143l Environmental Applications of Photocatalytic Tio_2 Films and Membranes

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MOTIVATION

New advances in environmental health are revealing that the presence of many microorganisms and naturally occurring organic and inorganic chemicals in water poses a serious health threat to humans and aquatic life. This is because many of these chemicals exhibit carcinogenic, mutagenic, endocrine-disrupting, or toxic properties. An emerging issue in drinking water supply, quality and treatment is the presence of biological toxins in sources of drinking water. In addition, these toxins are in the list of chemical and biological warfare agents. Despite tremendous efforts for securing and providing sufficient clean and safe water, the drinking water industry is now facing the necessity for the development and implementation of more innovative technologies for water treatment and purification.

BACKGROUND

Advanced oxidation technologies (AOTs) have a great potential to completely destroy harmful non-biodegradable and biocidal organic contaminants in water. These technologies proceed through the generation of highly reactive oxidizing species, which readily attack organic contaminants. Among them, TiO_2 photocatalysis has received great attention for environmental remediation due to the effectiveness of the TiO_2 catalyst to generate hydroxyl radicals along with its environmentally benign properties. Although TiO_2 photocatalysis is being researched for the destruction of a variety of recalcitrant organic pollutants and the killing of pathogenic microorganisms, the process suffers from a major disadvantage, which is the low efficiency of UV light utilization for catalyst photo-excitation. This is because the existing photocatalytic processes utilize TiO_2 with relatively low catalyst surface area, large crystallite size, low porosity, and less active crystal phase and material crystallinity.

CURRENT STATUS

Driven by the need of overcoming this disadvantage and developing new water treatment processes for the destruction of organic contaminants and toxins, we have recently synthesized novel and efficient TiO_2 photocatalysts with high photocatalytic activity, good homogeneity, tailor-designed pore structure and enhanced surface area. This result was the outcome of applying novel concepts of nanoscience and nanotechnology, inspired by the potential of this emerging field to provide new directions in the synthesis of advanced catalytic materials with unique hierarchical structures and functionalities. In particular, photocatalytic membrane reactors are an example of great interest because of their multiple functions such as the (i) destruction of recalcitrant organic pollutants, (ii) inactivation and killing of pathogenic microorganisms, (iii) physical separation of water contaminants, and (iv) self-antibiofouling action. However, to accomplish the development of TiO_2 photocatalytic membrane reactors, there is a need to apply novel material synthesis procedures to tailor-design the properties of TiO_2 material.

RESEARCH APPROACH

Since the first sol-gel synthesis of mesoporous TiO_2, different self-assembling strategies have been developed using a variety of organic molecules as nano-size templating materials to synthesize new TiO_2 catalyst. Controlling materials at the nano-level makes it possible to develop new types of products with improved properties and functionality for environmental applications. Common sol-gel methods employing direct addition of water molecules in a sol can lead to TiO_2 material with uncontrolled structure due to the rapid hydrolysis and condensation reactions between the highly reactive titania precursor and water. During the past decade, an interesting synthetic route of the Ti-O-Ti network in the

absence of externally added water molecules has been studied using acetic acid as a titania sol modifier. Compared to the case of externally added water, the hydrolysis reaction in the synthesis method applied in this study takes place with water released by the esterification reaction between alcohol and acetic acid. Consequently, the acetic acid-based sol-gel method modified with surfactant molecules applied in this work had the potential to better control the hydrolysis and condensation reactions, achieve stable incorporation of Ti-O-Ti network onto self-assembled surfactants and yield TiO_2 photocatalysts with enhanced structural and catalytic properties.

OBJECTIVES

The objective of this research is to investigate novel methods for synthesizing highly efficient TiO_2 catalysts with enhanced catalytic and structural properties and to evaluate the properties of these materials for the destruction of important emerging environmental contaminants. The methods should be simple and versatile for the synthesis of TiO_2 films and membranes. Fundamental research studies have been conducted to investigate (i) the structural and photocatalytic properties of TiO_2 catalysts prepared using this procedure, (ii) the role of surfactant in a titania sol on the formation of highly porous and active nanostructured crystalline TiO_2 catalysts, (iii) the properties of immobilized TiO_2 membranes on top of home-made porous alumina substrates in terms of water permeability and organic retention, (iv) the photocatalytic activity of TiO_2 catalyst for the destruction of water contaminants and toxins and the killing of pathogenic microorganisms, and (v) the development and scale-up of highly efficient photocatalytic reactors and membranes for water treatment.

EXPERIMENTAL

TiO_2 films and membranes are prepared through a new synthesis method employing surfactant molecules as a pore directing agent along with a novel acetic acid-based sol-gel route. The sol is composed of polyethylene glycol sorbitan monolaurate surfactant, acetic acid, titanium tetraisopropoxide, and isopropanol. Borosilicate glass or home-made alumina porous membrane supports are dip-coated with the sol, dried and calcined. For the characterization of the prepared TiO_2 material to study material crystal structure, morphology, nanostructure, elemental composition, and other characteristics, XRD, ASAP, HR-TEM, EDX, XPS, FTIR, and UV-Vis are used. TiO_2 films under near UV radiation at 365 nm are placed into borosilicate glass reactors containing one of the following organic contaminants: (1) methylene blue, which is a commonly used dye, (2) creatinine (2-imino-1-methylimidazolidin-4-one), which is usually found in urine and perspiration, (3) microcystin-LR (MC-LR), a cyanobacterial toxin known to cause skin irritations and liver damage, and (4) E. coli (ATCC 11229), which is a pathogenic microorganism. The water permeability and polyethylene glycol retention of the prepared TiO_2/Al_2O_3 composite membranes are tested with a home-fabricated membrane chamber.

IMPORTANT FINDINGS

The TiO_2 films and membranes had good structural and catalytic properties, including homogeneity without cracks and pinholes, high surface area and porosity, narrow pore size distribution, small crystallite size, high crystallinity, and active anatase phase. Organic contaminants such as methylene blue dye and creatinine were effectively destroyed by the photocatalytic activity of TiO_2 films. Destruction of MC-LR and inactivation of E. coli are currently being investigated. High water permeability and sharp polyethylene glycol retention of the TiO_2/Al_2O_3 composite membranes implied small hydraulic filtration resistance due to submicron size film thickness and much efficient rejection of water contaminants due to narrow pore size distribution in films without cracks and pinholes. We

believe that the methods and techniques introduced in this study are promising in preparing nanostructured TiO_2 films and membranes for environmental applications. Aiming at scaling up the photocatalytic film and membrane reactors, we are further investigating the synthesis conditions to better incorporate defect-free TiO_2 layer on the substrate, and design aspects to combine the separation function of TiO_2 layer with its photocatalytic action, which is one of the most difficult challenges in fabricating photocatalytic membrane reactors.