Create a project:

1. New project→Enter TiO2 SurfEngy as the project name→Click the OK button.
2. Right-click on the root icon in the Project Explorer→Select New | Folder, repeat this one more time→Rename the folders TiO2_rutile, TiO2_rutile (111).

To optimize bulk TiO2

1. In the Project Explorer, right-click on the TiO2_rutile folder and select Import→Navigate to Structures\Metal-Oxides→double-click on TiO2_rutile.msi (red: O, grey: Ti), which is a tetragonal phase of SGR=136 P42/MNM.
2. Right-click in the TiO2_rutile.xsd→Open the Display Style dialog→On the Atom tab, select Ball and stick→Close the dialog.
3. Module→ CASTEP→Calculation → Quality: Fine→Task: Geometry Optimization→ Click the More... button→Check the Optimize cell checkbox→Close the dialog→ Click the Run button→A message dialog about conversion to the primitive cell is displayed. Click the Yes button.
4. Open TiO2_rutile.xsd located in the TiO2_rutile CASTEP GeomOpt folder→Select Build | Symmetry | Conventional Cell→ Right-click in the 3D Viewer and select Lattice Parameters to check the lattice parameters of the optimized unit cell structure to be $a=b=c=4.66379$.
   Select File | Save Project, then Window | Close All from the menu bar.

To build the TiO2(111) surface file

Open TiO2_rutile.xsd in the TiO2_rutile CASTEP GeomOpt folder.

1. Build | Surfaces | Cleave Surface→Change the Cleave plane (h k l) from -1 0 0 to 1 1 1 and press the TAB key. Increase the Fractional Thickness to 3→Click the Cleave button and close the dialog.
2. Build | Crystals | Build Vacuum Slab→Change the Vacuum thickness to 10.00→Click the Build button.
3. Select File | Save As... →Navigate to the TiO2_rutile (111) folder→Click the Save button.
4. Select File | Save Project, then Window | Close All from the menu bar.
5. From the Project Explorer, open TiO2_rutile (111).xsd in the TiO2(111) folder→Module|CASTEP|Calculation→Task: Geometry Optimization. Ensure that the Optimize cell checkbox is unchecked→Close the dialog.
6. (Option for saving the computation time) Hold down the SHIFT key and select all the atoms except the uppermost layer. Select Modify | Constraints from the menu bar to open the Edit Constraints dialog. Check the Fix fractional position checkbox and close the dialog.

7. Click the Run button and close the CASTEP Calculation dialog.
8. Select File | Save Project then Window | Close All.