

Electronic Supporting Information

Curvature-induced hydrophobicity at imogolite-water interfaces

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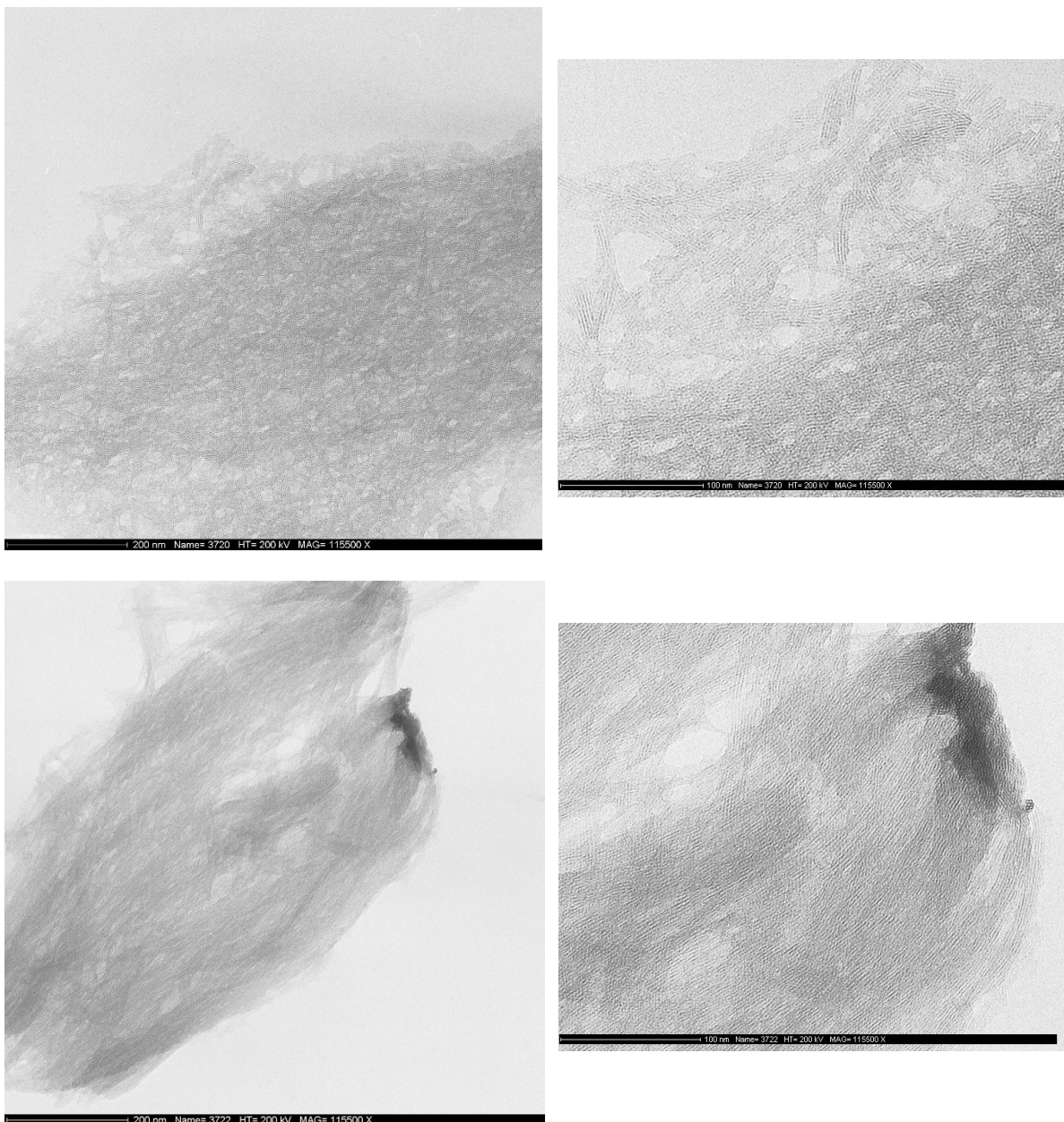


Fig. S1 Transmission electrons microscopy images of synthetic imogolite fibers at different magnifications. The large magnifications (left) show long fibers (up to ~50-100 nm long). The distance between fibers has been characterized to be in the range 2.0 – 2.2 nm, matching the expected external diameter of synthetic Si-imogolite.¹ The high magnification image (bottom right) shows the section of a few fibers, showing their open ends.

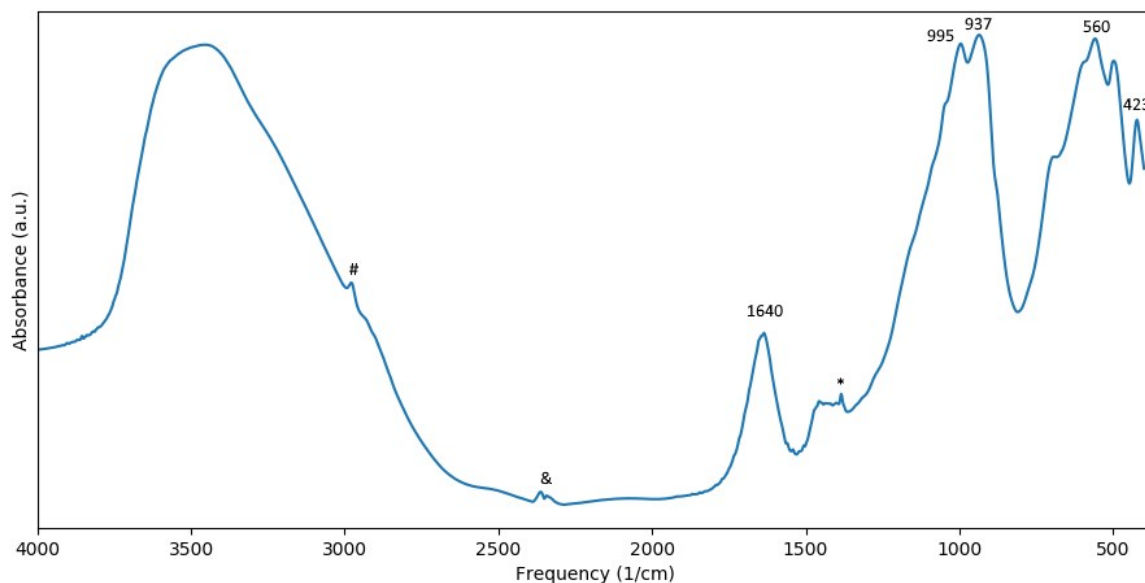


Fig. S2 Fourier Transform Infrared Spectroscopy (FTIR) absorbance spectrum of synthetic imogolite. Bands at frequencies 423, 560 and 937 have been identified as being characteristic of the imogolite structure, with high amount of water (1640 and 3500 cm^{-1}).^{2,3} The position of the band at 995 cm^{-1} corresponding to the Si-O stretching mode, shifts position depending on the Al:Si ratio. A low Al:Si ratio shifts the band towards higher wavenumbers.⁴ The peak at 995 cm^{-1} is indicative of a structure with a 2:1 Al:Si ratio, characteristic of imogolite. Other highlighted peaks indicate contamination with organics (#), atmospheric CO_2 (&) and residual nitrate from the synthesis (*).

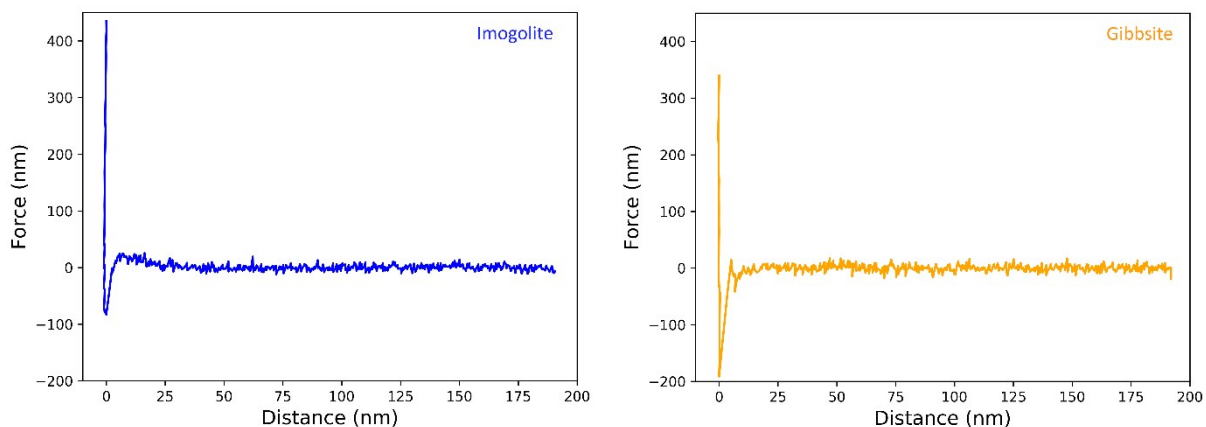


Fig. S3 Representative examples of force vs. distance curves showing a larger adhesion for gibbsite. The curves show the retraction force felt by the >SiOH terminated AFM tip during retraction from the surface. The distance $d = 0$ nm corresponds to the position of the surface. The negative force observed in both graphs at lower distances of retraction reflects the strength of the bond between the tip and the surface.

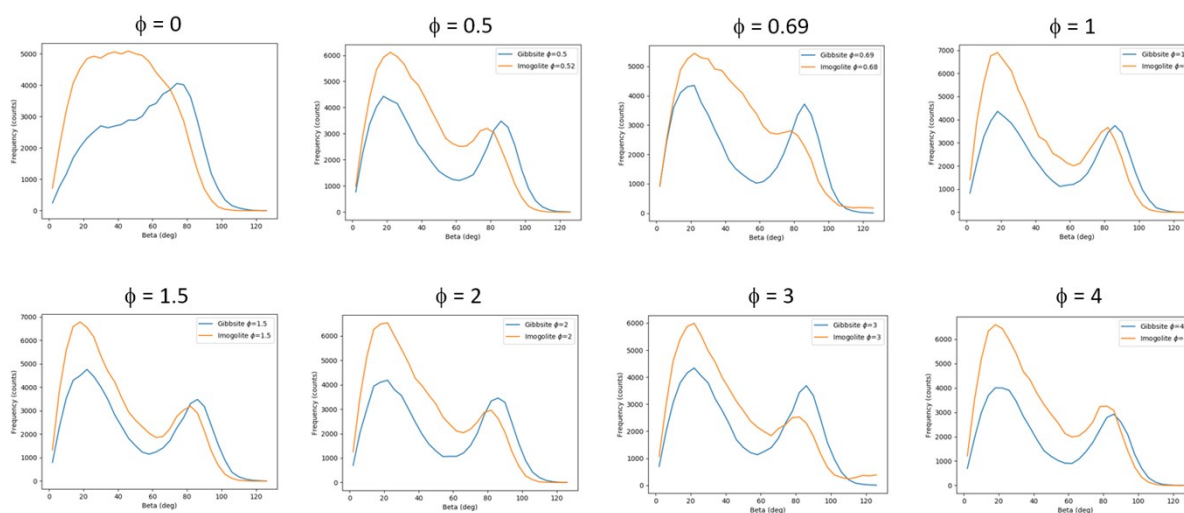


Fig. S4 Distributions of angle β formed between the surface hydroxyl vectors (\overline{OH}) and the vector normal to the surface, at different degrees of surface hydration (blue: gibbsite; orange: imogolite). The results show two main orientations of the hydroxyl groups, pointing mostly perpendicular ($\beta \sim 20^\circ$) and parallel ($\beta \sim 80^\circ$) to the surfaces, with a higher proportion of perpendicular hydroxyls for imogolite.

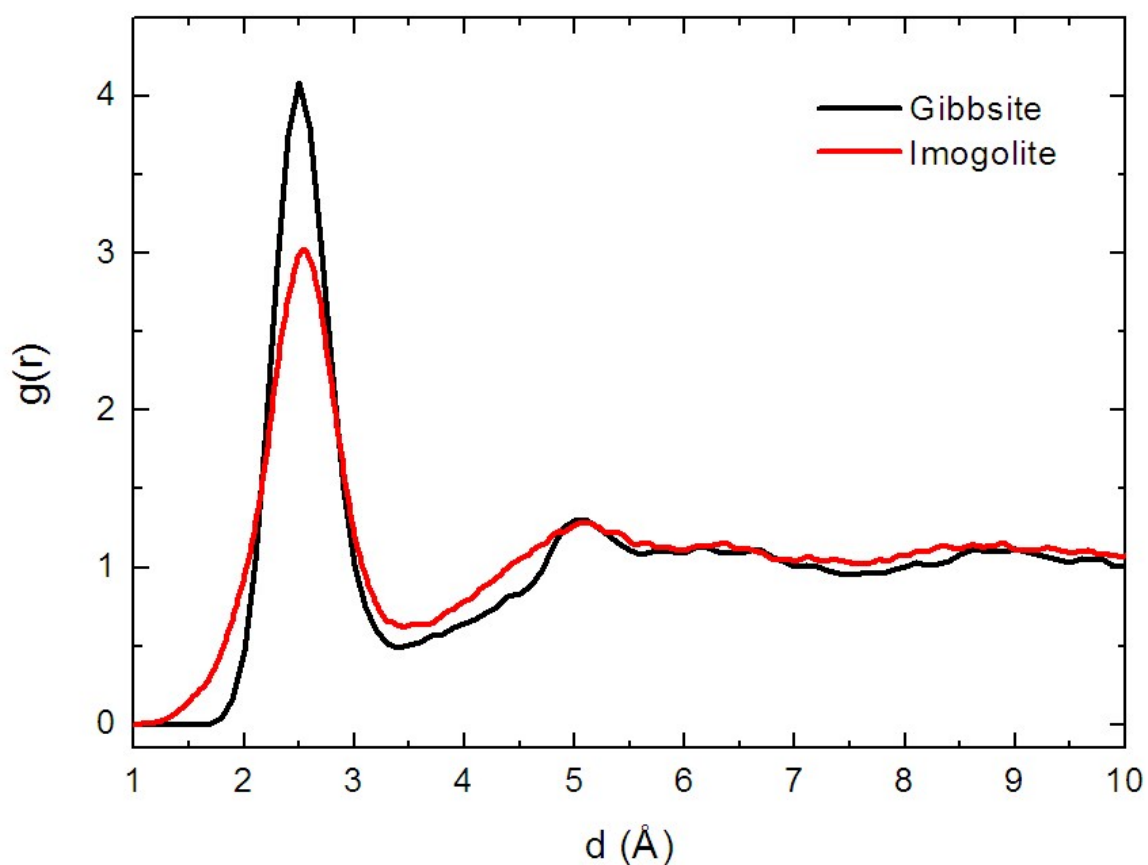


Fig. S5 Normalized water density profiles at the (001) gibbsite surface and at the external imogolite surface. The origin is placed at the positions of the surface O atoms. These plots have been generated from molecular dynamics trajectories in equilibrium (NVT ensemble), for an average of at least 0.5 ns.

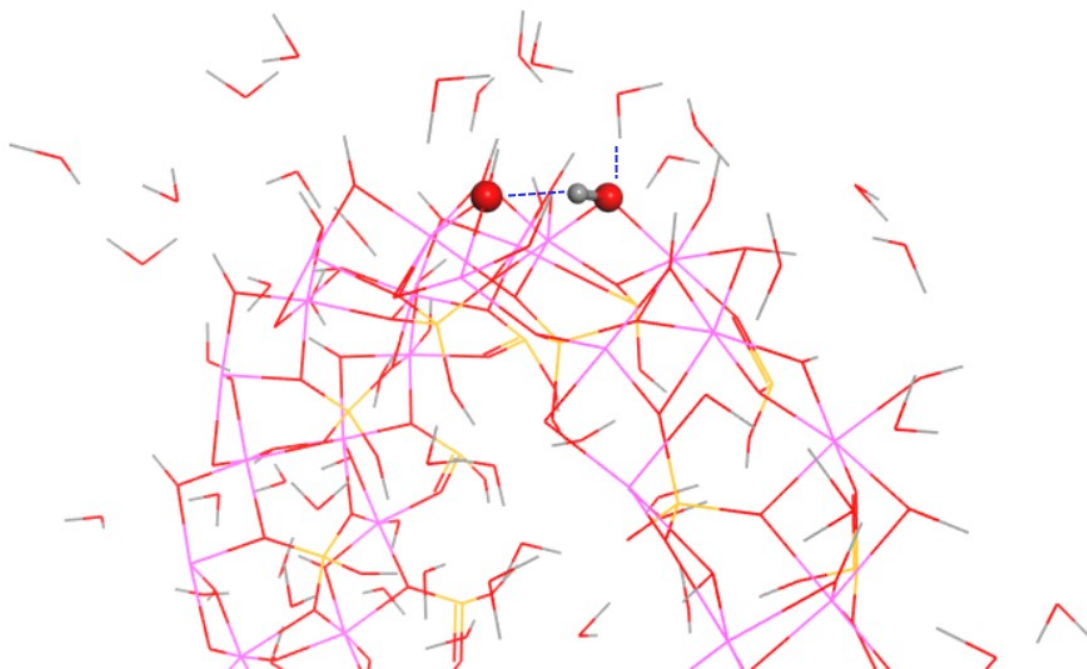


Fig. S6 View of the DFT-optimized structure of the imogolite-water interface. An A-type water molecule, donating a hydrogen bond to a surface oxygen, is highlighted (hydrogen bond in blue dashes). The surface hydroxyl is donating a hydrogen bond to a neighboring oxygen, in a direction almost parallel to the tube axis.

References

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