

# Simultaneous X-ray and Visible Spectroelectrochemistry of TiO<sub>2</sub> Nanocrystalline Films

D. J. Gosztola, Z. Saponjic, L. Chen, T. Rajh, and R. Rey-de-Castro

Argonne National Laboratory, Argonne, IL U.S.A.

## Introduction

The mechanism of semiconductor assisted radio- and photocatalysis is based on the principle that particulate semiconductors behave as miniature electrochemical cells driven by radiolytic or photoinduced charge separation. The efficiency of nanoparticulate wide band gap semiconductors is often determined by energy loss pathways such as charge recombination and charge trapping. It is important therefore to understand the complex interplay between structure and electronic properties and how they effect both the lifetime and chemical potential of charge carriers.

## Methods and Materials

Using a specially designed electrochemical cell (Fig. 1), we have recently been able to simultaneously measure both the X-ray absorption (near edge: XANES, extended: EXAFS) and the optical absorption spectra (400 - 900 nm) of a nanocrystalline TiO<sub>2</sub> film while controlling its potential. We have coupled spectroelectrochemical and X-ray absorption spectroscopies in order to begin to reveal the electronic nature of injected charge carriers and the structural changes due to their localization. In particular, localization of charge carriers may be manifested by changes in local oxidation state, local structure and symmetry, as well as in the appearance of new optical absorption transitions. Measurements were carried out in acetonitrile with LiClO<sub>4</sub> supporting electrolyte.

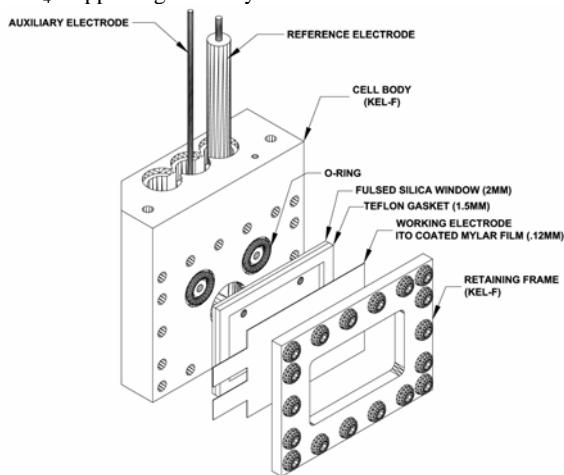


Fig. 1.

## Results

An increase in absorption throughout the visible-NIR region was observed (Fig. 2) which is attributed to the accumulation of electrons in the film. At potentials negative of -1.3 V (vs Ag/Ag<sup>+</sup>), electrons begin populating the conduction band giving rise to a weak broad band centered at 1030 nm. At potentials negative of -1.8 V, an absorption band appears at 750-800 nm which has been attributed to shallow surface inter-band trapped electrons[1]. Slowly growing in at potentials

negative of -2.6 V is a band at 500 nm which has been attributed deep surface state traps. X-ray absorption spectra in the near edge region (XANES) recorded simultaneously with these absorption spectra (Fig. 3) show that upon reduction, the X-ray absorption edge shifts to lower energies, consistent with a reduction in the formal oxidation state of Ti<sup>4+</sup>. In addition, a decrease in the fine structure was observed, consistent with a decrease in symmetry around Ti. These results are consistent with the formation of Ti<sup>3+</sup> either as Ti<sub>2</sub>O<sub>3</sub> or possibly as LiTiO<sub>2</sub> since at potentials negative of -1.8V, Li<sup>+</sup> ions are intercalated into the porous film[2].

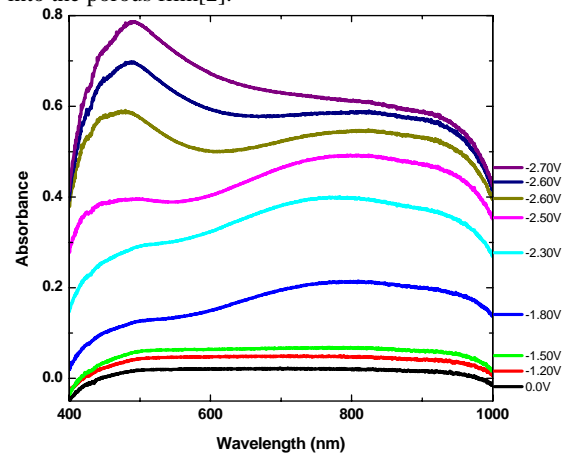


Fig. 2.

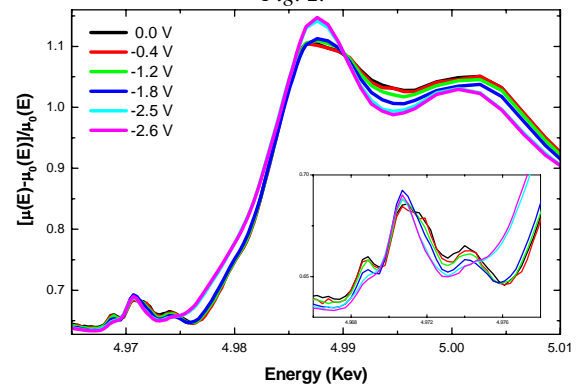


Fig. 3.

## Acknowledgement

This work was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy under Contract number W-31-109-Eng-38.

[1] T.-S. Kang, D. Kim, K.-J. Kim, *J. Electrochem. Soc.* **145**, 1982 (1998).

[2] M. Wagemaker, D. Lützenkirchen-Hecht, A. van Well,†R. Frahm, *J. Phys. Chem. B*, **108**, 12456 (2004).