Carbohydrate Polymers 126 (2015) 122–129

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

# The role of cellulosic chains of cotton in biosynthesis of ZnO nanorods producing multifunctional properties: Mechanism, characterizations and features

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ARTICLE INFO

*Article history:*
Received 16 February 2015
Received in revised form 15 March 2015
Accepted 18 March 2015
Available online 27 March 2015

*Keywords:*
In situ biosynthesis
*Keliab*
ZnO nanorod particles
Cellulosic fabric
Self-cleaning feature
Antibacterial efficiency

ABSTRACT

In situ synthesis of ZnO nanorods on cellulosic chains of cotton fabric was accomplished using natural plant source namely *Keliab* and zinc acetate. Hierarchical mechanism of nano ZnO generation and deposition on cellulosic chains of cotton fabric was discussed in details and several analytical techniques were used to characterize the formation of nano ZnO wurtzite structure. The morphology, crystal phase, and chemical structure of the fabric were characterized by scanning electron microscope, X-ray diffraction and energy dispersive X-ray spectroscopy. Further, interaction between ZnO and functional groups of cellulosic chains of cotton fabric was studied by Fourier transforms infrared spectroscopy. The influence of zinc acetate and *Keliab* solution on the self-cleaning activity of the treated cellulosic fabric was investigated with a central composite design based on surface response methodology. The treated fabrics showed self-cleaning activity toward methylene blue degradation under day light irradiation. The optimized treated sample showed high antibacterial efficiency against *Staphylococcus aureus* and *Escherichia coli* with enhanced tensile strength and higher crease recovery angle.



## 1. Introduction

Increasing awareness toward green chemistry and other biological processes has led to the development of eco-friendly approaches for synthesis of nanoparticles. Researchers have inspired from environmentally benign materials such as plant or plant extract, microorganism, fungi and enzymes for synthesis of nanoparticles (Abdel-Aziz, Eid, & Ibrahim, 2014; Mallikarjuna et al., 2011; Sangeetha, Rajeshwari, & Venckatesh, 2011). Plants and plant products as sustainable and renewable resources in the synthesis of nanoparticles have more benefit over prokaryotic microbes, which require an expensive method for maintaining microbial cultures and downstream processing (Narayanan & Sakthivel, 2011).

Zinc oxide nanoparticles (ZnO NPs) are an important semiconductor material with a wide band gap of 3.37 eV and large exciton binding energy (60 meV) due to interesting properties and potential applications in various fields (Bhatte, Sawant, Pinjari, Pandit, & Bhanage, 2012). Numerous methods have been employed for the synthesis of ZnO NPs such as sol–gel, thermal decomposition, chemical vapor deposition, spray pyrolysis, precipitation, pulsed-laser deposition, solvothermal technique, polyol (Bhatte, Sawant, Watile, & Bhanage, 2012; Chen, Liu, & Lu, 2008) and biological procedures (Singh et al., 2011). Synthesis of ZnO nanoparticles has been reported by using different plant, including *Aloe barbadensis Miller* (Sangeetha et al., 2011), *Physalis alkekengi* (Qu, Yuan, Wang, & Shao, 2011), *Acalypha indica* (Gnanasangeetha & Thambavani, 2013–2014), and *Cassia auriculata* (Ramesh, Rajendran, & Meenakshisundaram, 2014).

Cotton is one of the most important natural fibers that widely used in practical application due to their excellent properties including biodegradability, hygroscopic properties, flexibility, affinity to the skin, and low cost (Abd El-Hady, Farouk, & Sharaf, 2013; Ibrahim, Abou Elmaaty, Eid, & Abd El-Aziz, 2013; Ibrahim, Eid, et al., 2013; Ibrahim, El-Zairy, Abdalla, & Khalil, 2013; Zhang et al., 2013). There are also some undesirable properties such as easy wrinkling, easy soiling, and aptness for growth of microorganisms, low UV-protection and low strength (Ibrahim, Abou Elmaaty, et al., 2013; Ibrahim, Eid, et al., 2013; Ibrahim, El-Zairy, et al., 2013).

The application of ZnO nanoparticles to textile materials has been the object of several studies, to producing finished fabric with different functional performances (Ibrahim, Abou Elmaaty, et al., 2013; Ibrahim, Eid, et al., 2013; Ibrahim, El-Zairy, et al., 2013; Uğur et al., 2010). Nanoparticles were applied on textile materials

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http://dx.doi.org/10.1016/j.carbpol.2015.03.036
0144-8617/

into two main procedures, including ex situ and in situ processes (Montazer & Amiri, 2014). Most of literatures have reported ex situ method and there is few approaches nominated one-step or in situ synthesis of nanoparticles in which nanoparticles are synthesized and deposited simultaneously on the fabric. Yadav et al. prepared ZnO nanoparticles with an average size of 40 nm by wet chemical method and applied on bleached cotton fabric using acrylic binder. The nano ZnO coated cotton fabric showed better strength, air permeability and UV-absorption property (Yadav et al., 2006). Further, ZnO nanoparticles were in situ grown on $SiO_2$ coated cotton fabric through hydrothermal method followed by treatment with hot water (100 °C). The cotton fabric covered with needle-shaped nano ZnO indicated an excellent UV-blocking property (Mao, Shi, Zhang, & Cao, 2009). Sricharussin et al. prepared nano ZnO with various shapes (multi-petals, rod and spherical) and applied on cotton fabric through pad-dry-cure method to obtain UV-blocking and antibacterial properties (Sricharussin, Threepopnatkul, & Neamjan, 2011). Li et al. reported greatly improved UV-blocking property of the modified cotton fibers by assembling nano ZnO into the inner of cotton fibers via two-step hydrothermal method (Li, Zou, & Hou, 2011). Moreover, in situ generation and deposition of nano ZnO on cotton fabric were accomplished by using amino-terminated hyper-branched polymer (HBP-$NH_2$) to provide UV protection properties and antibacterial activity (Zhang et al., 2013). Further, Ibrahim et al. reported enhancing the antibacterial functionality and pigment printing properties of cotton/polyester blend by using bio-active additives consisting chitosan, choline chloride, triclosan derivative and hyper-branched polyamidoamine/silver or zinc oxide (Ibrahim, Abou Elmaaty, et al., 2013). Also, ZnO nanoparticles were assembled on the cotton fabric through layer by layer deposition formed multilayer film indicated excellent antibacterial activity against *Staphylococcus aureus* and UV protection property (Uğur et al., 2010). Further, nano ZnO was synthesized and loaded simultaneously on the cotton fabric by ultrasonic irradiation showed significant antibacterial activity against *S. aureus* and *E. coli* (El-Nahhal et al., 2013). ZnO NPs synthesized on cotton fabric through the formation of biologically activated ammonia from urea broth in the presence of ureolytic bacterial species *Serratia ureilytica* and reported antibacterial activity on the ZnO NPs loaded cotton fabric (Dhandapani, Siddarth, Kamalasekaran, Maruthamuthu, & Rajagopal, 2014).

Most of ex situ and in situ synthesis nanoparticles on cotton fabric were carried out by using chemical materials, or advanced technical equipment, which is expensive and harmful to the environment. Here, we describe in situ synthesis of ZnO nano particles by using natural plant source (*Keliab*) in facile hierarchical route. *Keliab* is producing by burning branches of *Seidlitzia rosmarinus* leading to extraction of dark viscous liquid and turning to grayish rough material similar to volcanic stones after cooling (Talebpour, Veysian, & Golfazani, 2013). The ash of *S. rosmarinus* is a source of alkali and contains a large amount of sodium and potassium carbonates (Hadi, 2009).

In our previous study, *S. rosmarinus* plant ashes namely *Keliab* was used for in situ synthesis of silver nanoparticles without any further reducing and stabilizing agents on the bleached cellulosic fabric to achieve antibacterial activity against *S. aureus* and *E. coli* (Aladpoosh, Montazer, & Samadi, 2014). In this paper, *Keliab* and zinc acetate dihydrate (Zn Ac) were utilized for in situ synthesis of ZnO nanorods on the cellulosic chains of cotton fabric imparting self-cleaning activity, antibacterial efficiency, and enhanced tensile strength with higher crease recovery angle. The self-cleaning activity of ZnO nanorods treated cellulosic cotton fabric was evaluated toward methylene blue (MB) degradation after 10 h under daylight irradiation. Moreover, the optimization of the self-cleaning treated fabric based on the precursor percentages (Zn Ac, w/v% and *Keliab*, v/v%) was investigated by central composite design (CCD). The proposed mechanism of ZnO nanorod particles synthesis on the cellulosic chains of cotton fabric and possible chemical reactions between the produced intermediates and cellulosic chains of cotton was discussed. Consequently, the multi-functional cellulosic cotton fabric was prepared by eco-friendly, easy, and economical method as a possible substitute for other conventional chemical methods.

## 2. Experimental

### 2.1. Materials

Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) as a primary metal salt was purchased from Sigma–Aldrich Co., and raw cellulosic cotton fabric with 148 g/m$^2$ was provided from Yazd Baf Co. (Yazd, Iran). Amylase and non-ionic detergent for desizing and scouring of raw cellulosic cotton fabric were supplied from local market (Tehran, Iran).

### 2.2. Instruments

X-ray diffractometer (XRD, model EQ uniox 3000, INEL, France) with nickel-filtered Cu Kα radiation was used to investigate the presence of crystalline phase of nanoparticles on the treated fabric. Nicolet FTIR was employed to study changes in the functional groups on the surface of cellulosic fabric from 400 to 4000 cm$^{-1}$. Scanning electron microscope (SEM, model xl30, Philips) was applied to study the morphology of the particles on the cellulosic cotton fabric and powder, also mapping images and energy-dispersive spectroscopy (EDX) was used to characterize the elemental composition of synthesized nano ZnO on cellulosic cotton fabric. INSTRON (Universal Testing Machine/INSTRON TM–SM, England) was applied to determine mechanical properties of the treated samples in both weft and wrap directions. SHIRLEY instrument was used to measure the crease recovery angle of the treated cellulosic fabrics.

### 2.3. Pre-synthesis

The raw cellulosic cotton fabric was pre-washed with 1 g/L non-ionic detergent at 60 °C for 20 min to remove surface contaminants and dirt and then desized with 1.5 g/L amylase at 80 °C for 45 min. Finally samples rinsed well with distilled water and dried at room temperature (liquor to goods ratio = L:G = 40:1).

*Keliab* stones were first milled, and then 10 g *Keliab* powder mixed well with 100 mL distilled water settled down over night, finally the alkaline supernatant liquid was separated and ready for use.

### 2.4. In situ synthesis of nano ZnO on cellulosic fabric

Nano ZnO was generated and deposited simultaneously on the desized cellulosic cotton fabric with different amount of $Zn(CH_3COO)_2 \cdot 2H_2O$ and *Keliab* solution according to Table 1.

To do this, first, the required amount of $Zn(CH_3COO)_2 \cdot 2H_2O$ and cellulosic cotton fabric was impregnated in the synthesis bath at L:G = 40:1 stirred for 30 min to obtain a transparent solution. Then, *Keliab* solution was slowly dripped into the synthesis bath, heated to 90 °C for 60 min. Introducing *Keliab* led to formation of a cloudy solution. Finally, the sample was taken out from the synthesis bath and dried at 80 °C for 30 min, cured at 150 °C for 3 min, rinsed with distilled water and dried at room temperature.