UCSD Jacobs School of Engineering | NANOENGINEERING

UCSD NANOENGINEERING SEMINAR SERIES

Date and Location Change:

Friday - February 3, 2012

1:30pm – 2:30pm

EBU II - Room 479

Tetracyanoquinodimethane and Dawson-Type Polyoxometalates as Catalysts for Water Oxidation in Ionic Liquid Media

Alan M. Bond

School of Chemistry, Monash University, Clayton, Victoria, 3800, Australia

Abstract: The synthesis of exceptionally long semiconducting silver tetracyanoquinodimethane (AgTCNQ) nanowires has been achieved in the room temperature ionic liquid, 1-n-butyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$) by photochemical reduction of TCNQ to $TCNQ^{-}$. The presence of Ag(I) in the ionic liquid allows formation of mm length AgTCNQ nanowires onto both conducting and insulating surfaces, via a nucleation and diffusion-controlled growth mechanism. Remarkably, photocrystallization is achieved using adventitious water present in the ionic liquid as the sacrificial electron donor. Oxidation of water produces O_2 as the counter reaction in the photoreduction of TCNQ. In contrast, irradiation in "dried" ionic liquids fails to induce any detectable photochemistry. Molecular structural differences, relative to the situation encountered in more conventional solvent media, are believed to account for the more favorable kinetics available for oxidization of water in ionic liquids.

Many polyoxometalates also photoactive and rich in their redox chemistry. We now show that photoreduction of $[S_2Mo_{18}O_{62}]^{4-}$ can be achieved in molecular solvents or ionic liquids, with adventitious or deliberately added water present in the solvent acting as an electron donor:

$$[S_2Mo_{18}O_{62}]^{4-} + h\nu \rightarrow [S_2Mo_{18}O_{62}]^{*4-}$$

$$2[S_2Mo_{18}O_{62}]^{*4-} + H_2O \rightarrow 2[S_2Mo_{18}O_{62}]^{5-} + \tfrac{1}{2}\, O_2 + 2H^{+}$$

Photoreduction of $[S_2Mo_{18}O_{62}]^{4-}$ to $[S_2Mo_{18}O_{62}]^{5-}$ was confirmed by rotating disk electrode voltammograms and visually by colour change, while the Clark-type electrode conferred the evolution of oxygen. In contrast, photoreduction of other Dawson-type polyoxometalates of interest in this study, $[P_2W_{18}O_{62}]^{6-}$ and $[S_2W_{18}O_{62}]^{4-}$, does not occur in neat water or when water is present in an organic solvent. However, it does occur when these polyoxometalates are dissolved in either protic or aprotic room temperature ionic liquids containing water. These studies highlights the significant role that water present as an adventitious impurity may play in photochemical studies in ionic liquids, and also suggest that ionic liquids may provide a favorable environment for photochemically based water splitting.

Biosketch: Professor Bond is currently R.L. Martin Distinguished Professor of Chemistry at Monash University, Victoria, Australia. Previously, he held Chairs of Chemistry at Deakin and La Trobe Universities. He received his Ph.D. (1971) and D.Sc. (1977) degrees from the University of Melbourne. Professor Bond's major research interests involve the development and application of modern electroanalytical techniques, and he is the author or co-author of over 700 papers, patents and books on this subject and is on the editorial board of fourteen journals. He is the recipient of several Australian Chemical Institute Awards which include the Analytical Chemistry Division Medal (1989), the Stokes Medal awarded by the Electrochemistry Division (1992), and the Burrows Medal awarded by the Inorganic Chemistry Division (2000). Awards from other societies include the Federation of Asian Chemical Societies Foundation Lectureship (1993), Royal Society of Chemistry Award for Electrochemistry (1997), the Governor General's Centenary Medal in 2003 and the Australian Academy of Science Craig Medal in 2004. In 1990, Professor Bond was elected as a Fellow of the Australian Academy of Science. In 1991 he was the recipient of the Robert Boyle Royal Society of Chemistry 150th Anniversary Fellowship, which enabled him to spend the period March - December at Oxford University as the Robert Boyle Professor. Professor Bond was awarded the Hinshelwood Lectureship by the Physical and Theoretical Chemistry Laboratory at the University of Oxford for the 1997/98 academic year. In the year 2002 Professor Bond concluded a three year period as Head of the School of Chemistry at Monash University and in 2003 he was awarded a 5 year Australian Research Council Professorial Fellowship. In 2004 Professor Bond become the R.L. Martin Distinguished Professor of Chemistry at Monash University and also the Vallee Visiting Professor of Chemistry at the University of Oxford. In 2005 Professor Bond obtained a 5 year Federation Fellowship.