EMSL Research and Capability Development Proposals

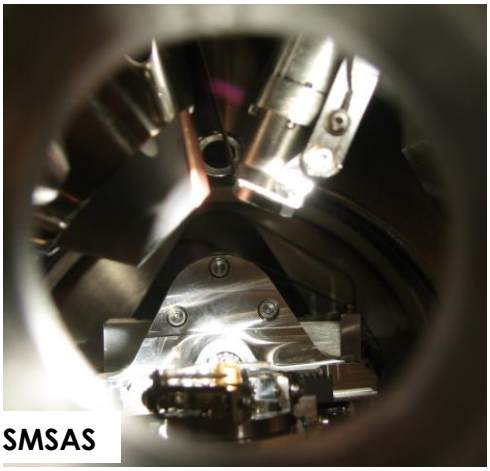
Developing in-spectrometer photochemistry and integration of molecular imaging techniques: Probing photo-induced electronic structure variations in dye-sensitized TiO_2 model system

Project start date: Spring 2009

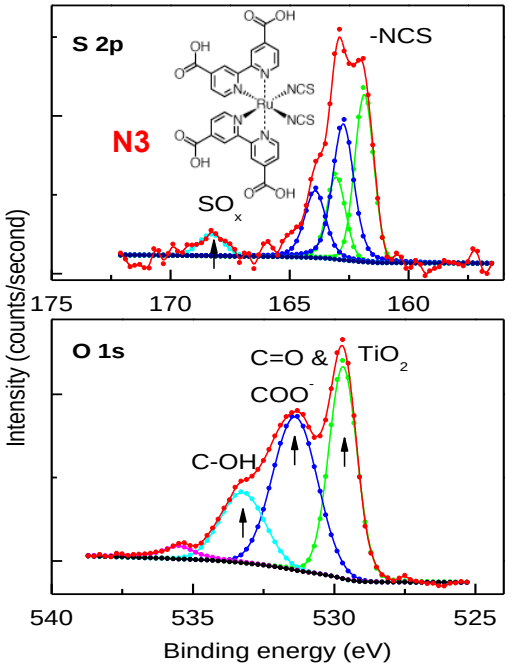
EMSL Lead Investigator:
Ponnusamy Nachimuthu, *Senior Research Scientist, EMSL Interfacial & Nanoscale Science Facility*

Co-investigators:
Zihua Zhu (*EMSL*), Kenneth M. Beck (*EMSL*), Z.Q. Yu (*EMSL*), A. Pandey (*EMSL*), Mike A. Henderson (*FCSD*), S. Thevuthasan (*EMSL*) and Donald R. Baer (*EMSL)*

The goal of this project is to develop capabilities that will advance the fundamental understanding of charge transfer and photochemical behaviors of organic molecular layers on surfaces as applicable to solar cells, sensors, and contaminant reduction. This would be accomplished by using model film systems, applying existing and newly developed tools to characterize the adsorbed ruthenium (Ru)-based dye molecules on the TiO_2 surface. This would disclose the nature of distribution and the geometrical structures using imaging techniques, as well as determine the photo-induced electronic structure variations and band alignments that will be correlated to understand the electron-transfer dynamics.



In order to achieve this goal, two novel capabilities were developed: 1) the photon exposure capability on the scanning multi-probe surface analysis system (SMSAS) for photocatalysis and photochemistry studies and 2) a fluorescent microscope with a mercury lamp as an excitation source on a time-of-flight secondary ion mass spectrometry system (ToF-SIMS) for understanding molecular distribution on the surface.



Using these capabilities, N3, N719, and Z907 Ru-based dye molecules (in powder form and adsorbed on TiO_2(110) surface using 0.25-1.0 mg/ml in ethanol) were studied. The X-ray photoemission spectroscopy (XPS) data show that one of the -NCS groups and one of the carboxylic acid groups in the N3 dye molecule are bound to the TiO_2(110) surface following adsorption. The valence band shows features at ~3.0eV and ~2.3eV characteristic of TiO_2 and N3 adsorbed on TiO_2, respectively. Based on these features, the relative energy levels are being determined. Similar studies are also being conducted on N719 and Z907 dye molecules on the TiO_2 surface, and the results are being correlated. Determination of the photo-induced electronic structure variations also is underway.

Products and Output

New Capability for EMSL Users

The following new capabilities have been developed and are now available for EMSL users:

1) The photon exposure capability on the SMSAS for photocatalysis and photochemistry studies

2) Fluorescent microscopy with a mercury lamp as an excitation source on a ToF-SIMS for identifying molecular distribution on surfaces.

Presentations

Nachimuthu P., A. Pandey, Z.Q. Yu, Z. Zhu, K.M. Beck, S. Thevuthasan, M.A. Henderson, and D.R. Baer. 2010. "Anchoring of N3, N719, and Z907 dye molecules on TiO_2(110) surface." to be presented at the *AVS 57th International Symposium and Exhibition*, October 17-22, 2010, Albuquerque, New Mexico.

Nachimuthu P., Z.Q. Yu, Z. Zhu, K.M. Beck, S. Thevuthasan, and M.A. Henderson. 2009. "Anchoring of N3 dye molecule on TiO_2(110) surface and its influence on energy level alignments." presented at the *AVS 56th International Symposium and Exhibition*, November 8-13, 2009, San Jose, California.