Surface Functionalization of TiO_2-CNF Films with Au and Ag Nanoclusters for Visible Light Photocatalysis

Abstract. *Titanium dioxide (TiO_2) nanoparticles were dispersed in a cellulose nanofiber (CNF) matrix to form composite films. Subsequently, gold (Au) and silver (Ag) nanoclusters were formed on the film surfaces using simple reduction techniques. Au- and Ag-doped TiO_2 films showed a wider spectral range for photocatalysis and enhanced mechanical properties. The ability of the films to degrade methylene blue (a model organic dye) in simulated sunlight has been demonstrated using UV-visible spectroscopy. Reusability and mechanical integrity of the films after irradiation were also investigated.*

Keywords. Cellulose nanofiber films, titanium dioxide, photocatalysis, gold, silver, reusable.

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Introduction. CNF provide a flexible, biocompatible matrix for particle dispersion with hydrophilic surfaces that are favorable for functionalization. Titanium dioxide (TiO_2) is a well-known photocatalyst that was incorporated into CNF to form films that were capable of photodegrading organic molecules under UV light. To expand the range of applications of the films to natural water sources, the catalyst system must be able to use solar energy efficiently. TiO_2 will become photocatalytically active upon visible light irradiation by coupling with noble metals such as Au and Ag [1]. In this work, Au and Ag nanoclusters were formed on the surface of TiO_2-CNF films by *in-situ* reduction methods. The effect of nanocluster formation on photodegradation, mechanical properties, and reusability was evaluated.

Methodology. Cellulose nanofiber suspension (0.5 wt% CNF aq.) was obtained from the USDA Forest Service, Forest Products Laboratory and was processed using a previously published procedure [2]. TiO_2 (~25 nm) was dispersed in water, added to the CNF suspension, and sonicated until evenly mixed. The TiO_2-CNF mixture was transferred to a Petri dish (8 cm diameter) and dried for several days in 65% relative humidity at 25°C. TiO_2-CNF films were immersed in silver nitrate solution and irradiated with UV light for 30 seconds to initiate photoreduction. Other dried films underwent citrate reduction using gold (III) chloride precursor to form Au nanoclusters on the surface of the films.

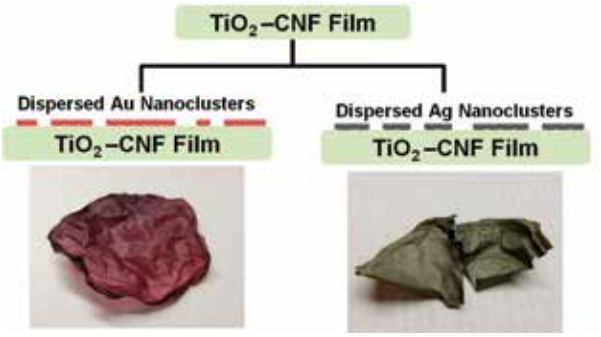

Figure 1. *Schematic and digital image of dried Au-TiO_2-CNF film (left) and Ag-TiO_2-CNF (right).*

The films were immersed in 25 mL of methylene blue (MB) solution and immediately irradiated for one hour with global AM 1.5 simulated sunlight (ASTM standard spectrum). 200 µL of solution was extracted every five minutes for analysis by UV-visible spectroscopy.

Results. Photoreduction of Ag and citrate reduction of Au proved to be simple, effective methods for *in-situ* formation of metal nanoclusters on TiO_2-CNF films. Both methods resulted in extensive surface coverage with bimodal average particle-size distributions. Discrete Ag particles were ~80 nm in diameter with nanoclusters averaging ~400 nm, while Au particles were ~70 nm in diameter with larger groups of particles, averaging ~250 nm.

All three sets of films were subjected to irradiation under simulated sunlight in MB dye solution for 60-minute intervals. The change in MB concentration was monitored using UV-Vis spectroscopy. Au-TiO2-CNF and Ag-TiO_2-CNF films (75% total degradation of original concentration) outperformed TiO_2-CNF films (60% total degradation), with the MB control solution showing only a slight change.

The films were also immersed in MB without irradiation to evaluate the extent of MB adsorption. Au-TiO_2-

CNF showed the strongest adsorption of MB from 0–35 minutes, likely due to roughness and the negative charge of the catalyst surface. The concentration drop may also be attributed to a strong affinity between Au and the MB thiol group.

After 60 minutes of irradiation, wet TiO_2-CNF films became weak and were prone to mechanical breakdown. Films with Au and Ag were much more durable and were able to undergo multiple cycles of irradiation. Reusability is an important feature of the films because it enables maximum use of the catalysts without mechanical failure. After several 60-minute irradiation cycles, photocatalytic performance of the Au-TiO_2-CNF (4 cycles) and Ag-TiO_2-CNF (5 cycles) films diminished to that of the original TiO_2-CNF system.

Mechanical properties of the films were also influenced by the presence of Au and Ag. Dynamic mechanical analysis performed on all films before irradiation indicated that Au-TiO_2-CNF and Ag-TiO_2-CNF films had higher values of elastic modulus and tensile strength than their TiO_2-CNF counterparts. Irradiation seems to weaken the CNF matrix of all films by a combination of water absorption and oxidation by TiO_2. Distribution of TiO_2 throughout the matrix can limit water absorption by the films compared to neat CNF, but it cannot be completely prevented. Au and Ag nanoclusters may have the ability to redirect electrons away from the matrix and distribute them more evenly across the surface, limiting damage to the CNF and enabling extended reusability. Despite the enhanced properties of the Au- and Ag-containing films, multiple irradiation cycles still led to considerable decreases in modulus and tensile strength. Ag-TiO_2-CNF films retained a significantly higher percentage of strength and stiffness than Au-TiO_2-CNF films. This accounted for the extended use (extra reusability cycles) of Ag-TiO_2-CNF films and may be attributed to continued photoreduction of Ag nanoclusters throughout the irradiation process.

Stability of the films was further confirmed by using UV-visible spectroscopy to monitor MB solutions for particle leaching during irradiation. Spectra collected throughout the irradiation cycles show no absorbance peaks in the 300–600 nm wavelength range, where characteristic peaks for TiO_2, Ag, and Au nanoparticles are known to appear [3].

Conclusions. Composite TiO_2-CNF films showed strong photocatalytic activity in UV light, and subsequent surface modification with Au and Ag nanoclusters enhanced photocatalytic efficiency in simulated sunlight. Functionalization of film surfaces with Au and Ag improved reusability of the TiO_2-CNF films by minimizing mechanical deterioration. Ag-TiO_2-CNF films proved most effective from the standpoints of photodegradation performance, reusability, and limitation of mechanical deterioration. Results of this study indicate that Ag-TiO_2- CNF and Au-TiO_2-CNF films are promising for future applications for degrading organic molecules in natural water sources.[4]

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Production and Applications of Cellulose Nanomaterials

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Cellulose nanocrystals incorporated within the overcoat varnish of the cover!

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