



### Urban Forestry Program - Research Publication Circulation

- Title:** Potentials of Nanotechnology Application in Forest Protection
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- Date:** 2011
- Source:** TAPPI International Conference on Nanotechnology for Renewable Materials 2011  
TAPPI Press  
ISBN: 9781618394408  
Pages: 972 (1 Vol) Format: Softcover  
Publisher: Curran Associates, Inc. (Apr 2012 )  
<http://www.proceedings.com/13868.html>
- Description:** This joint research project formed by Southern University, Louisiana State University and the USDA Forest Service focuses on applying nanotechnology in forest health and natural resource management. The targeted nanotechnology is derived from a new generation of renewable composite nano-material called Copper-Carbon Core-Shell Nanoparticles (CCCSNs), which have received increasing attention because of their low cost, unique stabilities, and demonstrated performance against Formosan termite and fungal diseases. This paper describes (1) the physical and chemical properties of CCCSNs and their interactions with environment, (2) CCCSNs uptake/distribution patterns within tree seedlings/mature trees and their effects on tree growth, and (3) the effects of CCCSNs on blue-stain and white rot fungi, and Formosa termite control. The goal of our research is to develop safe and effective formulations and treatment strategies, which use nanotechnology to protect forest and forest products against decay fungi and termites.
- Full paper:** <http://www.tappi.org/Downloads/Conference-Papers/2011/2011-TAPPI-International-Conference-on-Nanotechnology-for-Renewable-Materials/11NANO21.aspx>
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## Potentials of Nanotechnology Application in Forest Protection

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### Abstract

This joint research project formed by Southern University, Louisiana State University and the USDA Forest Service focuses on applying nanotechnology in forest health and natural resource management. The targeted nanotechnology is derived from a new generation of renewable composite nano-material called Copper-Carbon Core-Shell Nanoparticles (CCCSNs), which have received increasing attention because of their low cost, unique stabilities, and demonstrated performance against Formosan termite and fungal diseases. This paper describes (1) the physical and chemical properties of CCCSNs and their interactions with environment, (2) CCCSNs uptake/distribution patterns within tree seedlings/mature trees and their effects on tree growth, and (3) the effects of CCCSNs on blue-stain and white rot fungi, and Formosa termite control. The goal of our research is to develop safe and effective formulations and treatment strategies, which use nanotechnology to protect forest and forest products against decay fungi and termites.

### Introduction

The development of science and technology at the nanoscale revolutionizes our ability to manipulate and fabricate the engineered nanomaterials and nanosized subjects. Nanomaterials have generated tremendous interests because they offer many opportunities to deliver unprecedented material performance. Metal-based nanoparticles such as Cu, Au, Ag, etc., have been used as industrial chemicals, catalysts, optical media, electrode and magnetic materials. However, because of their high surface area-to-volume ratio, many metallic nanoparticles often have a high propensity to readily oxidize or otherwise undergo other chemical reactions. To minimize this problem a protective layer may be formed around the metal nanoparticles. Metal-carbon core-shell nanoparticles, which have a metallic core encased by a carbon shell, can extend the life and broaden the uses of metallic nanoparticles. The metal cores in such nanoparticles are protected against chemical reactions, and the carbon shells may be functionalized to have specific physical, chemical, and biological properties. There exists an unfilled need for metallic nanoparticles that are stable in air and water, yet still exhibit desirable chemical properties, as well as a method of generating such metallic nanoparticles that is cost efficient and scalable for industrial use. This paper introduces a new generation of renewable composite nano-material called Copper-Carbon Core-Shell Nanoparticles (CCCSNs), which have a copper core encased by a carbon shell. Because of their low cost, unique stability, and demonstrated performance against Formosan termite and fungal diseases, the CCCSNs have great potentials in applications for forest protection. In this paper, we describe (1) the basic physical and chemical properties of CCCSNs and their interactions with environment, (2) the CCCSNs uptake/distribution patterns in tree seedlings and their effects on tree growth, and (3) the effects of CCCSNs on blue-stain and white rot fungi, and Formosa termite control. This is part of a joint research project formed by Southern University, Louisiana State University and USDA Forest Service that focuses on applying nanotechnology in forest health and natural resource management. The goal of our research is to develop safe and effective formulations and treatment strategies that use nanotechnology to protect forest and forest products against decay fungi and termites, thus, helping secure our natural resources and economy.

### Characterization of Copper-Carbon Core-Shell Nanoparticles (CCCSNs)

The CCCSNs are produced under a technology patent (US Patent Pending 60/772.325) using cotton fiber as a template. The fabricated products contain CCCSNs in carbon black and yellow powder (Figure 1). The CCCSNs can be suspended in water and oil (Figure 1). Analysis by TEM shows that CCCSNs are embedded in the porous carbon black substrate (Figure 2, left) and the copper core and carbon shell structure is formed during one step fabricating process (Figure 2, left, inset). The size of CCCSNs averages 50 nm with a range of 20-60nm. The carbon shell averages 5nm with a range of 2-10nm. The CCCSNs possess a unique stability when immersed in water or exposed to air. For instance, after 36 months of immersion in water under the ambient atmosphere, the CCCSNs are able to maintain their original structure (Figure 2, right). X-ray diffraction shows little to no change in the

nanoparticle's copper core after the immersion exposure and the carbon shell protects the copper core, which remains as Cu zero (Figure 2, right, inset). Our research also shows that the CCCSNs possess good chemical stability in various pH solutions. The analysis of conductivity of CCCSNs in different pH solutions (pH4-pH9) over a two-month period indicates no significant copper ion leaching out of CCCSNs (Figure 3).

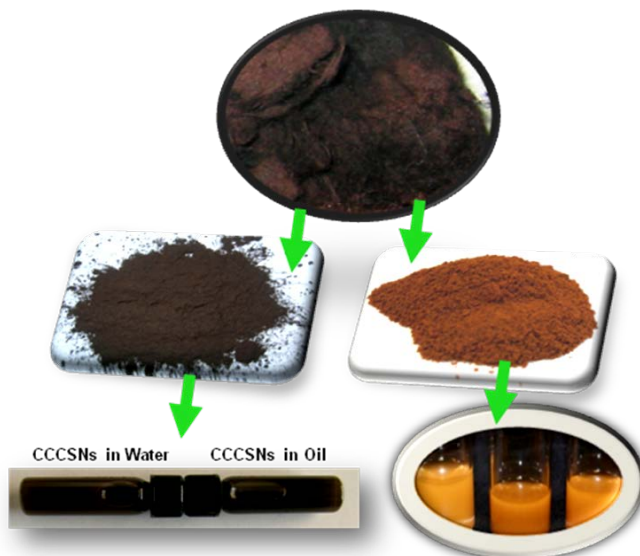


Figure 1. CCCSNs shown here are produced using cotton fiber and copper sulfate solution through one step processing. The fabricated products contain CCCSNs distributed in carbon black from cellulosic material (left) and yellow powder (right). The CCCSNs can be suspended in water and oil.

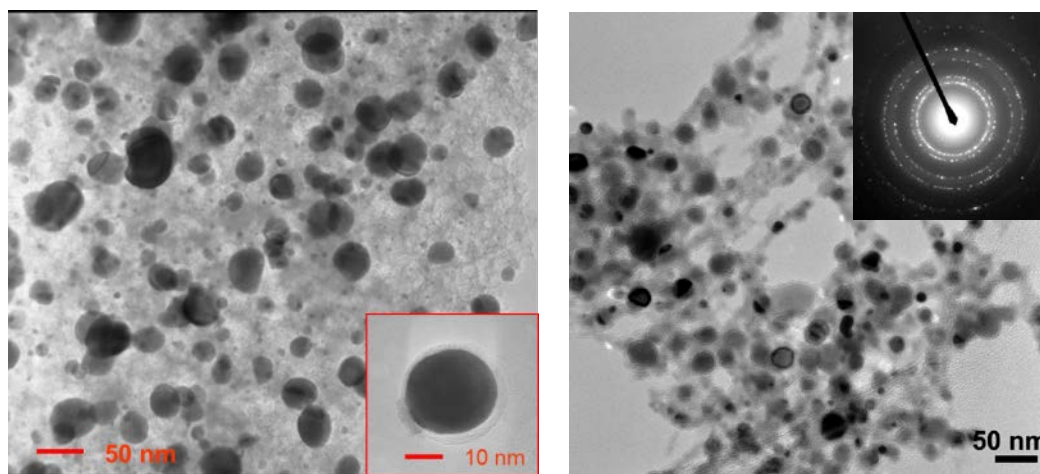


Figure 2. Left: TEM micrograph shows that CCCSNs are embedded in the porous carbon black substrate. The core shell structure (inset) is formed during one step fabricating process. Right: TEM image shows the stability of CCCSNs after 36 months of immersion in water under ambient atmosphere. X-ray diffraction (inset) shows no change to the nanoparticle's copper core after the exposure.

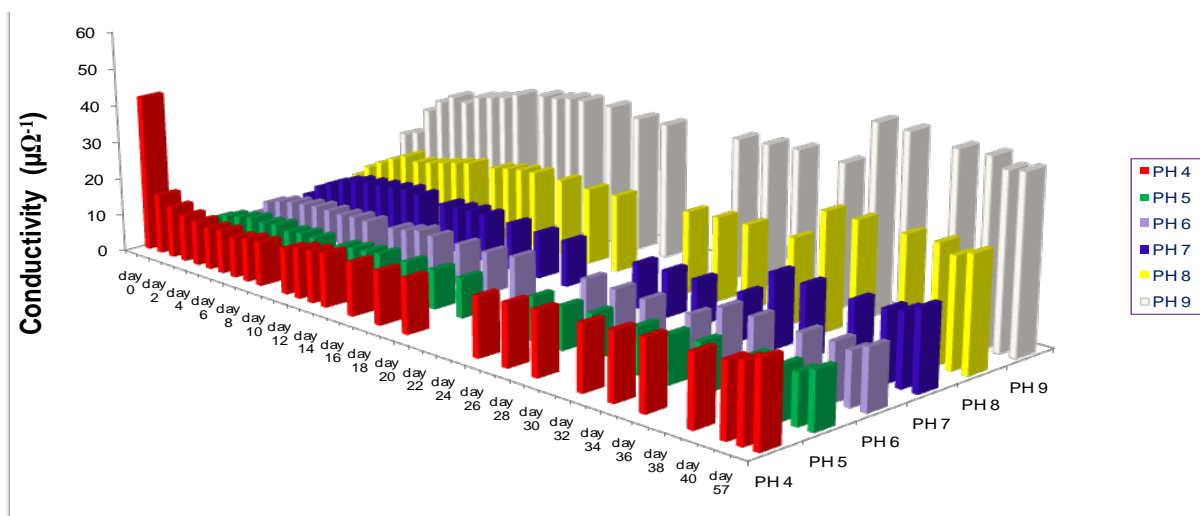


Figure 3. CCCSNs possess good chemical stability. The above chart shows the conductivity as a function of immersion time of carbon black powder containing CCCSNs in different pH solutions, indicating no significant copper ion leaching out of CCCSNs.

### CCCSNs Uptake/Distribution Patterns in Tree Seedlings and Their Effects on Tree Growth

Understanding the effects of CCCSNs on tree physiology is the first step toward any future application in forestry. In this case, we used bald cypress (*Taxodium distichum*) for a preliminary test. Bald cypress is a wetland species that is an ideal study subject for testing CCCSNs effects on tree physiology in water saturated environment (why?). Our study indicates that CCCSNs can enhance Cu uptake in bald cypress seedlings but show no significant effects on height, diameter, and biomass growth of the seedlings (Figures 4 and 5).

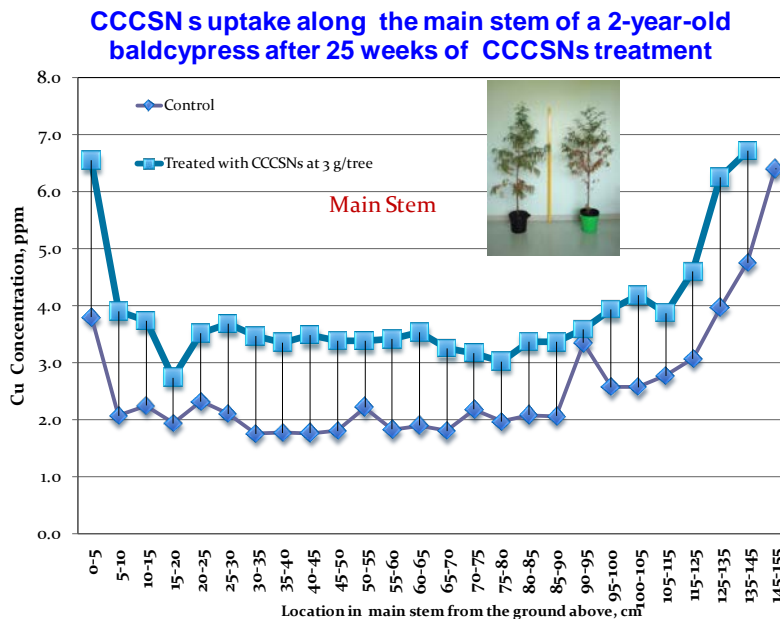


Figure 4. CCCSNs enhance Cu uptake along the main stem of a 2-yr-old bald cypress seedling after 25 weeks of CCCSNs treatment. The inset photo shows the bald cypress control (left) and CCCSNs treated (right) seedlings.

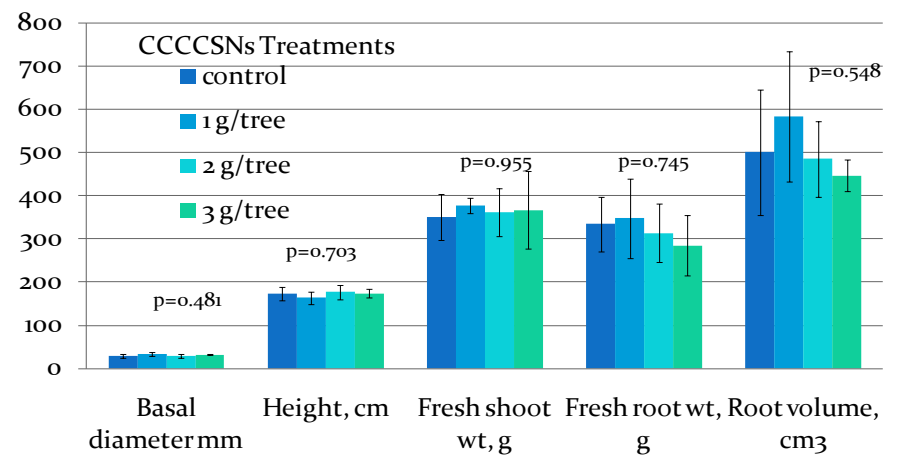


Figure 5. CCCSNs treatments show no significant effects on diameter, height, shoot and root weight, and root volume of bald cypress seedlings after 20 months of the treatments.

### Effects of CCCSNs on Blue Stain and White Rot Fungi, and Formosa Termite Control

Our studies have shown that wood treated with CCCSNs is highly resistant to a common white rot decay fungus (*Trametes versicolor*) (Figure 6). White rot fungi are a major group of fungi that cause tree decay and wood decay. The treatments of properly formulated CCCSNs can be used to increase the decay resistance of trees and commercial wood products.

Our *in-vitro* test against the Southern pine beetle associated blue stain fungus (*Ophiostoma Minus*) shows that proper formulation of CCCSNs possesses a strong antifungal property (Figure 7). The Southern pine beetle associated blue stain fungi are the number one natural enemy that causes huge destruction to loblolly pine and other southern pines, all of which are key commercial species for timber and forest product industries. Properly formulated CCCSNs treatment can be used to treat pine seedlings during planting and mature trees to increase their pest resistance against the blue stain fungi.

In Southern USA, Formosa subterranean termites (*Coptotermes formosanus*) are particularly destructive to residential homes that are made of wood. Current industrial treatments have come under attack when toxic elements such as arsenic are used. There is a great need to develop and to test new chemicals for wood-based treatments that *safely* secure residential structures. Our research has shown that wood treated with CCCSNs is highly resistant to Formosa subterranean termite attack (Figure 8). Actual copper content in CCCSNs treated wood is less than 0.25wt%, which is significantly lower than the copper content of commercially ACQ treated wood. The CCCSNs treatment can be used as a viable and environmental friendly alternative for wood treatment against Formosa termites and decay fungi.



Figure 6. Wood treated with CCCSNs shows remarkable decay resistance against white rot fungus, *Trametes versicolor*, after 16 weeks of testing based on AWPA E10 Method (for Decay test).



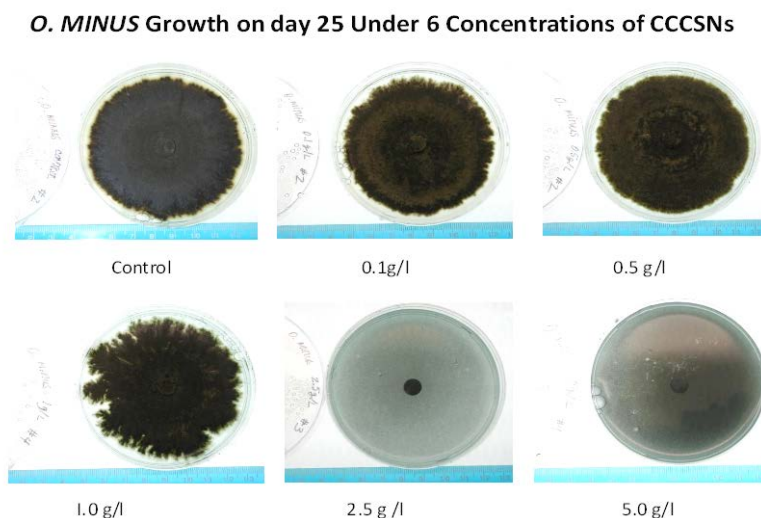
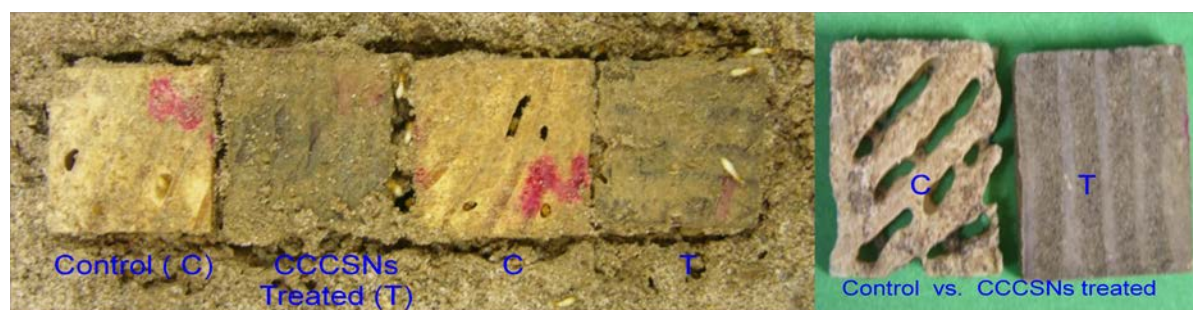


Figure 7. *In-vitro* test against Southern pine beetle associated blue stain fungus (*Ophiostoma Minus*) shows that the CCCSNs formulations at 2.5g/l and 5.0g/l possess a strong antifungal property.



Formosa Termite test: control (C) shows significant termite damage

Figure 8. Wood treated with CCCSNs is highly resistant to Formosa subterranean termite attack. The test was conducted based on the AWP A E1 Method (for Termite).

### Summary

Our research has shown that CCCSNs, a new generation of environmentally friendly nanomaterial, will have a great potential to be used for forest protection against decay fungi, blue stain fungi, and Formosa termites. This joint effort formed by Southern University, Louisiana State University and USDA-FS will significantly advance research on Southern pine beetle associated blue stain fungi and other important forest pests. Our long-term goal is to develop safe and effective formulations and treatment strategies for commercialization through industrial partnerships that use nanotechnology to protect our forest and forest products. This effort will lead to development of new nanotechnologies that protect forest products against woody decay and termites, thus, helping secure our natural resources and economy. This research may have broader applications in pest control in the field of Agriculture.

### Acknowledgements

The funding of the project was provided through USDA/NIFA/CBGP Grant No. 2008-38814-04771.

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