Supporting Information

Geometrical analysis of various amorphous titania structures is shown in Figures S1 through S5. In Figure S1 we show a comparison of radial distribution functions from our work with literature results. Figure S2 gives calculated coordination numbers from our work, also compared with literature results. Figure S3 shows radial distribution functions for two simulation cells, one containing 216 atoms and the other 1728 atoms, both using the DL_POLY molecular dynamics program. Figure S4 gives radial distribution functions for Ti-Ti pairs for different titania stoichiometries. Figure S5 shows the distribution of O-Ti-O-Ti dihedral angles for select stoichiometries. Figure S6 contains localized density of states plots with Ti and O electronic states indicated. Figure S7 shows electron density plots of the conduction and valence band edge orbitals for select stoichiometries. All optimized geometries for U = 4 eV can be found at the following website: https://github.com/Deskins-group/Structure-Files/tree/master/Amorphous-Reduced-Titania .

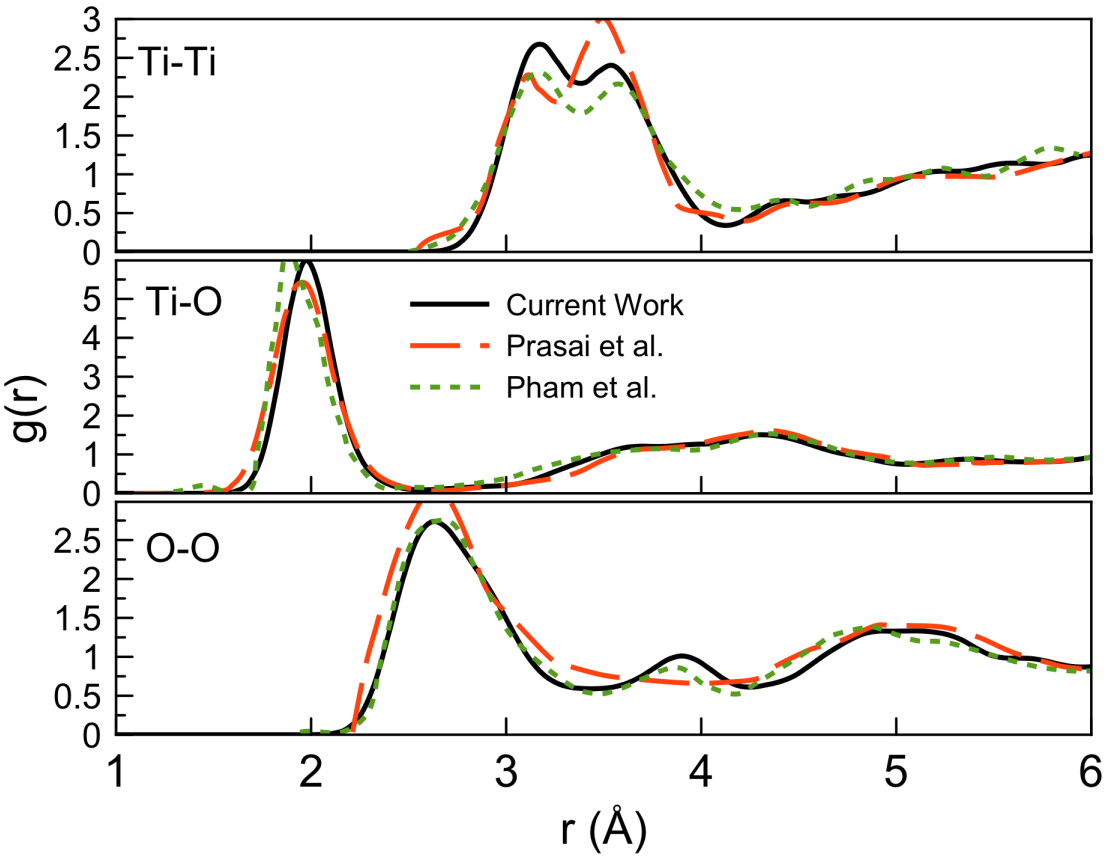

Figure S1: A comparison of our results with those of Prasai et al.[1] and Pham et al.[2] Shown is the calculated radial distribution function, g(r), for amorphous TiO_2.

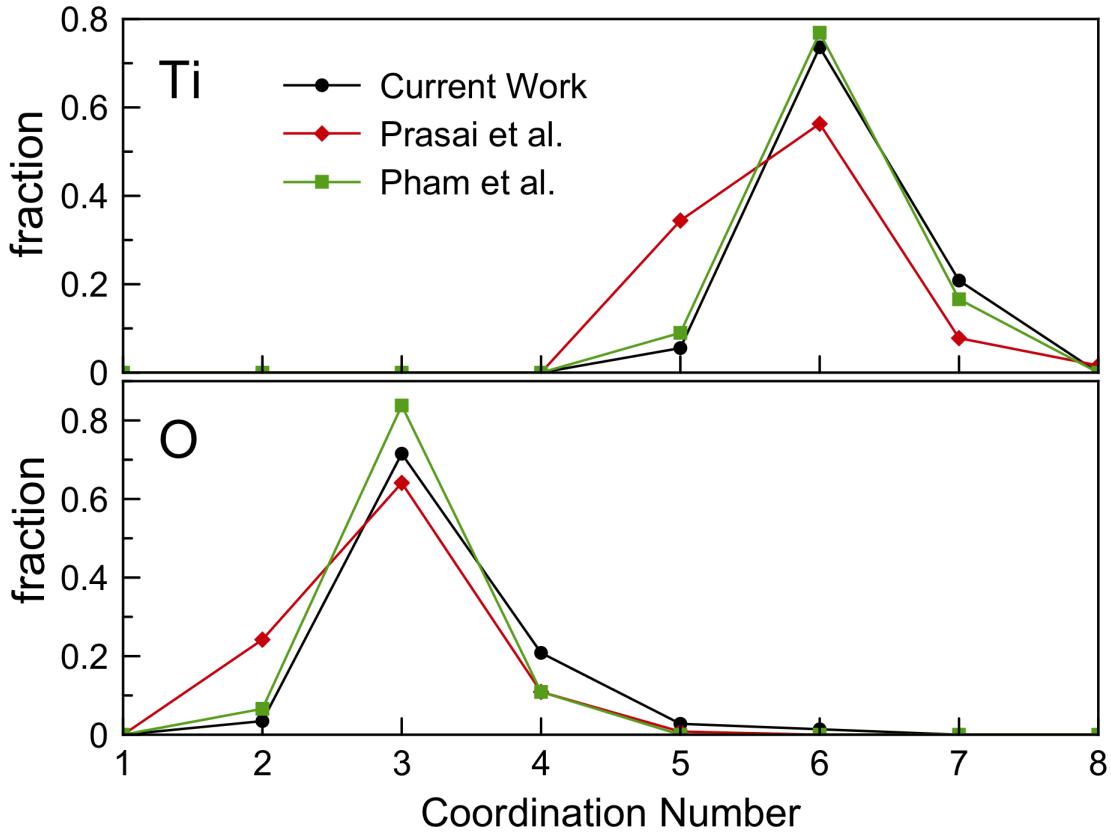

Figure S2: Calculated coordination numbers for amorphous TiO_2. Similar data from Prasai et al.[1] and Pham et al.[2] are shown for comparison.

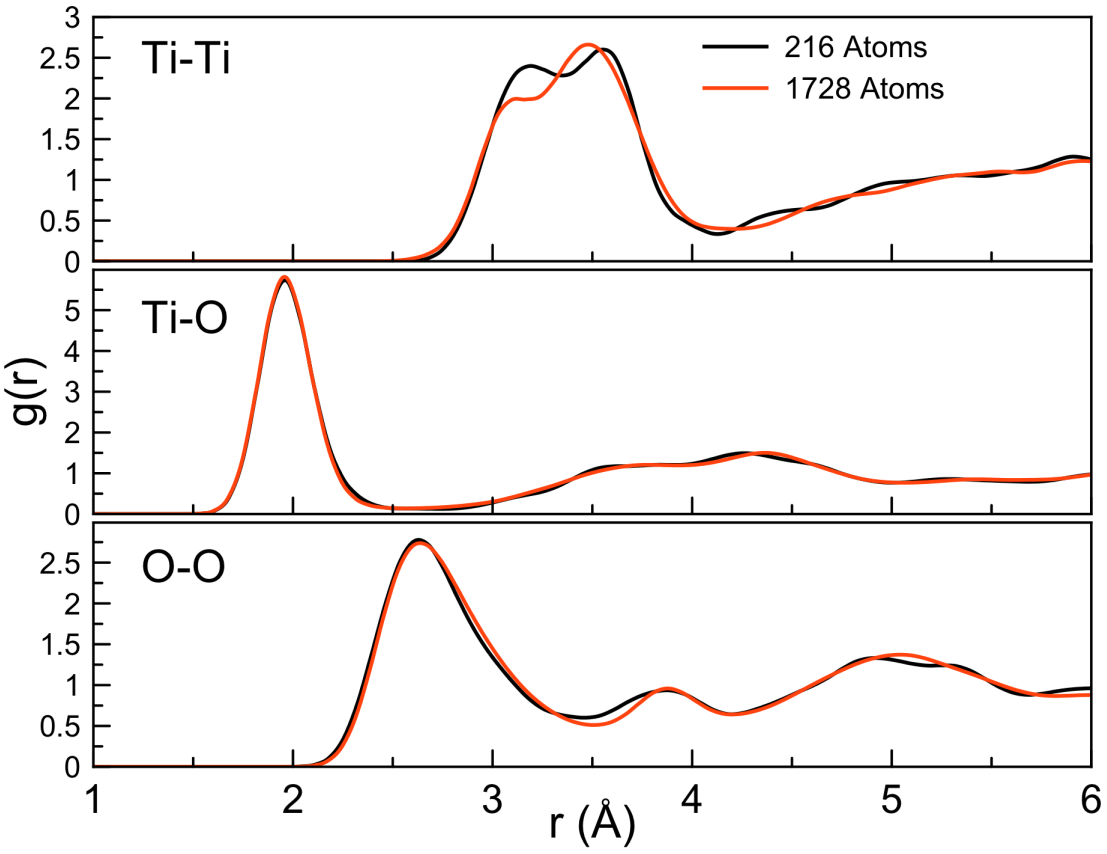

Figure S3: Radial distribution functions, g(r), for TiO_2 as calculated using the DL_POLY program. Different size simulation cells were used for the two data sets.

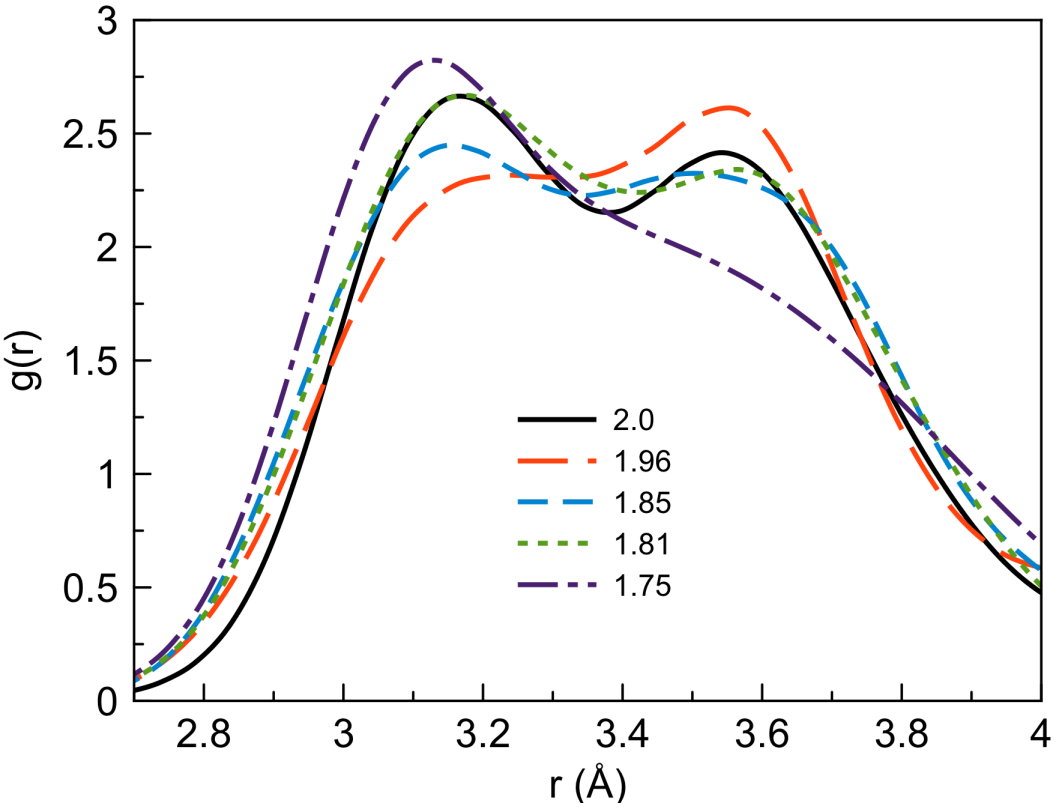

Figure S4: Pair radial distribution functions (Ti-Ti), g(r), for select TiO_x stoichiometries. First peak was attributed to edge-sharing octahedra and the second peak to corner-sharing octahedra.[3]

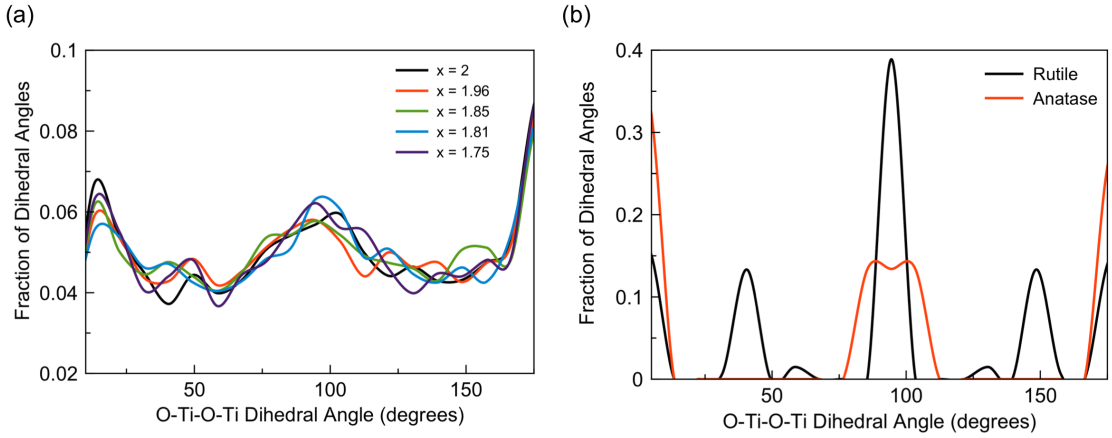

Figure S5: Dihedral angular distributions (O-Ti-O-Ti) for (a) select amorphous TiO_x stoichiometries and (b) crystalline titania.

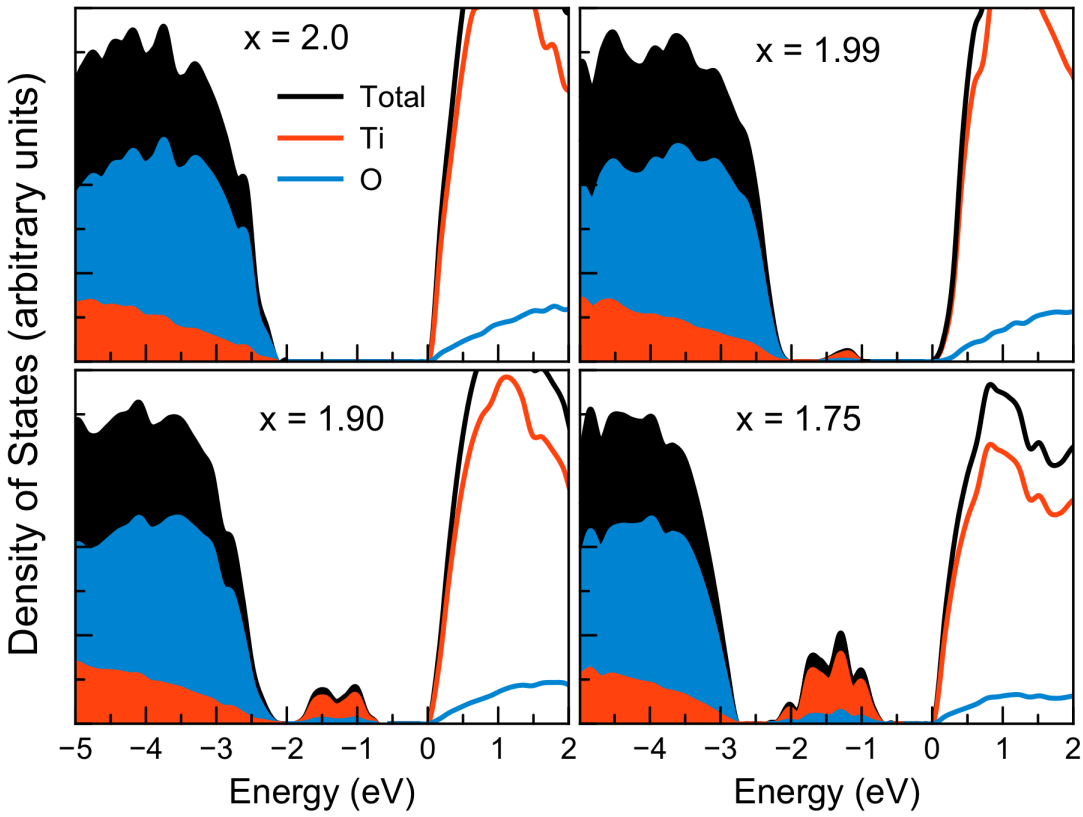

Figure S6: Calculated localized density of states for select stoichiometries showing electronic states on Ti and O atoms.

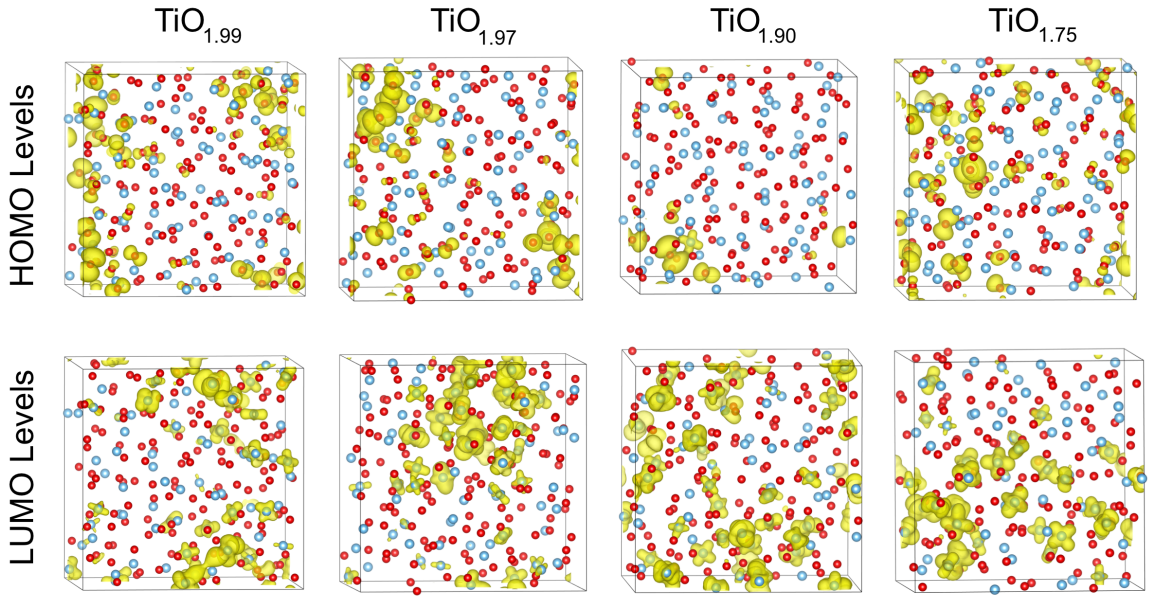

Figure S7: Illustration of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) states for select stoichiometries. All images show charge densities for electronic states within 0.1 eV of the highest occupied energy eigenvalue and lowest unoccupied energy eigenvalue.

References

[1] Prasai, B, Cai, B, Underwood, M, Lewis, J, & Drabold, D. (2012) Properties of amorphous and crystalline titanium dioxide from first principles. *Journal of Materials Science* **47**, 7515–7521.

[2] Pham, H. H & Wang, L.-W. (2015) Oxygen vacancy and hole conduction in amorphous tio2. *Phys. Chem. Chem. Phys.* **17**, 541–550.

[3] Petkov, V, Holzhüter, G, Tröge, U, Gerber, T, & Himmel, B. (1998) Atomic-scale structure of amorphous tio2 by electron, x-ray diffraction and reverse monte carlo simulations. *Journal of Non-Crystalline Solids* **231**, 17 – 30.