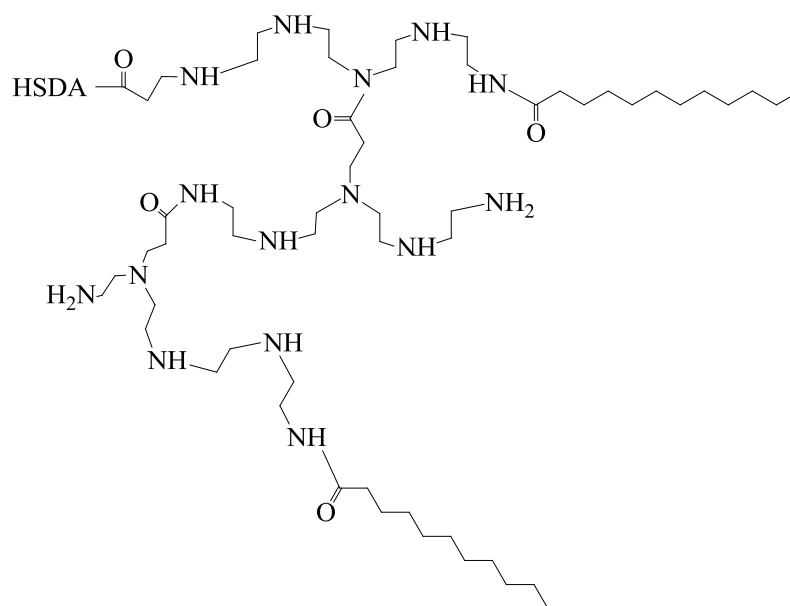


Figure 1 Schematic representation of the molecule structure of HSDA

## 5.2 Experimental

### 5.2.1 Materials

HSDA was synthesized as described in section 4.2.2 part 2. Bamboo pulp fabrics were purchased from Tanzhuzhuang, China. *Staphylococcus aureus* (ATCC 6538) and *Escherichia coli* (ATCC8099) were obtained from College of Life Science, Soochow University (China). Nutrient broth and nutrient agar were purchased from Scas Ecoscience Technology Inc,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was purchased from Sigma-Aldrich. All chemicals were used as received without any further purification or treatment.

### 5.2.2 Synthesis of ZnO nanoparticles on bamboo pulp fabric by in-situ method

An (0.01M) aqueous solution of  $\text{Zn}(\text{NO}_3)_2$  and 2g/L HSDA were prepared in a beaker. Bamboo pulp fabric was immersed in the solution, the bath ratio was 1:50. The beaker was then sealed and held in the 80°C water bath for 40min with constant stirring. At the end of the process the fabric was washed with deionized water several times to remove unfixed materials. The resulting bamboo pulp fabric was dried in drying oven at 100 °C for 2 min, 130 °C for 3min

### **5.2.3 Synthesis of ZnO nanoparticles on bamboo pulp fabric by immersion method**

Prepare  $\text{Zn}(\text{NO}_3)_2$  and HSDA solutions were prepared separately. The concentration of HSDA solution is 2g/L and the concentration of  $\text{Zn}(\text{NO}_3)_2$  is 0.1mol/L. Then 5 ml  $\text{Zn}(\text{NO}_3)_2$  solution (0.1 mol/L) was added in a dropwise manner into 45ml (2.2g/L) HSDA solution and stirred constantly at room temperature. The mixture was then heated till it boils for 2 minute and then the solution turned white in color. Deionized water was added to maintain the mixing solution is 50ml (0.01M of  $\text{Zn}(\text{NO}_3)_2$  and 2g/L HSDA)during the process.

The solution of ZnO/HSDA hybrid was prepared as mentioned above. The Bamboo pulp fabric was immersed in the solutions and held in the 80°C water bath for 40 min with constant stirring. The liquor-to-fabric ratio is 50:1 (v/m). Another sample was immersed in 50ml HSDA solution (2g/L) as control sample. The resulting bamboo pulp fabric was dried in drying oven at 100 °C for 2 min, 130 °C for 3min

### **5.2.4 Characterization of the ZnO Nanoparticles and ZnO treated bamboo pulp fabric**

The Whiteness of the fabrics was determined as described in section 2.2.7. (Htachi SEM scanning electron microscope model S-570, LaB6 gun, Kevex x-ray EDS) and X-ray photoelectron spectroscopy (XPS, XSAM 800 electron spectrometer) were used to observe morphology of ZnO nanoparticles on the surface of bamboo pulp fabric. The ultraviolet protection factor (UPF) were measured as described in section 3.2.3. ZnO content of the treated fabrics was determined by (ICP-AES) as described in section 2.2.7

### **5.2.5 Antibacterial test of bamboo pulp fabric**

The antimicrobial activity of Bamboo pulp fabrics was tested against E. coli and S. aureus by using a shaking flask method according to FZ/T 73023-2006 (China). The method are shown in section 2.2.7.

## 5.3. Results and discussion

### 5.3.1 Mechanism

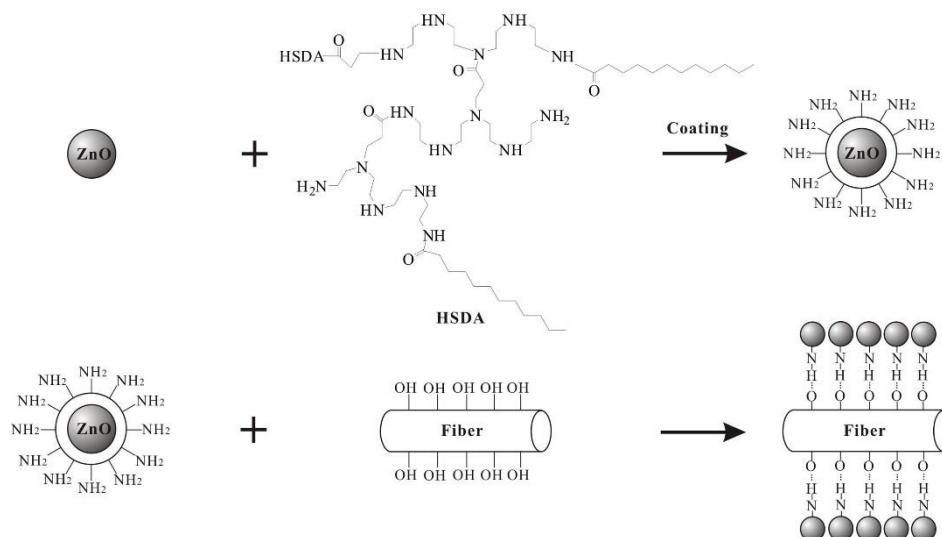


Figure 2 Schematic preparation of the ZnO nanoparticles coating on fabric

Compared to the traditional approach Fig.2 outlines our novel strategy for the solution scheme. Owing to the specific interior cavities and the outward oriented amino groups, HSDA can prevent nanoparticles from agglomerating. Cellulose has a weak negative charge at neutral and alkaline conditions.[12] They could be adsorbed on the fabric efficiently owing to the attractive force between the two of them: the positive nanocomposites and the negative fabric. Also the bamboo pulp fabric surface is rich of hydroxyl groups. Amino groups can adsorb onto bamboo pulp fabric substance by hydrogen bonding. The special structure of HSDA enables it to lie along-side cellulose fibers and maximize the Van-der-Waals, and hydrogen bonds. So in this process, HSDA served acts as a protective agent and capture agent to fix the ZnO nanoparticles on bamboo pulp fabric.

Fig.3 shows the UV-vis spectra of the prepared ZnO colloid nanoparticles. The HSDA  $\text{Zn}(\text{NO}_3)_2$  aqueous solution only have one characteristic peak at 298 nm. The mixing solution aqueous solutions were boiled for 2min. However, a new characteristic absorption of ZnO nanoparticles appeared at 368 nm. This confirms the nanocrystalline character of the result ZnO nanoparticles.[13, 14]

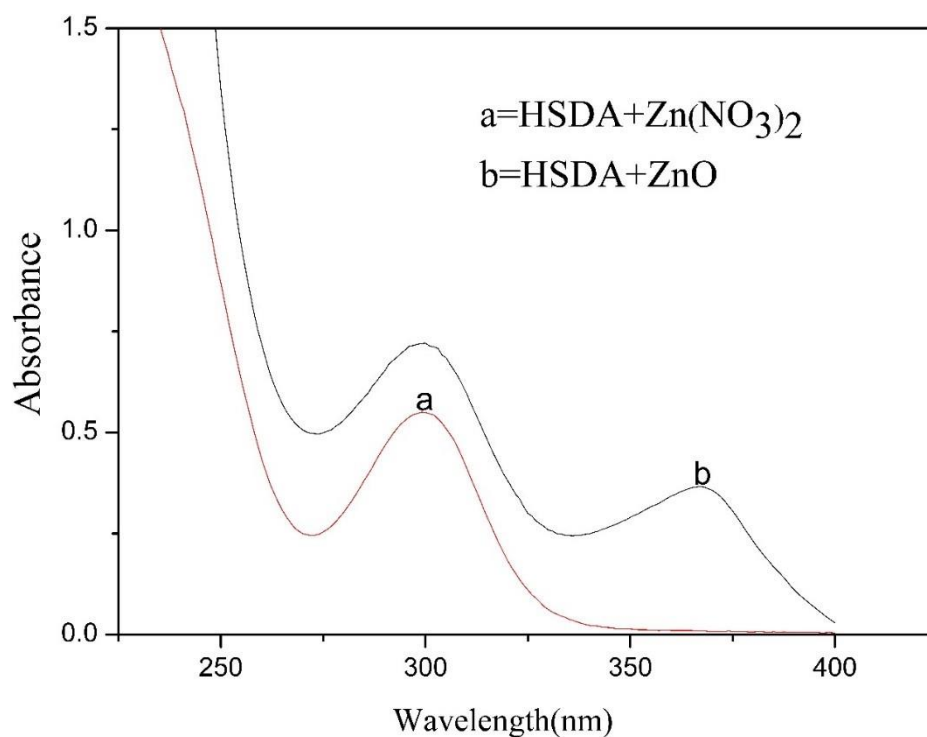
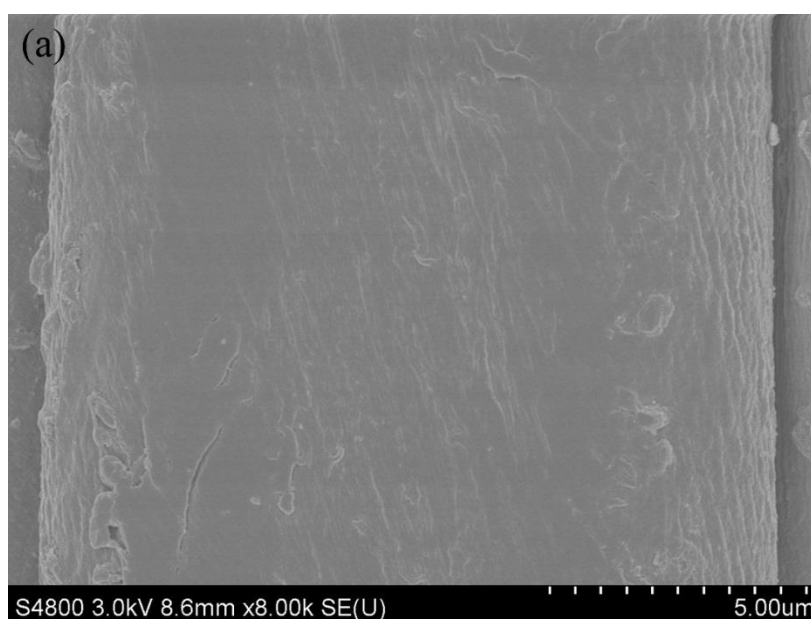


Figure 3 UV-vis spectra of the prepared ZnO colloid nanoparticles

### 5.3.2 Characterization of the ZnO nanoparticles on bamboo pulp fabrics by in-situ method

To confirm the formation of ZnO nanoparticles on the surface of the bamboo pulp fiber, the samples were analyzed with scanning electron microscope.





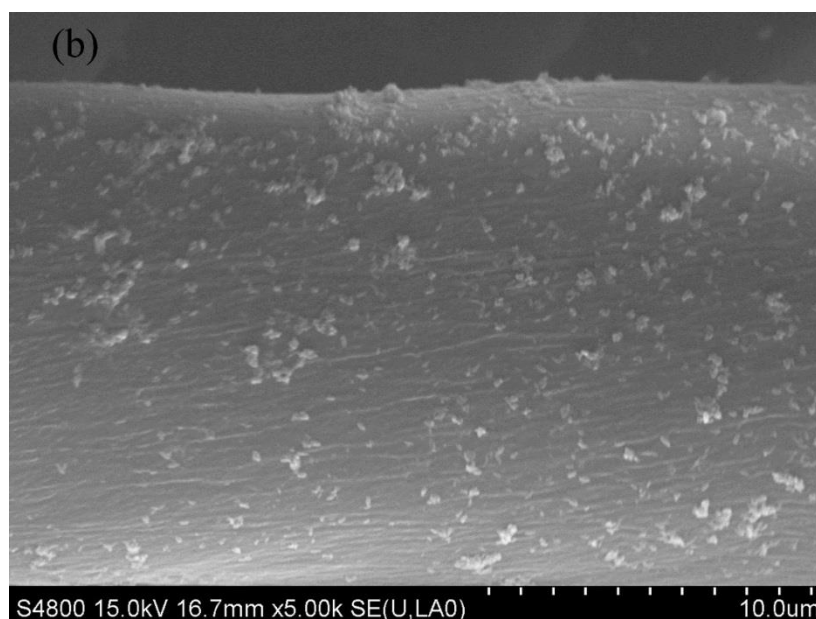


Figure 4 SEM images of (a) bamboo pulp fiber and (b) ZnO-treated bamboo pulp fiber

The surface morphology of bamboo pulp fiber and the ZnO-treated fiber can be seen in Fig 4. In terms of surface roughness there is an obvious difference the two fibers. As shown in fig.4 (a), the bamboo pulp fiber is made up of fibrils which are arranged along the length of the fiber basically, its morphology is straight stripes with a smooth, sleek shape. Fig.4 (b) reveals that nanograined ZnO nanoparticles were *in-situ* formed on the bamboo pulp fabric. Straumal et al. reported that the physical properties of ZnO nanoparticles depend on defects in amorphous intergranular regions, grain boundary character distribution and the presence of surfaces[15, 16]. According to the grain boundaries and free surfaces as well as the inherent properties of ZnO nanoparticles, the fabric with deposited ZnO nanoparticles may possess UV protection, ferromagnetic and antibacterial properties.[5, 6, 16]

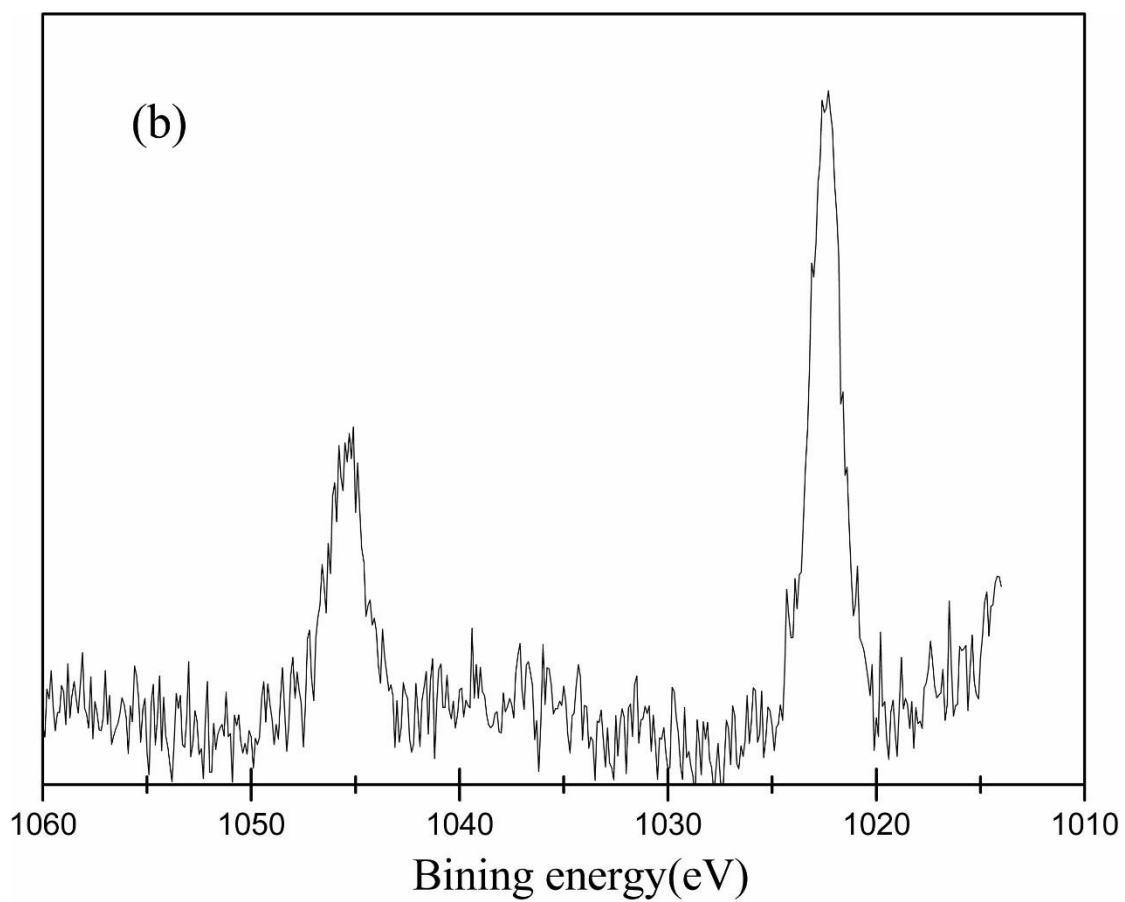
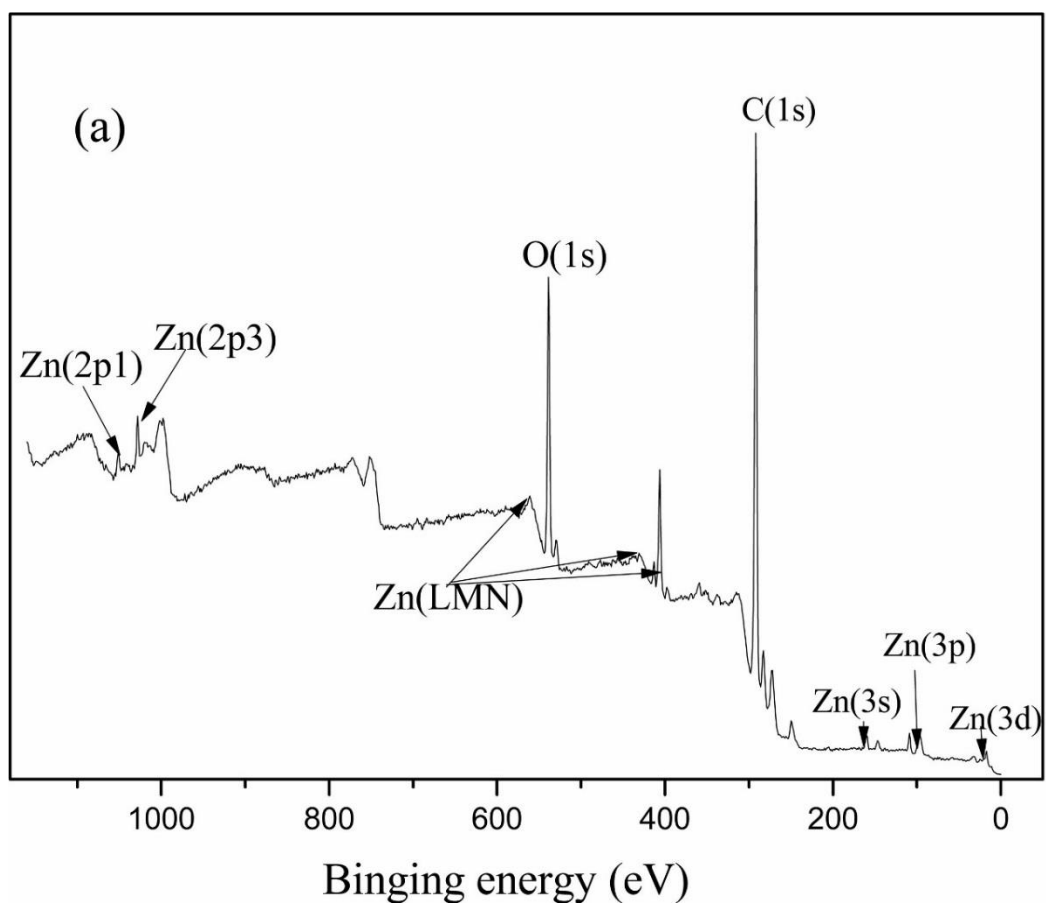


Figure 5(a) XPS spectrum of the bamboo pulp fabric (b)XPS spectrum of Zn 2p

XPS analysis was performed to identify the presence of ZnO nanoparticles. Fig.5 (a) shows the XPS spectra of the bamboo pulp fabric treated with ZnO nanoparticles. It can be seen that besides the C 1s and O 1s peaks such peaks as Zn 2p, Zn LMN, Zn 3s, Zn 3p, Zn 3d emerged, indicating that the modified bamboo pulp fabric was mainly composed of zinc, oxygen and carbon. The binding energy of Zn 2p<sub>3/2</sub> and Zn 2p<sub>1/2</sub> (as seen in Fig.5 (b)) is determined at 1022.5 and 1045.4 eV and the peak separation between them is 22.9 eV. According to the research results of Wei HY et.al and Zhang WJ et.al, the Zn ions are mainly in form of ZnO.[17, 18]

### **5.3.3 Characterization of the ZnO nanoparticles on bamboo pulp fabrics by immersion method**

Scanning electron microscope was used to observe the morphology ZnO nanoparticles on bamboo pulp fabric. It shows an obvious difference between the original bamboo pulp fabric and the ZnO-treated sample. Fig.6a shows the SEM image of the original bamboo pulp fiber. The morphology of bamboo pulp fabric is straight stripes with a smooth, sleek shape. Fig.6b demonstrates the SEM photographs of the ZnO nanoparticle covered bamboo pulp fibers. Compared with the untreated it is clear to see that the bamboo pulp fibers were covered with a uniform and dense of ZnO nanoparticles. The obtained ZnO particles were well faceted. To verify the nanoparticles on the bamboo pulp fibers were ZnO, elemental composition analysis was initially carried out via energy-dispersive X-ray spectroscopy (EDS). Fig.7 gives a typical EDS image recorded on the ZnO growth bamboo pulp fabric. Oxygen, zinc and carbon could be detected from the spectra. Carbon and oxygen arise from the bamboo pulp fabric. No other elements were detected, confirming that the particles are primarily ZnO.

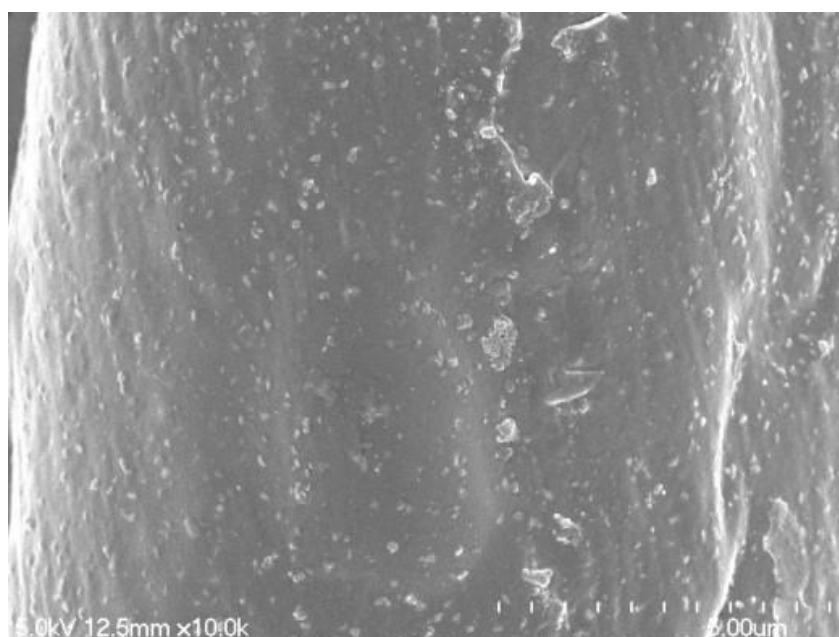
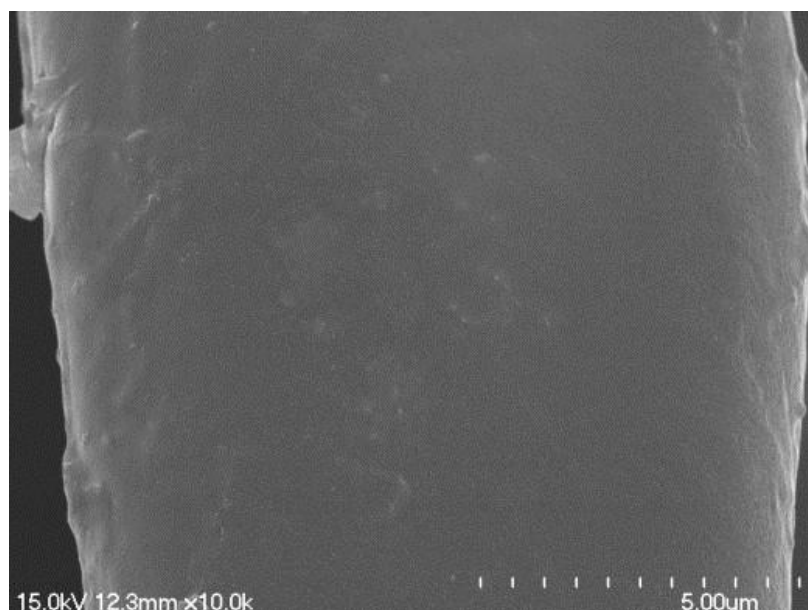


Figure 6 SEM images of (a) control bamboo pulp fiber, (b) ZnO nanoparticles treated bamboo pulp fiber

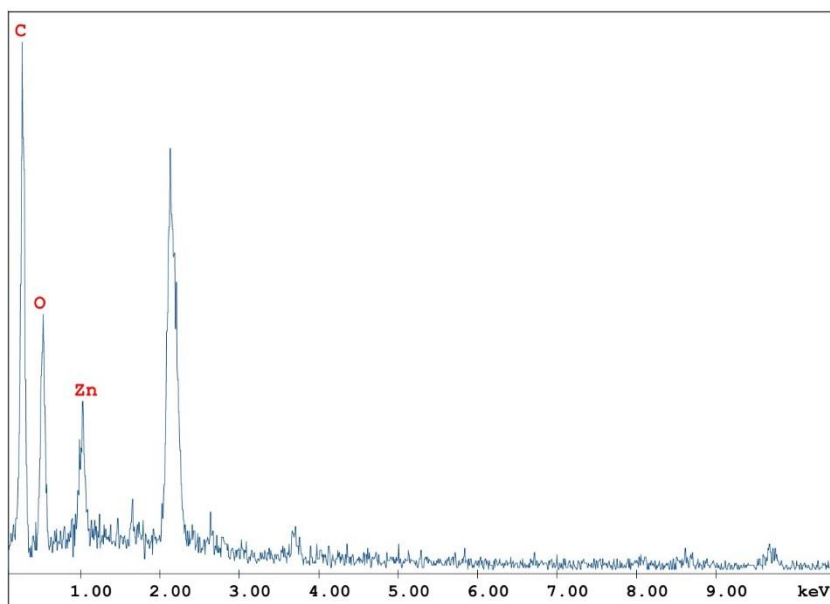


Figure 7 EDS of the ZnO nanoparticles on bamboo pulp fabric

#### 5.3.4 ZnO contents of the treated bamboo pulp fabrics

The results of scanning electron microscopy (SEM), X-ray spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS) confirmed that ZnO nanoparticles have been fixed and well dispersed on bamboo pulp fabrics by both in-situ method and immersion method. The contents of ZnO nanoparticles deposited on bamboo pulp fabric were shown in table 1.

Table 1 ZnO contents of the treated bamboo pulp fabrics

Sample	Concentration Of Zn(NO <sub>3</sub> ) <sub>2</sub> (mM)	Concentration of HSDA(g/L)	Content of ZnO (wt %)
In-situ method	10	2	1.97
immersion method	10	2	2.14

Table.1 indicated that the contents of ZnO deposited on bamboo pulp by in-situ method were the same as by immersion method. For convenience, we use immersion method for the functional finish of bamboo pulp fabric.

#### 5.3.5 UV protective properties of bamboo pulp fabrics

UPF is defined as the ratio of the average effective UV irradiance calculated for unprotected skin to the average UV irradiance calculated for skin protected by the fabric. The UV protective properties of the fabric can be directly evaluated by measuring its

UPF.

Sample	Concentration Of $\text{Zn}(\text{NO}_3)_2$ (mM)	concentration of HSDA(g/L)	UPF of fabric
Bamboo pulp fabric	-	-	9.02
Sample 1	4	0.5	26.09
Sample 2	6	1	60.24
Sample 3	10	2	90.38
Sample 4	14	3	87.51

Relationships between the UPF value of bamboo pulp fabric and the concentration of HSDA,  $\text{Zn}(\text{NO}_3)_2$  in the finishing liquid were studied. To prevent an over-dose of  $\text{Zn}(\text{NO}_3)_2$ , the increasing concentration of  $\text{Zn}(\text{NO}_3)_2$  keeps up with the increase concentration of HSDA. The results are shown in Tab 2 and the UV transmission spectra of bamboo pulp fabric are shown in Figure 8. Samples 1-4 represent the treated bamboo pulp fabrics under different concentrations of reactants as shown in Table 2. It clearly indicated that the UPF value of bamboo pulp fabric increased as the concentration of the  $\text{Zn}(\text{NO}_3)_2$  aqueous solutions increased. When the concentration of the  $\text{Zn}(\text{NO}_3)_2$  reached to 14mM, the UPF value of bamboo pulp changed very little. Therefore the optimum conditions for the anti-UV finishing of bamboo pulp is the finishing liquid contains 10mM  $\text{Zn}(\text{NO}_3)_2$  and 2g/L HSDA.

Table 2 Laundering durability of ZnO-treated bamboo pulp fabrics

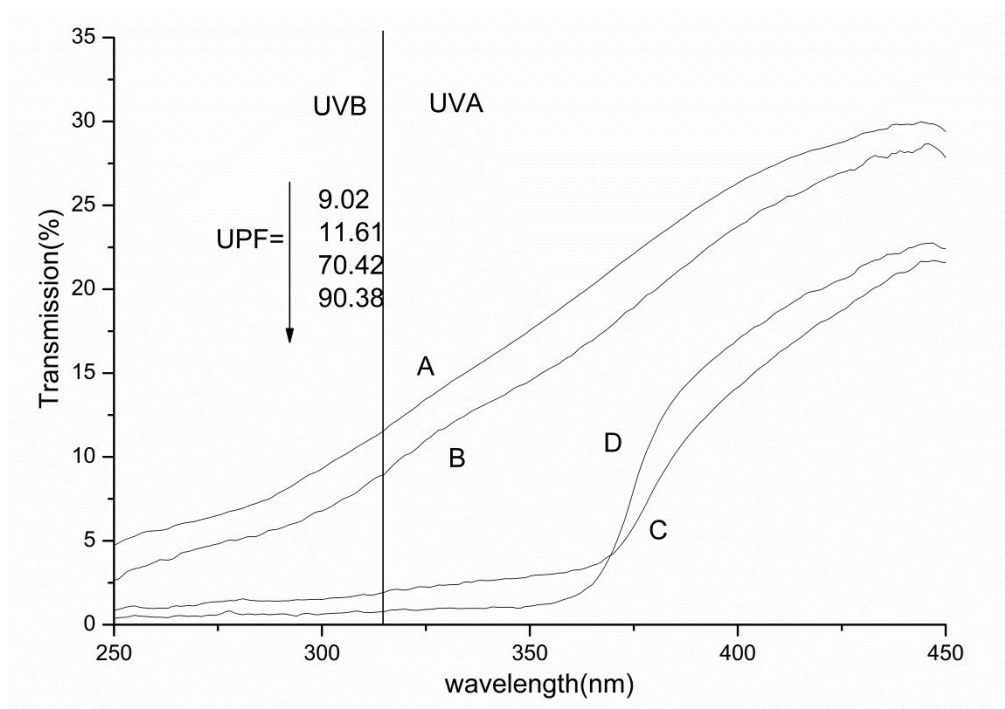


Figure 8 UV transmission spectra of bamboo pulp fabric and ZnO treated bamboo pulp fabric (A) original sample (B) treated by HSDA (C) ZnO covered bamboo pulp fabric (D) ZnO covered fabric washing for 20 times.

Fig. 8 shows that the bamboo pulp fabric and the fabric treated by HSDA has big UV transmittance and low UPF value, the UPF of the fabrics are only 9.02 and 11.61 (less than 15). While bamboo pulp fabric treated by ZnO nanoparticles has low UV transmittance and high UPF value. Its UPF value can reach to 90.38 (more than 50), which can be considered as good UV protective properties. The UPF value of treated fabric drops to 70.42 after washing for 20 times, but also keep good UV protective properties. The good laundering durability of the ZnO treated fabric may be caused by the strong adhesive power between the HSDA and the bamboo pulp fabric.

### 5.3.6 Antimicrobial activities of the bamboo pulp fabrics

The activities of bamboo pulp fabrics were evaluated by *S. aureus* and *E. coli*, cotton fabric was used as control sample. The whiteness (WI), antibacterial activity and washing durability of the ZnO nanoparticles treated fabrics (Table 2; sample3 was selected) were tested. Table 3 shows the whiteness and antibacterial activity of the bamboo pulp fabrics. As the numbers of surviving cells on bamboo pulp and cotton fabric are same, it could demonstrate that bamboo pulp fabric revealed no action against

*S. aureus* and *E. coli*. This also shows that bamboo pulp fiber has lost the antibacterial property inherent in bamboo resulting from the treatment with alkali in the processing. The bamboo pulp fabric treated with HSDA shows antibacterial activities, the bacterial reduction rates of *S. aureus* and *E. coli* is about 90 %. The antibacterial activities of fabric may be ascribed to the abundant amino groups on fabric. Which tend to deteriorate the cell membranes of bacteria and induce the leakage of intracellular components from bacterial cells, therefore, inhibiting the growth of bacteria effectively.[19] When covered with ZnO nanoparticles the antibacterial activity of bamboo pulp fabric was significantly improved, the bacterial reduction rates of *S. aureus* and *E. coli* have both reached above 99 %. Table 3 also shows that the functional finishing of bamboo pulp fabric has no effect on its whiteness.

Table 3 Whiteness and antibacterial activity of bamboo pulp fabrics

Sample	WI	Antibacterial activities			
		<i>S. aureus</i>		<i>E. coli</i>	
		Surviving cells CFU/ml	% Reduction	Surviving cells (CFU/ml) %	% Reduction
Cotton fabric	91.50	$2.32 \times 10^6$		$9.1 \times 10^6$	
Bamboo pulp fabric	90.20	$2.23 \times 10^6$	0	$8.7 \times 10^6$	0
HSDA treated fabric	90.10	$2.49 \times 10^5$	89.27	$9.3 \times 10^5$	89.7
ZnO treated fabric	90.18	$1.92 \times 10^3$	99.17	$2.54 \times 10^3$	99.97

In order to evaluate the durability against repeated launderings of the treated bamboo pulp fabrics, the fabrics were laundered 5, 10, and 20 cycles. The results are given in Table 4. With increasing laundering cycles only has a small negative impact on the retained antimicrobial activities of the bamboo pulp fabrics. Still over 98.93 % of bacterial reduction was maintained after 20 launderings.

Table 4 Laundering durability of ZnO-treated bamboo pulp fabrics

Sample	laundering cycles	Antibacterial activities			
		<i>S. aureus</i>		<i>E. coli</i>	
		Surviving cells (CFU/ml)	% Reduction	Surviving cells (CFU/ml) %	% Reduction
Cotton fabric	-	$2.32 \times 10^6$		$9.1 \times 10^6$	



Bamboo pulp fabric	-	$1.92 \times 10^3$	99.91	$2.54 \times 10^3$	99.97
	5	$1.63 \times 10^4$	99.29	$2.30 \times 10^4$	99.74
	10	$2.02 \times 10^4$	99.12	$7.9 \times 10^4$	99.13
	20	$2.27 \times 10^4$	99.02	$9.7. \times 10^4$	98.93

## 5.4 Conclusions

This work expanded the application of hyperbranched polymer in the textile industry and developed a new method to fabricate ZnO coated bamboo pulp fabric. The ZnO nanoparticles deposited bamboo pulp fabrics were fabricated via in situ and immersion method by HSDA. In this process, HSDA served acts as a reactant and capture agent to fix the ZnO nanoparticles on bamboo pulp fabric. The results of scanning electron microscopy (SEM), X-ray spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS) confirmed that ZnO nanoparticles have been fixed and well dispersed on bamboo pulp fabrics by both in-situ method and immersion method.

Bamboo pulp fiber has lost the antibacterial property lain inherently in bamboo, ZnO nanoparticles treated bamboo pulp fabrics showed excellent and durable antimicrobial effect against both *S. aureus* and *E. coli*. Still over 98.93 % of bacterial reduction was maintained even after exposure to 20 consecutive home laundering conditions. The UV protect properties of bamboo pulp fabric is very weak, bamboo pulp fabric treated with ZnO nanoparticles provided high UV protection property and good washing fastness, with UPF value 90.38(more than 50) even after exposure to 20 consecutive home launderings its UPF value can maintain 70.42.

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## **Chapter 6**

## **Conclusions**

## Chapter 6: Conclusions

In this research water-soluble multi-amide compound hyperbranched polymers RSD and HSDA were synthesized. RSD and HSDA were used to synthesize nano Ag and ZnO particles for the functional modification of bamboo pulp fabric to improve its anti-ultraviolet and provide it with antimicrobial properties. The main conclusions of the paper as follows:

### 1 Synthesis of silver nanoparticles and antibacterial property of bamboo pulp fabrics finished by silver nanoparticles

In this research we studied one-step synthesis of silver colloid nanoparticles by mixing  $\text{AgNO}_3$  aqueous solution and RSD aqueous solution under vigorous stirring. The synthetic process was carried out in aqueous solution and at room temperature, making the method versatile and environmentally friendly. RSD aqueous solution produced silver colloid nanoparticles having average sizes from 3 to 30 nm and narrow size distributions. The silver colloids prepared with initial  $\text{AgNO}_3$  concentration lower than 0.35 g/l showed good stability even after storing 2 months. The silver colloid nanoparticles prepared with initial  $\text{AgNO}_3$  concentrations 0.35 g/l in 2 g/l RSD aqueous solution showed high antibacterial activities against *S. aureus* and *E. coli*. The maximum concentration that should be used is 3.0  $\mu\text{g/ml}$  to give good antibacterial performance.

Bamboo pulp fabric was treated by the multi-amine compound (RSD) and silver nitrate mixed solution by in-situ method. The surface morphology, the whiteness, silver content, antibacterial activity and washing durability of the silver-treated fabrics were determined. The experiment of the antibacterial test showed that the silver-treated bamboo pulp fabrics showed excellent and durable antimicrobial effect against both *S. aureus* and *E. coli*

### 2 In-situ synthesis of ZnO particles on bamboo pulp fabric and its anti-UV property

Water-soluble multi-amide compound (RSD) was synthesized from methyl acrylate and diethylene triamine by melt polycondensation. Bamboo pulp fabric was

immersed in  $\text{Zn}(\text{NO}_3)_2$  and RSD mixing solution under hydrothermal condition, and then the ZnO particles were deposited on the surface of bamboo pulp fabric by in-situ method.

In the finishing process, RSD served as a binder to impart and fix the ZnO particles on the bamboo pulp fabric. All the results of UV-vis, XRD, SEM and TEM determinations confirmed that the ZnO particles were synthesized and the ZnO particles were deposited on the bamboo pulp fabric. Bamboo pulp fabric treated with ZnO particles provided high UV protection property and good washing fastness.

### 3 Preparation and characterization of ZnO nanoparticles/HSDA hybrid and study of their antibacterial activities

New multi-amide compound hyperbranched polymers HSDA-I and HSDA-II, were successfully synthesized from the modified of hyperbranched polymer (RSD). FTIR and TGA showed that HSDA were synthesized and they had good thermal properties. ZnO nanoparticles were easily obtained in one-step manner by mixing  $\text{Zn}(\text{NO}_3)_2$  and HSDA aqueous solution under hydrothermal condition. The results of TEM and UV-vis spectra indicated that ZnO nanoparticles had been formed in colloidal solution. Compared to HSDA-I, HSDA-II has a large molecular weight and long branches and the HSDA-II generated ZnO nanoparticles has a small size and highly dispersed.

The ZnO colloid nanoparticles, prepared with 0.74 g/l  $\text{Zn}(\text{NO}_3)_2$  aqueous solution in the presences of 2 g/l HSDA-II, showed good antibacterial activities against Gram-negative bacteria (*Escherichia coli*) and Gram-positive bacteria (*Staphylococcus aureus*). A very low concentration of ZnO nanoparticles (as low as 5.0  $\mu\text{g/ml}$  Ag) also gave excellent antibacterial performance.

### 4 Application of ZnO nanoparticles to enhance the antimicrobial activity and ultraviolet protective property of bamboo pulp fabric

This work expanded the application of hyperbranched polymer in the textile industry and developed a new method to fabricate ZnO coated bamboo pulp fabric. The ZnO nanoparticles deposited bamboo pulp fabrics were fabricated via in situ and impregnation method by HSDA. In this process, HSDA served acts as a reactant and

capture agent to fix the ZnO nanoparticles on bamboo pulp fabric. The results of SEM, EDS and XPS confirmed that ZnO nanoparticles have been fixed and well dispersed on bamboo pulp fabrics by both in-situ method and impregnation method.

ZnO nanoparticles treated bamboo pulp fabrics showed excellent and durable antimicrobial effect against both *S. aureus* and *E. coli*. Still over 98.93 % of bacterial reduction was maintained even after exposure to 20 consecutive home laundering conditions. Bamboo pulp fabric treated with ZnO nanoparticles also provided high UV protection property and good washing fastness.

### **List of publication**

1. **G.Y. Zhang**, H. Lin, H. Morikawa, M. Miura. In-situ growth of ZnO particles on bamboo pulp fabric and its anti-uv property. *Fibers and polymers* Vol. 14, No. 11, pp. 1803-1807(2013)
2. **G.Y. Zhang**, H. Morikawa, Y. Y. Chen, M Miura. In-situ synthesis of ZnO nanoparticles on bamboo pulp fabric *Materials letters* Vol. 97, pp 184-186(2013)
3. **G.Y. Zhang**, Y. Liu, H. Morikawa, Y. Y. Chen. Application of ZnO nanoparticles to enhance the antimicrobial activity and ultraviolet protective property of bamboo pulp fabric. *Cellulose* Vol. 20, pp 1877-1884(2013)

### **International Conference**

1. **G. Y. Zhang**, H. Morikawa, Y. Y. Chen, The Anti-microbial Property of ZnO Nanoparticles Deposited Bamboo Pulp Fabric, 2<sup>nd</sup> International Conference on Computational and Theoretical Nanoscience, T210387, 1-3 March 2013, Hongkong
2. **G. Y. Zhang**, H. Morikawa, Y. Y. Chen, The anti-UV property of in-situ growth nano ZnO bamboo pulp fabric, Polychar 21, PP-17, 11-15 March, 2013, KimDaeJung Convention Center Gwangju, Korea
3. **G. Y. Zhang**, H. Morikawa, Y. Y. Chen, Improving anti-UV performance of silk fabric based on multiamine compounds, 8th International Silk Conference, ISC-4-019, 8-10 September, 2013, Soochow university , China
4. **G. Y. Zhang**, H. Morikawa, Y. Y. Chen, Synthesis of ZnO nanoparticles in aqueous solution and their antibacterial Activities, 26th International Microprocesses and Nanotechnology Conference, 7P-7-61, 5-8 November, Royton Sapporo, Hokkaido, Japan
5. **G. Y. Zhang**, H. Morikawa, Y. Y. Chen, one step synthesis of Ag nanoparticles in aqueous solution and their antibacterial Activities. 38th International Conference and Expo on Advanced Ceramics and Composites, 26-31 Jan, Hilton Daytona Beach Resort and Ocean Center, USA

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