

Lithium Intercalation in Nanoporous Anatase TiO₂ Studied with RIXS

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INTRODUCTION

The interest of nanostructured TiO₂ is based on the possibilities of using the material in various applications as batteries, displays [1,2] and dye sensitized solar cells [3]. The electrode consists of interconnected nanocrystallites forming a nanoporous structure with an extremely large inner surface allowing for electrochemical reactions to take place in the entire volume of the electrode. High charging capacities are reported [1,2], when Lithium is intercalated in to the nanoporous anatase titanium dioxide electrode. Schematically the electrochemical intercalation reaction is written as $x \text{Li}^+ + \text{TiO}_2 + x e^- \leftrightarrow \text{Li}_x\text{TiO}_2$ where x is the mole fraction of lithium in the titanium dioxide. For technical devices, the reversibility of the reaction is of prime importance. A XPS/electrochemically technique was developed in Uppsala [4] to study these kind of systems and detect possible side reactions on the surface. With this setup the electronic structure of the anatase titanium dioxide was studied [5] and a Ti³⁺ state was detected shifted 2.1 eV towards lower binding energy in the Ti 2p spectrum in the intercalated electrode.

In this work we have studied the intercalated anatase titanium dioxide with Soft x-ray fluorescence spectroscopy. Soft x-ray originates from an electron transition between a localized core state and a valence state. The most striking features of characterizing SXES are (a) bulk probing ability due to comparably large photon attenuation lengths, (b) atomic and site selectivity due to transitions involving core levels, (c) orbital and symmetry selectivity by virtue of dipole selection rules and the use of polarized x-rays from synchrotron radiation sources. The excitation-dependence of Ti L_{2,3} soft x-ray emission showed to be a powerful tool to determine the magnitude of on-site Coulomb energy and crystal field splitting of La_xSr_{1-x}TiO₃ through the study of d-d and CT transitions [6]. In this report, we present resonant inelastic soft x-ray scattering (RIXS) spectra and soft x-ray absorption (XAS) spectra of Li_xTiO₂.

EXPERIMENTAL

The experiments were performed at beamline 7.0.1 at the *Advanced Light Source*, Lawrence Berkeley National Laboratory (LBNL). The intense, high-resolution radiation is produced by a undulator and a spherical grating monochromator (SGM). The electrode was prepared from a suspension of colloidal TiO₂ [3]. The electrochemical intercalation was made in a three-electrode setup, with the titanium dioxide electrode as the working electrode using an Eco Chemie PGSTAT10 potentiostat. The electrode/sample was after intercalation brought up from the solution and transferred into the vacuum system via a loadlock. The process was made under argon atmosphere in a glove bag attached to the loadlock, so the electrode was not to be in contact with air. The loadlock was pump down and the sample transferred into the experimental chamber within 20 minutes. The base pressure in the experimental chamber was 5×10^{-9} mbar. The x-ray absorption spectra (XAS) were obtained by measuring the total electron yield (TEY) from the sample as function of the incoming photon energy. The spectra were normalized to the photo current from a clean gold mesh introduced in the beam. A high-resolution grazing – incidence grating spectrometer [7] were used to record the emission spectra, with a resolution better than 0.4 eV. The bandpass of the exciting photon beam was set to 0.2 eV for absorption and 0.4 eV for the emission measurements.

RESULTS AND DISCUSSION

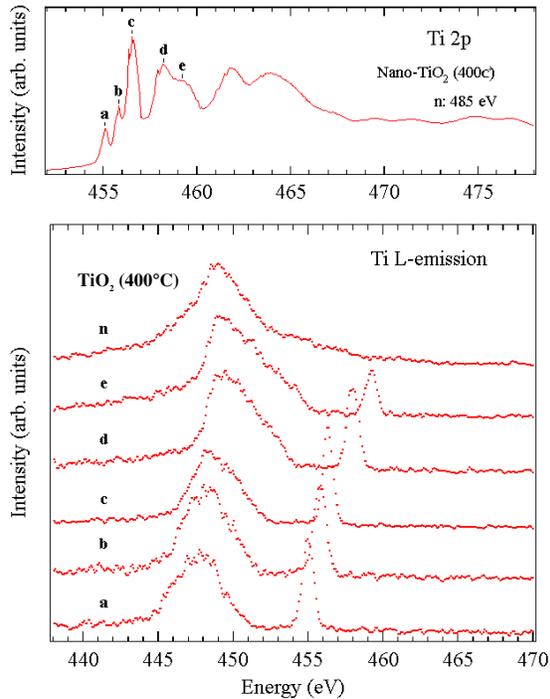


Figure 1 . Above, Ti 2p XAS spectra and below Ti L-emission spectra of nanoporous TiO_2 excited at the photon energies indicated in the XAS spectra

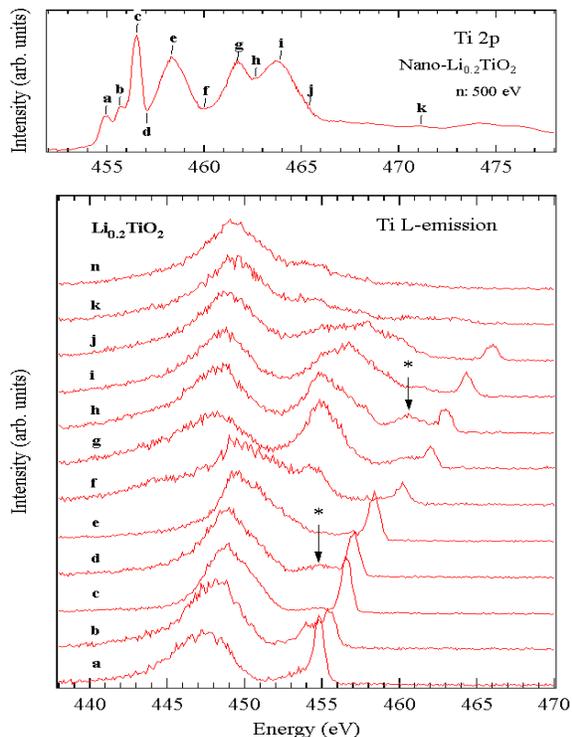


Figure 2 Above, Ti 2p XAS and below Ti L-emission of intercalated nanoporous $\text{TiO}_2/\text{Li}_{0.2}\text{TiO}_2$.

As a comparison, a few resonant excited (marked as a-e) and non-resonant excited SXES spectra were recorded on anatase, showed in

figure 1. The x-ray absorption spectra is derived from two parts of $L_3(2p_{3/2})$ and $L_2(2p_{1/2})$ that are furthermore split into a sharp t_{2g} (c) and double-splitting e_g (d and e) states due to the distortion from the O_h symmetry. The letters indicate the excitation energy used in the recording of the emission spectra. The emission spectra reflect the Ti 3d partial density of states. There are three components in the resonant excited SXES spectra. Normal emission features at fixed emission photon energy, elastic scattering features at same photon energy and inelastic scattering features including CT *charge-transfer* and d-d excitations. The sharp feature located at higher energy in all spectra, but “n”, is the elastic peak. The spectra labeled n, is non-resonant emission, that basically consists of Ti L_3 and L_2 emission.

Figure 2 and 3 shows the absorption and emission spectra recorded after intercalation of lithium ($x = 0.2$ and 0.5) into the titanium dioxide electrode. When comparing the absorption spectra we see that that the features a and b are reduced in intensity as the intercalation is increased. Changes are also observed in the e_g features. In the resonant excited emission spectra we see features that shift as the excitation energy is changed, this is inelastic scattering. This inelastic scattering/Raman shift corresponds to transition from occupied t_{2g} subband to an unoccupied e_g subband also referred as d-d transitions. And as we increase the fraction of lithium/doping, see figure 3, we observe that the relative intensity of these transitions increase. The relative intensities of d and e are sensitive to the crystal structure of TiO_2 . The marked feature (*) at ~ 2.4 eV below the elastic peak are not observed in the *undoped* TiO_2 spectra. In emission spectra indicated as a and b we can also observe a doping

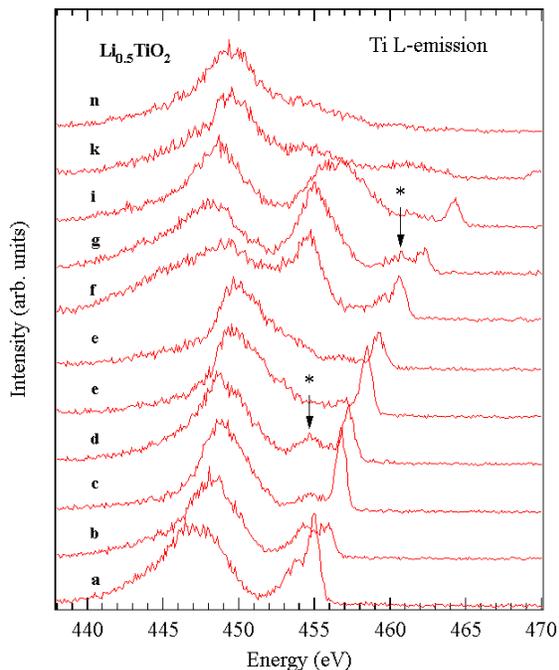
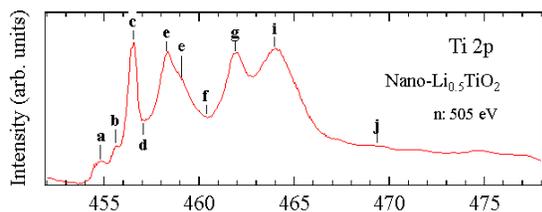


Figure 3 Above, Ti 2p XAS and below Ti L-emission of intercalated nanoporous $\text{TiO}_2/\text{Li}_{0.5}\text{TiO}_2$

dependent feature at ~ 1.1 eV below the elastic peak. There are also doping-sensitive features ~ 5 eV below that seems to follow the elastic peak (see resonant spectra *g* and *f*).

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