Supporting Information

Part I. The (101), (001), and (100) surfaces of TiO_2 modeled by the 1×1 surface cells consisting of 30, 18, and 7 atomic layers with a 20 Å thickness of vacuum layer above each slab, respectively.

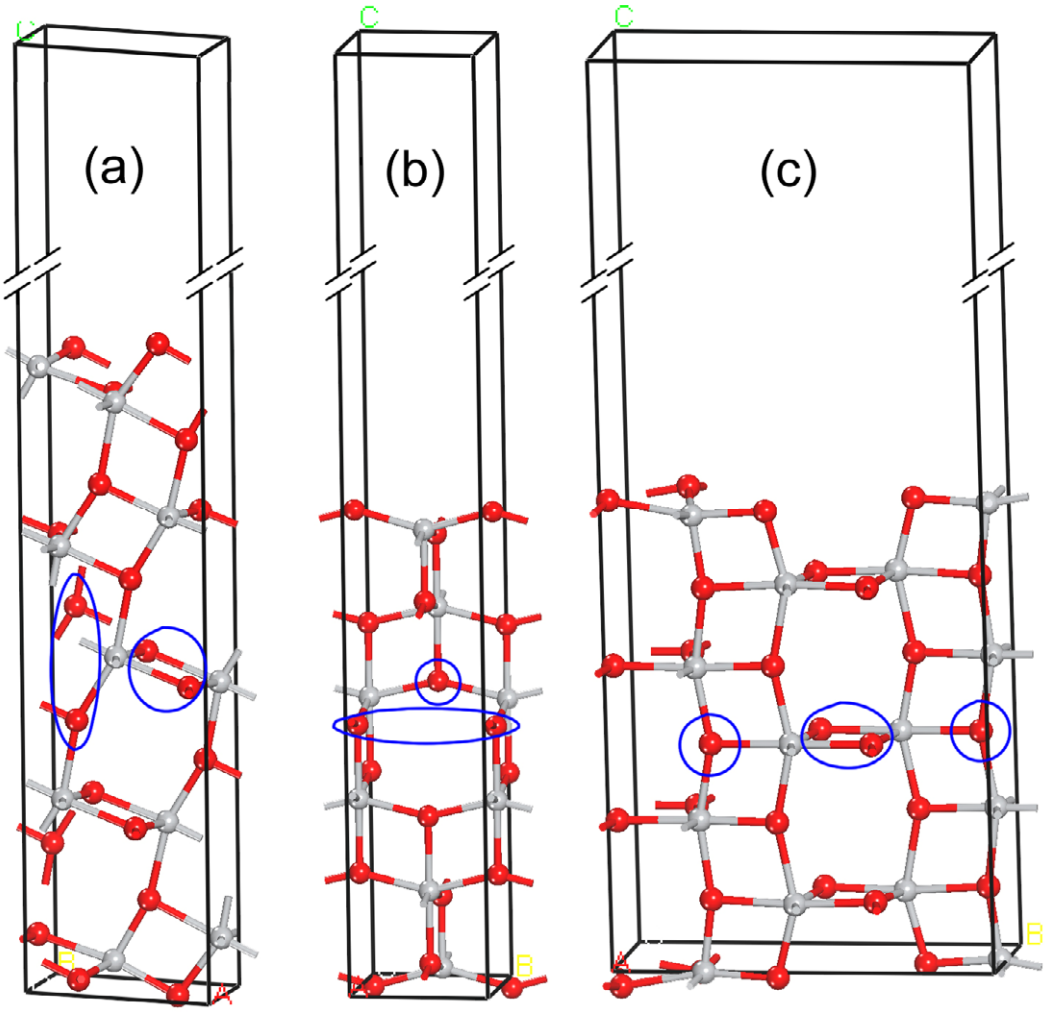

Figure S1. Slab models of (a) (101), (b) (001), and (c) (100) surfaces used in our calculations; the oxygen atoms in the circles are used to align the calculated DOSs of different surfaces, which is shown in figure S2. Note that 2×1 and 2×2 surface cells (not shown) are also used in the test calculations (see captions of table 1 and figure 1 in the manuscript).

Part II. Alignment of the DOSs.

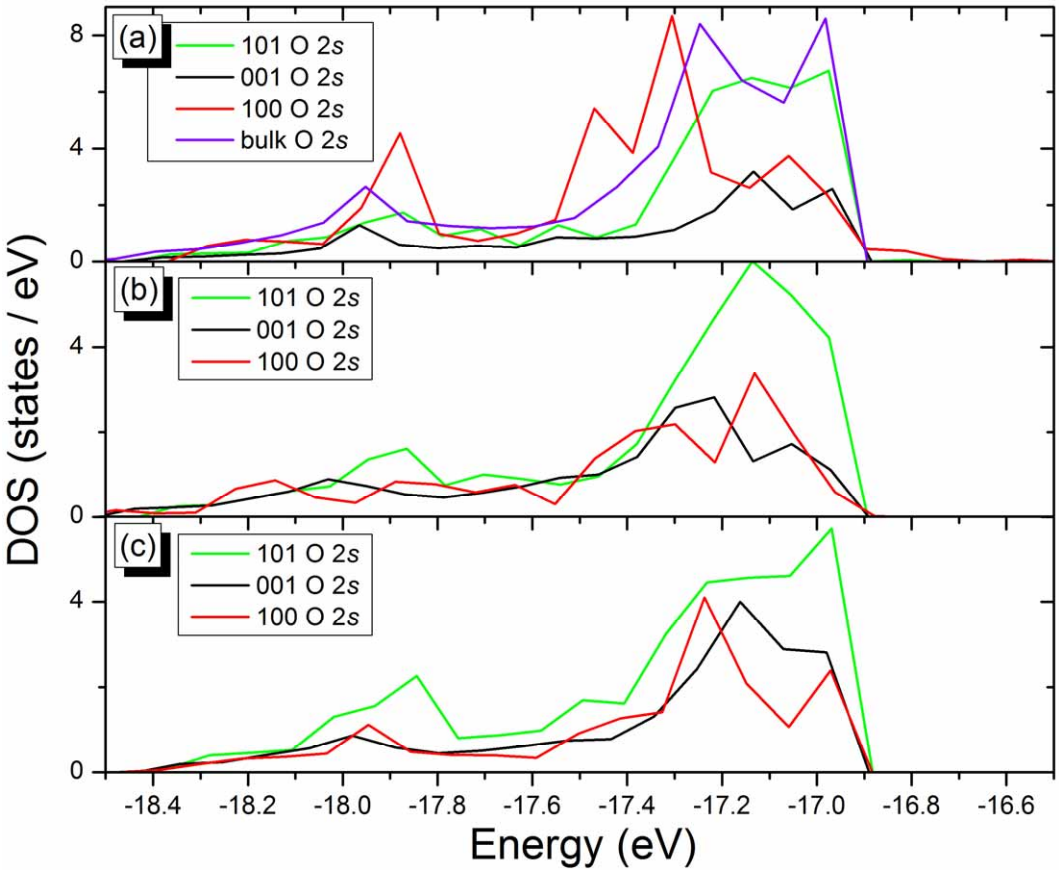

Figure S2. The aligned 2*s* states of the oxygen atoms in the surface slabs circled in figure S1 and those in the bulk.

The enough thickness of the surface slabs used in the calculations (see figure S1) allows the geometric structure around the deep oxygen atoms (circled in figure S1) do not change a lot relative to that of the bulk, which makes it possible that the deep 2*s* states of these oxygen atoms nearly do not affected by the surface effect. It can be seen from figure S2 that the DOSs of these O 2*s* states are very similar to those of the bulk, and the upper edges of them are sharp and can be easily aligned.

Part III. Details of the structural distortion.

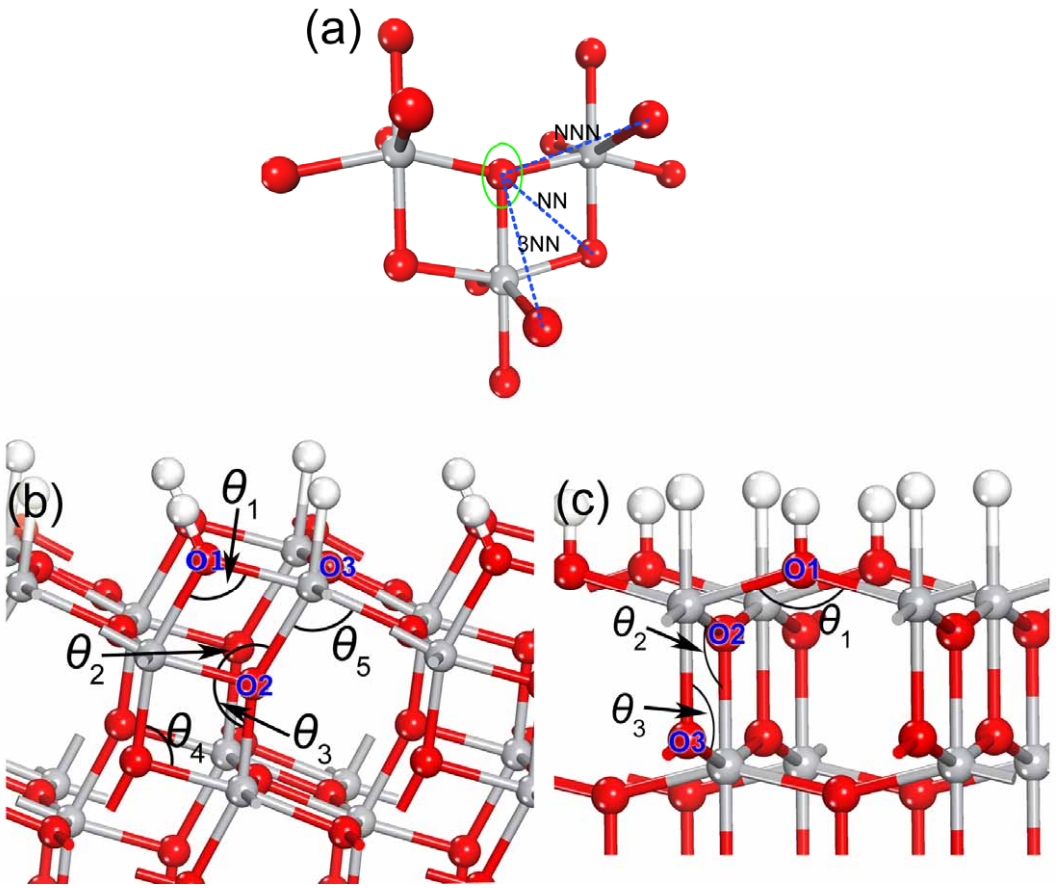

Figure S3. (a) Schematic illustration of the nearest neighbor (NN), next nearest neighbor (NNN), and third nearest neighbor (3NN) of an oxygen atom (the circled one) in the bulk. (b, c) Relaxed structures of (101) and (001) surfaces adsorbed H atoms, respectively. The red, gray, and white balls represent the oxygen, titanium, and hydrogen atoms, respectively.

It can be seen from figure S3a that one oxygen atom in the bulk is bonded with three Ti atoms, forming two shorter equivalent O-Ti bonds and one longer O-Ti bond, and there are two NNs, four NNNs, and four 3NNs oxygen atoms around it. The detailed variations of the bond lengths, bond angles, and distances between the neighbors of the (101) and (001) surfaces before and after hydrogenation are summarized in Table S1, S2, and S3, respectively. From the tables we can see that the hydrogenation induces obvious lattice distortions in (101) slab while the (001) slab is not so largely affected due to the tightly bonded structure of the surface layer terminated with the whole s-layer (see figure 1e).

Table S1. O-Ti bond lengths around the oxygen atom of (101) and (001) surfaces before and after hydrogenation.

		Bond length		
		Before (Å)	After (Å)	Variation (%)
101	O1	1.869	2.025	8.35
		-	-	-
		1.847	1.998	8.18
	O2	1.811	2.067	14.14
		2.04	1.95	-4.41
		2.062	1.927	-6.55
	O3	1.975	1.931	-2.23
		1.975	1.934	-2.08
		2.016	2.027	0.55
001	O1	1.96	1.969	0.46
		1.96	1.969	0.46
		-	-	-
	O2	1.934	1.942	0.41
		1.934	1.942	0.41
		1.995	2.055	3.01
	O3	1.942	1.936	-0.31
		1.942	1.936	-0.31
		1.961	2.082	6.17

Table S2. Bond angles (as illustrated in figure S3b, c) of (101) and (001) surfaces before and after hydrogenation.

	Angle	Before	After	Variation (%)
101	θ_1	99.52	103.693	4.19
	θ_2	93.946	104.719	11.47
	θ_3	103.263	100.367	-2.80
	θ_4	104.203	98.853	-5.13
	θ_5	102.59	95.678	-6.74
001	θ_1	148.842	146.975	-1.25
	θ_2	102.511	103.546	1.01
	θ_3	103.509	102.766	-0.72

Table S3. Distances between the oxygen atom and its nearest neighbors (NNs), next nearest neighbors (NNNs), and third nearest neighbors (3NNs) before and after hydrogenation.

			Before (Å)	After (Å)	Variation (%)
101	O1	NN	2.518	2.462	-2.22
		NNN	2.86	2.866	0.21
		3NN[a]	3.013	2.869	-4.78
			2.928	3.046	4.03
	O2	NN	2.523	2.516	-0.28
		NNN	2.782	2.818	1.29
		3NN[a]	3.051	3.185	4.39
			3.066	3.004	-2.02
			3.011	2.999	-0.40
	O3	NN	2.525	2.491	-1.35
		NNN	-	-	-
		3NN	3.287	3.273	-0.43
001	O1	NN	-	-	-
		NNN	2.832	2.857	0.88
		3NN	3.122	3.244	3.91
	O2	NN	2.437	2.492	2.26
		NNN	2.832	2.857	0.88
		3NN	3.099	3.134	1.13
	O3	NN	2.437	2.492	2.26
		NNN	2.823	2.808	-0.53
		3NN	3.122	3.244	3.91

[a] More than one values for the 3NN indicates that the equivalent distances between the oxygen atom and its 3NNs are split into more than one values.

Part IV. Isosurface contor plots of selected lowest unoccupied wave functions on hydrogenated (100) surface.

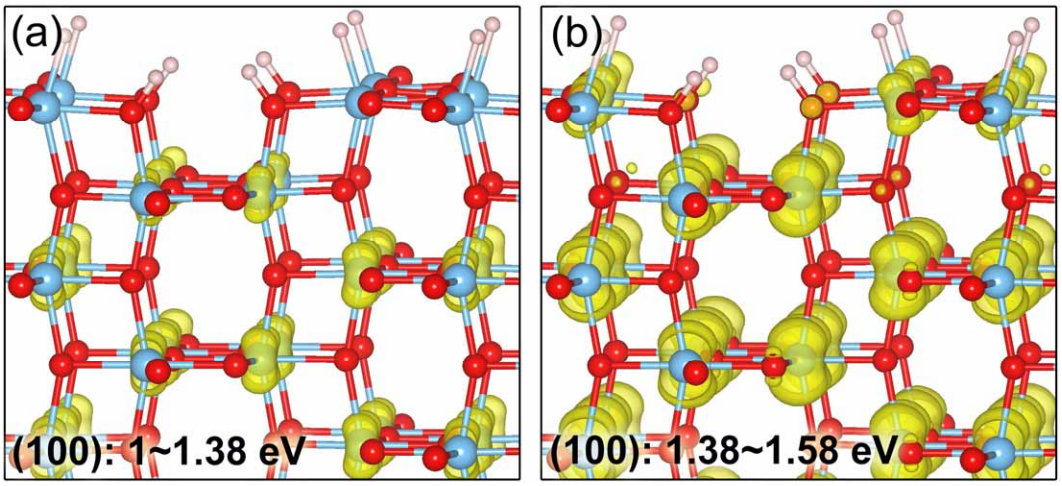

Figure S4. 3D isosurface contor plots of selected lowest unoccupied wave functions (LUWFs) on hydrogenated (100) (Eigen values indicated in the figures are correspond to the energies in abscissa axis of figure 1c). The isosurface value is set as ± 0.001 eÅ^{-3}. The red, light blue, and light red balls represent the oxygen, titanium, and hydrogen atoms, respectively.

From the DOSs (figure 1c) and LUWFs (figure S4), it can be seen that the hydrogenated (100) surface has almost very similar electronic structure to that of (101) surface, which indicate that it may not make significant sense to merely increase the exposed (100) surface that has been considered as an active facet of clean TiO_2 nanocrystal for the hydrogenated nanocrystals.