Development of SiO_2/TiO_2 Nanostructured Aerogel Photocatalysts for Environmental Applications

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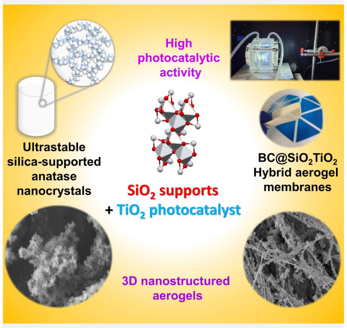

In the present presentation we overview on recent studies on development of SiO_2/TiO_2 based aerogels to design high performance photocatalysts for water purification. We emphasize the use of SiO_2 nanostructured supports as a versatile approach to enhance the structural, textural, and photocatalytic properties of TiO_2. By using novel $TiCl_4$ sol-gel routes, we reported preparation of silica-titania aerogels with high thermal stability (anatase nanocrystalline phase stable up to 1000 ºC) and exceptional photocatalytic activity. In a follow-up study, we explored similar synthesis routes to grown SiO_2 layers and TiO_2 aerogel porous structure on bacterial nanocellulose scaffolds to develop hybrid BC@SiO_2/TiO_2 aerogel for in-flow photocatalytic water purification, a promising advance on the usage of aerogels for photocatalytic water treatment.

Introduction

TiO_2 remains the predominant material utilized as a semiconductor photocatalyst for various environmental applications, including water and air purification. The potential for employing TiO2-based materials in such contexts has spurred extensive research into developing titania nanostructured materials with properties aimed at enhancing photocatalytic performance, such as high surface area, optimal crystallinity, and precise control over crystalline phase composition. Among the various morphologies and forms in which TiO_2 materials can be synthesized, TiO_2-based aerogels emerge as significant candidates for the development of high-performance photocatalysts for diverse applications.[1] Aerogels represent a distinctive class of 3D nanoporous materials prepared through controlled drying of wet gels (e.g., Freeze Drying or Supercritical Drying). Aerogels exhibit unique structural and textural properties, including high surface area, substantial pore volume, and macroscopic monolithic structure facilitating easy handling and recovery. However, nanometric TiO_2 suffers from drawbacks such as agglomeration tendency, phase transformation, and surface area reduction upon thermal treatment necessary for crystallization [2]. These challenges are even more pertinent for highly porous 3D structures like titania-based aerogels, which exhibit high surface area in the as-synthesized form but lose this desirable characteristic upon thermal treatment. To address these issues, our team has spent the past years developing various silica-titania nanostructured aerogel photocatalysts demonstrating high photocatalytic activity in degrading water contaminants and ultra-high thermal stability. By employing different forms of silica-based nanostructures as functional supports, we have been able to design silica-titania aerogel photocatalysts with tailored physicochemical and structural properties for optimized photocatalytic performance [3]. Additionally, utilizing a bacterial cellulose (BC) biopolymer gel scaffold, we have created BC@SiO_2/TiO_2 hybrid aerogel membranes suitable for efficient, in-flow photoassisted removal of dyes and pharmaceuticals from water [4]. In this presentation, we will provide an overview of our recent research endeavors focusing on silica-titania-based aerogel photocatalysts

Material and Methods

Silica-titania aerogels were synthesized through epoxide-assisted gelation and thermohydrolysis of $TiCl_4$ in the presence of SiO_2 aerogel particles (SiO_2/TiO_2 composite aerogel) or SiO_2 wet gels (SiO_2@TiO_2 core-shell aerogels) as functional supports. The aerogels were obtained by CO_2 supercritical drying and annealed at various temperatures for crystallization (600ºC, 800ºC, and 1000ºC). For the BC/SiO_2/TiO_2 hybrid aerogel membranes, we developed a combined sol-gel method for SiO_2 coating on the BC scaffold, followed by epoxide-assisted gelation synthesis of the TiO_2 gel network on BC@SiO_2 support membranes. The TiO_2 gel was crystallized through soft hydrothermal treatment at 150ºC for 24 hours and BC@SiO_2/TiO_2 hybrid aerogels were obtained by CO_2 supercritical drying. Further details on the synthesis methods can be found in our published studies [3,4]. Materials characterization involved several techniques, including XRF, SEM, TEM, XRD, FTIR, Raman, and N_2 physisorption. The photocatalytic properties were assessed through Rhodamine B (RhB) dye photocatalytic degradation under UV-vis illumination. Hybrid BC@SiO_2/TiO_2 aerogels were utilized for in-flow photo-assisted removal of Methylene Blue (MB) dye and Sertraline drug (SER) using a specifically designed membrane photoreactor.

Results and Discussion

Using two novel straightforward $TiCl_4$-based sol-gel routes, SiO_2/TiO_2 nanocomposite and SiO_2@TiO_2 core-shell aerogels with exceptional photocatalytic performance even after annealing at temperatures as high as 1000 °C were developed. SEM and TEM analysis revealed microstructure consisting of porous 3D networks of interconnected SiO_2 and Anatase TiO_2 nanoparticles. The silica-titania aerogels exhibit excellent structural and textural properties, including high surface area, large pore volume, and impressive stability against thermal treatments, as revealed by N_2 physisorption and XRD analysis. While SiO_2@TiO_2 aerogels prepared by thermo-induced deposition method show higher and unprecedented thermal stability, epoxide-assisted gelation method allows preparation of highly photoactive anatase/rutile bicrystalline silica-titania SiO_2/TiO_2 composite aerogels. Furthermore, the robust mesoporous structure and silica's ability to inhibit the anatase-rutile phase transformation and crystal growth induced by thermal treatments result in an increase in photocatalytic activity with increasing calcination temperature. Of particular note is the high photocatalytic activity of the SiO_2/TiO_2 composite this material exhibiting superior photocatalytic efficiency compared to untreated and thermally treated commercial P25 photocatalyst. While developed inorganic silica-titania aerogels materials show outstanding structural, thermal and photocatalytic applications, their application for practical water purification is still hindered by limitations related to their mechanical stability. While inorganic aerogels can be obtained in macroscopic forms such as monolithic bodies, they are typically very fragile and lose their macroscopic shape upon immersion in water due to capillary forces. This restricts their use to powders or suspensions, limiting applications due to the economic, energy-related, and operational difficulties associated with material recovery. To address such issue, in a follow-up study we explored bacterial nanocellulose-based aerogels as a porous, mechanically-stable and flexible support for SiO_2/TiO_2 inorganic aerogel layers aiming to develop practical BC@SiO_2/TiO_2 hybrid aerogel for in-flow photocatalytic water purification. By combining sol-gel, hydrothermal, and supercritical drying techniques, we achieved controlled deposition of compact SiO_2 layers grown around cellulose nanofibrils and the deposition of a high surface area titania aerogel layer on the resulting BC@SiO_2 membranes. The silica interlayer significantly influenced the membrane's structure and composition, as evidenced by various materials characterization techniques. Developed BC@SiO_2/TiO_2 aerogel membranes significantly outperformed silica-free BC/TiO_2 membranes and other supported based materials previously reported, when assessed for in-flow photo-assisted contaminants removal under similar conditions. Finally, the optimized photoactive aerogel membrane efficiently removed SER drug, an emerging water contaminant, thus highlighting its promising potential for the advancement of in-flow photocatalytic water purification systems.

Conclusions

SiO_2 nanostructured supports offers a versatile approach for enhancing thermal stability and optimizing the structural/textural properties, thereby improving the photocatalytic properties of titania-based aerogels. While studies highlight such approach for the development of highly photoactive, thermally stable anatase inorganic SiO_2/TiO_2 aerogel powder photocatalysts, as well as hybrid BC/SiO_2/TiO_2 aerogel membranes for in-flow photo-assisted water purification.

Acknowledgments

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