Mesoporous nanocrystalline TiO_2 deposited on Bacterial Nanocellulose membrane scaffolds through a low-temperature method: an active membrane for methylene blue photocatalytic degradation

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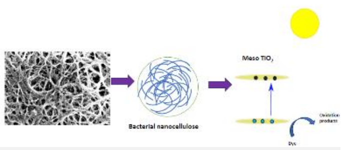

Environmental pollution in water is one of the most alarming ecological problems facing humanity. Heterogeneous photocatalysis is a promising alternative to cope with it due to the possibility of using light and robust semiconductors to efficiently decompose a variety of pollutants. Mesoporous TiO_2 presenting high surface area and nanocrystalline walls have been studied for photocatalysis applications, either as powders or thin films. However, the study of self-supported membranes and the use of low-temperature methods that lead to active photocatalysts is less explored. We demonstrate a method to process nanocrystalline titania on a bacterial nanocellulose scaffold. This nanocomposite represents an alternative to explore new and sustainable flexible substrates with high active surface area that could increase the photocatalytic degradation of emergent pollutants in water. TiO_2-X% was morphologically, structurally and optically characterized. The photocatalytic activity was evaluated using the degradation of methylene blue under UV light as a model reaction.

Introduction

The increase in emerging pollutants in water is one of the environmental problems currently affecting humanity. Among the alternatives to deal with this environmental issue, heterogeneous photocatalysis stands out due to its ability to utilize solar light, achieve complete degradation of contaminant molecules in short periods, and enable the possible reuse of the photocatalyst.[1]

The textural and morphological properties (i.e., high surface area, controlled pore size, crystalline character) of mesoporous and nanocrystalline TiO_2 make this semiconductor a promising material to be studied as a high-performance photocatalyst.[2,3] On the other hand, hybrid aerogel membranes possess mechanical stability and excellent textural properties of bacterial nanocellulose (BC), making this material promising as a template for nanostructured semiconductors. [4] Therefore, using membranes as support for mesostructured TiO_2 appears to be a valuable alternative to combine the best properties of mesostructured TiO_2 and bacterial nanocellulose, combining the enhanced adsorption and photocatalytic performance in the degradation of emerging pollutants in water with optimized processability. In order to combine a flexible biopolymer substrate and a nanocrystalline inorganic component, soft methods that permit to extract templating agents and lead to low-temperature crystallization have to be developed.

In this work, we studied the effect of different synthesis routes for mesoporous nanocrystalline TiO_2 deposited on bacterial nanocellulose and its impact on the structural, morphological, and optoelectrical properties of the composite material. We aimed at self-sustaining membranes with high exposed surface area and nanocrystalline walls. This study aims at assessing the photocatalytic properties of these hybrid nanocomposites for the degradation of methylene blue in water.

Material and Methods

The mesostructured TiO_2 over bacterial nanocellulose was synthesized through the combination of sol-gel synthesis and Evaporation-Induced Self-Assembly (EISA). Pristine nanocellulose membranes were obtained from hydrated BC membranes produced from *Komagataeibacter xylinus* (ATCC 53,524) and supercritically dried.[3] The titania-modified membranes were created by dip-coating the pristine membrane into a mesoporous precursor TiO_2 sol ($Ti:C_2H_6O:F127:HCl:Acac:H_2O$; 1:40:0.005:4:1:15; TiO_2-100%). Different amounts of TiO_2 were studied:10%, 20%, 40%, and 100%. Subsequently, the membranes were dried at 40°C overnight in an oven. Finally, the membranes underwent solvothermal treatment in ethanol for 12 hours at 180°C in a hydrothermal Teflon vessel. The final samples were collected and dried at 40°C overnight. All the samples were structurally characterized by XRD, SEM, UV-vis (DRS), N_2 adsorption, and TGA analysis. The degradation of methylene blue evaluated the photocatalytic activity of the photocatalyst in a designed membrane photoreactor (Microtube), under UV⁻Vis illumination from a 200 W Xe⁻Hg arc lamp (Lightningcure LC8, Hamamatsu, λ = 250⁻600 nm.

Results and Discussion:

After EISA, TiO_2-X% hybrid samples showed a biphasic system in which fiber-like textures and porous titania could be identified. Low-temperature treated samples presented amorphous titania. SEM images showed very well-defined arrays of TiO_2 nanoparticles smoothly coated over the nanofibers (**Figure 1**). The amount of TiO_2 on the nanofibers varied, correlating with the amount of sol used in the synthesis. In addition, XRD patterns (**Figure 2**). of solvothermally treated samples reveal anatase as the crystalline structure of the TiO_2; in addition, the XRD peaks belonging to the bioscaffold shift to higher angles, suggesting a contraction in the nanocellulose framework. FTIR of these samples indicate a decrease in the $\nu_{C\text{-}H}$ signals, suggesting that the templating agent is mostly removed. We can advance that the solvothermal process leads to a significant reorganization of the titania network that leads to crystallization, accompanied by changes in the nanocellulose that become more compact. DRS analysis indicated that TiO_2-X% membranes have the main absorption region in the UV light, (λ < 335 nm) consistent with the band gap for nanostructured TiO_2. N_2 adsorption revealed an increase in the superficial area of TiO_2-X%compared with the area shown by the pristine material.

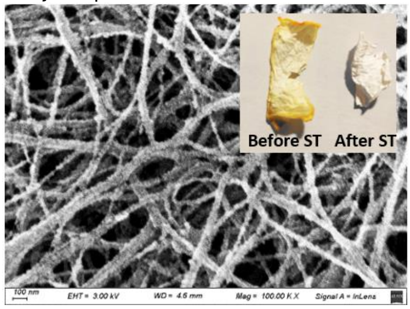

Figure 1. SEM micrograph of TiO_2-20%

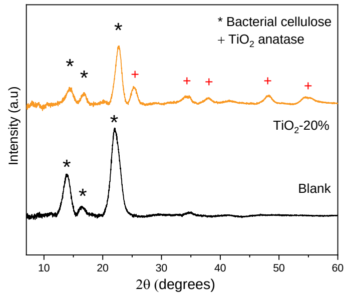

Figure 2. XRD of the pristine membrane and TiO_2-20%.

All samples exhibited methylene blue degradation under UV light. The photocatalytic performance demonstrated an increase in dye degradation compared to that achieved with photolysis and the pristine membrane. Dye degradation is lower in the samples studied with respect to P-25, which can be attributable to a lower crystallization degree. However, these samples are reusable, and their ease of use is promising. Work in progress is aimed at optimizing the solvothermal treatment to increase crystallinity.

Conclusions

The sol-gel synthesis and EISA method enable the coating of mesostructured TiO_2 over bacterial nanocellulose, modifying the structural, morphological, and optical properties of the membrane. The use of TiO_2-X% membrane improves methylene blue degradation under UV light.

Acknowledgments

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