Hydration structure of brookite TiO₂ from first-principles molecular dynamics and experiment

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A promising application of TiO₂ is the photocatalytic reduction of atmospheric CO₂ into hydrocarbons. Of the ambient polymorphs of TiO₂, we target the hydration structure of brookite for increasing our understanding of the reduction process on this relatively unexplored surface. Using density functional theory molecular dynamics simulations and high-resolution atomic force microscopy, we unravel the structural, electronic, and vibrational properties of the interface of TiO₂ brookite (210) and water.

Below: The brookite (210) surface. Right: At low coverages, water mainly adsorbs through covalent Ti-O bonds and hydrogen bonding. Only 3-4% of surface oxygens are hydroxylated.

Above: Histogram of lateral ionic positions. Red dots signify bridging O₂c-, light green dots signify Ti₅c. At bulk H₂O coverage, about 15% of surface oxygens are hydroxylated. The rows of Ti₅c are covered by H₂O molecules, adsorbed through weak covalent Ti-O bonds and through hydrogen bonds to nearby O₂c pairs, as well as OH fragments (see panel below).

Top left: The electronic density of states is featureless near the band gap. Bottom left: Hydroxilation leads to proton transfer at the interface. Right: electronic density in a plane through an OH fragment.

The OH stretching band of H₂O is drastically red-shifted at the solid-liquid interface. We are currently planning experimental measurements to test this theoretical prediction for the vibrational spectrum.

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