Distribution of zinc oxide nanoparticles on unbleached and bleached bamboo paper via in-situ approaches

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Abstract. Metal oxide nanoparticles such as zinc oxide are increasingly being recognized for potential use in research and health-related application. It is usually incorporated in the modern healthcare products functioning as antimicrobial properties. These inorganic compounds could be applied for antimicrobial paper. Therefore, the objective of this study is to investigate the growth distribution of zinc oxide nanoparticles prepared via in-situ approaches on unbleached and bleached pulps. In order to produce these pulps, hydrothermal method is used throughout the study. The micrograph obtained from the scanning of Field Emission Scanning Electron Microscope exhibited that zinc oxide nanoparticles appeared in the range of 64.1 nm to 87.5 nm supported by the analysis of Field Emission Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis, as high as 27% zinc and 39% oxygen. As expected, zinc oxide nanoparticles decreased the mechanical properties of paper due to the interference of fiber bonding. Antimicrobial test demonstrated acceptable results which required further test.

1. Introduction
Zinc oxide is applied as traditional medicinal ointments for boils and carbuncles since 2000 B.C. [1]. In modern technologies, zinc oxide has gone far in electronic, optic and biomedical applications [2]. The slurry form containing zinc oxide has been used in calamine lotion which is suitable for rashes skinner [1]. Moreover, zinc oxide has served effectively to reduce the microbial growth and has been used as biomimetic membrane in bioscience area [3]. To the extent that, zinc oxide can be nano-synthesized via hydrothermal method, sol-gel method, wet chemical reaction and biological technique [4-6].

In terms of papermaking, zinc oxide has been used as prior source in optoelectronic printing which allow detection and controlling of light. Tetrapodal zinc oxide microstructures are applied to produce such photosensor [7]. Paper also is treated with nanorod zinc oxide in order to function as effective protein concentrator for biomarker in heart disease [8]. Ma et al., [9] and Martins et al., [10] produced antimicrobial paper by coating the paper surface with zinc oxide-starch nanocomposites and nanofibrillated cellulose composites with zinc oxide nanoparticles (NFC/ZnO nanocomposites) respectively. Previously, a study has been conducted by Li et al., [11] which showed resistance of antibacterial activity by immersing nano-zinc oxide cotton fabrics against salt and alkaline artificial sweat solution.
Unbleached paper is widely used as food packaging or paper bag materials in most developed countries. Some countries like Japan used it as writing printing paper that is more environmental friendly material, as it escapes bleaching process. However, bleached papers are more preferred for some official correspondence like writing and printing; has better mechanical properties such as tensile, elongation and tear indices by lignin removal[12]. Brightness of paper that available in market is related to the application of acid, chlorine dioxide and hydrogen peroxide during bleaching process [12-14]. In order to improve the pulp and paper properties, combination of mechanical pulping and chemical bleaching are carried out which further influence the size and distribution of pore [15].

Chen et al., [16] stated that size of pore can influence the ability of fibres to absorb chemical additives. Therefore, a study was conducted in order to investigate the distribution of zinc oxide nanoparticles via hydrothermal method on both unbleached and bleached paper using in-situ techniques. According to Guo et al., [17] , the technique was simple and effective especially for small-scale laboratory application.

2. Materials and methods

2.1. Materials and chemicals

Bamboo culms of Gigantochloa scortechinii (Semantan) were purchased from Sungai Siput, Perak, Malaysia. The bamboo was received 2 m in length prior to chipping process. The chemicals involved in bleaching process were sodium hydroxide (NaOH), sodium chlorite (NaClO₂), acetic acid (CH₃COOH) and hydrogen peroxide (H₂O₂). Other chemicals listed as zinc acetate dihydrate (Zn(CH₃COO)₂.2H₂O), zinc nitrate hexahydrate (Zn(NO₃)₂.6H₂O) and hexamine (C₆H₁₂N₄) were used in synthesizing zinc oxide nanoparticles. All chemicals were purchased from R&M Chemicals.

2.2. Preparation of unbleached and bleached pulps of bamboo

Bamboo culms were grinded into chips until 2-3 cm width and length. These chips were cooked using soda pulping technique, 17% sodium hydroxide in twin digester at 170 ℃ for 90 mins. After pulping process, unbleached pulp was washed and screened using Somerville Fractionator. At this stage, unbleached pulp was obtained. In order to produce bleached pulp, bleaching need to be carried out on unbleached pulp. However, prior to bleaching, the unbleached pulp needs to be beaten until 6,300 revolutions by using PFI-mill according to TAPPI T248 Standard Method. The next step was bleaching process which involved delignification stage (D) and extraction stage (Ep) following D₁EpD₂ bleaching sequences. During D₁ stage, unbleached pulp was put in the transparent plastic bag containing 2 % of NaClO₂ and 3 % of CH₃COOH. This pulp was placed in water bath at 70 ℃ for 180 mins. In order to continue bleaching process, a mixture of NaOH at 1.5 % and H₂O₂ at 1 % was applied to the pulps for 90 mins. Finally, D₂ stage involved the immersion of pulps was carried out for another 90 mins by adding NaClO₂ and CH₃COOH at 1.25 % and 3.00 % concentrations accordingly.

2.3. Synthesis of zinc oxide nanoparticles

Nanoparticles of zinc oxide was synthesized using hydrothermal method[4]. Firstly, zinc acetate dihydrate was stirred in ethanol until the mixture was completely dissolved. Then, this mixture was poured into another mixture of sodium hydroxide and ethanol. The stirring continued for 2 hrs at 70 ℃. The latter solution promptly changed into cloudy after adding the mixture of sodium hydroxide, zinc nitrate hexahydrate and hexamine. The solution was stirred at 90 ℃ for another 3 hrs in order to allow optimum growth of zinc oxide. The solution was then filtered and dried in the oven at 100 ℃. Finally, whitish solid powder was attained and sent for characterization purpose. This experiment was conducted in order to prove that the produced powder was obtained in nano-size.

2.4. Preparation of zinc oxide unbleached and bleached paper via in-situ approach

The in-situ approach was conducted for both unbleached and bleached pulps by generating zinc oxide nanoparticles in the pulp slurry. The solution of sodium hydroxide and zinc acetate dihydrate was heated and stirred for 2 hrs. An amount of 24 g unbleached or bleached pulps was soaked for 30 mins
and dried for another 30 mins at room temperature. The soaking process was repeated for three times. The pulps were then stirred in the solutions of hexamine and zinc nitrate hexahydrate at 90 °C for 3 hrs. This solution was sonicated at 450 Hz for 30 mins and disintegrated before preceding the papermaking process. Papermaking was done using laboratory handsheet machine.

2.5. Characterization of zinc oxide nanoparticles, zinc oxide unbleached and bleached paper

The zinc oxide nanoparticles which were hydrothermally synthesized were observed using Field Emission Scanning Electron Microscope (Model: FESEM JEOL JSM 7600F). Besides, another 4 samples were prepared which comprises of unbleached paper, bleached paper, zinc oxide unbleached paper and zinc oxide bleached paper. The formation and distribution of zinc oxide for these papers were observed using FESEM. In addition, the Energy Dispersive X-ray (EDX) was also applied in order to detect the elements that attached on the fibers that formed a sheet of paper.

2.6. Characterization of optical, physical and mechanical properties of paper

The optical properties of paper involved paper brightness and opacity. Physical properties of paper consisted of grammage and bulk thickness while mechanical properties contained paper tensile strength, tear strength and folding endurance. All test were referred to TAPPI Standard Methods namely as following : TAPPI Standard T 452 om-02 for brightness [18], TAPPI Standard T425 om-01 for opacity [19], TAPPI Standard T411 om-97 for thickness [20], TAPPI Standard T414 om-98 for tear resistance [21], TAPPI Standard T511 om-02 for folding endurance [22], TAPPI Standard T404 cm-02 for tensile [23].

2.7. Antimicrobial test

The test was carried out by using method from Cavalieri et al., [24], by placing 6 mm diameter of paper disc onto a plate of agar with microbes. The microbe culture was standardized to 0.5 McFarland standards which was approximately 10⁸ cells [25]. An amount of 100 mg/ml of streptomycin standard were used for each bacteria with three replicates for each plates; Staphylococcus aureus (ATCC 43300), Salmonella choleraesuis (ATCC 10708) and Escherichia coli (ATCC 25922). These plates were inverted and incubated at 30-37 °C for 18-24 hrs, until the sufficient growth has occurred. After incubation, each plate was examined. The diameters of the zones of complete inhibition were measured, including the diameter of the disc. Zones were measured to the nearest whole millimeter, using sliding calipers or a ruler, which was held on the back of the inverted petri plate.

3. Results and discussion

3.1. Morphological observation of zinc oxide nanoparticles and zinc oxide papers

The morphological observation of control paper and zinc oxide nanoparticles which observed via FESEM were exhibited as in Figure 1 and 2. There were two type of shapes observed in the powder which namely as rod-shape and spherical-shape. The spherical-shape is also known as nano-seeds of zinc oxide nanoparticles. The micrograph showed the size distribution was 356 nm in diameter and 1.52 μm in length of nanorod. On the other hand, the nano-seeds of zinc oxide achieved nano-sized with range of 64.1 nm to 87.5 nm. The distribution of particles size of zinc oxide–starch nanocomposites studied by Ma et al., [19] was from 35 nm to 45 nm of spherical shapes while Xu & Cai, [8] obtained nanorod shapes of zinc oxide with diameter 40 nm to 60 nm with 300 nm to 450 nm in length.

The occurrence of these two shapes might be due to duration of heating during synthesis process. The same conditions were obtained by Baruah et al., [26]. In the processes of producing photocatalytic paper using zinc oxide, the paper sheets are dipped in pretreatment solutions containing zinc acetate dihydrate and sodium hydroxide. The dipping was done until three times and was dried at 90 ℃ for 15 mins which temperature was higher. Besides that, the nanoseed zinc oxide paper is dipped into solutions of zinc nitrate hexahydrate and hexamine for 10 hrs at 90 ℃ and dried at 70 ℃ for 6 hrs. Hence, this explains the reason of the presence of two shapes of nano-zinc oxide.
Figure 1. Surface of control paper is observed via FESEM at 500X magnification showing (a) bleached control paper, and (b) unbleached control paper.

Figure 2. Flocs of zinc oxide particles observed via FESEM at 50kX magnification showing nano-rod and nano-spherical shapes.

Figure 3. FESEM image of unbleached paper which contained zinc oxide nanoparticles at 50kX magnification. Majority of zinc oxide was observed in lumps.

Figure 4. FESEM images of bleached paper which contained zinc oxide nanoparticles at 50kX magnification. Majority of zinc oxide was observed in spherical form.
Figure 3 and 4 exhibited the micrographs of zinc oxide unbleached and bleached paper accordingly. The distribution of zinc oxide was found more in bleached paper which most part of paper were located with spherical nano-particles of zinc oxide. On the other hand, majority of zinc oxide also existed on unbleached paper in lump form but fewer than on unbleached paper surfaces. Although the distribution types were different but zinc nanoparticles on both unbleached and bleached paper were ranged similarly as 57 nm until 143 nm. In order to confirm the existence of zinc oxide, EDX scanning was carried out which results are shown in Graph 1.

The deposition of nanoparticles on paper is confirmed as zinc oxide which occurs as zinc and oxygen on both unbleached and bleached papers. The element composition of zinc and oxygen on bleached paper was found higher at 27.25 % (zinc) and 38.72 % (oxygen) than unbleached paper at 25.27 % (zinc) and oxygen 33.72 % (oxygen). This may be due to the surface properties of both pulp as explained by Andreasson et al., [15]. The Total Chlorine Free bleached pulps were analyzed using Nuclear Magnetic Resonance (NMR) having larger average pore radius up to 16.5 nm compared to unbleached pulps with 15.0 nm. The pores were reduced to 14.8 nm after treated with high pH and salt concentration. Porosity test measures void of fraction in a material and Kamel et al., [27] stated that increment of paper porosity can consequently enhance the retention of any polymer solution due to the adsorption on surfaces and high potential penetration to fill in the voids.

![Graph 1. Percentage of zinc and oxygen on unbleached and bleached paper scanned via EDX.](image)

3.2. Physical, optical and mechanical properties of zinc oxide paper

There are three category of paper testing were carried out namely as physical, optical and mechanical paper properties. All test results were performed in Table 1. Paper physical test involved grammage and thickness of each paper sample. The grammage achieved by zinc oxide paper either unbleached or bleached are higher compared to the control papers. The addition about 13.26% and 15.13% of grammage for unbleached and bleached respectively most probably were due to the existence of zinc oxide nanoparticles. These results clearly proved that the in-situ synthesis was successfully done. The thickness showed a slight increment after incorporating the zinc oxide nanoparticles. This can be related to the presence of these particles which affect the arrangement of fibers that formed the papers.

| Paper testing       | Control paper | Zinc oxide paper |
|---------------------|---------------|-----------------|
|                     | Bleached      | Unbleached      | Bleached | Unbleached |
| Grammage (g/m²)     | 55.30         | 56.20           | 65.16    | 64.79      |
| Thickness (μm)      | 125.68        | 128.60          | 130.00   | 136.77     |
| Opacity             | 81.80         | 96.60           | 81.81    | 98.99      |
Optical paper properties involved paper opacity and brightness. The results showed that the presence of zinc oxide nanoparticles enhance the brightness of the paper by 0.40 % and 5.40 % for unbleached and bleached paper respectively. The opacity percentages of bleached and unbleached papers were slightly increased about 0.01 % and 2.39 % accordingly. The nanoparticles are observed to improve the brightness and opacity of papers which reacted as fillers. Mineral fillers such as precipitated calcium carbonate, clay and other functional filler materials in papermaking improve paper opacity and printability as well. Producing bright and opaque paper with good white colour has been generally achieved by applying zinc pigments and zinc oxide [28]. In instance, starch-zinc oxide and alginic acid-zinc oxide may modify fibre sheets up to 89.9 % and 93.1 % of opacity respectively compare to control fibre sheets which has 88.3 % of opacity [29]. Bulk zinc oxide coated paper is thicker and more opaque than base paper by having intensity of XRD spectra peaks from bulk-zinc oxide that is reduced to 60 % of intensity from the base paper [30].

Mechanical properties of paper consist of tensile, tear and folding test. Huge decrement of 22.2 % in tensile properties was detected by unbleached paper. However, the decrement of tensile properties for bleached paper was lower, about 10.7 %. Bleached fibres are more fibrillated and flexible compared to unbleached fibres due to the bleaching process that provide chemical action to the fibre surfaces. However, unbleached reading was higher than bleached papers due to the chemical treatments that have been carried out. According to Fišerová et al., [31], chemical treatments could reduce fibre strength and length because fibre bonding is condensed, and according to Hossain et al., [32], changes of interfibrillar region caused by chemical treatment contribute to rearrangement of fibrils along the tensile loading direction as this consequently applied higher stressed in the fibre which certainly reduce tensile strength. Tear properties of both unbleached and bleached paper presented same trend as tensile properties. The reductions percentages of both unbleached and bleached papers are 46.23 % and 37.35 %. Folding endurance showed 62.27 % and 13.51 % of decrement for unbleached and bleached papers. This degradation in terms of mechanical properties is expected because any presence of fillers on the surface of fibers which later formed into paper will affect greatly the fibre bonding. Interruption of fibre bonding creates crucial effects to paper strength mechanically.

3.3. Antimicrobial test

Referred to Table 2, it was found out that no inhibition zones are observed from the three bacteria tested. This happened might be because of low concentration of zinc oxide in paper sample as stated by Cavalieri et al., (2005)[24]. He showed that the concentration of the ampicillin interpretive’ categories for the break-point panel provide resistant interpretive of 32.0 mcg/ml (0.032 mg/ml) via Minimal Inhibitory Concentration (MIC) testing. The diameter of zinc oxide particles also could be the factor of percentage of inhibition growth such as study done by Baruah et al., (2010)[26], showed that particles size at 8 nm and 30 nm to 10 nm caused inhibition growth of S. aureus (95%) and E. coli (100%) respectively, compare to particles size at 50 nm to 70 nm for only 50% inhibition growth. Conversely, the paper sample gives the zinc oxide paper a mild antimicrobial properties by not spreading new bacteria or fungal on agar media as can be seen in Figure 5.
Figure 5. The inhibition zone and paper samples for standard with Streptomycin using S. aerus.

Table 2. Antimicrobial screening results

| Types of bacteria         | Screening results | Observation |
|---------------------------|-------------------|-------------|
| **Escherichia coli**      |                   |             |
| (gram negative)           | CB                | -           |
|                           | CUB               | -           |
|                           | T1-B              | -           |
|                           | T1-UB             | -           |
| **Salmonella choleraesuis**| CB                | -           |
| (gram positive)           | CUB               | -           |
|                           | T1-B              | -           |
|                           | T1-UB             | -           |
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\[ \begin{array}{c|c}
\text{Staphylococcus aeurus} & \text{(gram positive)} \\
\hline
\text{CB} & - \\
\hline
\text{CUB} & - \\
\hline
\text{T1-B} & - \\
\hline
\text{T1-UB} & - \\
\end{array} \]

*CB = control bleached, CUB = control unbleached, T1-B = hydrothermal bleached, T1-UB = hydrothermal unbleached

4. Conclusion
This study showed nano-ZnO synthesized using hydrothermal method is highly distributed on bleached paper as for its pore size of paper is more dispersed compare to unbleached paper prepared via in-situ approach. As expected the physical, optical and mechanical properties of paper were affected due to the presence of zinc nanoparticles. Antimicrobial test demonstrated promising results however more testing need to be carried out in next study.

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