

# Electronic Supplementary Information for

## Photoinduced Hardness Change on TiO<sub>2</sub> Single Crystal Surfaces

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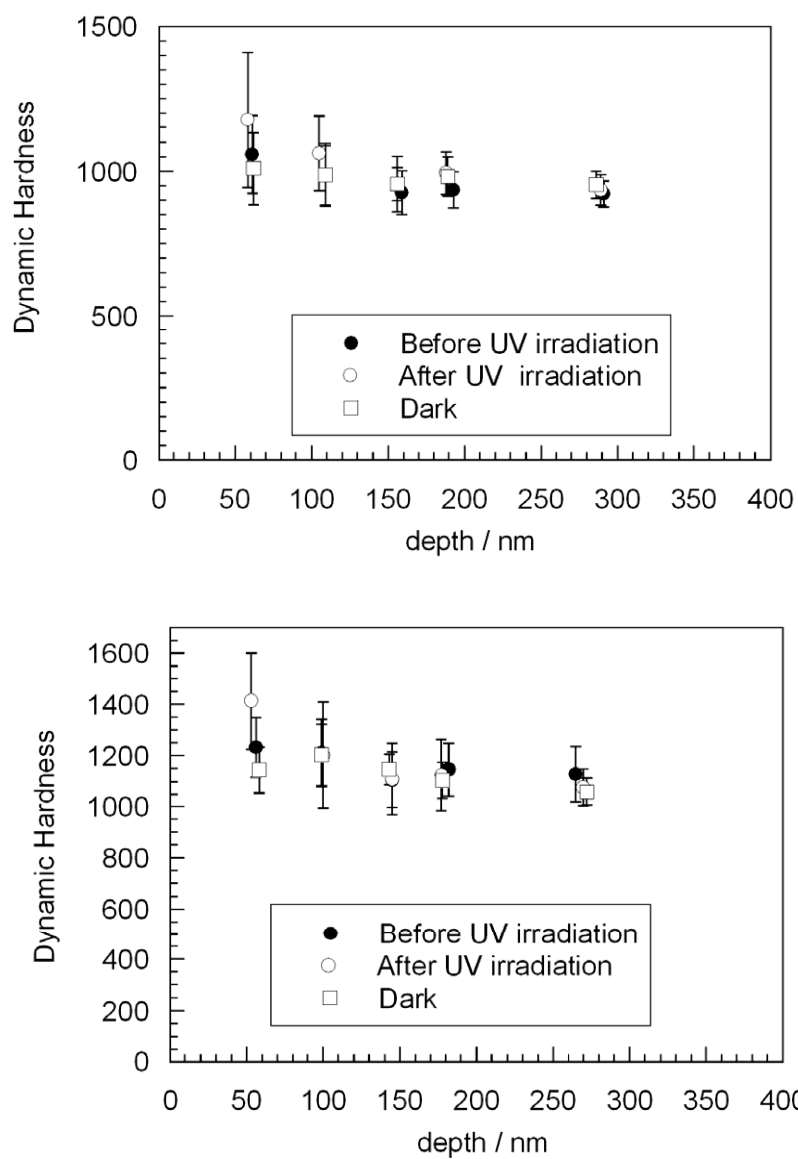
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## Electronic Supplementary Information, S1

In previous works by the authors (ref. 2 and Adv. Mater. 1998, 10, 135), it was shown that UV irradiation onto single-crystal TiO<sub>2</sub> substrates with defined crystallographic orientation actually leads to amphiphilic surfaces as a result of the formation of alternating nanoscale hydrophilic and hydrophobic domains, the former possibly attributable to newly introduced hydroxyl moieties. Based on such previous findings, one could expect that the indentation measurement values could largely depend on the specific surface location on which the load is applied. However, we could not measure the hardness separately on such nanoscale hydrophilic and hydrophobic domains due to following reasons. The domain size that we have reported is approximately 30×80 nm. Thus, the domain area is 2,400 nm<sup>2</sup>. In contrast, the projected area (denoted as A) of the trace produced by the diamond nanoindenter is defined as  $24.56 \times h^2$ , where h is the penetration depth. Here, the penetration depth ranges from 50 to 300 nm, and thus we calculate the A value using an intermediate h value of 100 nm. Therefore, A is 245,600 nm<sup>2</sup>, and the hardness we measured is the average of approximately one hundred nanoscale hydrophilic and hydrophobic domains.

## Electronic Supplementary Information, S2

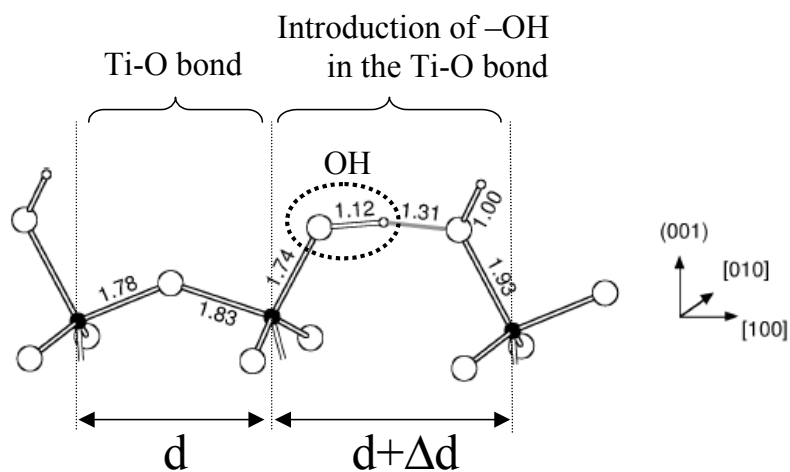
In addition to the rutile (100) single crystal surface, changes in dynamic hardness of the (110) and (001) surfaces were also measured, as shown in Figs. S1(a) and S1(b). Similar to (100), the hardness of the rutile (110) and (001) surfaces, with initial hydrophobic states ( $\theta = \sim 70^\circ$ ), showed nearly constant values regardless of the indentation depth. In contrast, the hardness of the illuminated samples at ~50 nm showed higher values than those at ~300 nm.



**Fig. S1** Dynamic hardness as a function of indentation depth for rutile **(a, upper)** (110) and **(b, lower)** (001) single crystals.

### Electronic Supplementary Information, S3

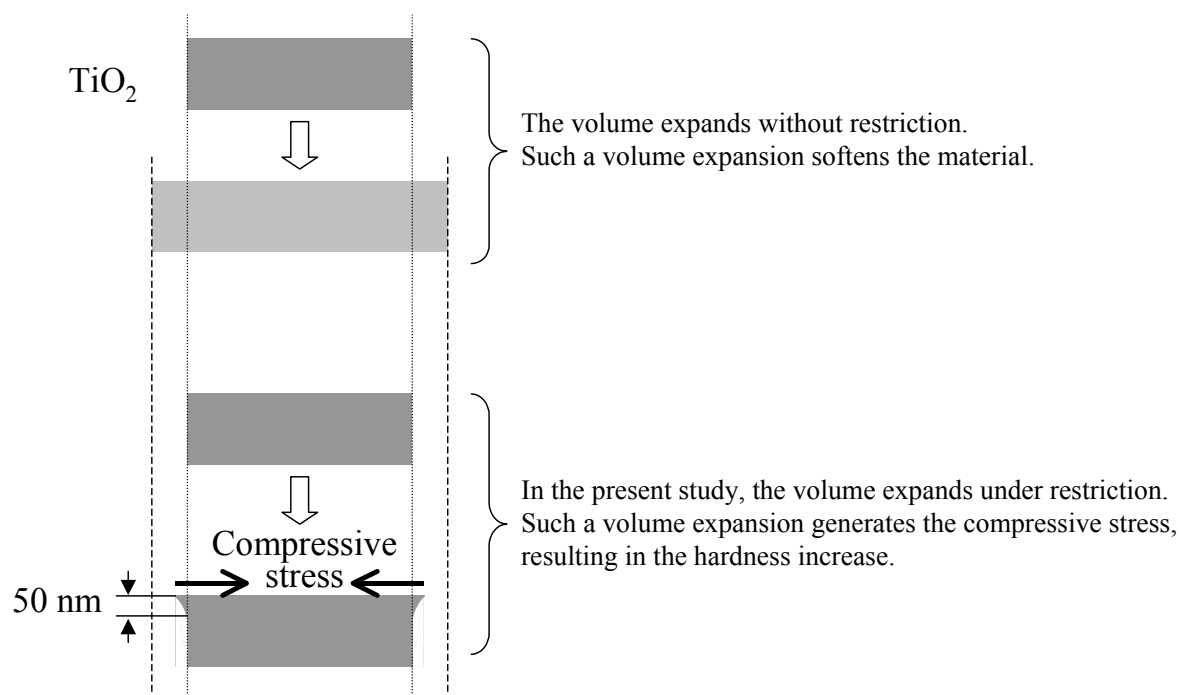
According to Vittadini *et al.* (ref. 20), when introducing the hydroxyl group (-OH), the bond length seemed to increase as shown in Fig. S2.



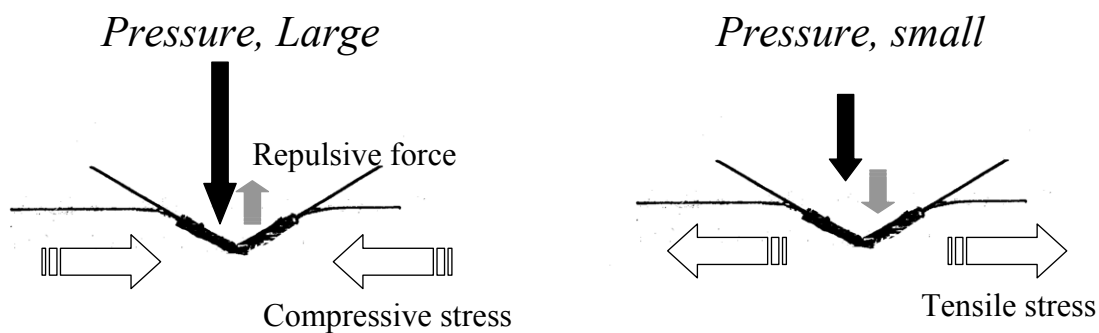
**Fig. S2** Atomic structure (side view) for adsorbed water molecule in dissociated state on anatase (001). A gray line denoted 1.31 indicates hydrogen bond. Bond length is in angstrom. Large empty and small filled circles represent O and Ti atoms, respectively, and small empty circles represent hydrogens (ref. 20).

## Electronic Supplementary Information, S4

The present volume expansion occurs only in the near surface region, not in the interior (bulk) region. In fact, the hardness increased only in the near surface region (~50nm) but kept constant in the interior region (~300nm). This means that the volume expands in the near surface region under the restriction from the bulk lattice. That is, the volume expansion in the near surface region does not proceed freely, resulting in the lattice increase less than that when the volume expansion proceeds freely. Accordingly, the volume expansion in the near surface region under the restriction cannot be completely accomplished, due to the force against the expansion from the bulk lattice, resulting in the generation of the compressive stress only in the near surface region, which does not resemble the expansion under the restriction-free condition (Fig. S3). In general, the generation of the compressive stress hardens the material as shown in Fig. S4.



**Fig. S3** Schematic illustration as for the volume expansion without and with restriction.



**Fig. S4** Schematic illustrations for the large indentation pressure in the presence of compressive stress and for the small indentation pressure in the presence of tensile stress when the penetration depths are the same. So, the surface with the compressive stress is hardened, compared to the ones without stress and with tensile stress.

## Electronic Supplementary Information, S5

We have detected the increase in the surface hydroxyl groups on the rutile TiO<sub>2</sub> (110) single crystal as shown in Fig. S5. We already reported such the increase in the ref. 4, R. Wang, N. Sakai, A. Fujishima, T. Watanabe, K. Hashimoto, *J. Phys. Chem. B* 1999, **103**, 2188.

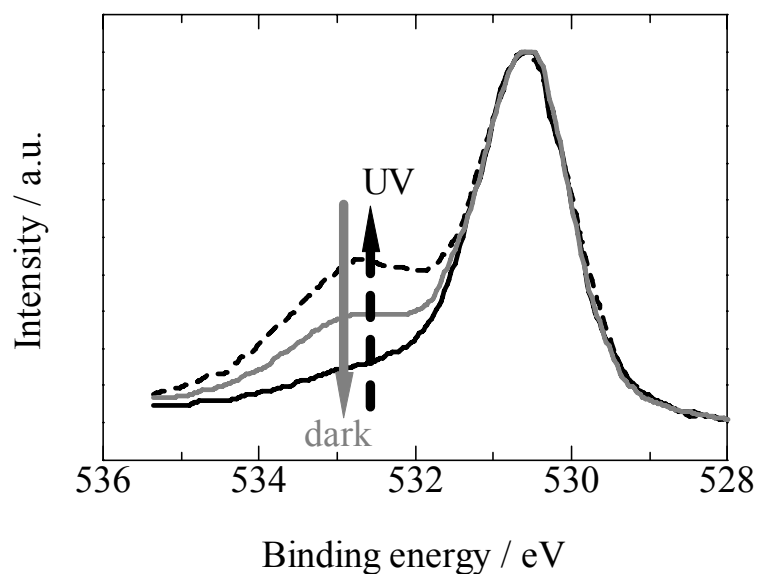


Fig. S5 XPS spectra of O 1s for a TiO<sub>2</sub> (110) single crystal surface. Black line: Less-hydrophilic state before UV irradiation stored in the dark; broken line: Highly-hydrophobic state after UV irradiation; gray line: Less-hydrophilic state stored in the dark after UV irradiation. The shoulder peak at ca. 533 eV originated from the increase of hydroxyl groups was observed after UV light irradiation. After stopping UV irradiation, the peak intensity at 533 eV decreased.