Supporting information

Structure, stability and water adsorption on ultra-thin TiO_2 supported on TiN

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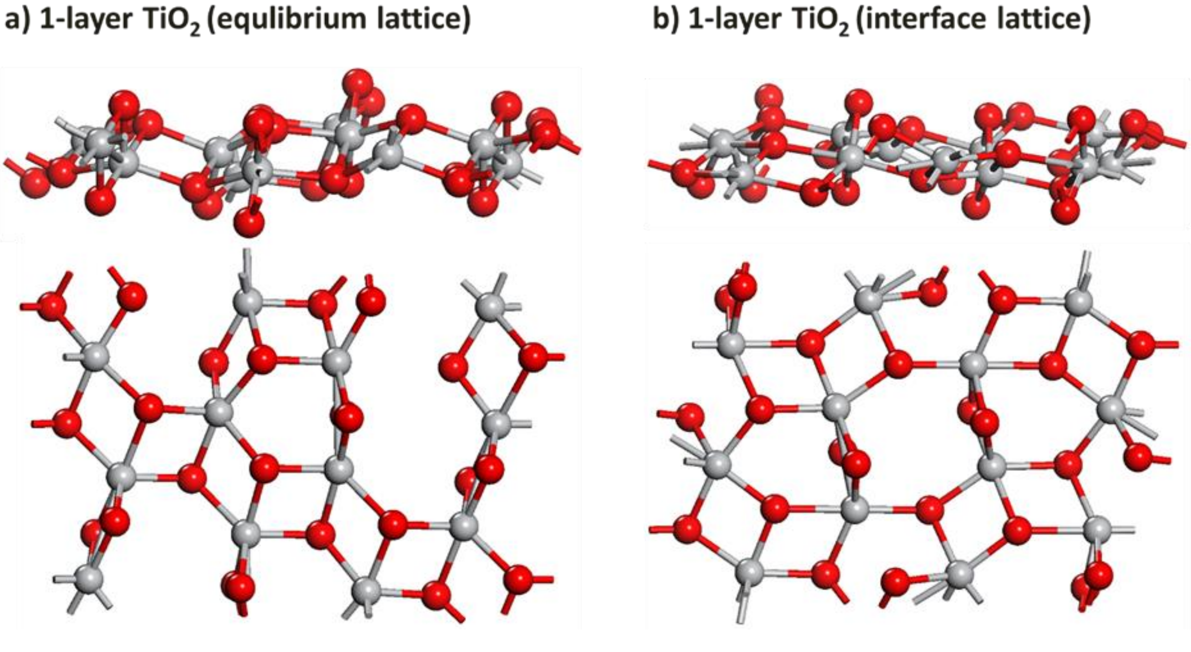
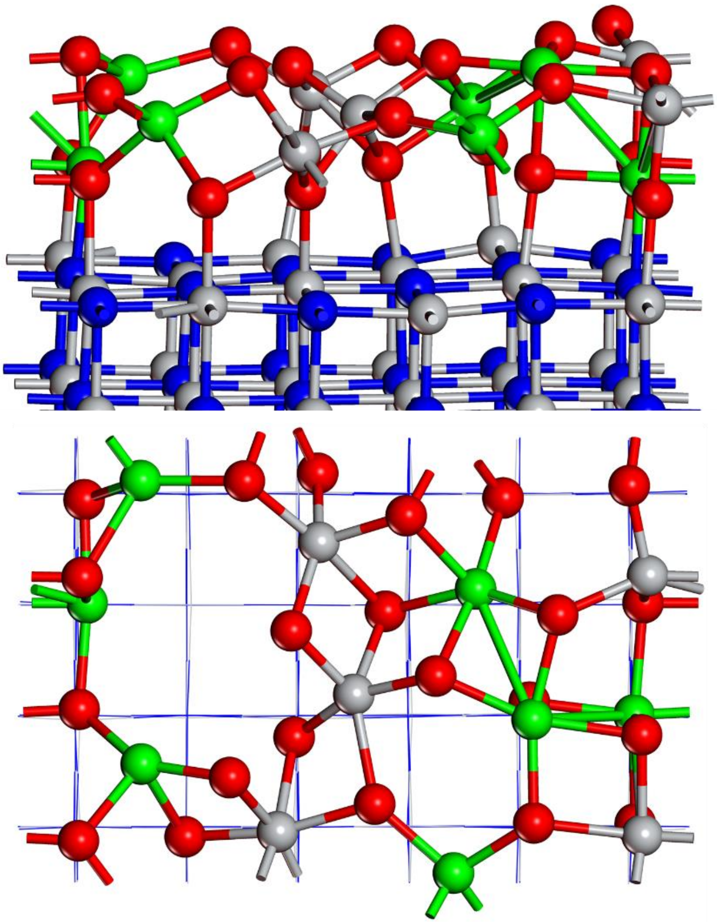
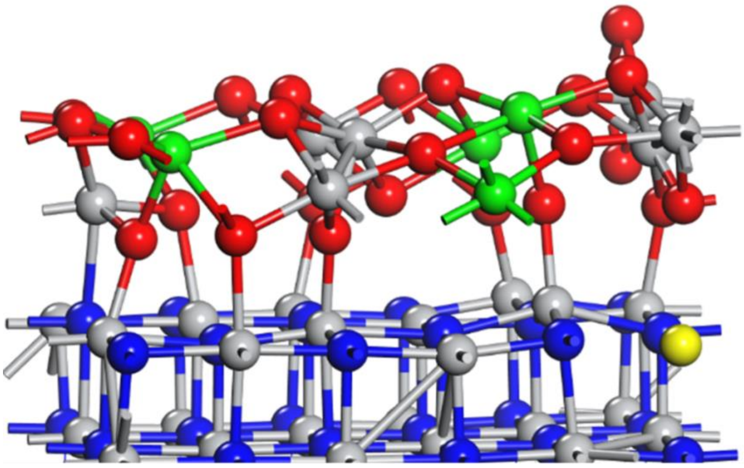


Figure S1. DFT+U relaxed structure of the free-standing rutile TiO_2 (110) monolayer at (a) equilibrium TiO_2 lattice and (b) interface TiN (100) lattice. The front-perspective view of the slab is presented on the top panel and the top view is on the bottom. Ti and O atoms are represented by grey and red spheres, respectively. The structure is strongly disordered compared to the original rutile (110). The formation of Ti-O bonds in the inter-layer is promoted in the compressed model (interface lattice), due to the proximity between neighbours. The calculated total energy of the compressed layer is 0.93 eV higher than the equilibrium structure.



E_{vac} ($2O_{vac}$) = 5.71 eV

Figure S2. Structure of 1-layer thick rutile TiO_2 (110)–TiN (100) interface with 2 O vacancies simultaneously created. The front-perspective view of the slab is presented on the top panel and the top view is on the bottom. The vacancy formation energy is presented under the figure. Reduced Ti^{3+} atoms in TiO_2 are represented are green, Ti^{4+} atoms in TiO_2 and all Ti in TiN are grey, N atoms are blue and O atoms are red.



E_{vac} (Ti) = 4.62 eV

Figure S3. Structure of Ti defect in 1-layer thick rutile TiO_2 (110)–TiN (100) interface The Ti vacancy formation energy calculated taking as reference the energy of bulk Ti is presented under the figure. The Ti vacancy site in TiN is represented by a yellow sphere, reduced Ti^{3+} atoms in TiO_2 are represented are green, Ti^{4+} atoms in TiO_2 and all Ti in TiN are grey, N atoms are blue and O atoms are red.

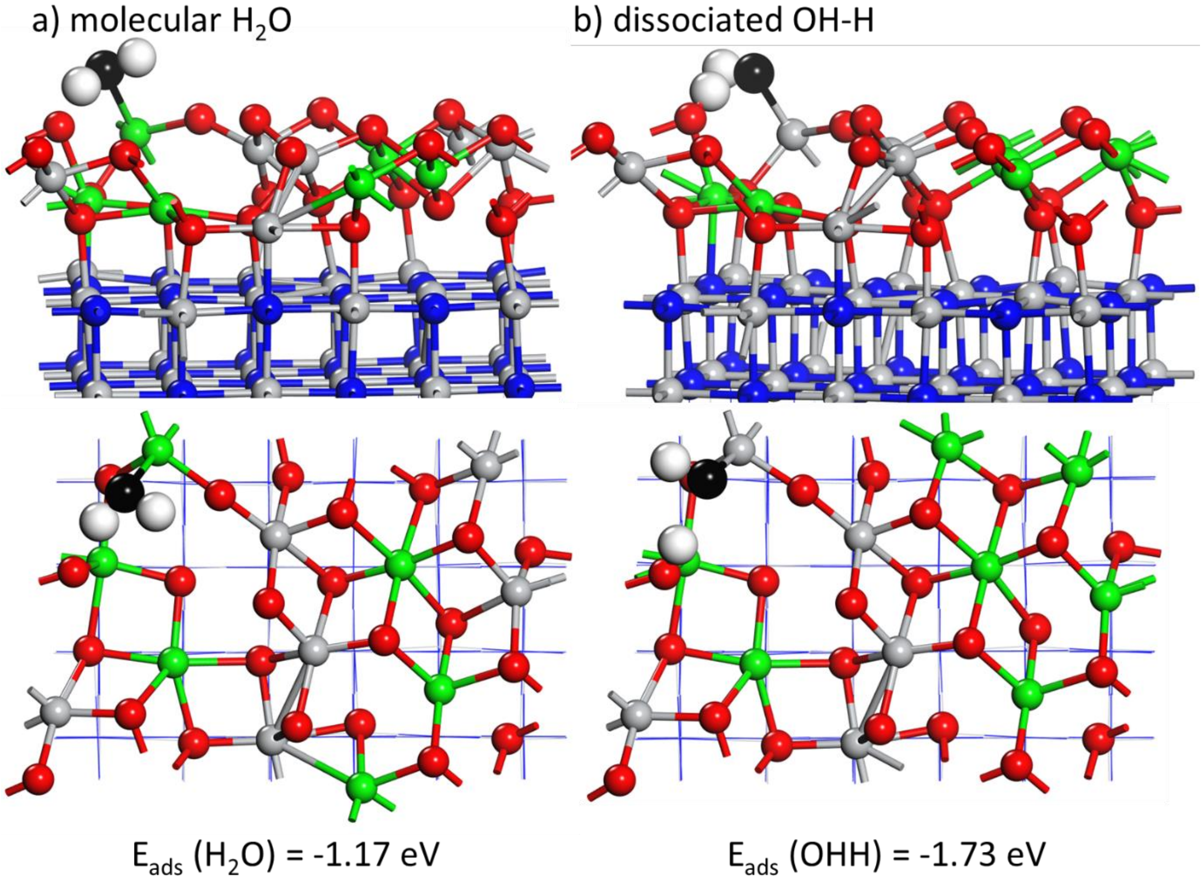
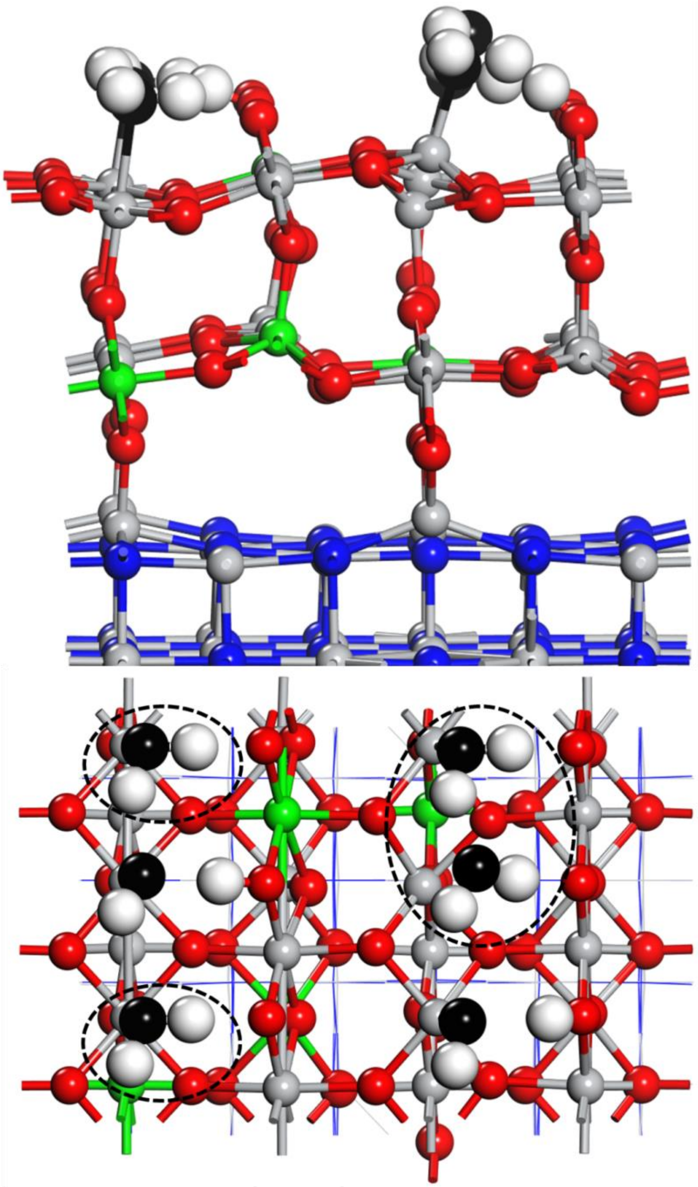


Figure S4. Structures of single water adsorbed at 1-layer thick O-defective TiO_2–TiN interfaces in (a) molecular and (b) dissociated modes. The adsorption energy values per adsorbed water are presented under figures. The Ti^{3+} atoms in TiO_2 are represented by green spheres, Ti^{4+} atoms in TiO_2 and all Ti in TiN are grey, N atoms are blue, O atoms from TiO_2 are red, O atoms from adsorbed water are black and H atoms are white.



E_{ads} (OHH) = -0.81 eV

Figure S5. Structure of DFT+U relaxed dissociated water monolayer (fully hydroxylated) on perfect 2-layer thick rutile (110) TiO_2–TiN interface. The adsorption energy per water is presented under figures. Molecular H_2O formed from OH+H reassociation are indicated with dashed rings. The Ti^{3+} atoms in TiO_2 are represented by green spheres, Ti^{4+} atoms in TiO_2 and all Ti in TiN are grey, N atoms are blue, O atoms from TiO_2 are red, O atoms from adsorbed water are black and H atoms are white.

	1-layer TiO_2				2-layer TiO_2					
	Stoichiometric		1xO-vac		Stoichiometric		$6xO_{vac}$ (slab)		$6xO_{vac}$ (etched)	
Coverage	H_2O	OH-H	H_2O	OH-H	H_2O	OH-H	H_2O	OH-H	H_2O	OH-H
1 x H_2O	-1.78	-2.33	-1.17	-1.73	-0.68	-1.09	1.24	1.65	1.54	0.60
H_2O ML	-0.81	-0.83			-0.89	-0.81	-0.55	-0.71	-1.73	-1.66

Table S1. Adsorption energy (expressed in eV) water on rutile TiO_2 (110)–TiN (100) interfaces. Molecular (H_2O) and dissociated (OH-H) adsorption modes with increasing surface coverage are distributed in lines. The ideal stoichiometric 1-layer thick perfect and O-defective TiO_2-TiN, stoichiometric 2-layer thick TiO_2-TiN and $6xO_{vac}$ 2-layer thick $TiO_{1.75}$-TiN etched, and slab model interfaces are represented in columns.

	1-layer TiO_2		2-layer TiO_2					
	Stoichiometric		Stoichiometric		$6O_{vac}$ (etched)		$6O_{vac}$ (slab)	
Surface Coverage	Ti-O	O-H	Ti-O	O-H	Ti-O	O-H	Ti-O	O-H
isolated (H_2O)	2.23	1.02	2.19	0.97	2.11	0.97	2.20	0.97
		0.98		1.01		1.09		1.04
isolated (OH-H)	2.05	0.97	1.91	0.97	1.91	0.97	1.89	0.98
	2.18	0.98		0.98		0.99		0.97
full (H_2O)	3.45	0.98	2.26	0.99	2.24	0.98	2.27	1.01
	2.22	0.99	2.33	1.02	2.20	1.00	2.12	0.98
	2.23	1.04	2.32	0.99	2.21	0.97	2.20	0.97
	2.33	1.00	2.44	1.02	2.13	1.09	2.23	1.03
	2.22	1.02	2.29	0.99	2.09	0.98	2.27	1.04
	2.25	0.97	2.28	1.02	-	1.04	-	0.97
		0.99		0.98		1.01		0.97
		0.99		1.01		0.98		1.03
		0.97		0.99		0.97		1.98
		1.12		1.02		1.00		1.00
		1.02		0.99		-		-
		0.97		1.02		-		-
full (OH-H)	1.97	1.00	2.25	1.00	1.94	0.97	1.89	0.98
	2.15	0.98	2.01	1.04	1.97	0.99	1.93	0.97
	2.17	1.01	2.27	0.98	1.85	0.97	2.21	0.97
	2.14	1.02	2.24	1.01	1.99	0.99	1.96	0.98
	2.77	0.97	3.51	0.99	1.92	1.00	1.95	0.99
	2.83	1.09	1.90	1.01	-	0.97	-	1.02
		1.01		1.00		0.98		0.97
		0.99		1.03		0.97		0.97
		0.99		0.97		0.97		1.00
		0.97		0.99		1.01		1.00
		0.99		0.99		-		-
		0.99		0.99		-		-

Table S2. Bond distances (expressed in Å) between O from adsorbed water and surface Ti atoms and H, after adsorption on rutile TiO_2 (110)–TiN (100) interfaces. Molecular (H_2O) and dissociated (OH-H) adsorption modes with increasing surface coverage are distributed in lines. The ideal stoichiometric 1-layer thick TiO_2-TiN, stoichiometric 2-layer thick TiO_2-TiN and $6O_{vac}$ 2-layer thick $TiO_{1.75}$-TiN etched and slab model interfaces are represented in columns. Top-down listed distances represent adsorption sites following an order from left-to-right and back-to-front as represented in the corresponding figures as within the manuscript. Each pair of O-H distances for molecular H_2O correspond to the molecular bonds in water and are given in left-to-right order, as presented in the manuscript. For dissociated OH-H, the distances stand for the O-H bond in the hydroxyl and the bond formed between the surface O in TiO_2 and the adsorbed H from water and are also given following a left-to-right order.

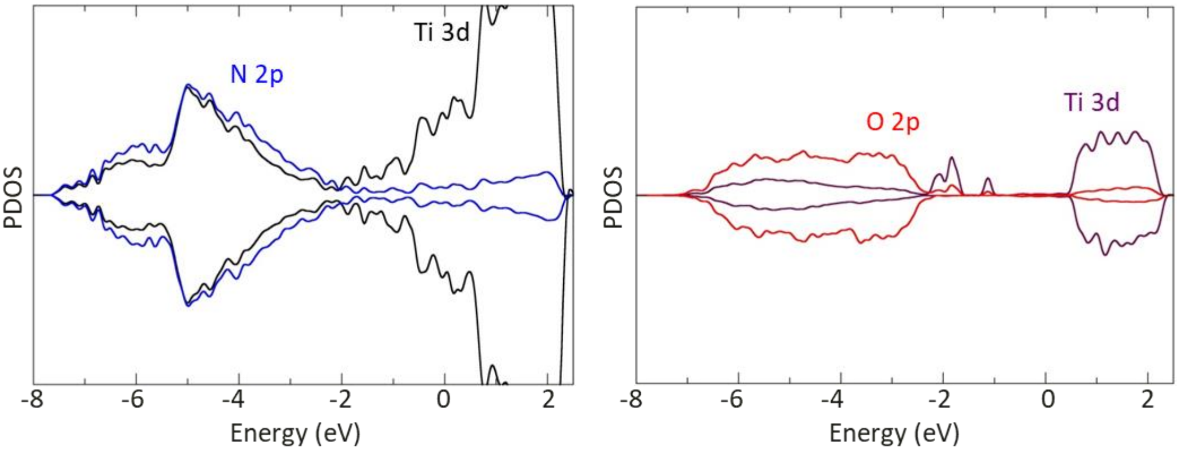
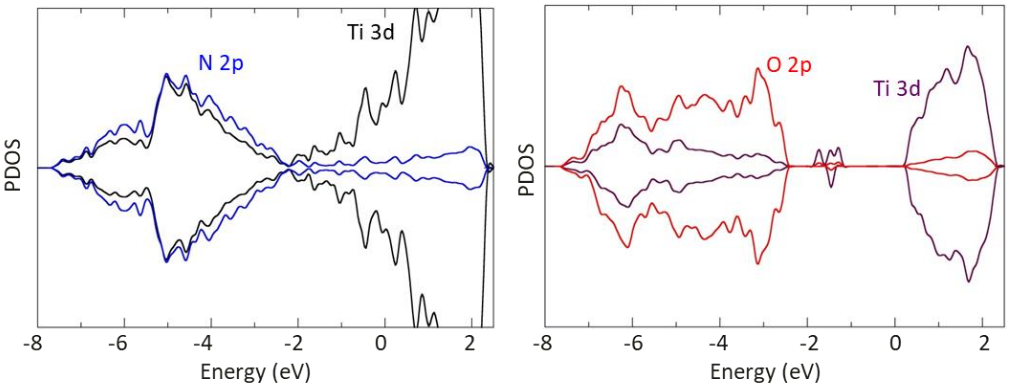
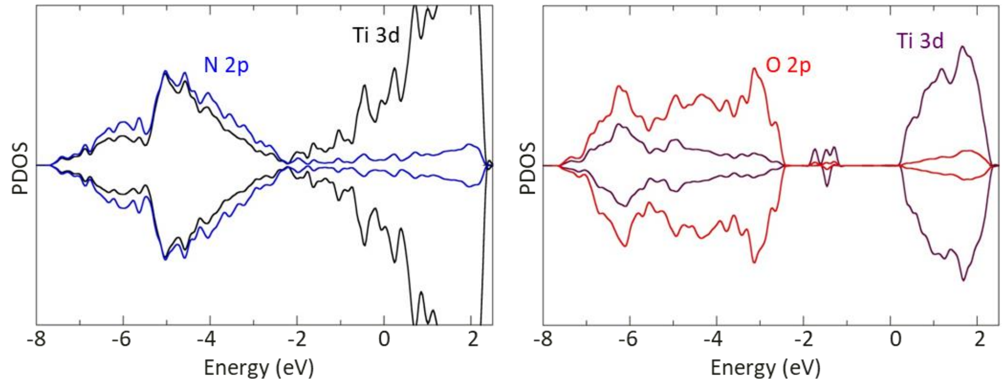


Figure S6. Spin-polarized Partial Density of States (PDOS) of O-defective 1-layer thick TiO_2-TiN interfaces. The Ti^{3+} states lay between the top edge of the valence band and -1.6 eV below E_F, which contribute to an energy gap narrowing to 2 eV. The mid-gap peak is centred -1.1 eV from E_F. In line with the content presented in the main text, the graphs on the left and right panels represent TiN and TiO_2 contribution. Ti 3d electrons from TiN are represented with black lines, N 2p electrons in blue, Ti 3d electrons from TiO_2 in purple, and O 2p electrons from TiO_2 in red. The accumulated contribution of each species was considered for the total PDOS. The upper and lower halves of the graphs represent the spin-up and spin-down components respectively. The 0 eV energy stands for the Fermi level.

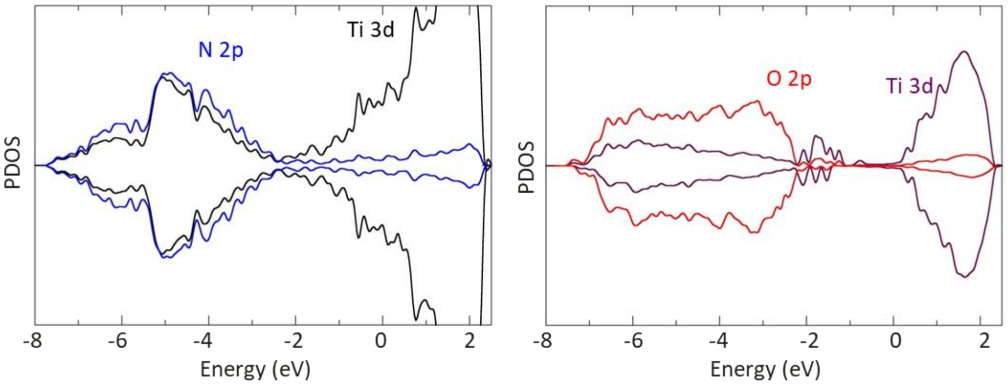
a) 2-layer TiO_2-TiN



b) 2-layer 1xO vacancy (inteface) TiO_2-TiN



c) 2-layer 6xO vacancy TiO_2-TiN (etched)



d) 2-layer 6xO vacancy TiO_2-TiN (slab)

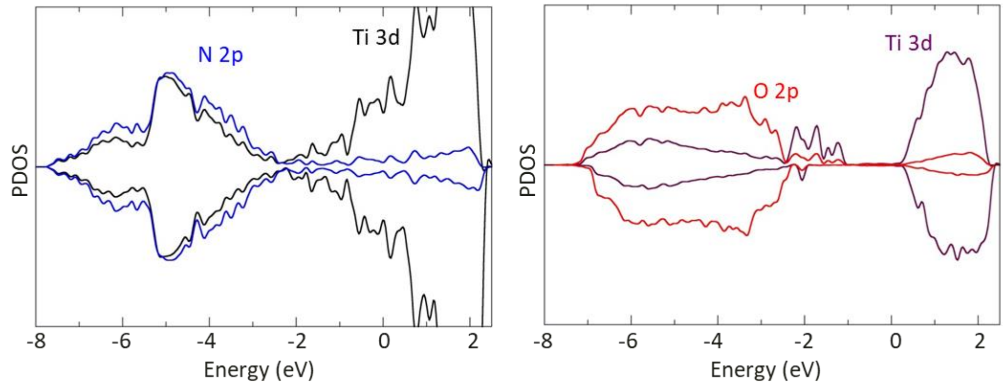


Figure S7. Spin-polarized Partial Density of States (PDOS) of 2-layer thick TiO_2–TiN interfaces (a) stoichiometric, (b) O-vacancy system, (c) etched model of $Ti_{1.75}$-TiN and (d) slab model of $Ti_{1.75}$-TiN. The graphs on the left and right panels represent TiN and TiO_2 PDOS.

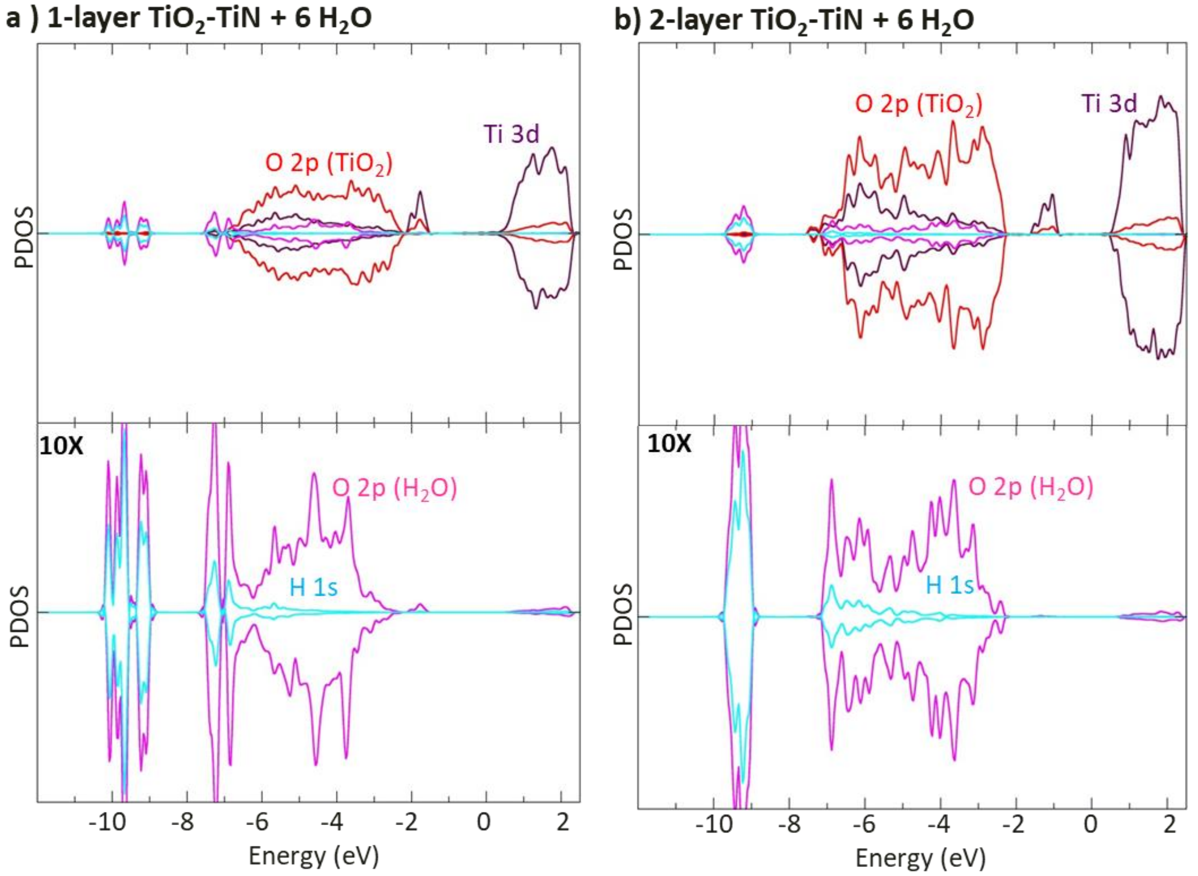


Figure S8. Spin-polarized Partial Density of States (PDOS) of TiO_2 for the fully covered (a) 1-layer TiO_2–TiN with molecular H_2O and (b) 2-layer TiO_2-TiN with molecular H_2O. The legend with the contribution of each species is included in the graphs. Ti 3d electrons from TiN are represented with black lines, N 2p electrons in blue, Ti 3d electrons from TiO_2 in purple and O 2p electrons from TiO_2 in red. The accumulated contribution of each species was considered for the total PDOS. The individual contribution of O 2p states from water is shown under the main graphs and amplified by a factor of 10 with respect to the contribution of one single atom. The upper and lower halves of the graphs represent the spin-up and spin-down components, respectively. The 0 eV energy stands for the Fermi level.

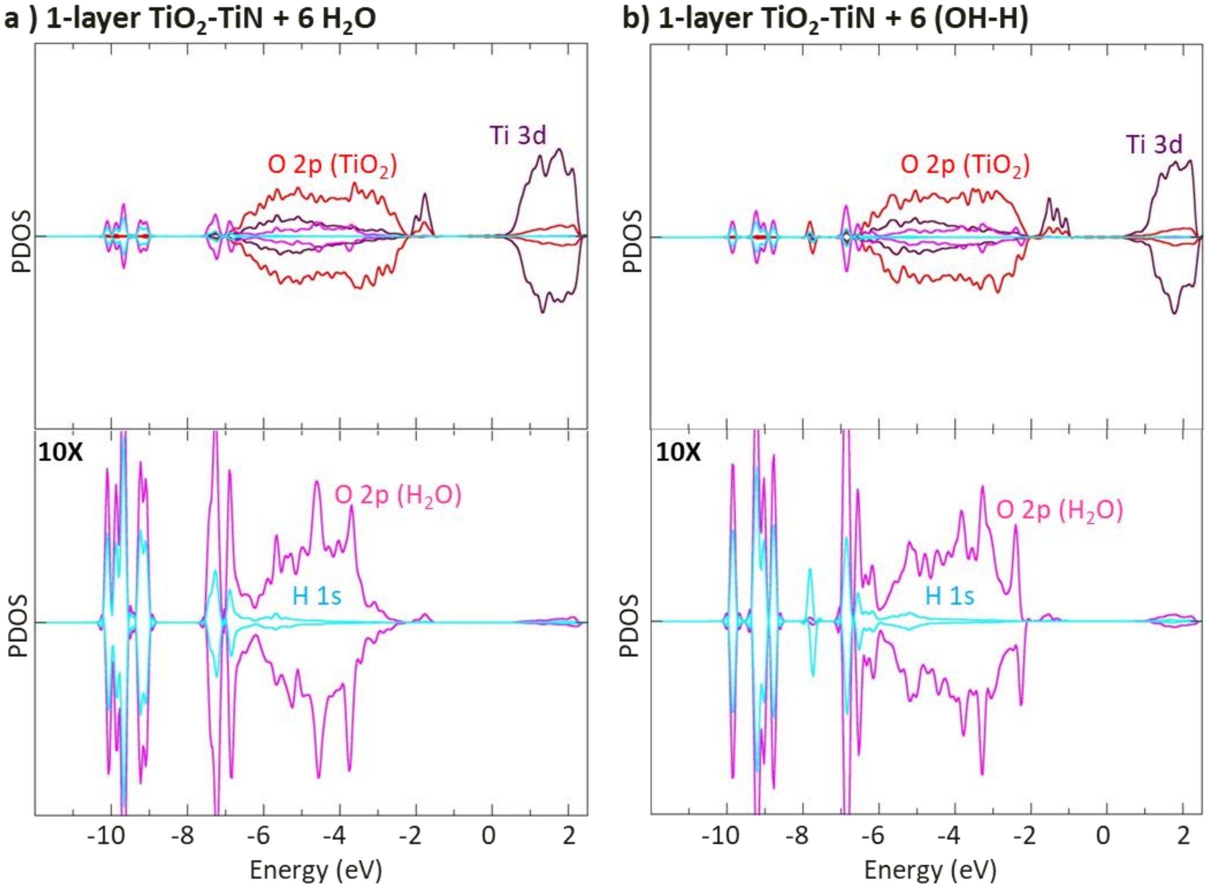


Figure S9. Spin-polarized Partial Density of States (PDOS) of TiO_2 for the fully covered 1-layer TiO_2–TiN interfaces with (a) molecular H_2O and (b) dissociated OH-H water adsorbed on the surface. The legend with the contribution of each species is included in the graphs. Ti 3d electrons from TiN are represented with black lines, N 2p electrons in blue, Ti 3d electrons from TiO_2 in purple and O 2p electrons from TiO_2 in red. The accumulated contribution of each species was considered for the total PDOS. The individual contribution of O 2p states from water is shown under the main graphs and amplified by a factor of 10 with respect to the contribution of one single atom. The upper and lower halves of the graphs represent the spin-up and spin-down components, respectively. The 0 eV energy stands for the Fermi level.

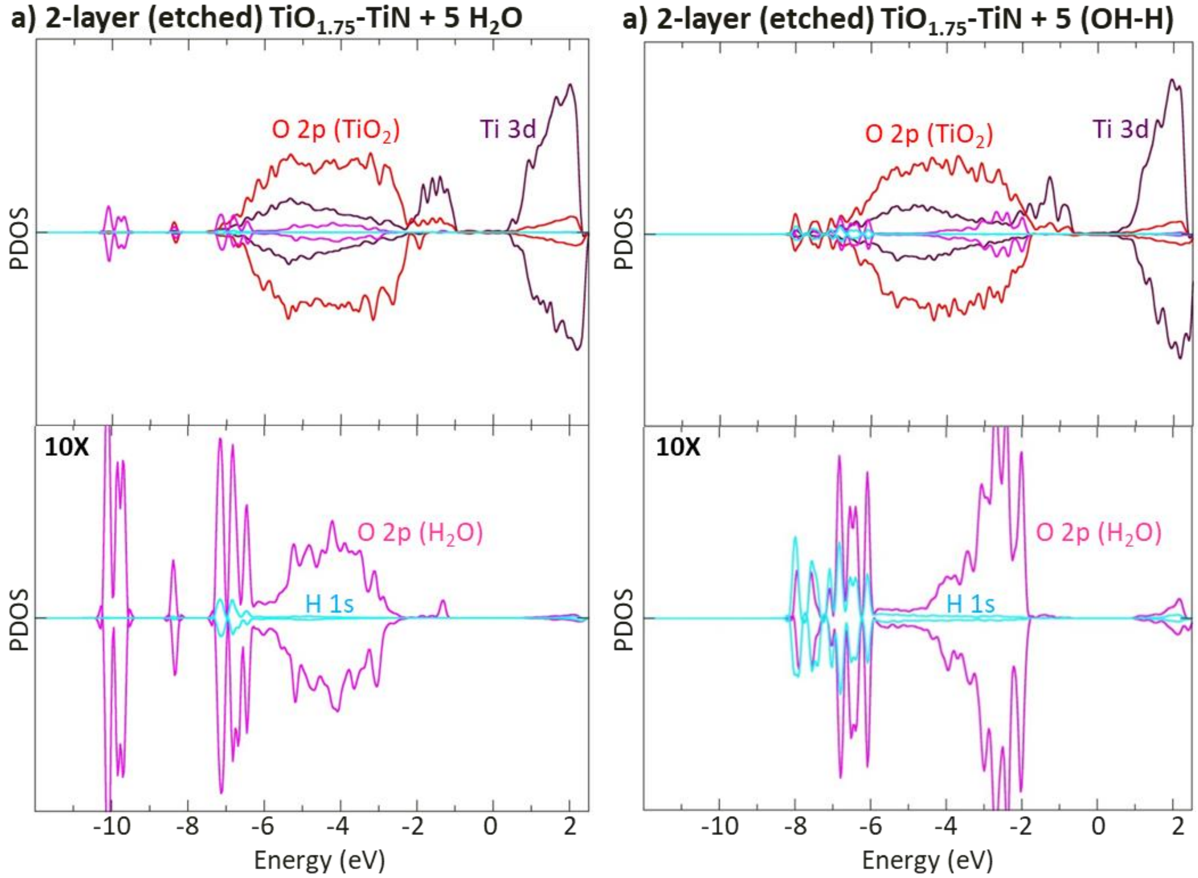


Figure S10. Spin-polarized Partial Density of States (PDOS) of TiO_2 for the fully covered 2-layer TiO_2–TiN etched model interfaces with (a) molecular H_2O and (b) dissociated OH-H water adsorbed on the surface. The legend with the contribution of each species is included in the graphs. Ti 3d electrons from TiN are represented with black lines, N 2p electrons in blue, Ti 3d electrons from TiO_2 in purple and O 2p electrons from TiO_2 in red. The accumulated contribution of each species was considered for the total PDOS. The individual contribution of O 2p states from water is shown under the main graphs and amplified by a factor of 10 with respect to the contribution of one single atom. The upper and lower halves of the graphs represent the spin-up and spin-down components, respectively. The 0 eV energy stands for the Fermi level.

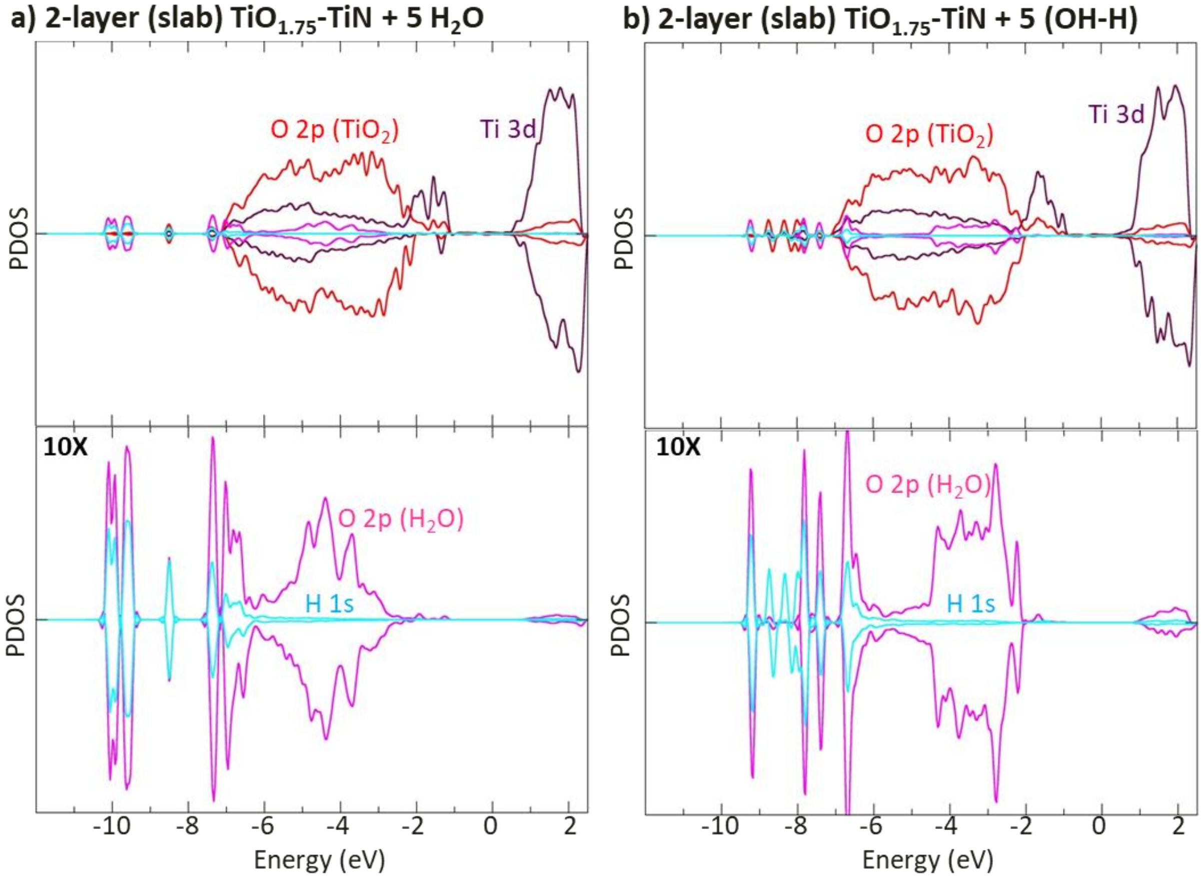


Figure S11. Spin-polarized Partial Density of States (PDOS) of TiO_2 for the fully covered 2-layer TiO_2TiN etched model interfaces with (a) molecular H_2O and (b) dissociated OH-H water adsorbed on the surface. The legend with the contribution of each species is included in the graphs. Ti 3d electrons from TiN are represented with black lines, N 2p electrons in blue, Ti 3d electrons from TiO_2 in purple and O 2p electrons from TiO_2 in red. The accumulated contribution of each species was considered for the total PDOS. The individual contribution of O 2p states from water is shown under the main graphs and amplified by a factor of 10 with respect to the contribution of one single atom. The upper and lower halves of the graphs represent the spin-up and spin-down components, respectively. The 0 eV energy stands for the Fermi level.