SUPPORTING INFORMATION

Curved TiO_2 Nanoparticles in Water:

Short (chemical) and Long (physical) Range Interfacial Effects

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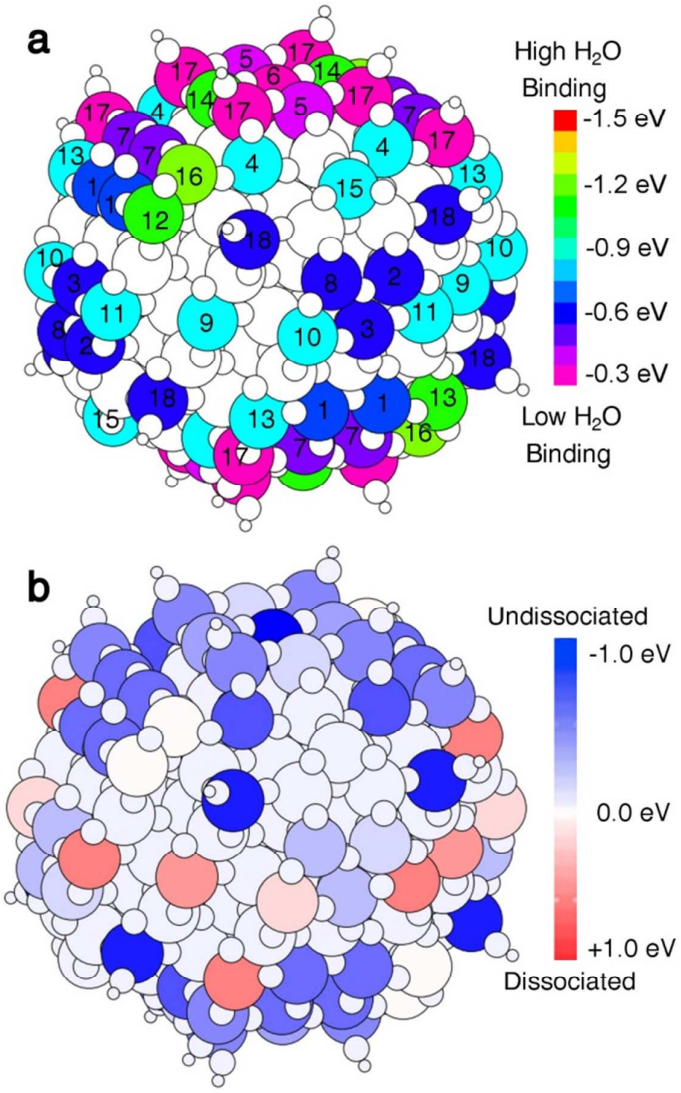

Figure S1. a. Graphical representation of the distribution of binding energies for molecular water molecules on each undercoordinated Ti site of the **NS** model in vacuum, as obtained with the DFTB method. The numbering refers to inequivalent Ti undercoordinated sites on the **NS** surface. **b.** Total energy difference between the molecular and dissociative adsorption modes for each Ti site on the surface of the **NS** model in vacuum. A positive sign (red color) indicates that the dissociative mode is favored, a negative sign (blue color) that the molecular mode is preferred.

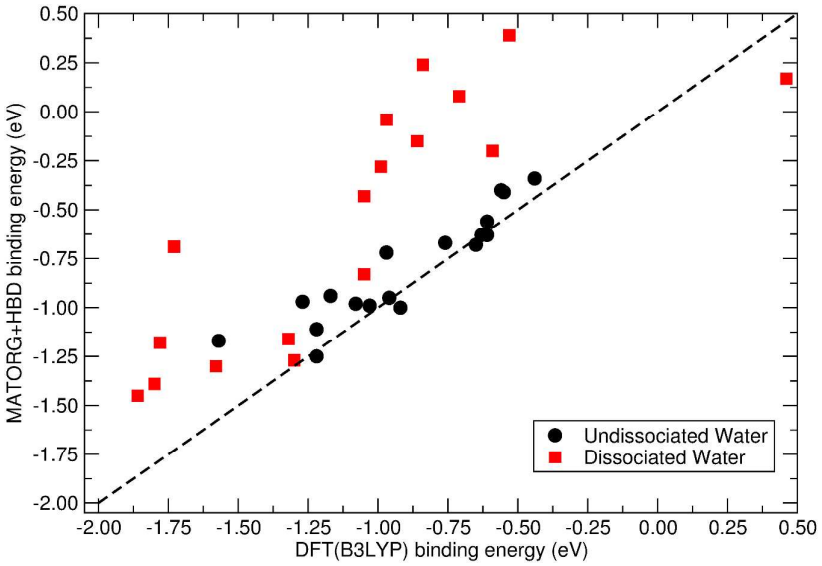

Figure S2. Correlation between the binding energy of undissociated (black circles) and dissociated (red squares) water molecules as obtained with DFT(B3LYP) and DFTB(MATORG+HBD) approaches.

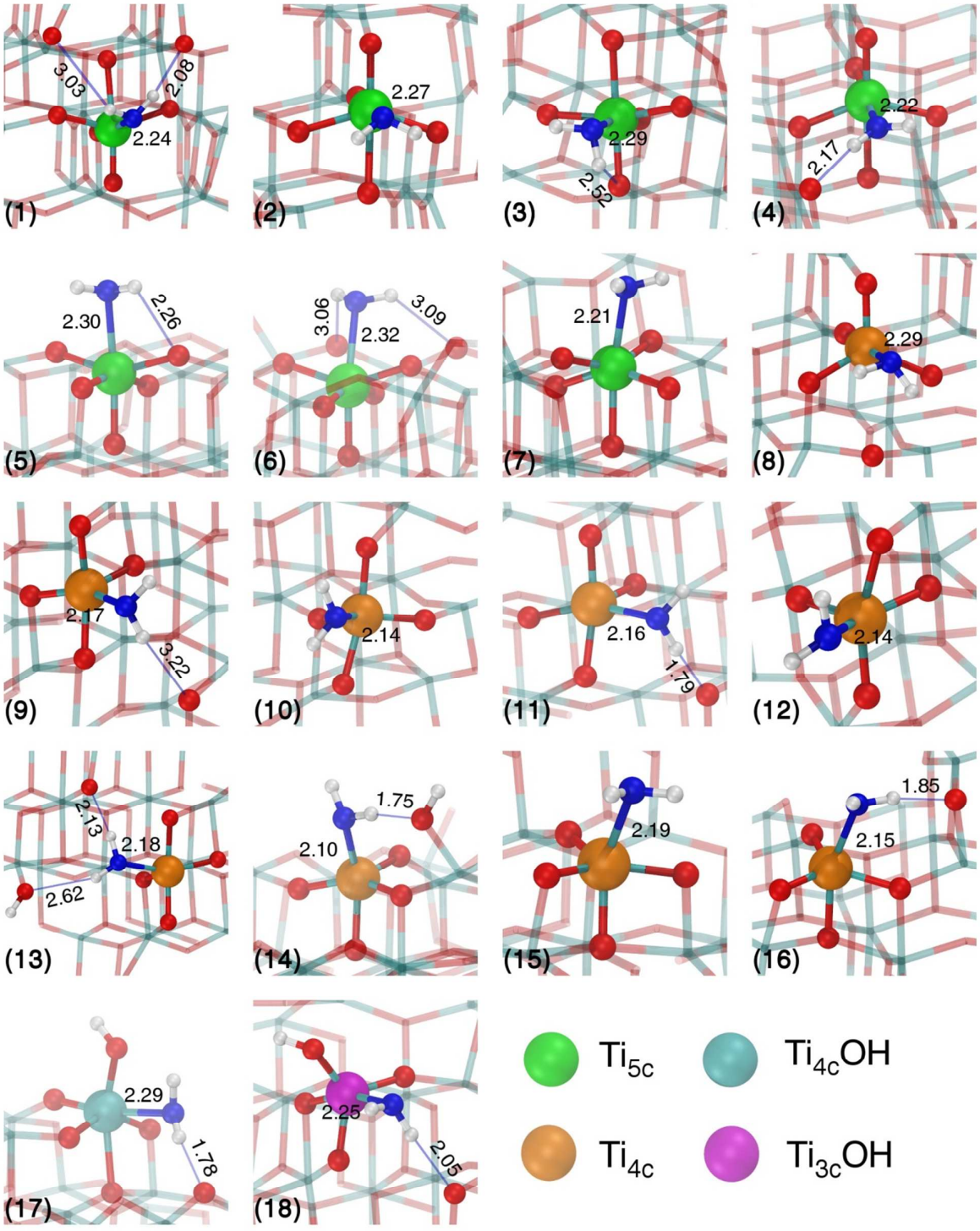

Figure S3. Ball-and-stick representation of the molecular water adsorbates on all the undercoordinated Ti sites on the surface of the **NS** model. The adsorption site and its next-neighbouring atoms are evidenced by larger spheres: Ti atoms are colored according to their coordination pattern, as given in the color code in the bottom right; H atoms are shown in white, lattice and hydroxyl O atoms in red, water O atoms in blue. Relevant hydrogen-bonds are represented by thin blue lines. Distances are in Å.

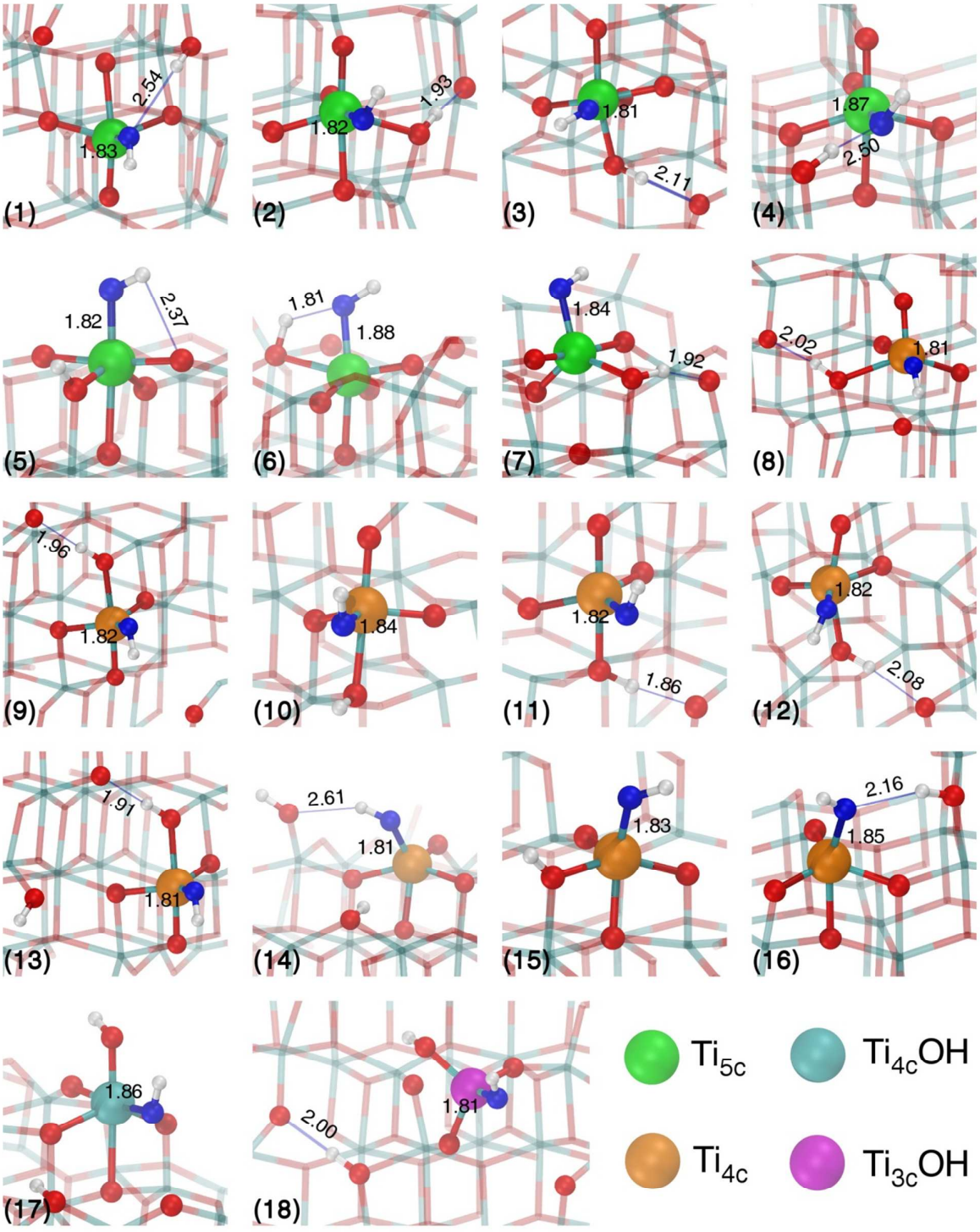

Figure S4. Ball-and-stick representation of the dissociated water adsorbates on all the undercoordinated Ti sites on the surface of the **NS** model. The adsorption site and its next-neighbouring atoms are evidenced by larger spheres: Ti atoms are colored according to their coordination pattern, as given in the color code in the bottom right; H atoms are shown in white, lattice and hydroxyl O atoms in red, water O atoms in blue. Relevant hydrogen-bonds are represented by thin blue lines. Distances are in Å.

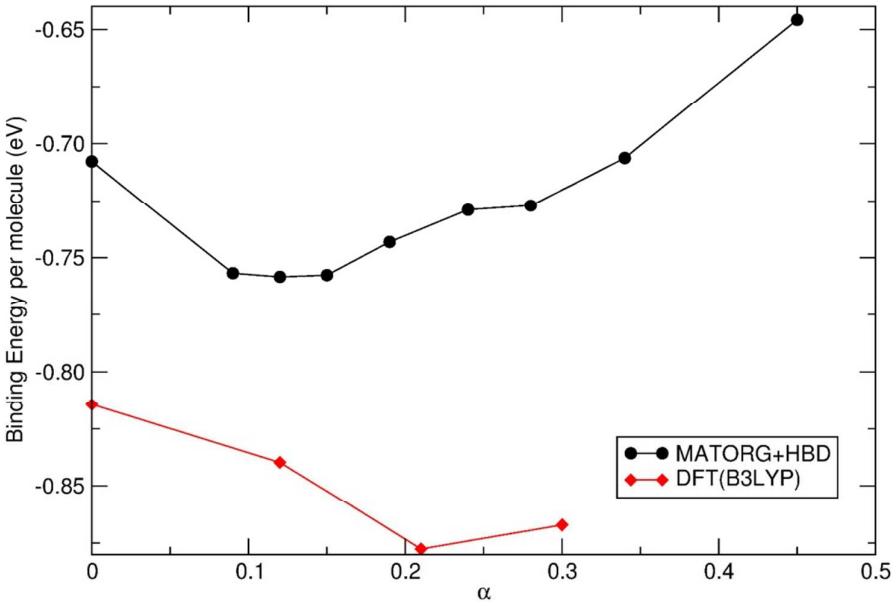

Figure S5. Binding energy per molecule as a function of the extent of dissociation α for the water monolayer (134 H_2O molecules) adsorbed on the NS model as obtained with DFTB(MATORG+HBD) and DFT(B3LYP) methods.

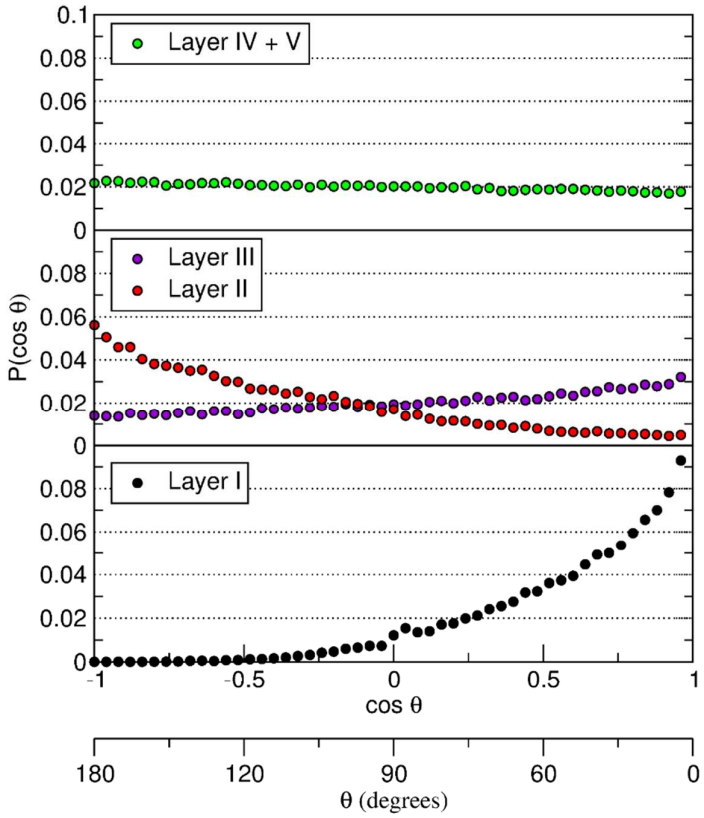

Figure S6. Probability distribution P(cos θ) of the angle θ between the O–H bond vector and the vector connecting water O atom to the center of the NS model for the molecules of the water multilayer (treated at the DFTB level of theory) immersed in a droplet of water (treated at the MM level of theory) within Layer I (bottom panel, in black), Layer II and III (as red and violet points, respectively, in middle panel) and Layer IV and V (as green points, in top panel). A cos θ equals to 1 means that the O–H bond is directed outwards, whereas a value close to −1 means that the O–H bond is oriented towards the center of the nanosphere.

Table S1. Comparison between the binding energies (E_b, in eV) for a water molecule on each specific site of the **NS** model with the DFTB and the DFT(B3LYP) method. Both the molecular and the dissociated adsorption mode are considered. The preferred adsorption mode for each site is highlighted in bold. The mean absolute errors (MAE, in eV) of DFTB values with respect to DFT for undissociated and dissociated water are also given.

Site	**Label**	DFTB (eV)		DFT (eV)	
		Molecular	Dissociated	Molecular	Dissociated
Ti_{5c}	1	**–0.72**	–0.04	**–0.97**	–0.97
	2	–0.68	–0.43	–0.65	–1.05
	3	**–0.67**	–0.28	–0.76	**–0.99**
	4	**–1.00**	–0.15	**–0.92**	–0.86
	5	**–0.41**	–0.20	–0.55	**–0.59**
	6	**–0.34**	1.71	–0.44	**0.51**
	7	**–0.56**	–0.08	**–0.61**	–0.54
Ti_{4c}	8	**–0.63**	–0.24	–0.61	**–0.84**
	9	–0.98	**–1.30**	–1.08	**–1.58**
	10	–0.99	**–1.16**	–1.03	**–1.32**
	11	–0.94	**–1.45**	–1.17	**–1.86**
	12	–1.11	–1.18	–1.22	-1.78
	13	–0.97	**–1.39**	–1.27	**–1.80**
	14	**–1.17**	–0.69	–1.57	**–1.73**
	15	**–0.95**	–0.83	–0.96	**–1.05**
	16	–1.25	**–1.27**	–1.22	**–1.30**
$Ti_{4c}OH$	17	**–0.40**	0.17	**–0.56**	0.46
$Ti_{3c}OH$	18	**–0.63**	0.39	**–0.63**	–0.53
MAE		0.12	0.64		

Table S2. Binding Energy per molecule (in eV) for the water monolayer on the **NS** and **NC** models with a different degree of dissociation (α) as obtained with DFT and DFTB methods. The number of terminal OH (OH_t), water molecules bound (H_2O_{Ti}) or not bound (H_2O_{HB}) to titanium atoms is also given. The same quantities for a monolayer of water on the faceted $(TiO_2)_{260}$ anatase TiO_2 nanoparticle (**NC**) are reported.

Nanoparticle	α	Binding Energy per molecule	Number of water adsorbates		
			OH_t	H_2O_{Ti}	H_2O_{HB}
DFT					
NS	0.00	–0.814	0	109	25
	0.12	–0.840	16	100	18
	0.21	**–0.878**	**28**	**88**	**18**
	0.30	-0.867	40	79	15
NC	0.03	-0.746	4	111	11
DFTB					
NS	0.00	–0.708	0	105	29
	0.09	–0.757	12	95	27
	0.10	**–0.758**	**14**	**90**	**29**
	0.19	–0.743	25	82	27
	0.24	–0.729	32	79	23
	0.28	–0.727	37	74	23
	0.34	–0.706	45	67	22
	0.45	–0.646	61	56	17
NC	0.03	-0.666	4	101	21