Report as of FY2009 for 2009MO99B: "Visible Light-activated Titanium Dioxide-based Photocatalysts: Synthesis and Potential Environmental Applications "

Publications

Project 2009MO99B has resulted in no reported publications as of FY2009.

Report Follows

Visible Light-activated Titanium Dioxide-based Photocatalysts: Synthesis and Potential Environmental Applications

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ABSTRACT

Titanium dioxide (TiO_2) has been widely used as a photocatalyst for the advanced oxidation treatment of organic contaminants and disinfection when coupled with ultraviolet (UV) radiation. Much efforts has recently focused on modifying TiO_2 so it can be activated with visible light (VIS), which could result in much broader environmental applications. TiO_2 doped with elements such as carbon and nitrogen (N) are found to exhibit photocatalytic effects in VIS region. The efficiency of these modified photocatalysts, however, is still low. The objective of this proposed study is to synthesize and characterize the N-doped TiO_2 nanomaterials capable of significant visible light absorption and evaluate their photocatalytic reactivity under visible light radiation for the degradation of petroleum hydrocarbons. Our long-term goal is to prepare solid thin-film and nano-structured photocatalysts with a superior quantum yield and explore their environmental applications such as degradation of petroleum hydrocarbons, disinfection of treated municipal wastewater prior to final discharge to rivers and lakes, and destruction of indoor air pollutants. The techniques developed in the project will help the State of Missouri and the Nation to better treat various waste streams with less cost and enhance public health. The outcomes will be documented by peer-reviewed publications that contribute to the knowledge base of the scientific and engineering communities in the field of visible light photocatalysis. The project will help train students for research and develop their critical thinking skills. Also this project represents a new but promising research direction for the PI; the result from this project will greatly enhance PI's ability to attract external funding in this focus area for further research and development.

Visible Light-activated Titanium Dioxide-based Photocatalysts: Synthesis and Potential Environmental Applications

Nature, Scope and Objective of Research:

Since the discovery of its photoactivity in 1972 (Fujishima and Honda 1972), titanium dioxide (TiO_2) has been widely used as a photocatalyst for disinfection and contaminant degradation (Chen and Mao 2007). However, original TiO_2 can only be activated by ultra-violet (UV) radiation due to its high energy band gap. Since less than 10% of the total solar radiation to the earth's surface is in the UV range, photocatalytic processes mediated by TiO_2 require an anthropogenic UV source. Much effort has recently been devoted to modifying TiO_2 to achieve activation in the visible light region (Asahi et al. 2001). Notably nitrogen (N)-doped TiO_2 is found capable of absorbing visible light (Asahi and Morikawa 2007; Chen and Mao 2007). However, applications of N-doped TiO_2 nanomaterials in water treatment have not been explored.

The objective of this proposed study is to synthesize and characterize the N-doped TiO_2 nanomaterials capable of significant visible light absorption and evaluate their photocatalytic reactivity under visible light radiation for the degradation of petroleum hydrocarbons. This is an integral part of our long-term goal to prepare solid thin-film and nano-structured photocatalysts with a superior quantum yield and explore their environmental applications such as degradation of petroleum hydrocarbons, disinfection of treated municipal wastewater prior to final discharge to rivers and lakes, and destruction of indoor air pollutants.

This proposed study is built on mature TiO_2/UV processes that have been widely used for disinfection and advanced oxidation of organic contaminants. The result from this study could extend the photocatalytic treatment processes to visible light region, avoiding the need for an UV source. Degradation of petroleum hydrocarbons is selected as the first model system for application because oil spills occur frequently; and it is envisioned that if an effective photocatalyst could be prepared that utilizes visible light radiation, application of the catalyst to the contamination sites could be a new and economical approach of contamination degradation. Another application is for the treatment of produced water associated with gas and oil production. Dissolved aromatics hydrocarbons in the produced water include benzene, toluene, ethyl benzene and xylene (BTEX), which are potent carcinogens. Currently, produced water is mainly treated with physical treatment techniques such as filtration, gravity separation and flotation. These techniques are expensive and not able to treat the water to meet standards for reuse. Drinking water standards are even more rigid, which are 0.005, 1, 0.7, and 10 ppm for benzene, toluene, ethyl benze ne and xylene, respectively (http://www.epa.gov/safewater/contaminants/index.html#listmcl). The proposed research could potentially provide a cost-effective approach for the produced water treatment and reuse.

Methods and Procedures of Research:

This is a two-year project focused on synthesis and optimization of N-doped TiO_2 nanomaterials capable of significant visible light absorption and evaluation of their photocatalytic reactivity towards degradation of petroleum hydrocarbons. One Ph.D. graduate student and one undergraduate research assistant will be involved in the project to complete the following two main tasks.

Task 1: Synthesis and characterization of VIS-activated N-doped TiO_2 photocatalysts

Two approaches will be employed to prepare N-doped TiO_2 photocatalyst nanomaterials in this research. The first approach is to prepare a thin solid film of N-doped TiO_2 by the chemical vapor deposition method. In this approach, the N-doped TiO_2 will be either prepared by atmospheric pressure chemical vapor deposition (APCVD) or plasma enhanced chemical vapor deposition (PECVD). Implementation of APCVD and PECVD is derived from the works of Guo et al. (2007). Precursors including $TiCl_4$, O_2 (as air) and NH_3 gas react at glass substrate surface of 500-600^oC for 1 minute, resulting in deposition of TiO_2 and TiN on a substrate of glass. The glass with deposited layer containing TiO_2 and TiN are then annealed at 500^oC in nitrogen atmosphere. Conditions for sample preparation will be altered including the reactant concentration and treatment time in order to obtain the best materials with the highest catalytic activity. Equipments for chemical vapor deposition and plasma enhanced chemical vapor deposition are available from Professor Hao Li's laboratories in the Department of Mechanical and Airspace Engineering of University of Missouri. PI for this project has been collaborating with Prof. Li on another project and has access to the facility. The second approach is to prepare nano-structured N-doped TiO_2 following the sol-gel method by hydrolysis of titanium isopropoxide (TIIP) in ammonia solution, as reported in the literature (Yu et al. 2001). TIIP is applied to ammonia solution drop-wisely. The collected sol is aged for 1 hour inside ultrasonic bath, then to be annealed at 500^oC in nitrogen atmosphere. It is expected that nanorods of TiO_2 will be achieved. As-prepared samples then can undergo further treatment by plasma with carrier gas of NH_3.

The prepared photocatalyst samples from different approaches will be characterized by X-ray diffraction spectroscopy (XRD) for crystal structures and sizes - peak positions and magnitudes in XRD spectroscopy provide information on the crystal type (e.g., anatase or rutine) and nanoparticles size, as illustrated by Figure 1. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) analyses will be used to examine nanostructures or induced layer of TiO_2 at the surface of prepared photocatalysts. Light absorption efficiency of the samples will be measured by UV-VIS optical absorption analysis. Specific surface area of the prepared samples will be determined by BET method using multi-point nitrogen adsorption.

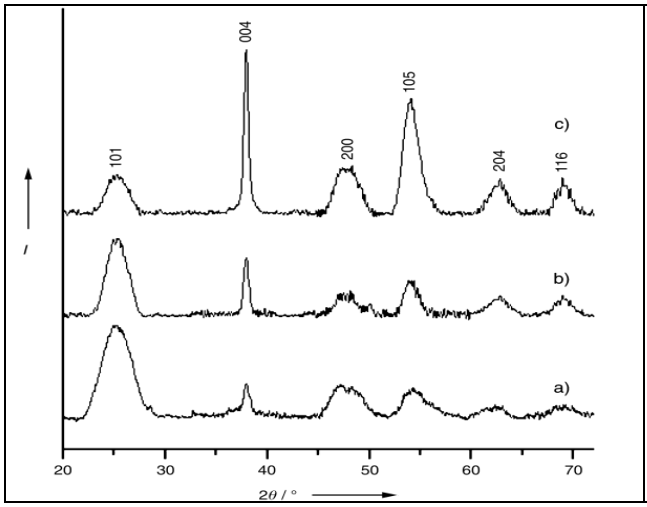

Figure 1. Powder XRD patterns of TiO_2 nanomaterials of different sizes, adapted from Zhang et al. (2005). When the nanoparticle size increases, the peak is narrowed: (a) = spherical particles, (b) = 16-nm nanorod, and (c) = 30-nm nanorod.

Task 2: Evaluation of the photocatalytic reactivity of N-doped TiO_2 under visible light

In this task, we will evaluate the photocatalytic oxidation of the prepared N-doped TiO_2 samples under simulating solar radiation in batch reactors, with BTEX as model contaminants. Degussa P25 titanium dioxide will be used as a reference catalyst to compare the reactivity of prepared samples. Dark control tests and controls without any catalyst will be included to allow proper data interpretation. The catalytic reaction will be examined as a function of solid loadings from 0 – 1.0g/L, pH (3 – 11), common ions in water (e.g., Ca^{2+}, Na^{+}, HCO^{-}, Cl^{-}), mixing intensity, and temperature (5 – 40 ^{o}C). Temperature will be controlled with a recirculating water bath capable of maintaining temperature within 0.5 ^{o}C of the set range. Degradation of organic contaminants will be examined at several complexity levels: from BTEX compounds spiked individually to the mixture of BTEX and then to the produced water samples collected from the field sites. Several produced water samples have already been collected from gas producing facilities at Farmington, New Mexico, which could be used for this study.

Concentration of dissolved petroleum hydrocarbons in batch reactors will be measured as a function of time, pH, dissolved oxygen, and alkalinity, and oxidation-redox potential (ORP). BTEX and other aliphatic hydrocarbon concentrations will be measured by gas chromatography-mass spectrometry (GC/MS). Reaction intermediates and products will also be identified by GC/MS. A Total Organic Carbon (TOC) analyzer will be employed to determine the final total concentration of hydrocarbons in water, which should be particularly useful when field produced water samples are examined and identification of individual components is often difficult and too expensive. The proposed study will provide quantitative information on the degradation kinetics of BTEX in simple and complex systems. The interpretation of the kinetic data relies on the understanding of the reaction mechanism and how various parameters affect the reaction. If the effect of reaction products are found affecting the overall reaction kinetics, the initial rate method will be adapted for kinetic data collection and analysis (Swinbourne, 1971). Catalytic reaction kinetics will be modeled by the established approaches (Lasa et al., 2005). Catalytic reaction networks can normally be described by coupled differential equations. A software program, Scientist (MicroMath Scientific Software, 1995), can be used to solve linear ordinary differentiation equations determined by the reaction mechanisms.

Relevance of Project:

N-doped TiO_2 nanomaterials with greatly enhanced ability for visible light absorption will have wide environmental applications such as degradation of produced waters associated with gas and oil production, cleanup of gasoline spills in surface water, disinfection of treated municipal wastewater prior to final discharge to rivers and lakes, and destruction of indoor air pollutants (e.g., aldehyde). If successful, the technique developed in the project will help the State of Missouri and the Nation to better treat waste streams with less cost and enhance public health. The outcomes of the project will be documented by peer-reviewed publications and will contribute to the knowledge base of the scientific and engineering communities in the field of photocatalyst.

Practical environmental applications of VIS-activated photocatalysts are limited because of the lack of good catalysts. This study aims to develop N-doped TiO_2 photocatalysts with strong visible light absorption ability for potential environmental applications. It is a kind of high risk/high reward project that is highly valued by funding agencies such as National Science Foundation (NSF) and Department of Energy. With the transformational nature of this project and preliminary data that will be collected from this project, the PI believes that we will be able to attract external funding from NSF and other agencies, including Environmental Protection Agency, Department of Energy, NASA, Department of Defense, and ACS Petroleum Research Funds, and American Petroleum Institute.

One Ph.D. graduate student and one undergraduate will be working on this project under close supervision of PI. The graduate student will write his/her thesis on the synthesis and modification of VIS-activated photocatalyst based on titanium dioxide and their implications in water/wastewater treatment. It is expected that an undergraduate will do research along with the graduate research. Support for the undergraduate student will come from the Honor's Research Program in the MU College of Engineering, which provides $1000 each semester to support an undergraduate researcher.

Research Synopsis:

The following are research results to-date:

In the first year of this project, we had prepared 1-dimension TiO_2 nanomaterials under the form of arrays containing nanotubes with opening diameters of 100-200 nm on titanium metal foil. The prepared nanotubes were then subjected to plasma processing with reactive gases containing nitrogen and carbon monoxide. Various plasma operating conditions were experimented, including plasma types, power input and treatment duration. We had also prepared a thin film of Degussa P25, a popular type of TiO_2 in the industry, on a titanium metal foil for comparison purposes.