

Liquid-Jet X-ray Photoelectron Spectra of TiO₂ Nanoparticles in
an Aqueous Electrolyte Solution

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Supporting Information

A Photoemission survey spectra collected at 1200 eV photon energy is presented in Figure S1. No presence of carbon was detected in the survey, nor was it found in narrow energy scans of the C1s region of the spectrum. For oxygen, the O1s photoemission lines (~ 538 eV) and Auger KLL (~ 700 eV) are observed. Ti2p of titanium dioxide (~ 465 eV) and N1s of NO_3^- (~ 412 eV) are also apparent in the survey; precise characterization of the nitrogen was unsuccessful due to the weak signals. Finally, valence band of the solution can be seen in the spectrum at low energies ($\sim 0 - 40$ eV).

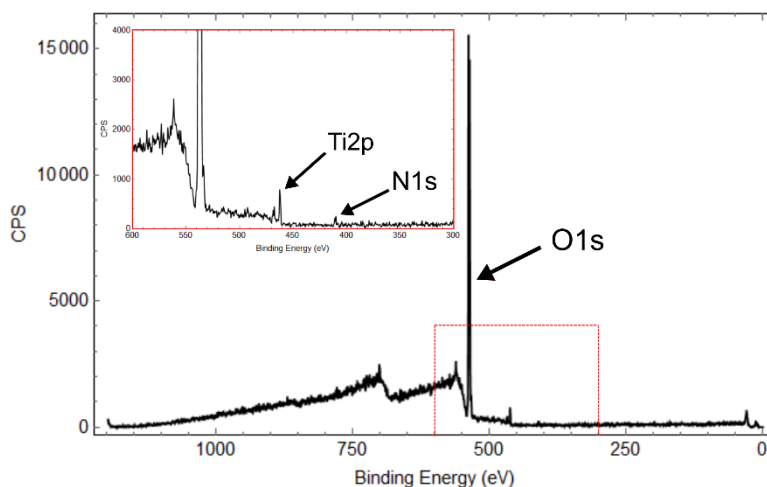


Figure S1: Survey spectrum of the TiO_2 solution at 1200 eV photon energy. Inset is the magnified region from 300 eV to 600 eV, to clearly show the existence of titanium and nitrogen.

Photoemission spectra of O 1s at the eleven excitation energies between 765 eV and 1435 eV as a function of binding energy, are displayed in Figure S2 and normalized such that TiO_2 lattice oxygen O 1s maximum intensities are the same. Lattice titanium dioxide and liquid water O 1s fits are presented as black and blue curves, respectively, while the raw data are displayed as black points. The difference between the experimental data and the total fit indicating the high quality of the fit is shown as the red line in the plots.

Fits of all spectra were obtained using the standard fitting program, CASAXPS.³³ Shirley backgrounds were applied to each spectrum and Gaussian line shapes were used to fit individual peaks. No constraints to relative binding energies, areas or widths were applied.

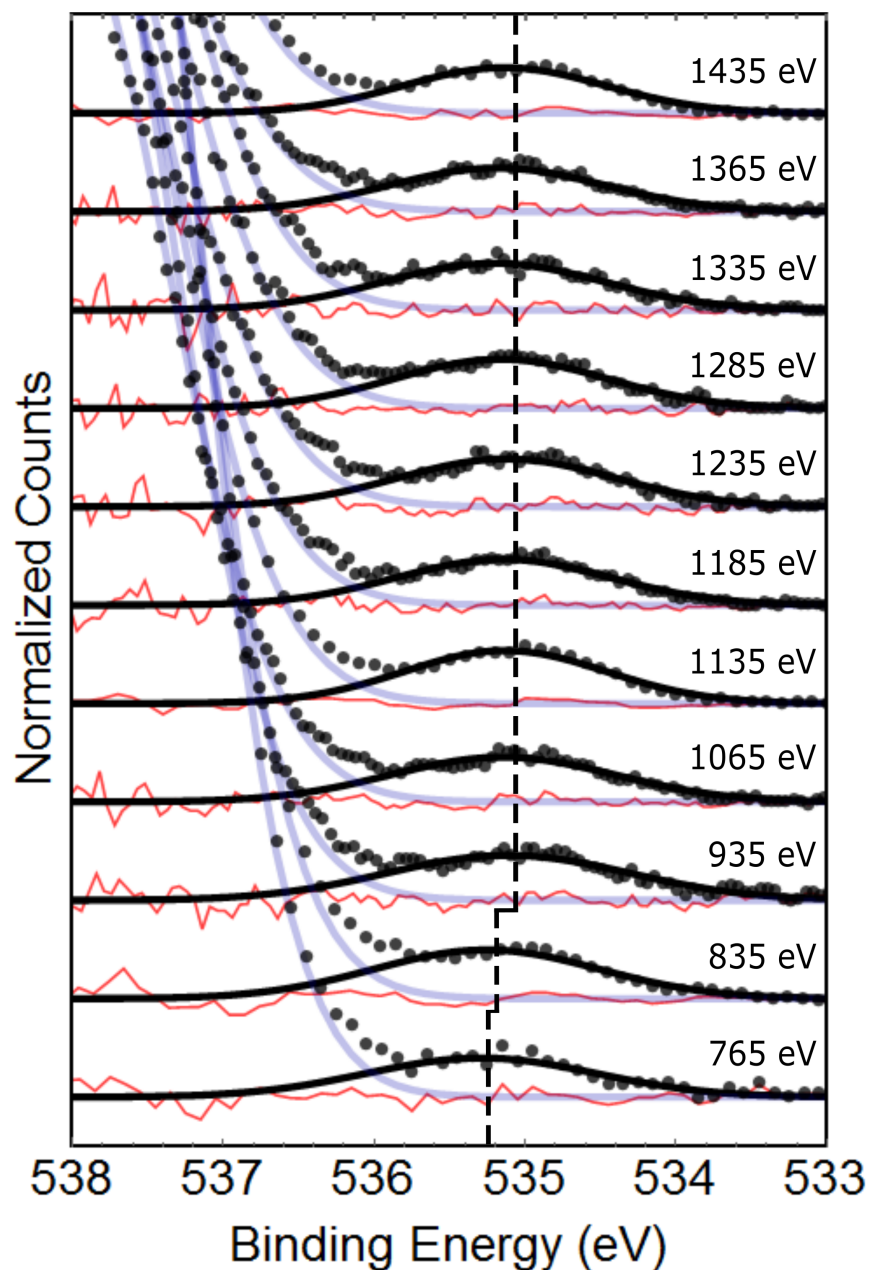


Figure S2. Photoemission spectra of O 1s, magnified to clearly show the lattice oxygen, at the eleven photon energies used in the experiments. Raw data are displayed as points. The black curve is the fit to the lattice oxygen, O 1s, and the blue lines are the fit to the liquid water O 1s. In each case the red curve shows the difference between the data points and the fit. Each spectrum is normalized such that the lattice O 1s maximum intensity is the same.

Duplicate experiments were carried out at six photon energies (765 eV, 835 eV, 1135 eV, 1185 eV, 1335 eV, 1435 eV) covering the entire range of energies used in this study to demonstrate the experimental reproducibility. Data from duplicated measurements are plotted in red in Figure 2b and Figure 3 of the manuscript. The duplicate measurements were carried out at two different beam times spaced by more than one month. Between beam times the liquid-jet chamber is removed from the ambient pressure electron energy analyzer, and re-assembly is done at the beginning of the next beam time. At each beam time spectra were obtained at different photon energies in random sequence (i.e., not in ascending or descending order). In addition, other spectral regions (e.g., Ti 2p) were scanned between collection of the O1s spectra discussed in the manuscript. The reproducibility of the data shown in Figure 2b and 3 of the manuscript is very good and typical of what we have observed in our studies of a wide range of aqueous solutions.