Reactivity of anatase (001) surface from first-principles many-body Green's function theory

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S1 The binding energy

The stability and possibility of formation of the reconstructed ADM and AOM also could be investigated by comparing the binding energy which is calculated by $E_b = \frac{1}{n_T}\left(E_{TiO_2} - n_{Ti}E_{Ti} - n_O E_O\right)$, where E_{TiO_2} represent the total energy of the TiO_2 crystal and E_{Ti} and E_O represent the energy of individual Ti atom and O atom. n_T, n_{Ti} and n_O are is the total number of atoms, the number of Ti atoms and the number of O atoms in TiO_2 crystal. The computed binding energies of ADM and AOM structures are shown in table S1. It can be seen that the ADM is the most stable, implying the ADM is most likely to be formed. Although the unreconstructed shape is more stable than the AOM, the AOM is possible to exist due to the very small binding energy difference between them. The results are in accordance with the analysis results on the formation energy.

Table S1 Computed binding energies (in eV/atom) of the unreconstructed (001), ADM and AOM structures.

Structures	E_b (eV/atom)
unreconstructed	-6.97
ADM	-7.01
AOM	-6.93

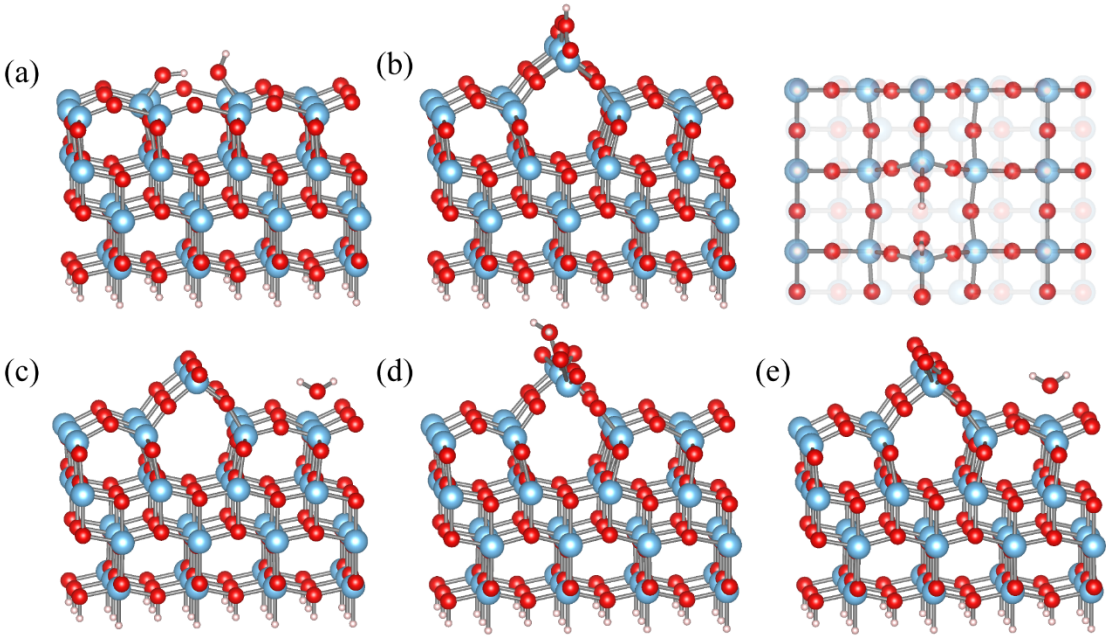

Figure S1 Structures of the (001)/water interface. (a) the clean anatase (001)/H_2O interface. (b) the ADM-R/H_2O interface; left: front view; right: vertical view. (c) the ADM-T/H_2O interface; (d) the AOM-R/H_2O interface; (e) the AOM-T/H_2O interface;

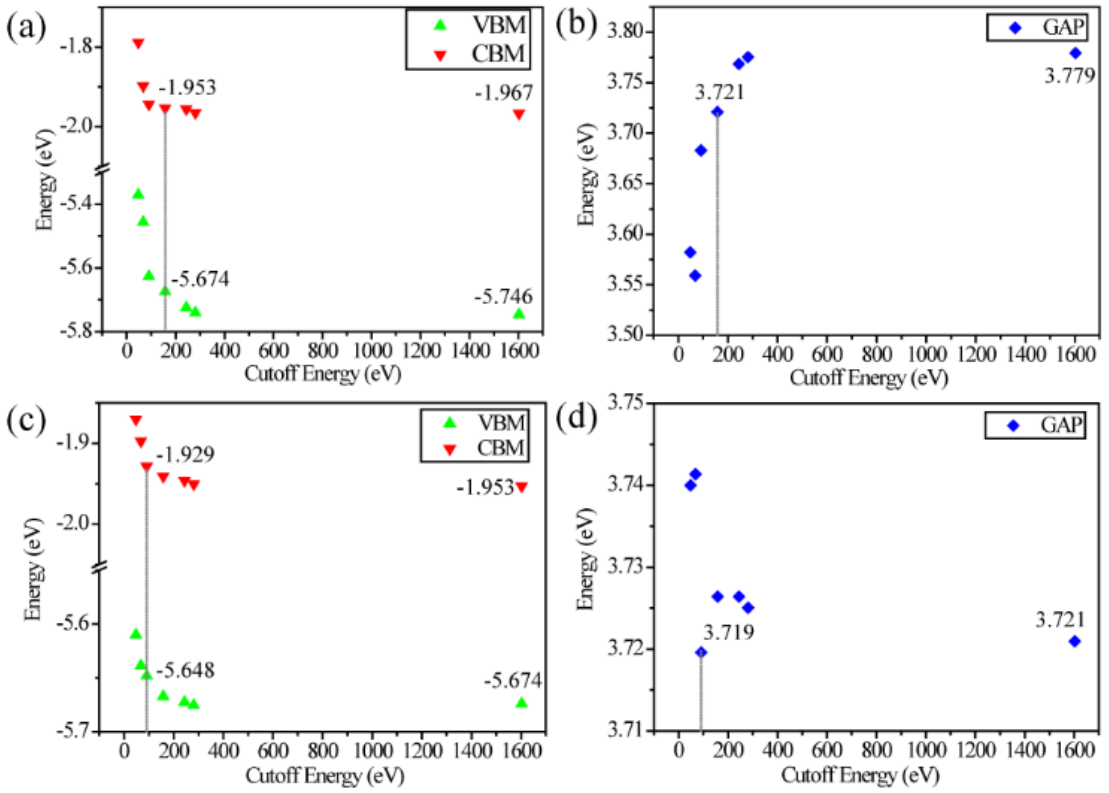

Figure S2 Evolution of the energies of VBM and CBM at Γ point calculated by GW for unreconstructed (001) surface with the cutoff energy applied in the band summation over unoccupied orbitals for the evaluation of self-energy ((a) and (b)) and electronic

screening ((c) and (d)) in GW. In the convergence test for self-energy, there is no cutoff in the evaluation of electronic screening. In the convergence test for electronic screening, cutoff energy is set to 158 eV in the evaluation of self-energy. Cutoff energies adopted in realistic calculations are indicated by grey dotted lines.

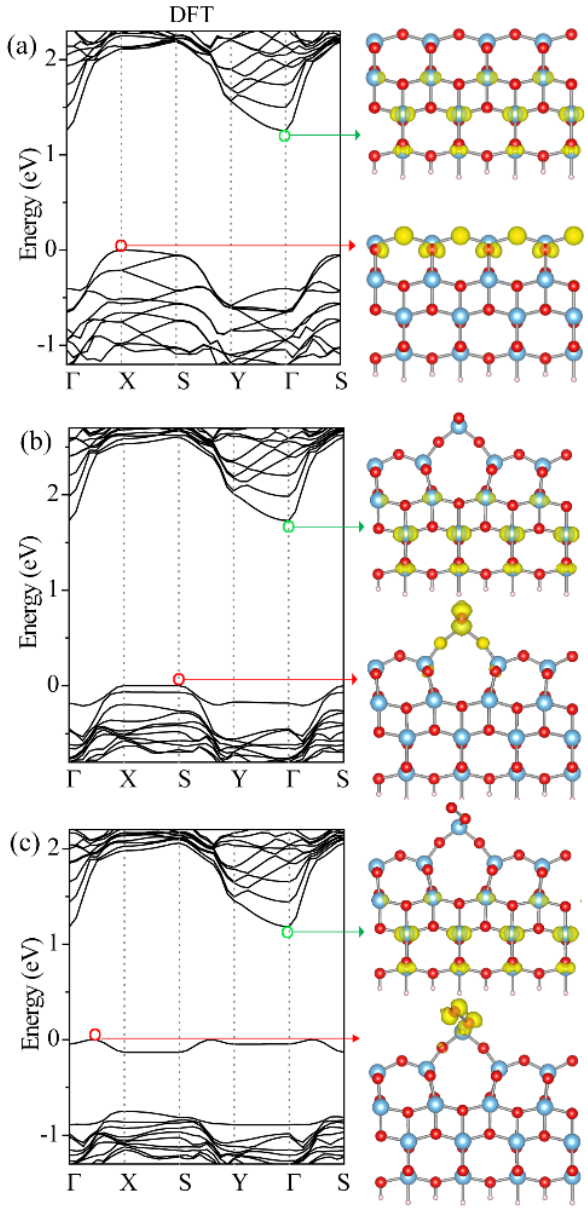

Figure S3 DFT-LDA band structures of the unreconstructed anatase (001) (a), ADM (b) and AOM (c). VBM and CBM of the band structures in each panel are marked by red circle and green circle, respectively. The VBM is set to zero in each panel. The charge distributions of VBM and CBM calculated by DFT for three surfaces are in the right of figures (a)-(c).

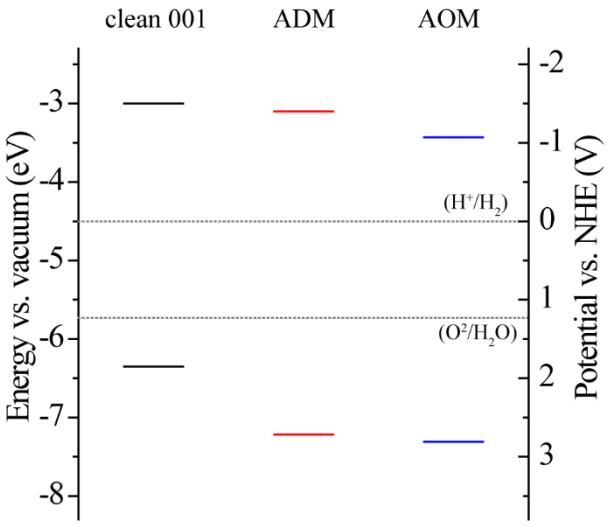

Figure S4 VBM/CBM positions for the unreconstructed anatase (001), ADM and AOM relative to vacuum and NHE scales.

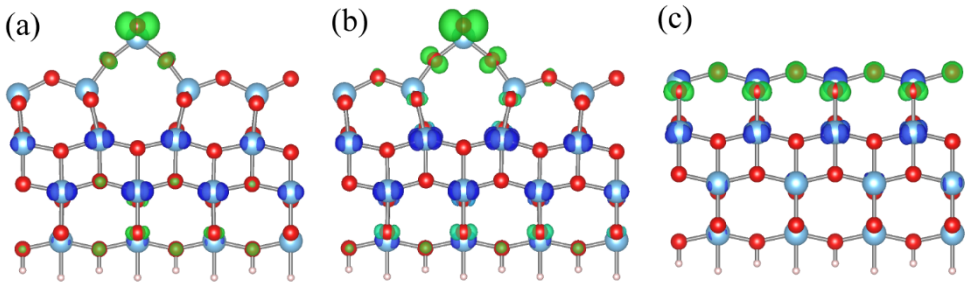

Figure S5 Exciton distributions for the excited states at 3.80 eV (a), 3.98 eV (b) of ADM and the excited state at 3.45 eV of the unreconstructed 001 surface, respectively. Electron and hole are represented in blue and green isosurfaces, respectively.