



Reusable photocatalytic titanium dioxide–cellulose nanofiber films

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ABSTRACT

Titanium dioxide (TiO₂) is a well-studied photocatalyst that is known to break down organic molecules upon ultraviolet (UV) irradiation. Cellulose nanofibers (CNFs) act as an attractive matrix material for the suspension of photocatalytic particles due to their desirable mechanical and optical properties. In this work, TiO₂–CNF composite films were fabricated and evaluated for photocatalytic activity under UV light and their potential to remove organic compounds from water. Subsequently, gold (Au) and silver (Ag) nanoclusters were formed on the film surfaces using simple reduction techniques. Au and Ag doped TiO₂ films showed a wider spectral range for photocatalysis and enhanced mechanical properties. Scanning electron microscopy imaging and energy dispersive X-ray spectroscopy mapping were used to evaluate changes in microstructure of the films and monitor the dispersion of the TiO₂, Au, and Ag particles. 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 were also investigated.

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1. Introduction

Cellulose nanomaterials (CNs) have gained considerable interest as an abundant biocompatible material with potential applications in a wide variety of fields ranging from tissue scaffolds to flexible electronics. Two general classes of CNs are cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs), both of which exhibit interesting physiochemical behavior and possess mechanical properties that are superior to bulk cellulose [1]. CNs have previously been studied as reinforcement materials for various polymer matrices [2,3], but have recently been integrated into biosensors [4], packaging [5], protective coatings [6], drug delivery systems [7], and antimicrobial films [8]. For these new functional composite systems, the individual CN particle surfaces or CN composite surfaces are functionalized with other polymers/chemicals [9], or inorganic nanoparticles [10–12]. Since, CNs are flexible, hydrophilic biopolymers that can be cast into films of different shapes and sizes, and have surfaces that are readily functionalized, they seem well suited for use as a matrix for nanoparticle dispersions [1]. Furthermore, the renewability, degradability, and non-toxicity of CN reduce concerns about negative environmental impact from the matrix material.

Titanium dioxide (TiO₂) is a well studied, stable photocatalyst capable of degradation of organic molecules via electron hole pairs that are formed upon irradiation with UV light that exceeds the material's bandgap [13]. This photocatalytic ability makes TiO₂ an ideal model material for investigating novel photocatalytic configurations. Although TiO₂ nanoparticles have been used for water decontamination applications in the past [14,15], their subsequent collection and removal is difficult. The presence of inorganic nanoparticles throughout a natural water supply or even a wastewater treatment reservoir presents concerns to human health [16,17]. Therefore a photocatalytic configuration with such nanoparticles being incorporated in a durable, biocompatible matrix has the potential to both enhance the stability of the photocatalytic nanoparticles and allow water treatment without further contamination.

Anatase, with a relatively large bandgap (~3.2 eV) is the TiO₂ phase that displays the most efficient photocatalytic activity in the UVA region of the electromagnetic spectrum (400–315 nm) [13]. Expansion of the photocatalytic properties of such particles into the visible region would lead to a more efficient use of solar energy, increasing the range of applications of TiO₂ photocatalysts. One way to increase the minimum wavelength of irradiation necessary for photocatalysis is through surface functionalization with noble metals (e.g. Au and Ag). The presence of metal nanoparticles has been shown to enhance the electron distribution and transfer on the surface of TiO₂ [18,19]. Increased charge separation between electrons and holes decreases the speed and amount of recombination, thereby facilitating enhanced oxidation of

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molecules adsorbed on the TiO₂ [20]. Several noble metal doped TiO₂ composites have been fabricated as nanoparticle systems, but not as substrate-free supported catalyst films [18–21].

Previous studies investigated functionalization of paper [22] or regenerated cellulose [23] with TiO₂, however, this is the first study on the processing and design of photocatalytic TiO₂-CNF-based films that are usable across the entire solar spectrum. Our group previously functionalized alpha synuclein protein with nanoparticles before progressing to functionalizing biopolymer fibers. This study investigated the photocatalytic properties of CNF films that incorporated TiO₂, Au-TiO₂ and Ag-TiO₂ nanoparticles towards the decomposition of the model organic compound methylene blue (MB), which is used to examine their potential to degrade organic compounds in water.

2. Materials and methods

2.1. Materials

Titanium dioxide (anatase), methylene blue, silver nitrate, gold (III) chloride, and trisodium citrate were obtained from Sigma-Aldrich (St. Louis, MO). Cellulose nanofiber suspension (0.5 wt% CNF, 1.3 mmol COONa per g CNF, aq.) was obtained from the USDA Forest Service-Forest Products Laboratory (Madison, WI). The cellulose processing followed a previously published procedure [24]; a brief description is given here. Purified Eucalyptus pulp was suspended in water containing (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO), sodium bromide (NaBr), sodium hydrogen carbonate (NaHCO₃) and sodium carbonate (Na₂CO₃). The oxidation process consisted in slowly pouring sodium hypochlorite (NaClO) at room temperature for five hours under constant mixing. After reaction completion, the TEMPO-oxidized pulp was then passed through refiners (0.1 mm and 0.05 mm gap) and microfluidizer to get a 0.5 wt% CNF suspension in water. From TEM images the CNFs were determined to be 4–20 nm in diameter. Due to the interconnected nature of the CNFs on the TEM grids, exact lengths of individual fibers were difficult to determine with observed values ranging from 200 nm to greater than 1000 nm.

2.2. Fabrication of TiO₂-CNF composite films

A stock dispersion of TiO₂ was prepared by dispersing TiO₂ nanoparticles (~21 nm, 2 g/L) in water through a combination of mechanical mixing and sonication. The TiO₂ solution (5 mL) was then mixed with as-received CNF solution (40 mL) and sonicated until well dispersed and free from agglomeration. The pH of each solution was adjusted using NaOH and HCl. Dilute aqueous solutions (1 mL) of TiO₂ and CNF were injected into the cell and zeta potential was measured using a zeta sizer nano-z, (Malvern Instruments, Westborough, MA). Electrophoretic mobility was converted to zeta potential using the Smoluchowski model. The CNF-TiO₂ mixture was then transferred to a Petri dish and dried in a controlled humidity chamber (~65% relative humidity, 25 °C) for several days until all water was removed. The resulting films had a consistent diameter of 8 cm and thickness of 30.25 μm ± 4.35.

2.3. Photodeposition of silver on TiO₂-CNF film

The dry TiO₂-CNF film was immersed in a silver nitrate solution (11.8 mM, pH 7, aq.). The system was then irradiated with UV light (~400 W) for 30 s with a noticeable change in color of the film from white to gray. The film was removed from the solution, rinsed with water, and dried overnight.

2.4. Citrate reduction of gold on TiO₂-CNF film

Trisodium citrate (8 g) was added to a gold (III) chloride solution (15 mM, pH 12, aq.). The TiO₂-CNF film was added to this solution and heated to 60 °C. After 15 min, the solution and film began to turn dark pink/purple. The reaction continued for 6 h, and then the film was rinsed with water and dried overnight. No oxidation or leaching of particles from the surface was observed visually, via UV-visible spectroscopy of the solutions, or via XPS analysis of the film surfaces.

2.5. Characterization of films

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were performed on the top surface of the films using a Philips XL40 SEM in SEI mode at 2000× magnification. No special sample preparation or coating was performed on the films in order to avoid any interference with EDS results. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Kratos spectrometer. Tensile stress-strain tests were conducted using a TA Instruments Q800 Dynamic Mechanical Analyzer (DMA) used in controlled force mode, from which elastic modulus and ultimate tensile strength of CNF films were determined. The tensile tests were performed at 27 °C and 50% relative humidity using a 1.0 N/min load rate and initial pre-load of 0.005 N. Tensile specimens approximately 2 mm wide and 12 mm long (as measured by micro-caliper) were then carefully mounted onto the DMA. The lengths for determining strain were measured with calipers as the distance between DMA grips. Eight to ten tensile specimens were tested and averaged for each condition.

2.6. Photodegradation of methylene blue

The films were immersed in 25 mL of methylene blue solution (0.01 g/L, aq., initial absorbance of 1.27 ± .070) and immediately placed under the xenon arc solar simulator (Sol3A Class AAA Solar Simulator IEC/JIS/ASTM, Newport Corporation, Irvine, CA). The system was irradiated for one hour with global AM 1.5 simulated sunlight (ASTM standard spectrum) and 200 μL of solution was extracted every 5 min for analysis by UV-visible spectroscopy (Molecular Devices, Sunnyvale, CA).

3. Results and discussion

3.1. Film fabrication and optimization

Several parameters were varied to optimize the film fabrication process. The pH of the TiO₂ and CNF solutions was changed over a range of 3.5–10, and zeta potential was measured to better understand particle interactions. The CNF remained negatively charged over this entire pH range (Supplementary Fig. S1). Anatase TiO₂ has a measured isoelectric point around pH 8–8.5, with a negative surface charge occurring at pH > 8.5 [22]. The least particle agglomeration in the films was observed when mixing pH 10 CNF and TiO₂ dispersion due to electrostatic repulsion.

Resulting films displayed some TiO₂ agglomeration upon drying, but the surface distribution was good enough that the small loss of surface area did not significantly affect its photocatalytic ability. Use of surfactants limited agglomeration; however, these films showed decreased photocatalytic performance, which may be attributed to greater electron-hole recombination by the polymer surrounding the catalyst particles. Wrinkling of the films that occurred upon drying (Fig. 1) is believed to be inconsequential since the tests are performed in an aqueous environment (e.g.

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