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A Study on the Effect of Nanocellulose Coating for Effective Deposition of Metallic Nanoparticles on Textile Substrate

Md. Mehdi Hasan[*], *Md. Shariyar Parvej, Md. Shakhawat Hossain*
Department of Textile Engineering, Khulna University of Engineering & Technology, Khulna-9203, BANGLADESH

ABSTRACT
Cellulose is one of the most abundant and important substances among natural and synthetic polymeric materials. Fibrous cellulosic materials are capillary porous disperse systems with high specific surface areas. The degraded low molecular weight product, micro and nano-cellulose is highly renewable. Nanocrystalline cellulose (NCC) has gained a great attention of the researchers because of their inherent sustainability, renewability and unique physical and chemical properties. NCC has been extracted using sulfuric acid hydrolysis process of sugarcane bagasse and ultrasonic treatment. This process effectively removes the amorphous part of cellulose, which yields low molecular weight nanoparticles and form stable cellulose nanocrystal suspension. NCC has showed potential as versatile support for metallic nanoparticles. In this study, a novel method to produce uniform NCC layer on textile substrate using spin coater has been presented and the effect of NCC coating for effective deposition of silver nanoparticles (AgNPs) on regular textile surface has been investigated. The amount of AgNPs deposited on the nanocellulose precoated textile has been found 27 per cent of the original weight of the substrate whereas the regular substrate without NCC coating showed only 5.5 per cent of AgNPs deposition on surface which is significantly lower. The study effectively demonstrates that the NCC coating significantly improve the capability of metallic nanoparticle deposition on textile surface, which may potentially enhance the functional properties of textile materials.

Keywords: Nanocellulose, Nanoparticles, AgNPs, Spin Coating

1. Introduction

Cellulose $(C_6H_{10}O_5)_n$ is the most abundant organic carbohydrate polymer of β-D glucopyranose repeating unit and consists of three hydroxyl groups per anhydroglucose unit (AGU) which provides high degree of functionality [1]. The materials based on cellulose and its derivatives have been used for a wide variety of applications e.g. food, paper production, biomaterials and pharmaceuticals [2]. Presence of Hydrogen bond network provides cellulose polymer enhanced stability, which prevents from dissolving in common aqueous solvents and does not possess fixed melting point. The cellulose fibers have a good flexibility and elasticity unlike mineral fibers which allows them to maintain a high aspect ratio in the process of manufacturing [3,4]. Hydroxyl groups of cellulose induce the formation of several hydrogen bonds, and high stereo regularity contributes to the high crystallinity of cellulose [5,6]. Pretreatment enhances the interaction with reactants by altering the structure of cellulosic materials. This is a necessary element in bioconversion of lignocellulosic materials to fuels and chemicals. Crystalline cellulose in microcrystalline (MCC) and nanocrystalline (NCC) form are crucial value-added part of cellulosic materials. [7,8]. NCC possesses properties like nanoscale dimension, high specific strength and modulus, high surface area, unique optical properties, etc when compared to cellulose fibers [2]. Highly crystalline cellulose can be prepared by different selective methods from lignocellulosic sources by removing or separating the crystalline part. The NCC can be prepared by vigorous acid hydrolysis or by the combination of acid hydrolysis [9] and ultrasonic treatment [10]. Acid hydrolysis followed by ultrasonic treatment is also reported for the preparation of transparent aqueous gel of NCC [11].

Nanotechnology has enabled the alteration and improvement of textile materials at the molecular level to improve the durability and performance beyond the assortments of existing products. Nanomaterials coated and impregnated textile materials exhibit superior surface properties while maintaining as-manufactured surface texture or comfort. Functional surface properties i.e. antibacterial surface, UV-resistance, stain resistance, wrinkle resistance, water repellency, flame retardancy, moisture transmission, targeted drug delivery, and self-cleaning properties are being explored in the realm of nanofinished textiles [12, 13]. Additionally, metal nanoparticles induce presence of surface plasmons that impart different colors by varying their size and shape. Nanotechnology has evolved into a crucial tool to bring revolutionary transformation into the traditional textile industry by offering value to the textile product in near future [14].

Nanocellulose has showed great potential in catalysis, and use as support, stabilizer and/or reducing agent in the synthesis of various metal nanoparticle recently [15]. Size controls the important physical and chemical properties e.g. conductivity, catalysis and fluorescence of nanoscale materials [16]. Gradual disappearance of the band structure of metals while discrete energy levels become dominant and the rules of quantum mechanics replace the principals of classical physics size decreases below a certain level [17]. Today, metal nanoparticles are celebrated materials in a variety of scientific fields. The remarkable size-, surface-and shape-dependence of

* Corresponding author. Tel.: +88-01303164266
E-mail addresses: mehdihasan1421009@gmail.com

the physical, chemical and optical properties of nano-materials make them excellent candidates in modern chemistry. The importance of anisotropic nanoparticles rapidly increasing due to several reasons. The approaches to understand the intrinsic shape dependent properties of metal and semiconductor nanocrystals are motivated by their synthesis. It is possible to predict and systematically manipulate the resultant nanocrystal structure through the particle growth mechanism. Unique structural features i.e. optical and electrical properties have made those desirable in various emerging fields of technology. Moreover, generation of different nanostructures which depend on novel template materials are being benefited by these nanomaterials [18].

Disinfectants comprise of metals/organic compounds are used for the antimicrobial finishes of polymers and fibers [19,20]. Silver exhibits antiseptic properties by binding with protein molecules and inhibiting cellular mechanism to eradicate microbes [21]. Nanosilver is biocompatible, nontoxic and effectively reduce bacterial counts on textile materials i.e. filtration media, medical textiles, which come into direct contact with human skin [22,23]. Nanocelluloses has gained attention as metal NP support in the past decade. Metal NPs possess unique properties compared to the bulk or macromolecular counterparts [24]. Metal NPs are thermodynamic instability leads to the aggregation and formation of bulk metal when capping agents, ligands or supports are not used in their synthesis. Nanocelluloses are attractive supports for metal NPs due to their high surface area, reductive surface functional groups and water suspendability [25].

The main objective of this work is to examine how the nanocellulose coating affect silver nanoparticle deposition on textile substrate. This novel work can pave the way of efficient functionalization of textile.

2. Materials and Methods

2.1 Materials

Sugarcane Bagasse was collected from local juice bar of Khulna. Sodium Chlorite ($NaClO_2$), Sodium Hydroxide (NaOH), Sulfuric Acid (H_2SO_4), Silver Nitrite ($AgNO_3$), Aqua Ammonia (NH_4OH) and Glucose ($C_6H_{12}O_6$) was donated by the Wet Processing Laboratory of Department of Textile Engineering at Khulna University of Engineering and Technology. A single jersey knit fabric of 110 GSM was collected from Micro Fibre Group Ltd, Narayanganj, Dhaka, Bangladesh.

2.2 Preparation of NCC

NCC was prepared using acid hydrolysis method. The procedure was as follows. Sugarcane bagasse was washed with water and dried under direct sunlight for a day. Then SCB were cut into small pieces. 10 grams of SCB were treated with 250 mL 3% (w/w) NaOH in IR laboratory dyeing machine at 95ºC for 4 hours. Then the samples were washed with tap water to adjust pH to 8 and kept overnight. pH was adjusted to 12 by adding 50 mL 3% (w/w) NaOH. Then it was treated using Sodium Chlorite (0.02 gram per gram SCB) at 90ºC for 2 hours 30 minutes. Acid hydrolysis was performed using 64 wt% sulfuric acid for 90 minutes. Acid was preheated to 45ºC and hydrolysis was continued at this temperature with vigorous stirring at 1000 rpm using hot plate magnetic stirrer. Acid to fiber ratio was 1:20. Hydrolyzed solution was ultrasonicated for 20 minutes at 70% strength. Ultrasonicated sample was centrifuged at 4000 rpm and precipitated gel was washed and centrifuged till pH of solution was stable at 6. Sample was freeze dried and then air dried to make powder NCC sample.

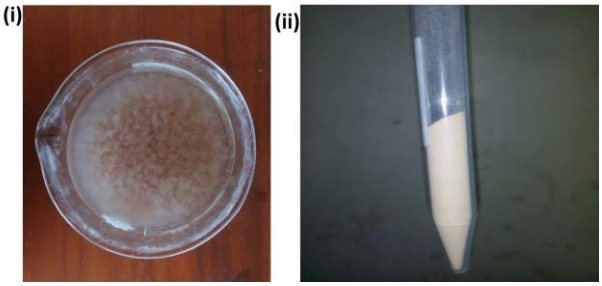

Figure 1. (i) NCC sample after acid hydrolysis and ultrasonication (ii) Powder NCC sample

2.3 Characterization of NCC by X-Ray Diffraction (XRD)

It is well known that the physical and chemical properties of cellulose products have strong correlation with the crystallinity and crystal structure. To determine the crystal structure and crystallinity, XRD patterns of the NCC was measured by Rigaku Smartlab SE. Before testing, samples were dried in a vacuum oven at 40°C for 6 hours to remove moisture.

2.4 Coating of Fabric with NCC

The fabric sample was oven dried at 80ºC and cut into size of 5mm×5mm. Then the fabric was coated using 2 wt% NCC suspension by spin coater. Then NCC coated fabric sample was dried in oven at 60ºC for 10 minutes.

2.5 Coating of Fabric with Silver Nanoparticles (AgNP)

Here, sample 1 is NCC coated fabric and sample 2 is the fabric without NCC coating. Both samples undergo alkali treatment i.e. the samples were treated with 10 wt% aqueous sodium hydroxide (NaOH) solution at room temperature for 10 min and later rinsed with distilled water. To prepare transparent colorless $[Ag(NH_3)_2]^+$ solution, 28 wt% aqua ammonia was added into a 0.1 M $AgNO_3$ aqueous solution dropwise with stirring. The alkali-treated textiles were dipped into the $[Ag(NH_3)_2]^+$ solution for 1 h followed by transferring into a stock solution of 0.1 M glucose. The remaining $[Ag(NH_3)_2]^+$ solution was also added into the glucose solution after 5 minutes and continued for 15 min to complete the reaction. Finally, the samples were rinsed with water and dried in the air.

2.6 Calculation Amount of AgNP Deposited on Samples

Amount of AgNP deposited on samples were calculated by taking weight of samples before and after AgNP coating. Amount of weight gain was expressed as percentage of weight before AgNP coating.

% of weight gain= [(weight after coating-Weight before coating)/Weight before coating]×100%

3. Result and Discussion

3.1 Acid Hydrolysis of Cellulosic Materials

Since the cellulose contains both amorphous and crystalline structures, the highly crystalline cellulose can be prepared from selective methods based on the source of the cellulose. Among them NCC is derived by sulfuric acid hydrolysis to remove the amorphous parts and separate the particles consisting of needle-like nanocrystals.

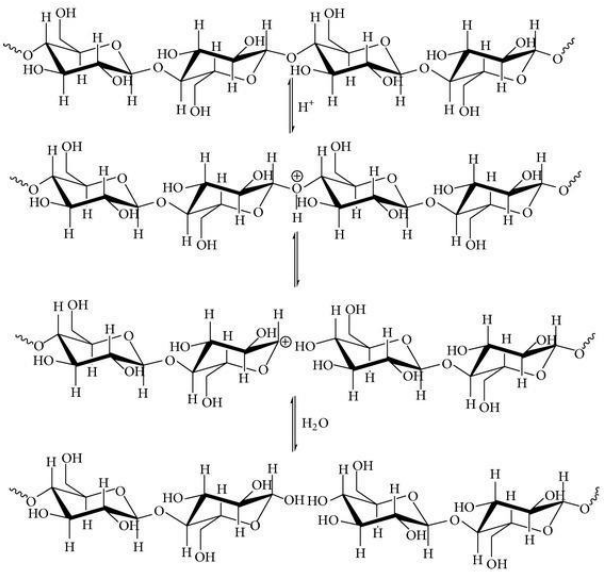

Figure 2. Acid-catalyzed hydrolysis mechanism of cellulose by cleavage of β-1-4- glycosidic bond

3.2 Characterization of X-Ray Diffraction (XRD)

An empirical method for determining the crystallinity of the produced nanocellulose was studied with an X-ray diffractometer using the focusing and transmission techniques. The influence of fluctuations in the primary radiation and in the counting and recording processes has been determined. The intensity of the 200 interference and the amorphous scatter at $2\theta = 18^0$, 22.5^0 was measured. The percent crystalline material in the total cellulose was expressed by an x-ray "crystallinity index." This was done for powdered nanocellulose sample produced by sulfuric acid hydrolysis. The results indicate that the crystallinity index is a time-saving empirical measure of relative crystallinity. Crystallinity index of the sample was calculated using OriginPro software and found 74.6%.

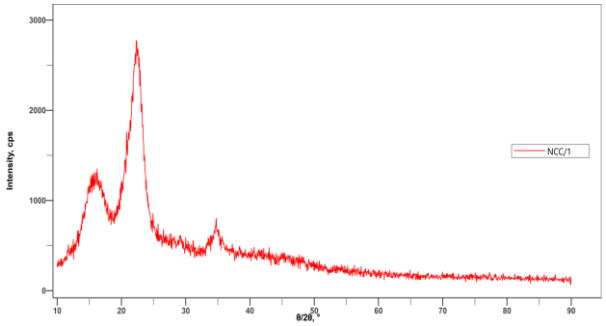

Figure 3. XRD pattern of prepared NCC

Table 1. Grain size of NCC from XRD

2θ °	Size Å
15.95868	23.868
22.56911	32.5921
34.89264	70.8933

3.3 Amount of AgNP Deposition on Textile Substrate

Weight of NCC coated sample (Sample 1) was 0.11 grams and 0.14 grams before and after AgNP deposition respectively. On the other hand, weight of sample without NCC coating (Sample 2) was 0.18 grams and 0.19 grams before and after coating respectively. Weight of NCC coated sample (Sample 1) increased by 27.27% whereas weight of sample without NCC coating (Sample 2) increased 5.56%.

In this project, spin-coating method has been used to create a thin layer of self-assembled NCC. Although, spin-coating has been utilized to prepare free-standing film of NCC [26], we have demonstrated the capability of producing the same on the textile substrate. Sulfuric acid hydrolysis yield negatively charged sulfate groups by reacting with surface hydroxyl groups and induce crystals to arrange in a way that minimizes existing electrostatic interactions [27,28], thus self-assembled layer form on the textile surface. This negatively charged particles facilitates attachment of Na^+ molecules which later reduce Ag^+ ions. Fragmentation of long cellulose polymer chains and high surface area of nanoparticles on textile surface may have played critical role for increasing metallic nanoparticles deposition.

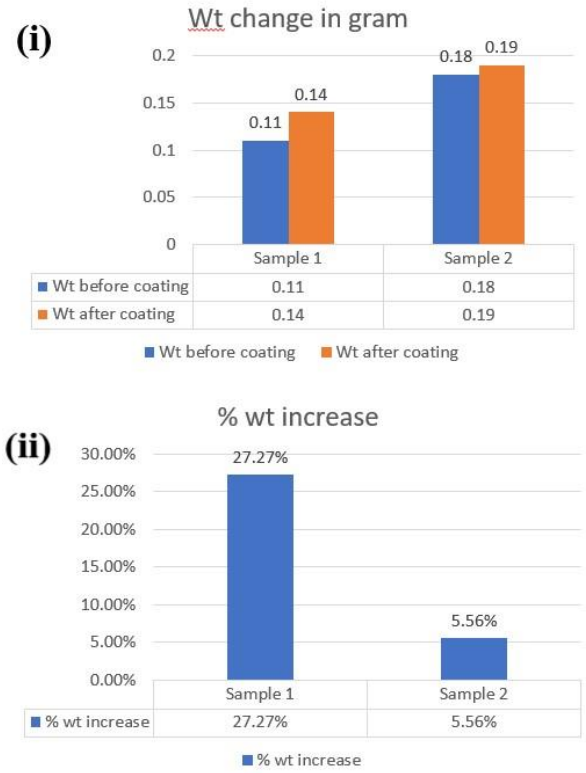

Figure 4. Amount of AgNP deposition (i) in gram (ii) as percentage

4. Conclusion

Transparent gel and its powder form was successfully prepared using sulfuric acid hydrolysis. NCC was prepared by using 64 wt% sulfuric acid at 45ºC, time was 1hour 30 minutes and acid to SCB ratio was 1:20.

XRD showed NCC was crystalline in nature and grain size was between 2-7 nm. Crystallinity index was 74.6%.

NCC coating on fabric showed great potential for supporting metallic nanoparticle deposition on textile substrate. Amount of AgNP deposition increased dramatically for NCC coated sample. NCC coated sample weight gain was higher than the sample without any coating. With higher degree of purity of NCC sample, we expect more higher deposition of metallic nanoparticle deposition.

Some tests i.e. FESEM, FTIR and TGA should be carried out for further characterization of NCC sample.

Further work can be carried out to find out optimum condition for NCC preparation from SCB and to find out optimum condition for NCC coating on textile substrate. Conditions include optimum concentration of NCC solution, proper binder, optimum ultrasonication time and temperature and ratio of binder to NCC for proper deposition of NCC on textile substrate without decreasing its capability to increase metallic nanoparticle deposition on textile substrate.

NCC is an exciting material for future. Extensive research on its modification and application can lead to its use on groundbreaking emerging fields like green electronics, nanocomposite, and medical field.

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NOMENCLATURE

NP : Nanoparticles
AgNP: Silver nanoparticles
XRD : X-Ray diffraction
FE-SEM : Field emission scanning electron microscopy
TGA : Thermo gravimetric analysis
FTIR : Fourier-transform infrared spectroscopy