



Preparation of the CNC/Ag/beeswax composites for enhancing antibacterial and water resistance properties of paper

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ABSTRACT

An effective method of preparing composites containing inorganic (Ag) and organic (beeswax) particles was established in this study. Ag nanoparticles were first immobilized on the cellulose nanocrystals (CNC) during the reduction of AgNO₃ in the presence of CNC, then mixed with beeswax by high speed stirring. Scanning transmission electron microscopy (STEM) images indicated that Ag and beeswax particles were uniformly dispersed and stable in the network structure formed by CNC. Upon coating on a paper surface, a layer of beeswax film was evident based on scanning electron microscopy (SEM) images. The dynamic contact angle and antibacterial activity tests indicated that the contact angle of coated paper reached 113.06° and the growth inhibition of *Escherichia coli* increased to 99.96%, respectively, at a coating amount of 21.53 g/m². When applied onto paper surface by coating, the CNC/Ag/beeswax composites can impact paper with antibacterial property and improved water resistance.

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1. Introduction

Inorganics and organics composites have received much attention in recent years because they can impact multi-functional properties to materials when applied. Ag nanoparticles (NPs), a type of inorganic material, have excellent antibacterial activity against a wide range of bacteria and viruses. However, its application in paper products is limited due to their aggregation in aqueous solution (Xiong, Lu, Wang, Zhou, & Zhang, 2013; Shi, Liu, Xue, Lu, & Zhou, 2014; Guibal, Cambe, Bayle, Taulemesse, & Vincent, 2013). Beeswax is a mixture of various long chain alcohols, fatty acids and their esters, and it can be used as a water-resistance agent for paper due to its excellent barrier property (Zhang & Xiao, 2013; Zhang, Xiao, & Qian, 2014). A variety of antibacterial or water-resistance agents, such as chitosan, rosin, and carboxymethyl cellulose are available for papermaking industry, but paper additives with both antibacterial and water resistance properties are rather limited. Although Ag NPs and beeswax composites can provide both antibacterial activity and water resistance property for paper, it is still rather challenging to prepare dispersible and stable composites of Ag NPs

and beeswax due to their high aggregation trend and poor compatibility.

Due to the presence of large number of ionic groups, cellulose nanocrystals (CNC) can be well dispersed and stabilized in a diluted system (Shafiei-Sabet, Hamad, & Hatzikiriakos, 2014; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011; Boluk, Lahiji, Zhao, & McDermott, 2011; Fukuzumi, Tanaka, Saito, & Isogai, 2014; Kurihara & Isogai, 2014; Fujisawa, Saito, & Isogai, 2012). CNC have been used as carriers or dispersants for medical purposes, protein or nanoparticles because of their high dispersibility and stability. For example, Wen, Yuan, Liang, and Vriesekoop (2014) prepared a highly stable D-limonene pickering emulsions using CNC as stabilizer. Sun, Hou, He, Liu, and Ni (2014a), Sun, Hou, Liu, He, and Ni (2014b) investigated CNC as carriers and dispersants for hydrophobic spirooxazine (SO)-based dye and alkenyl succinic anhydride (ASA) and found that CNC can improve the stability of SO-based dye and ASA.

In this work, CNC were used for dispersing Ag NPs and beeswax simultaneously in an aqueous solution, so that Ag NPs and beeswax composites with high dispersibility and stability can be prepared. Ag NPs were synthesized by following a reduction method using sodium borohydride as the reducing agent in the presence of CNC. Then beeswax was added to the CNC/Ag composites to prepare CNC/Ag/Beeswax composites. The final composites were coated on the surface of paper to produce multi-functional paper with enhanced antibacterial and water resistance properties.

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The antibacterial activity of the coated paper was tested against *Escherichia coli* (*E. coli*, ATCC 11229) by a shaking flask method, while the water resistance property was studied by measuring the dynamic contact angle.

2. Materials and methods

2.1. Materials

Cellulose nanocrystals (CNC) (3.5%, w/w) were obtained from Tianjin Haojia Cellulose Co. Ltd. (China). Refined beeswax, silver nitrate, sodium borohydride, phosphate buffered saline (PBS) and LB Broth with agar were purchased from Sigma-Aldrich Reagent Co. Ltd. All other chemicals were of analytical grade and used without further purification.

2.2. Methods

2.2.1. Preparation of CNC loaded with Ag NPs

A solution of 2 g CNC (3.5%, w/w) with 33 g of water was prepared and placed in an ultrasonic dispersion machine for 6 min with an on/off pulse interval of 6/3 s. A silver nitrate solution was prepared by adding 0.003 mol silver nitrate into 5 g of water. The dispersed CNC was then poured to a three-neck round-bottom flask along with the silver nitrate solution, which was kept in an ice water bath and stirred at 400 rpm. About 0.006 mol sodium borohydride was diluted with 10 g of water, the sodium borohydride solution was then added drop by drop to the suspension and left to react for 30 min. Finally, 50 g of CNC/Ag composites were obtained.

2.2.2. Preparation of CNC loaded with Ag NPs and beeswax

For 50 g of CNC/Ag composites, 1 g of beeswax was weighed and added. The CNC/Ag composite solution was heated to 80 °C to make the beeswax melt completely. The melted beeswax was then stirred by using a T-25 digital Ultra-turrax running at 15,000 rpm for 3 min. The dispersed beeswax particles were contained and rapidly cooled in iced water to prevent large solid wax particles from forming.

2.2.3. Coating of paper

A filter paper (dia. 5.5 cm, 75 g/m²) was first placed in a glass petri dish, the CNC/Ag/beeswax composites were then added into the glass petri dish. After the composites were coated on the paper in the petri dish completely, the petri dish was then kept in an oven at 105 °C for 30 min. The amount of the composites coated on paper was listed in Table 1.

2.2.4. Characterization of the CNC/Ag/beeswax composites

The CNC/Ag/beeswax composites were analyzed using an Ultraviolet–visible (UV–vis) Spectrometer (Genesys 10-S, Thermo Electron Corporation, USA). UV–vis spectra were recorded between 300 and 700 nm at room temperature.

2.2.5. STEM analysis

The CNC and CNC/Ag/beeswax composites were analyzed by a Scanning transmission electron microscopy (STEM, JEOL 2010; Japan) operating at a voltage of 200 kV. A drop of sample was placed on a 200 mesh carbon coated copper grid and dried overnight at room temperature.

2.2.6. SEM analysis

The surface morphology of the blank paper and coated paper was investigated using a Scanning Electron Microscope (SEM, JSM-6400, JEOL; Japan). The surface of the sample was carbon coated and then gold coated for conductivity at the SEM accelerating voltage of 15 kV.

2.2.7. Antibacterial activity measurement

The antimicrobial activity of the coated paper was tested against *Escherichia coli* (*E. coli*, ATCC 11229) using the shaking flask method. This method was conducted as described (Zhang & Xiao, 2013): About 4.5 ml of 0.01 M phosphate buffered saline solution was mixed with 0.5 ml *E. coli* (10⁵ CFU/ml) in a sample tube, and 0.1 g blank paper or coated paper was added into the above solution. The sample tube was then immersed in a water bath shaker and shaken at 37 °C for 1 h. About 0.1 ml of each culture was transferred and seeded on an agar plate, the plate was then kept in an incubator at 37 °C for 24 h. The number of colonies was counted, and the inhibition of bacterial growth was calculated by the following equation:

$$\text{Growth Inhibition of Bacteria (GIB)}(\%) = \frac{A_0 - A_1}{A_0} \times 100 \quad (1)$$

where, A_0 and A_1 were the number of colonies detected from the blank paper and coated paper, respectively.

2.2.8. Contact angle measurement

The hydrophilicity of the coated paper was studied using a contact angle measuring machine (Attension Theta). The blank and coated paper samples were first cut into rectangular specimens with a width of 15 mm and length of 50 mm, and then a water droplet was dropped on the specimen for 10 s. Pictures were taken and the contact angles were determined by the machine. All the measurements were performed at room temperature.

3. Results and discussion

3.1. Characterization of the CNC/Ag/beeswax composites

It is well known that the Ag NPs tend to aggregate in aqueous solution (Wu, Zhao, Zhang, & Xu, 2012). In order to overcome this shortcoming, the Ag NPs were prepared by reducing AgNO₃ using sodium borohydride (NaBH₄) in the presence of CNC. The use of CNC enabled the Ag NPs to be dispersible and stable in aqueous solution. The formation of Ag NPs in the presence of CNC can be confirmed by the UV–vis spectra (Fig. 1). As shown in Fig. 1, an absorption band at 410 nm, which was typical of Ag NPs (Bhui & Misra, 2012; Ibrahim, Eid, & El-Batal, 2012), was evident for the CNC/Ag composites, demonstrating the immobilization of Ag NPs on CNC. Manivannan et al. studied the *N*-[3-(trimethoxysilyl)propyl] diethylenetriamine matrix embedded Ag NPs by UV–vis absorption spectra and observed a characteristic absorption at 409 nm (Manivannan, Krishnakumari, & Ramaraj, 2012).

Good dispersibility and stability of CNC/Ag/beeswax composites can be confirmed using Fig. 1. It can be seen that the CNC suspension exhibited good dispersibility, but the prepared Ag NPs in absence of CNC exhibited high aggregation and coagulation in aqueous solution. On the other hand, the composites prepared using Ag NPs, beeswax and CNC, were highly dispersible and stable even after storing at room temperature for three months.

Table 1
Antibacterial activities of paper coated with different amount of CNC/Ag/beeswax composites.

Coating amount (g/m ²)	0	1.25	5.64	11.08	21.53	37.92	53.1
Ag amount (g/m ²)	0	0.29	1.31	2.57	5	8.81	12.34
GIB (%)	–	26.09	89.13	99.93	99.96	99.98	100

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