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Supporting Information

Interface sensitivity in electron/ion yield X-ray absorption spectroscopy: the TiO_2-H_2O interface

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S1 Sample preparation

S1.1 Thermal evaporation of Au and Cr

Commercial SiN_x membrane windows (Norcada NX10100C) with window dimensions of 1 mm×1 mm×100 nm and frame dimensions of 10 mm×10 mm×0.2 mm was loaded on the sample plate of a commercial thermal evaporator system (Denton DV-502A at the Molecular Foundry, Lawrence Berkeley National Laboratory). Before loading the sample plate, a gentle flow of N_2(g) was used to ensure that the windows were dust-free. Au pellets were loaded in a W evaporation boat and Cr was evaporated using a Cr-plated W rod (Midwest Tungsten Service, Cr purity of 99.9% and W purity of 99.95%). The system was evacuated using a scroll pump and a turbomolecular pump. The system reached a stable pressure, typically around the mid 10^{-5}-Pa range after *ca.* 12 h. Before growing the thin films, the evaporation sources were outgassed, and the sample plate was heated to approximately 373 K. Cr was evaporated by passing a current of 68–69 A through the rod until a thickness of 2–3 nm was reached with a rate of 1 nm/minute, measured using a quartz crystal microbalance. During the Cr deposition, the pressure was $(3–5)\times10^{-3}$ Pa. Au was evaporated by passing a current of 46 A through the boat until a thickness of 10–12 nm was reached with a rate of 1 nm/minute. The samples were allowed to cool to near room temperature before taking them out and storing them in a N_2 box.

S1.2 Plasma-enhanced atomic-layer deposition of TiO_2

The TiO_2 films were grown on the Au/Cr-coated SiN_x membranes by plasma-enhanced atomic layer deposition (ALD) using a Cambridge Nanotech Fiji F200 system in the Marvell nanolab, University of California, Berkeley. For the TiO_2, O_2 and tetrakis(dimethylamino)titanium ($Ti[N(CH_3)_2]_4$, TDMAT) were used as precursors with Ar as the carrier gas. The gas delivery line was heated to 423 K, the precursor was preheated to 348 K, and both the chamber and sample holder were kept at 523 K during the deposition. A single ALD cycle consisted of a 100-ms TDMAT dose, a 5-s purge, a 20-s O_2 plasma dose at 300 W, and another 5-s purge. The growth rate, 0.044 nm per cycle, was calibrated by ellipsometry performed *ex situ* on TiO_2 deposited on Si and Au substrates.

S2 Sample characterization

The Fourier-transform infrared (FTIR) measurements were conducted with a Thermo Nicolet iS50 FTIR spectrometer using diamond crystal attenuated total reflectance (ATR). The spectra were collected with a resolution of 4 cm^{-1} in the spectral range from 4000 cm^{-1} to 500 cm^{-1} averaging over 64 scans and normalized to the light intensity measured on a Au film without TiO_2.

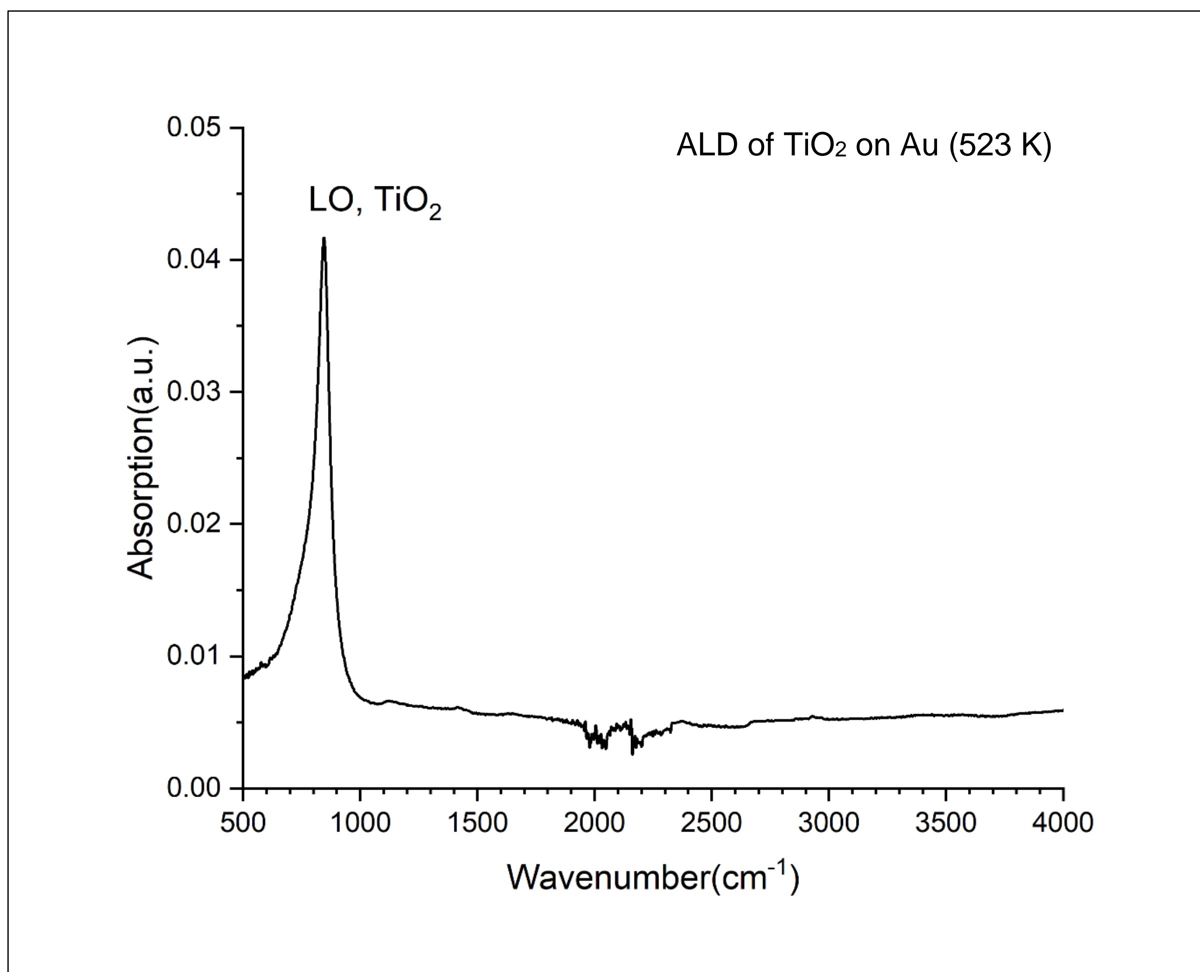

Figure S1 ATR-FTIR spectrum of ALD TiO_2 film (13.5 nm) deposited on a 50-nm Au film on a Si wafer using the same evaporation and ALD procedure as outlined in section S1.

The longitudinal optical (LO) mode at 845 cm^{-1} agrees well with previously reported polycrystalline TiO_2 film in anatase form grown by ALD[1] and spin-coating[2]. The peak position at such high wavenumber might be induced by the Berreman effect.[3]

S3 Beamline measurements

The data for Fig. 2 were measured at beamline 8.0.1.4 of the Advanced Light Source at the Berkeley Lawrence National Laboratory, California, USA. This beamline uses a U5 undulator as source with a plane-grating monochromator with 380-lines/mm grating with the entrance and exit slits set to 80 µm.

The data for Figs 3 & 4 were measured at beamline 23-ID-2 (IOS) of the National Synchrotron Light Source II at the Brookhaven National Laboratory, Upton, New York, USA. This beamline uses an EPU49 undulator as source with a plane-grating monochromator with a 1200-lines/mm grating and the exit slits set to 15 µm.

Both beamlines provided linearly polarized X-rays in the horizontal plane. The endstations were separated from the respective beamlines by a SiN_x membrane of 100-nm thickness. The spectra were corrected for energy-dependent variations in photon flux by dividing the spectra by the photocurrent emitted from a Au mesh (8.0.1) or a photodiode (IOS) located upstream from the SiN_x membrane separating the endstation from the beamline.

The partial fluorescence yield at the IOS beamline was collected using a Vortex EM silicon drift detector.

All measurements were performed with the reference electrode floating and without applying an external bias on any of the electrodes. Furthermore, the beam intensity was not modulated using a chopper, unlike previous work.[4–6] During the measurements, the pressure in the main chamber was in the high-vacuum regime, around 1×10^{-6} Pa.

After the beamline experiments, the sample was visually inspected and compared with the state prior to the experiments; no changes were observed, which is a further indication of the stability of TiO_2 in the beam.

O K-edge spectra of Fig. 3 are divided by (1) the output of a photodiode to correct for energy-dependent variations in the photon flux and (2) the theoretical X-ray transmission[7] through Si_3N_4 to correct for the attenuation by the SiN_x membrane(s), two 100-nm-thick membranes for Fig. 3a and one 100-nm-thick membrane for Fig. 3b. Data are otherwise plotted as measured.

The difference spectrum (black, Fig. 4) was obtained by subtracting Fig. 3b from 3a after (1) subtracting a linear background from each and (2) scaling the TiO_2−UHV spectrum to match the O $1s\rightarrow t_{2g}$ peak intensity (531.1 eV).

S4 Partial fluorescence measurements

The partial-fluorescence-yield spectra recorded simultaneously with the drain current measurements (Fig. 3) are depicted in Fig. S2. The partial-fluorescence-yield spectrum of TiO_2−H_2O appears very similar to the partial-fluorescence-yield spectra of self-assembled monolayers adsorbed on Au/SiN_x in contact with H_2O(l).[8] The spectra in Fig. S2 are divided by the output of a photodiode to account for energy-dependent differences in the photon flux. No other data corrections have been applied. The spectrum for the TiO_2 in water is dominated by contributions from H_2O(l), although saturation effects significantly distorted the spectrum. This reduced the intensity of the main edge (538 eV), making the pre-edge feature at 535 eV appear unrealistically large compared to the main edge. Furthermore, a small shoulder around 531.8 eV is visible. Similarly, self-absorption effects possibly made this feature appear larger compared to the H_2O(l) features. Although the origin of this feature is uncertain, it is tentatively ascribed to a defective, oxidized layer on the outside of the SiN_x membrane.[9,10] Oxygen in the TiO_2 could have contributed as well, even though that contribution would have been small,

because the TiO_2 layer is only 20 nm thick and because of the attenuation of the incoming and fluorescent X-rays by the 100-nm thick SiN_x membrane (attenuation of around 0.5).

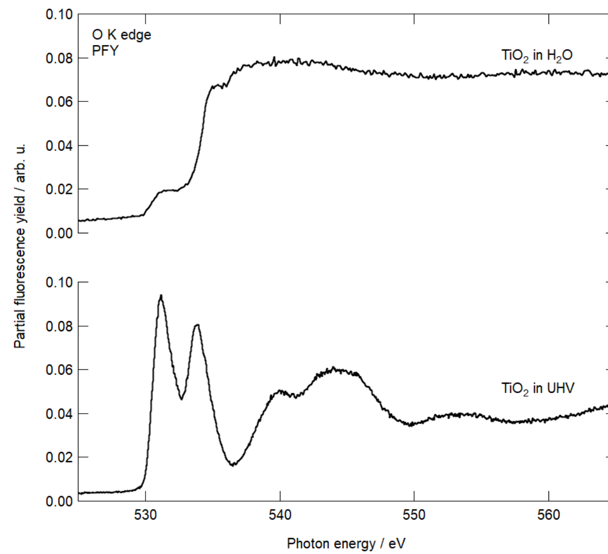

Figure S2. O-K-edge spectra obtained via partial fluorescence yield of the TiO_2 in contact with bulk H_2O(l), top, and in ultra-high vacuum (UHV), bottom.

S5 Fitting of the water difference spectrum

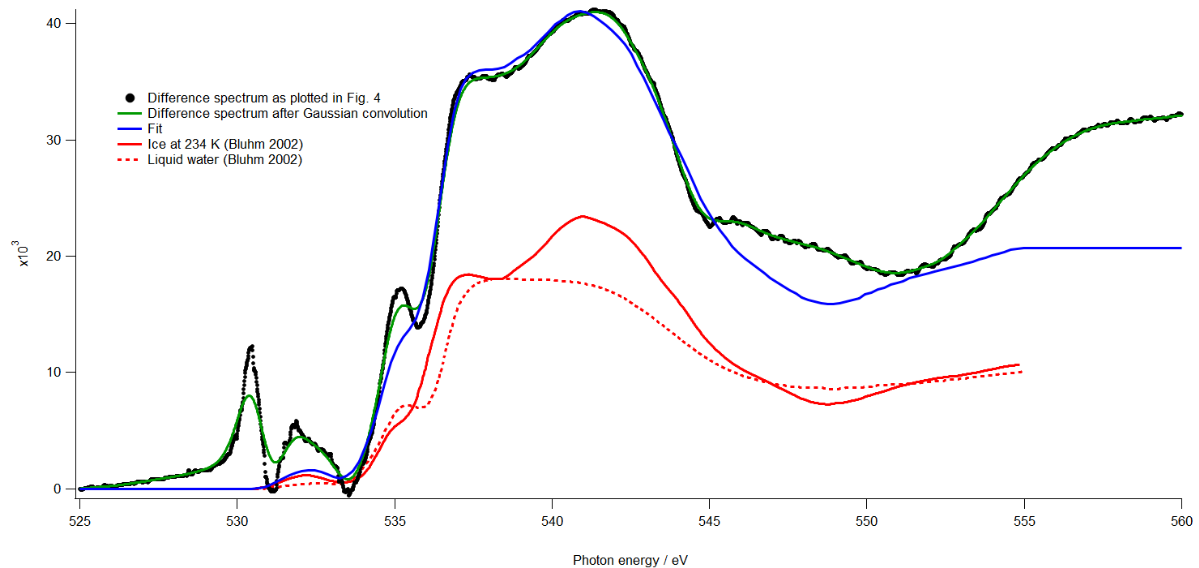

Figure S3. Fitting the difference spectrum (Fig. 4) by a linear combination of the spectra for H_2O(l) and H_2O(s), taken from Bluhm *et al.*[11] The difference spectrum was convoluted with a 0.3-eV wide Gaussian to account for the lower resolution in Ref. 11. Furthermore, the spectra of H_2O(l) and H_2O(s) were allowed to shift in position on the x axis. The optimal fitting parameters were a=6766, b=7141, c=−0.016, and d=−0.114 for the formula $fit(x)=a\times I_{water}(x+c)+b\times I_{ice}(x+d)$.

References

[1] K. Bernal Ramos, G. Clavel, C. Marichy, W. Cabrera, N. Pinna, and Y.J. Chabal, Chem. Mater. **25**, 1706 (2013).

[2] B.C. Trasferetti, C.U. Davanzo, and R.A. Zoppi, Electrochem. Commun. **4**, 301 (2002).

[3] D.W. Berreman, Phys. Rev. **130**, 2193 (1963).

[4] J.J. Velasco-Velez, C.H. Wu, T.A. Pascal, L.F. Wan, J. Guo, D. Prendergast, and M. Salmeron, Science **346**, 831 (2014).

[5] C.H. Wu, T.A. Pascal, A. Baskin, H. Wang, H.-T. Fang, Y.-S. Liu, Y.-H. Lu, J. Guo, D. Prendergast, and M.B. Salmeron, J. Am. Chem. Soc. **140**, 16237 (2018).

[6] R.S. Weatherup, C.H. Wu, C. Escudero, V. Pérez-Dieste, and M.B. Salmeron, J. Phys. Chem. B **122**, 737 (2018).

[7] B.L. Henke, E.M. Gullikson, and J.C. Davis, At. Data Nucl. Data Tables **54**, 181 (1993).

[8] D. Schön, R. Golnak, M.F. Tesch, B. Winter, J.J. Velasco-Velez, E.F. Aziz, and J. Xiao, J. Phys. Chem. Lett. **8**, 5136 (2017).

[9] Y. Yamashita, S. Yamamoto, K. Mukai, J. Yoshinobu, Y. Harada, T. Tokushima, T. Takeuchi, Y. Takata, S. Shin, K. Akagi, and S. Tsuneyuki, Phys. Rev. B - Condens. Matter Mater. Phys. **73**, 1 (2006).

[10] Y.S. Lee, W.J. Lee, S.K. Kang, and S.K. Rha, Jpn. J. Appl. Phys. **49**, 08JF05 (2010).

[11] H. Bluhm, D.F. Ogletree, C.S. Fadley, Z. Hussain, and M. Salmeron, J. Phys. Condens. Matter **14**, 227 (2002).