Hybrid Bacterial Cellulose@SiO2-TiO2 Hybrid Aerogel for In-Flow Photo-assisted Removal of Water Contaminants

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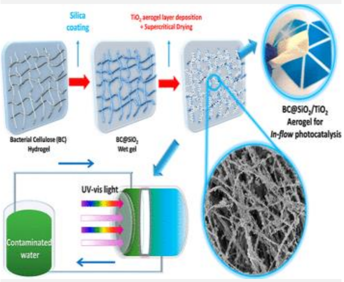

Hybrid aerogels were prepared by a sequential layered sol-gel deposition of SiO_2 and porous TiO_2 onto BC, forming a high surface area and crystalline aerogel after supercritically drying. The silica interlayer between the biopolymer and the titania photocatalyst shown deep correlation on the structure and composition of the hybrid aerogel membranes. The optimized $BC@SiO_2–TiO_2$ hybrid aerogel displayed a 12-fold decoloring of methylene blue for *in-flow* photocatalytic in contrast with $BC@TiO_2$ material, improvement even juxtapose with most supported-titania materials reported. Moreover, the material developed herein was applied to sertraline drug removal, which is a model emergent contaminant, thus further demonstrating their potential for water purification.

Introduction

In recent years, nanostructured materials have become key players in water treatment, offering efficient pollutant removal thanks to their unique properties. TiO2-based nanomaterials, renowned for their photocatalytic activity, face challenges in practical use due to separation difficulties and environmental concerns. To overcome this, functional nanocomposites like photocatalytic aerogels are being developed, combining efficient contaminant removal with easy handling [1].

Nanocellulose, especially bacterial cellulose (BC), emerges as a promising support for nanostructured membranes in water purification. By integrating BC with silica and TiO2 aerogels, researchers aim to enhance both mechanical stability and photocatalytic performance [2]. Hence, coating BC membranes with silica interlayers to protect against degradation and improving pollutant degradation, may result in highly effective BC@SiO2@TiO2 aerogel membranes for water purification.

The procedure and results displayed here have been already published on *ACS Appl. Mater. Interfaces* 2023, 15, 19, 23146–23159.

Material and Methods

Bacterial cellulose (BC) is biosynthesized by *Komagataeibacter rhaeticus* (BAA 2831) as described before [3]. Briefly, a Hestrin-Schramm (HS) media is used for cell cultivation, while a HS glucose-rich media is used to grow the bacteria and cellulose sheets production.

To coat the BC fibers with silica, two membranes were submerged in different tetraethylorthosilicate (TEOS):H_2O mixture diluted in 15 mL ethanol, yielding different covering morphologies. After 24h on orbital shaker, NH_4OH was added, kept under agitation for another 24h, later washing with ethanol, obtaining $BC@SiO_2$. Conditions used are shown in Table 1.

Table 1. Experimental conditions to obtain $BC@SiO_2$

Sample	TEOS / µL	H_2O / µL	NH_4OH / µL
BCS1	1125	360	250
BCS2	2250	360	250
BCS3	2250	720	500
BCS4	4500	720	500
BCS5	4500	1080	750

After SiO_2 coating and washing, or pristine, the membranes could undergo a porous titania coating, submerging the membranes into 15 mL ethanol, 1750 µL Titanium *tert*-butoxide (TBOT), 250 µL HCl, 360 µL H_2O, and remained 24h on orbital shaker. The following day, 2 mL of propylene oxide (PO) was added to previous solution, inducing TiO_2 gel formation. Subsequent to 24h gel-aging, the membranes were separated from the gel, and washed with ethanol.

Followed by proper titania coating process, samples underwent a hydrothermal treatment for 24h at 150 °C to crystallize TiO_2. Later, these samples, and samples without titania, went through a supercritical CO_2 drying, obtaining the aerogel structures.

Results and Discussion

Initially, to have a glimpse on the morphological aspect of the material, scanning electron microscopy analysis was made on dried samples, and the results can be observed in Figure 1. It is possible to infer that the silica synthesis forms a homogenously coat on BC fibers, growing thicker as the silica amount increases, but keeping the morphology almost unchanged. On the other hand, titania coating over the silica results in spheres, or agglomerates, randomly distributed on its surface.

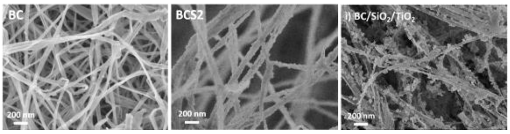

Figure 1. SEM micrographs of pristine BC, BC@SiO$_2$, and BC@SiO$_2$@TiO$_2$

To achieve a good photocatalytic activity, TiO$_2$ anatase crystal phase is desired. Samples with different SiO$_2$ amount, but same TiO$_2$ synthesis was measured in XRD, and results are display in Figure 2. Asterisks represents crystalline peaks of bacterial cellulose (4.4°, 16.8°, and 22.6°), other peaks represent titania phases. It is important to indicate that sample without silica (BC-T) present a peak at 30.6° referent to brookite crystal phase, contrasting with the other samples. Thus, silica may have contributed in anatase stabilization, represented by remaining peaks, when compared with reference (PDF 21-1272), especially the higher intensity peak at 25°.

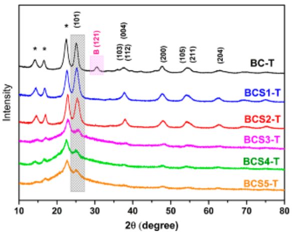

Figure 2. XRD patterns of BC@TiO$_2$ and BC@SiO$_2$@TiO$_2$ aerogels.

As follows, samples were submitted to photocatalytic tests under UV light using an *in-flow* membrane reactor. Methylene blue (MB) degradation for different samples can be observed in Figure 3. The different samples different were tested in the same conditions (5 ppm MB), highlighting the synergetic effect of silica on degradation of this model emerging contaminant.

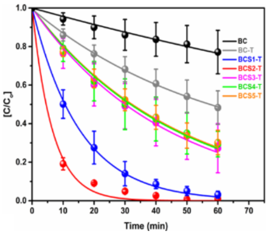

Figure 3. Comparison of the kinetic profile of different samples for MB removal performance.

Not only the material presents itself as good candidate for MB degradation, it is also capable of degrading Sertraline (another emerging contaminant), and has been tested up to five recyclability cycles, maintaining its activity higher than 80%.

Conclusions

In essence, a hybrid aerogel composed SiO$_2$ and TiO$_2$ supported on BC was developed with outstanding photocatalytic response using an in-flow reactor. Controlling the amount of silica on BC fibers, properties such as porosity, surface area, Ti loading and photocatalysis rate could be tuned, thus, an optimal condition was obtained from experiments performed. Using BC membrane as support, and having produced a material that can be recycled, the hybrid designed could be applied in larger scales or under real sunlight exposition.

Acknowledgments

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