A facile approach towards self-reinforced antibacterial paper (SRAP)

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ABSTRACT

A facile process to prepare self-reinforced antibacterial paper (SRAP) was developed by in situ synthesis of zinc oxide (ZnO) in partially dissolved cellulose. The SRAP was fabricated by impregnating filter paper in zinc chloride (ZnCl₂) solution and then reacting with sodium hydroxide (NaOH). Filter paper was firstly impregnated with ZnCl₂ solution of 65 wt% concentration for 5 seconds at 80 °C, and then pressed at 3.85 kPa for 5 seconds to remove excess liquid. Subsequently, the paper was soaked in a 0.8 wt% NaOH solution for 1 hour, and then washed with deionized water, and dried finally to yield SRAP. Energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) and scanning electron microscope (SEM) were used to characterize the SRAP. The results revealed that the SRAP contained intact cellulose fibers as the skeleton, gelled cellulose as the matrix, and clusters of nano ZnO particles as the filler. The SRAP had a much higher density, tensile and burst strength, compared with the untreated cellulose paper, and the folding strength was enhanced by more than fifteen times. In addition, the SRAP had outstanding antibacterial properties due to the presence of nano ZnO particles.

Keywords: cellulose; self-reinforced; antibacterial paper; zinc chloride; ZnO; nano particles

1. INTRODUCTION

Due to wide concerns about the environmental problems, the utilization of renewable resources is becoming more and more important. As one of the most abundant renewable natural and environment-friendly materials, cellulose is widely used in papermaking industry. Cellulose-based paper is considered to be an environmentally friendly and cost-effective alternative packaging material.1 However, the traditional cellulose-based paper cannot prevent the invasion of bacteria. Organic antibacterial agents, such as quaternary ammonium salt and chlorine disinfectant, have been used industrially to prepare antibacterial papers, but some of them are volatile and exhibit a poor stability at higher temperatures or pressures. Furthermore, some monomers are emitted when used during a long period, which limits their application in food packaging.2 Cellulose fibers were modified by metallic salts or surface graft polymerization to yield antibacterial papers. However, these methods are neither cost-effective nor environment friendly.3

Some antibacterial inorganic oxides such as zinc oxide (ZnO), titanium dioxide (TiO₂), magnesium oxide (MgO), and calcium oxide (CaO) are very stable under harsh conditions, and they are regarded as very safe materials for human beings and animals.4-9 TiO₂ and ZnO have been used to prepare various personal care products. Unlike TiO₂, ZnO has antimicrobial properties even without photo-activation.10-12 Besides, ZnO nanoparticle could be coated on the cellulose fibers by a simple ultrasonic approach.13 The ZnO particles could be synthesized on the surface of cellulose fibers with a precursor solution of a zinc compound, such as zinc nitrate (ZnNO₃), zinc acetate (Zn(CH₃COO)₂), or zinc sulfate (ZnSO₄), and an aqueous solution of base like sodium hydroxide (NaOH), potassium hydroxide (KOH) or ammonium hydroxide (NH₄OH).14-17 Goncalves et al. prepared ZnO/cellulose nanocomposites using a two-step synthesis: firstly, the nucleation of ZnO seeds at the surface of cellulose fibers done by 2-propanol solutions of 3.5 mmol/L zinc acetate and 2.0 mmol/L NaOH, and secondly, the growth of ZnO nanostructures was promoted by 25 mmol/L Zn(NO₃)₂ aqueous solution and equal molar concentration of the hexamethylenetetramine. XRD and Raman analysis showed rod-shaped ZnO particles at the cellulose surface. The ZnO/cellulose nanocomposites showed photoluminescence and antibacterial activities.14,15

John et al. prepared a cellulose film using LiCl/DMAc solvent system to dissolve cellulose. Then generated a cellulose-ZnO hybrid film by using the mixture of 0.01 mol/L Zn(NO₃)₂ and 0.01 mol/L triethanolamine (TEA) as precursors of ZnO to immerse the cellulose film. In that study, XRD patterns, SEM images and AFM pictures demonstrated numerous ZnO nanoparticles ranging from 100 to 250 nm in size embedded in the cellulose film. But the cellulose-ZnO hybrid film had lower strengths.15

Yadav et al. prepared ZnO nanoparticles using 0.2 mol/L zinc nitrate and 0.4 mol/L NaOH as precursors under 0.5 wt% cooked starch as a stabilizing agent. An average size of 40 nm ZnO was coated on a cotton woven fabric using acrylic binder. That ZnO-cotton woven fabric showed lower frictional property. However, a large quantity of water or organic solvent was needed through these methods, and due to the very low concentration of ZnO precursors, the prepared composites show very poor mechanical properties.

In our previous studies, the paper mechanical properties, grease resistance and antibacterial properties could be
improved as it was treated in 8% NaOH/12% urea/0.25% ZnO solution at -12 °C for 120 min. However, the harsh treating condition at -12 °C limits the possibility in pilot and industrial production. On the other hand, when the paper was treated in 65 wt% ZnCl₂ solution in a mild condition, such as at 80 °C for 5 seconds, the treated paper exhibited a high strength performance and grease resistance, but unfortunately, the treated paper had no antibacterial properties. However, it is well known that zinc chloride aqueous solution is not only a cellulose solvent but also a precursor solution for ZnO particles. In 65 wt% zinc chloride aqueous solution, Zn²⁺ could interact with the hydroxyl group of the cellulose molecular chain, leading to lower intermolecular hydrogen bonding, which results in partial dissolution of the paper surface layers. The Zn²⁺ could be rinsed out from cellulose matrix and the partially dissolved cellulose formed a matrix with intact fibers embedded in the cellulose regeneration processes, which imparted high mechanical strength properties to the treated papers. It was reported that Zn(OH)₂ was predominantly formed from the reaction of Zn²⁺ and OH⁻ at pH 6.0–9.0, while ZnO was mainly obtained at pH above 9.0. It was also known ZnO can form stronger hydrogen bonds with cellulose than NaOH hydrate. During the cellulose regeneration process, water is replaced by NaOH aqueous solution as coagulation liquid. As the pH increases to above 9, ZnO nucleates, grows and stably attaches to the surface of fibers or the cellulose matrix, rendering the paper antibacterial properties. However, few studies have focused on the route to fabricate self-reinforced antibacterial paper via partial dissolution of cellulose and in situ synthesis of zinc oxide (ZnO) technology.

The key objective of this work is to develop an environmentally friendly technology for the production of paper with good antibacterial properties and high mechanical strength properties by in situ synthesis of ZnO nano particles. Figure 1 shows schematically the process for the preparation of the self-reinforced antibacterial paper.

2. EXPERIMENTAL

2.1 Materials
All the reagents were analytical grades and used without any further purification. Zinc chloride and sodium hydroxide were analytical grades from Nanjing Chemical Reagent Factory, China. Filter paper of 103 g/m² basis weight and 18.5 cm diameter was purchased from Fisher Scientific International Inc. (Pittsburgh, UK). The paper was made with cellulose fibers which had a degree of polymerization (DP) of about 830.

2.2 Preparation of SRAP
65 g zinc chloride was dissolved with 35 g distilled water to make an aqueous solution. Then the solution was heated to 80 °C. The filter paper was immersed in this solution for five seconds. Subsequently, the samples were pressed for 5 minutes at 3.85 kPa between two clear plastic sheets at an ambient temperature. Then, the papers were impregnated with 0.8% sodium hydroxide solution for several hours, and then they were rinsed with deionized water for several times. Finally, the samples were constrained on a stainless-steel disk with clips and dried in an oven for 12 h at 60 °C.

2.3 Characterizations of the SRAP
Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) of the treated filter paper (SRAP) were performed on a JEOL JSM-6400 scanning electron microscope (JEOL, Tokyo, Japan). The chemical bonding states of Zn and O were identified by X-ray photoelectron spectroscopy (XPS), using an AXIS Ultra DLD system (UK).

2.4 Mechanical properties of SRAP
The SRAP paper was conditioned at 23 °C and 50% relative humidity (RH) for 48 hours before testing. Density was calculated from the grammage and thickness of paper. The paper grammage was measured based on TAPPI method T 410 om-02. Thickness was measured in accordance with TAPPI method T 551 om-12. Tensile strength and burst strength were measured in accordance with TAPPI T 494 om-01 and T403 om-02 respectively. Folding strength was tested according to TAPPI method T 511 om-02. The average value and standard deviation of
tensile index and burst index were calculated from at least 5 parallel tests.

2.5 Antibacterial assessment of SRAP

Inhibition effects of control samples or treated samples were measured according to GB/T 20944.1-2007 disk diffusion method. *Escherichia coli* (One gram-negative bacterium) and *Staphylococcus aureus* (one gram-positive bacterium) were used in the experimentation. The culture medium for the aforementioned microorganism was a mixture of 17 g of agar, 15 g of beef extracts, 5 g of peptone and 5 g of NaCl in 1000 mL of water. The pH value was adjusted to 8.0 using 1 mol/L HCl or 1 mol/L NaOH. Then, 0.1 mL of the bacterial suspension (approximately 10⁶ CFU/mL) was spread on the agar plates, and circular samples of the coated papers (diameter 15 mm) were placed on the surface of agar. Then, the dishes were placed in an incubator at 37 °C for 24 h. The antibacterial activity was evaluated by measuring the diameter of the inhibition zones.

2.6 Determination of free zinc ions

To examine the release of zinc ions from treated paper, the paper sample was weighed, and cut into 1cm×1cm pieces, and then immersed in vials with 10ml of distilled water for one week in 37 °C in an orbital shaker at 100 rpm shaking. The liquid phase was then analyzed by an AA900T flame atomic absorption spectrometry (FAAS) (Perkin Elmer, USA) with HCl-HNO₃ digestion.

3. RESULTS AND DISCUSSION

3.1 Mechanical properties and antibacterial activity

The mechanical properties of the self-reinforced antibacterial paper were shown in Table 1. The self-reinforced antibacterial paper had a higher density, which resulted in a double increase in both tensile strength and bursting strength, compared with the untreated cellulose paper. Moreover, the folding strength was enhanced more than fifteen times. ZnCl₂ swelled and partially dissolved the filter paper. The dissolved cellulose served as a glue to join the un-dissolved fibers together. As a result, the treated paper becomes less porous and stronger.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Density (g/cm²)</th>
<th>Tensile index (N/m²)</th>
<th>Burst index (kPa.m²/g)</th>
<th>Folding strength (times)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filter paper</td>
<td>0.54±0.004</td>
<td>19.33±0.16</td>
<td>1.32±0.08</td>
<td>5±1</td>
</tr>
<tr>
<td>Treated paper</td>
<td>0.96±0.031</td>
<td>51.10±0.96</td>
<td>1.65±0.01</td>
<td>80±3</td>
</tr>
</tbody>
</table>

The antibacterial activity of treated papers was shown in Figure 2. Apparent inhibition zones against *S. aureus* and *E.coli* were observed around treated paper samples. The inhibition zone against *S. aureus* was larger than that against *E.coli*. This indicated *E.coli* strain showed a higher resistance against ZnO than *S.aureus* strain. Some research reported gram-negative bacterial strains of *E. coli* had smaller inhibition zones than those of gram-positive bacterial strains *S. aureus* in the presence of ZnO nanoparticles¹⁸,²². The present results are consistent with the results of these reports.

In order to investigate whether there was a significant amount of ZnO or Zn²⁺ released from the treated paper, the treated paper was soak in deionized for one week, and the water was tested by flame atomic absorption spectrometry (FAAS). No absorption of Zn was detected by FAAS, which implied that there was no Zn released from the treated paper and ZnO was stably fixed to the paper substrate. Therefore, the treated paper should be safe as package materials and other functional substrates.

Fig. 2 Antibacterial properties of papers (A- against *E. coli*, B- against *S. aureus*, a- untreated paper, b- treated paper).

3.2 Characterization of self-reinforced antibacterial paper

3.2.1 EDS and XPS analysis

To determine the elemental composition of the self-reinforced antibacterial paper and the presence of ZnO in the self-reinforced antibacterial paper, EDS and XPS analyses were performed in this study. According to the results in Figure 3, the self-reinforced antibacterial paper was composed of C, O, Zn and Cl elements, and the XPS results show that besides the C1s and O1s peaks, peaks of Zn 2p, Zn 3s, Zn 3p, Zn 3d were also present, indicating that the modified paper was mainly composed of zinc, oxygen and carbon. The Zn 2p spectrum illustrated a doublet peaks, and the binding energies were 1021.6 and 1044.7 eV, which can be identified as the Zn-2p3/2 and Zn-2p1/2 lines, respectively. The binding energy differences between the two lines are 23.1 eV, which is close to the standard reference value for ZnO²¹. These results support the conclusion that the Zn in the treated paper was in the form of ZnO²⁴,²⁵.
Fig. 3 EDS pattern and XPS spectrum of the self-reinforced antibacterial paper (A- EDS pattern, B- XPS spectrum)

Fig. 4 SEM images of (A-1) the surface of the untreated filter paper; (B-1) the surface of the self-reinforced antibacterial paper; (A-2) the cross-section of the untreated filter paper; and (B-2) the cross-section of the self-reinforced antibacterial paper.

3.2.2 SEM observation
SEM of the untreated and treated filter papers were used to evaluate the distribution of ZnO in the paper surface in Figure 4. The blank filter paper (A-1, A-2) showed a bulk network of entwined cellulose fibers with wide pores. The self-reinforced antibacterial paper (B-1, B-2) was highly compacted and less porous. Moreover, flower-like ZnO layers were observed on the surface of the self-reinforced antibacterial paper (B-1). The flower-like ZnO layers coated on the cellulose fibers were nano-size flakes. These observations indicated that the some of the cellulose fibers were partially dissolved in 65 wt% ZnCl₂ aqueous solution, and the paper was filled and coated with the dissolved cellulose. The dissolved cellulose served as a binder to form a compact and strong fiber network. Simultaneously, the presence of Zn ions in higher concentration induced the formation of clusters of ZnO nano flakes on cellulose during the regeneration process, resulting in the formation of flower-like ZnO layers on the cellulose substrate. These flower-like ZnO layers imparted to the self-reinforced antibacterial paper a high antibacterial activity.

4. CONCLUSIONS
A novel self-reinforced antibacterial paper (SRAP) was successfully fabricated by in-situ zinc oxide synthesis and partial dissolution of the cellulose paper substrate. Partial dissolution of the cellulose paper substrate with ZnCl₂ solution resulted in a dense paper structure with high mechanical strength properties. Flower-like ZnO nano
flakes were formed and fixed on the paper substrate to provide excellent antibacterial properties. This antibacterial paper had stable physical and chemical properties, and could potentially be used for food packaging materials and for medical applications.

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