PROJECT 2

Title: Enhancement of Photocatalytic Activity in Nanosized Titania through the Optimisation of Crystal and Surface Chemistry

Supervisors: Prof. Jim Leckie (Stanford) and Dr. Tim White (NTU)

Other researchers involved: Prof. Darren Sun and Dr. Li Ying

Since Fujishima & Honda obtained H_2 by decomposition of H_2O and Frank & Bard oxidized CN^- to OCN^- using TiO_2 as a photocatalyst in the 1970s, TiO_2 has attracted substantial attention as a potential material for photoelectrochemical energy production and photocatalytic removal of various organic toxins from air and water. The basic principle of semiconductor photocatalysis involves the migration of photon-generated electrons and holes to exposed surfaces where they can react with adsorbed reactants as redox sources, leading to the decomposition of pollutants. Photocatalysis can be extended by electrochemical techniques that enable ceramic membranes to photoplate heavy metals onto a counter electrode making this process favourable for remediating mixed waste streams.

Compared with other semiconductor compounds, TiO_2 has high photocatalytic activity, excellent chemical stability, is not toxic, and is abundant. In recent years, researchers and engineers have paid special attention to nanosized TiO_2, which has several advantages compared to the bulk TiO_2 including:

- Quantum size effect
- Reduced recombination of electron-hole pairs
- Increased active surface area

The major disadvantages of contemporary semiconductor photocatalysts:

1. photoreactions operate most efficiently with UV rather than visible light which reducing efficiency and increasing operating costs;
2. nanoparticle morphologies can be challenging to handle and recovery for reuse is difficult; and
3. control of surface structures and states is not easily achieved or robust.

Objectives:

This project will focus on the synthesis of nanosized metal-doped titania photocatalysts with visible light band gaps, the development of techniques to characterise and validate the bulk and surface chemistry of such particles, and photoreaction mechanisms and intermediates. Specific objectives will be:

1. Synthesis of nanosized titania doped with band-gap shifting metals including tungsten and vanadium;
2. Structure determination by advanced diffraction methods, including Rietveld analysis of electron diffraction patterns collected from individual nanoparticles;
3. Correlation of the surface structure and chemistry with photocatalytic properties;
4. Investigation of photoreaction pathways for model pollutants.

Research Approach and Research Tasks:

The student will synthesise and conduct in-depth characterisation of a range of photocatalyst compositions. Advanced characterisation methodologies using electron microscopy and X-ray analysis will be developed and proven.

Specific Research Tasks:

1. Soft chemical methods based on the controlled hydrolysis of metal alkoxides will be used to synthesise homogeneous nano-titania powders. The relationship between nano-particle structure and processing parameters will be investigated systematically.
2. Electron diffraction patterns will be collected using energy-filtering and manipulated by image processing to produce data suitable for crystal structure refinement. Rietveld methods, modified to take account of electron scattering, will be used to refine understanding of the crystal structures of nanosized titania. Crystal structure determinations by X-ray and electron diffraction methods will be compared and rationalised.
3. Screening for catalytic activity will be undertaken by UV-Vis spectroscopy and photoreactor studies of an indicator compound such as methyl blue.
4. Surface structure and reactions will be studied by in situ observation using XAFS in a reaction cell installed on a beam line at the Singapore Synchrotron Light Source.
5. The mechanisms and intermediate products arising from oxidation of waste pollutants will be studied using standard test protocols.

Organisation and Training:

Electron microscopy and X-ray diffraction will be undertaken in CARE using a JEM 3010 TEM, a Panalytical Xcellerator XRD, and a Bruker 5001 XRD fitted with environmental hot cell. XAFS will conducted at the SSLS using a beamline jointly under development with CARE.

The effort will be closely linked with ongoing efforts on photocatalytic treatment of waters and wastewaters being conducted in the laboratory of Stanford Professor James Leckie. Professor Leckie's group has extensive experience in the study of oxide mineral surface chemistry and their impact on aqueous contaminants.

The SSP student will spend substantial time in residence at Stanford. In addition to working with the Leckie group the student will take Stanford graduate courses, choosing from among Stanford's wide range of offerings including materials science, chemistry, chemical engineering, and environmental science. Finally the student will have the opportunity to link up with the geochemistry group in Stanford's School of Earth Sciences. This group has extensive collaborations with Stanford's Environmental and Water Studies program and for 25+ years has been in the forefront of development and utilization of XAS techniques in environmental surface chemistry.