

X-ray Absorption Study of TiO₂ Nanoparticle Films under Electrochemical Control

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Introduction

The electrochemistry of and at nanoparticle semiconductor films has been used as the basis of electrochromic devices, batteries, photovoltaics, photoelectrochemical catalysts, and sensors. One of the most useful techniques for studying such films is spectroelectrochemistry, which typically combines electrochemical techniques, such as cyclic voltammetry or chronoamperometry/voltammetry, with simultaneous uv-visible absorption spectroscopy. This combination of electrochemical and spectroscopic methods gives much more information about the system than does either method alone. Spectroelectrochemistry of TiO₂ films in both aqueous and nonaqueous solvents has shown that as the electrode potential is made more negative, electrons accumulate in the nanoparticle film, and (depending on whether the solvent is protic or aprotic and on the supporting electrolyte), positive counter ions may intercalate into the film.

In order to gain a better understanding of charge accumulation in TiO₂ films, a “universal” spectroelectrochemical cell was designed and built. It enables us to measure not only uv-visible absorption and fluorescence but also x-ray absorption under electrochemical control. The addition of x-ray absorption (both x-ray absorption near-edge structure [XANES] and x-ray absorption fine structure [XAFS]) gives a more direct measure of the oxidation state of titanium and indicates any structural changes that might occur in the nanocrystalline film.

Methods and Materials

The spectroelectrochemical cell was designed for both transmission and reflectance/fluorescence and is loosely based on previous thin-layer designs. Figure 1 shows an exploded view of the cell. The cell body holds a pair of reference electrodes, the platinum auxiliary electrode, and a small reservoir of solvent/electrolyte solution. A fused silica slide forms one window of the cell. It has a series of holes drilled through it to allow for the passage of solvent from the cell-body reservoir. The front window is separated from the back window by a Teflon[®] gasket that is typically 1.5-mm thick. The front window acts as the working electrode and is coated with a transparent, conductive indium-tin oxide (ITO) layer. For x-ray experiments, the front window is ITO-coated Mylar[®], whereas for visible wavelengths, the front window is ITO-coated fused silica.

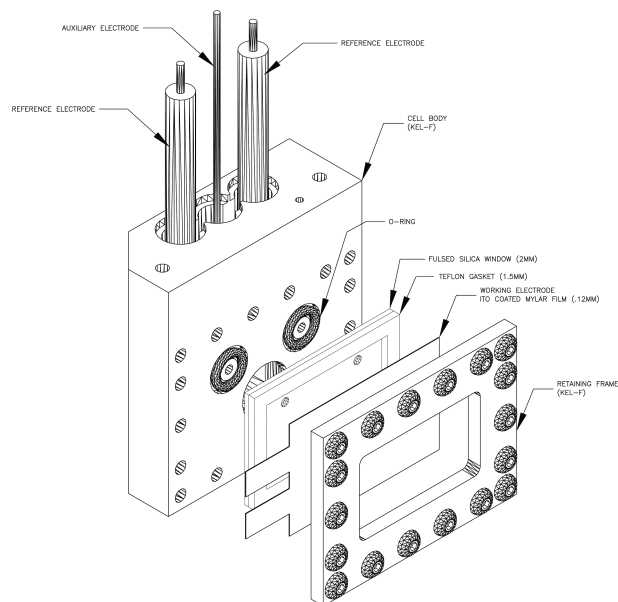


FIG. 1. Spectroelectrochemical cell.

The TiO₂ nanoparticle film was deposited on the ITO side of the window. The cell is assembled and held in place with a retaining frame. For x-ray absorption experiments, the cell was placed in a helium-purged box at a 45° angle to the x-ray beam. A 13-element detector was placed at a 90° angle to the x-ray beam to detect the x-ray fluorescence.

Results

Preliminary results show that the cell works as desired. Figure 2 shows XANES and Fourier transform (FT)-XAFS spectra of the TiO₂ nanoparticle film in acetonitrile/LiClO₄ at 0 V (versus Ag/AgCl) and at -1.9 V and a powder sample of Ti₂O₃. The shift of the absorption edge to lower energies when -1.9 V is applied is consistent with the reduction of the oxidation state of Ti⁴⁺. However, the edge position of this reduced TiO₂ film is still higher in energy when compared with Ti³⁺ in Ti₂O₃. In addition, the XAFS spectra suggest that the local coordination environment of Ti is almost unchanged upon the accumulation of electrons in the film. This accumulation is verified by the film turning a deep blue color. When the potential is returned back to 0 V, the

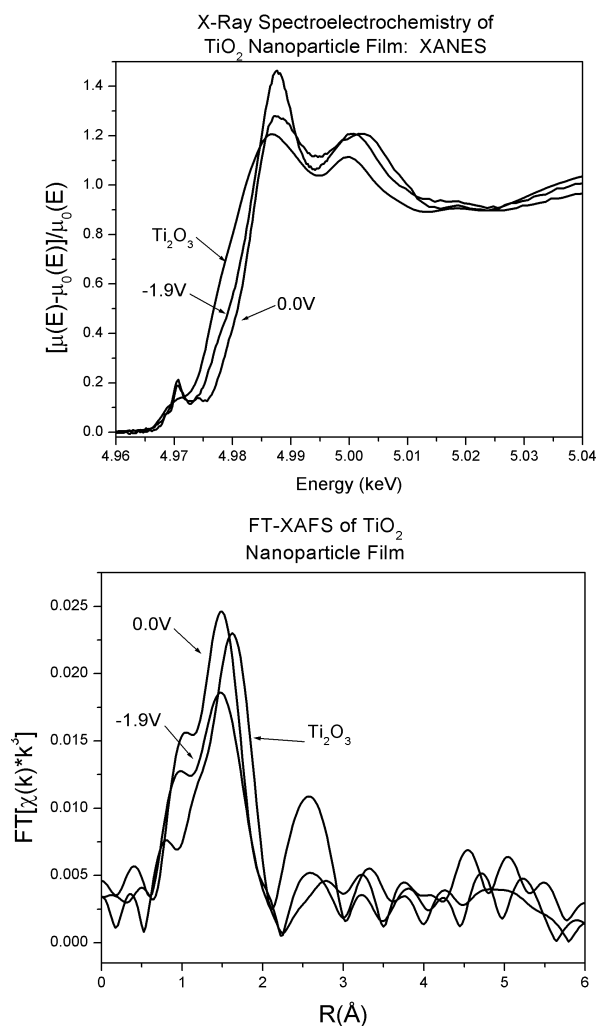


FIG. 2. Upper panel shows XANES of TiO₂ film at 0.0 V and -1.9 V and Ti₂O₃ powder. Lower panel shows FT-XAFS of same.

edge returns to the starting position for Ti⁴⁺, indicating the reversibility of the reaction.

Modifications to the spectroelectrochemical cell are currently underway to allow simultaneous uv-visible absorption and x-ray absorption spectroelectrochemical measurements to be carried out.

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