X-ray Standing Wave Study of Zn^{2+} Adsorption at the Rutile/Aqueous Interface

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Beamline(s): **X15A**

Introduction: Chemical reactions at the aqueous/oxide interface are technologically important, but far from well understood. The electrical double-layer (EDL) was introduced over a century ago as a model for the ion distribution near the solid-liquid interface, but many aspects of its physical description is still unresolved. The X-ray Standing Wave (XSW) method is a powerful tool to probe the EDL structure. Rutile (TiO_2) is one of the most studied oxide surfaces [2], and represents an important model system for understanding the EDL structure. In our earlier work [1], we studied the adsorption of Sr^{2+} and Rb^{+} at the aqueous/TiO_2 (110) interface with XSW and EXAFS. We are presently studying the adsorption of Zn^{2+} on TiO_2 (110) surface. As a first step we have performed an ex-situ XSW analysis of this interface.

Methods and Materials: The TiO_2 single crystal ($10\times10\times1mm^3$) was cleaned twice with ultrasonic baths in acid (pH=2 HCl), methanol, and deionized water in order to remove any pre-absorbed impurities. The crystal was exposed to 0.1mM or 1.0mM NaCl solution containing 1μM Zn^{2+} at pH≅9 for 15 minutes. It was removed from the solution without leaving a droplet on its surface. The sample was measured with XSW under dry N_2 gas immediately after preparation.

The measurements were performed at beamline X15A at National Synchrotron Light Source. A 6° miscut Si (111) monochromator was used to select the x-ray energy at 11.5keV. The single crystal TiO_2 (110) reflection was measured. The fluorescence detector was setup to collect the fluorescence signal from the crystal surface at a take-off angle less than 5°. The coverage of the Zn^{2+} ions on the surface was calibrated with a Ga implanted standard. We measured a surface coverage of ca. 0.1 monolayer (ML).

Results: The experimentally measured (110) reflectivity $R(\theta)$ and Zn^{2+} XSW fluorescence yield $Y(\theta)$ are presented in Fig.1, along with the best-fit curves to the data. The corresponding coherent fractions and the coherent positions of Zn^{2+} are shown in the figure. The (110) coherent position is close to unity, indicating that the Zn^{2+} ions occupy the same position along the surface normal direction as Ti atoms do in the bulk crystal of TiO_2.

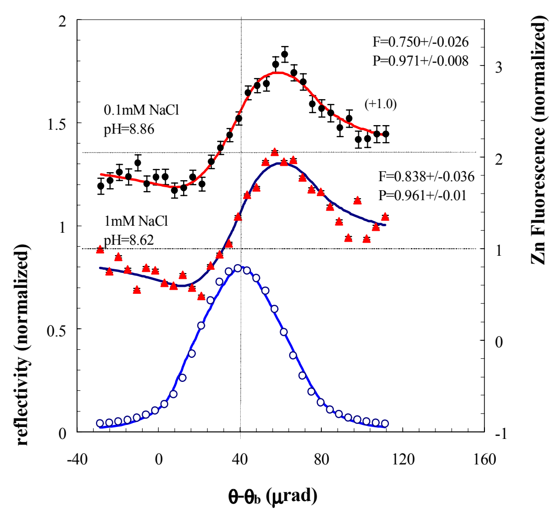

Figure 1. *Ex-situ* XSW results for Zn^{2+} absorbed on TiO_2 (110) surface.

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References: [1] P. Fenter, L. Cheng, S. Rihs, M. Machesky, M.J. Bedzyk, and N.C. Sturchio, “Electrical Double-Layer Structure at the Rutile-Water Interface as Observed in Situ with Small-Period X-ray Standing Waves,” Journal of Colloid Interface Science, **225**, 154, 2000; [2] G. E. Brown, et. al., “Metal Oxide Surfaces and Their Interactions with Aqueous Solutions And Microbial Organisms,” Chemical Review. **99**, 77 1999;