Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Structure and reactivity of water-covered anatase TiO_2 (001) surface

Xiufeng Lang,*[,a] Yanhong Liang,[a] Jing Zhang,[b] Lei Li,[c] Liqin Cao,[d] Hongsheng Zhang[d]

[a] Material Simulation and Computing Laboratory, Department of Physics, Hebei Normal University of Science & Technology, Qinhuangdao, 066004, China
[b] Institute of Bismuth Science & College of Science, University of Shanghai for Science and Technology, Shanghai, 200093, China
[c] School of Sciences/Key Laboratory of Cosmetric, China National Light Industry, Beijing Technology and Business University, Beijing, 100048, China
[d] College of Environment and Chemical Engineering, Yanshan University, Qinghuangdao, 066004, China

Email: lxf518@csrc.ac.cn

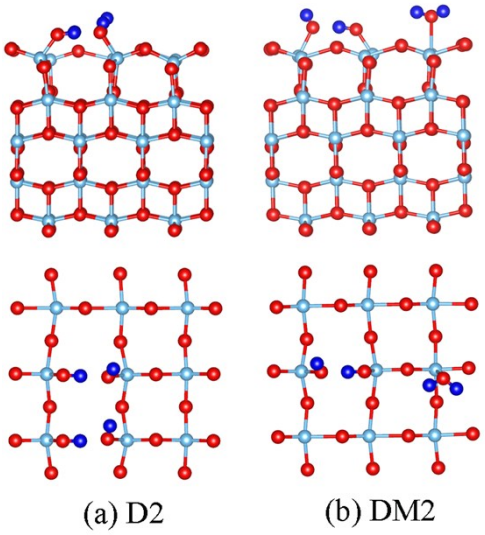

Fig. S1. (a) and (b) show top and side views of two kinds of adsorption structures of water molecules on TiO_2(001)-(1×1) surfaces for θ = 0.22, respectively. H, Ti and O atoms are represented by blue, light blue, and red spheres, respectively.

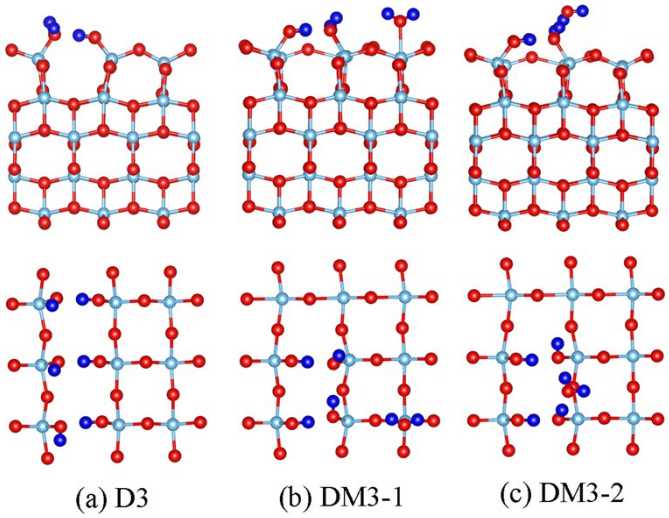

Fig. S2. (a)-(c) show top and side views of three kinds of adsorption structures of water molecules on TiO_2(001)-(1×1) surfaces for θ = 0.33, respectively. The representation for H, Ti and O atoms is the same as that in Figure S1.

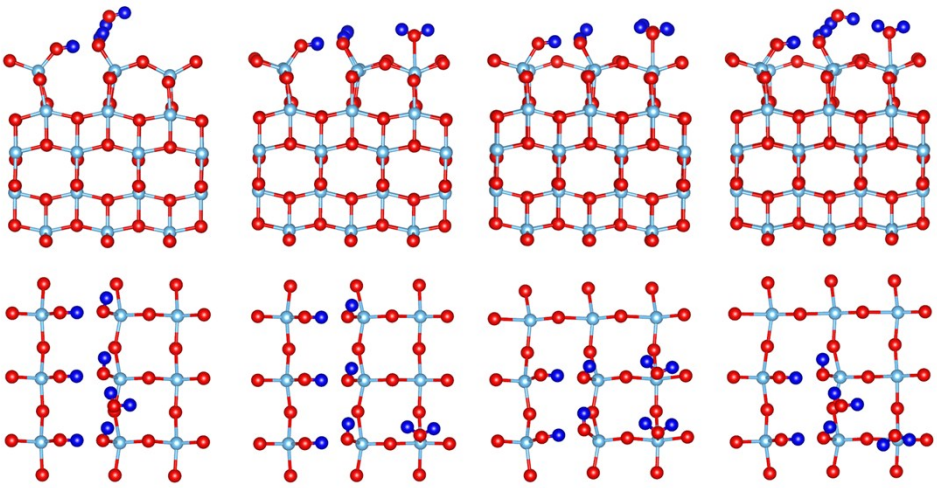

Fig. S3. (a)-(d) show top and side views of four kinds of adsorption structures of water molecules on TiO_2(001)-(1×1) surface for θ = 0.44, respectively. The representation for H, Ti and O atoms is the same as that in Figure S1.

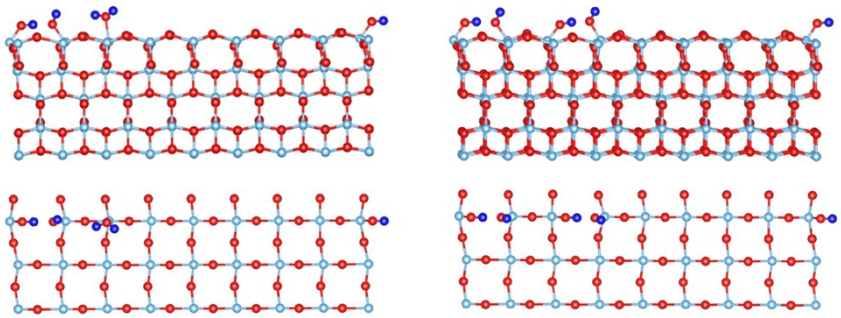

Fig. S4. (a) and (b) shows top and side views of adsorption structures of two water molecules on TiO_2(001)-(1×1) surface modeled by a (3×8) supercells. The representation for H, Ti and O atoms is the same as that in Figure S1.

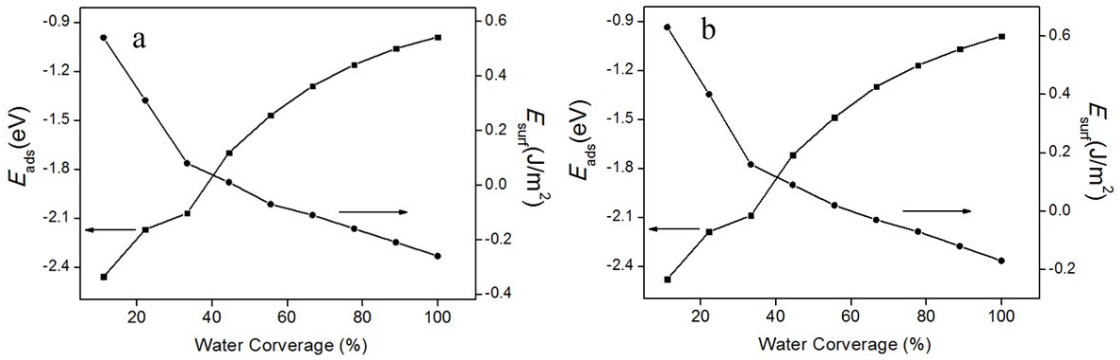

Fig. S5. Average adsorption energies (E_{ads}) (rectangles) and surface energies (E_{surf}) (black balls) of different hydrated (001) surface structures in Fig. 2 for cutoff energy 400 eV and k-point mesh 1×1×1 (a) and cutoff energy 450 eV and k-point mesh 2×2×1 (b).

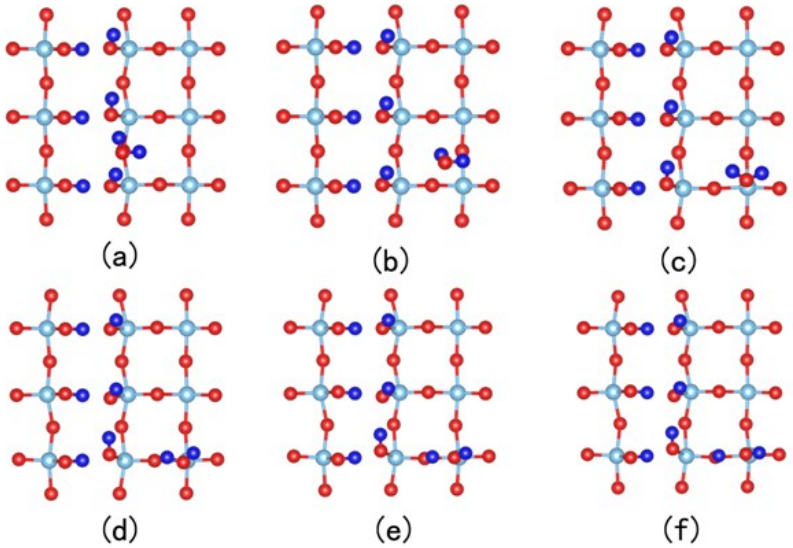

Fig. S6. Atomic configurations of a-f labeled in the potential energy profile in Figure 5 are separately shown in (a)-(f) in the pathway including water diffusion and dissociation on TiO_2(001)-(1×1) surface. The representation for H, Ti and O atoms is the same as that in Figure S1.

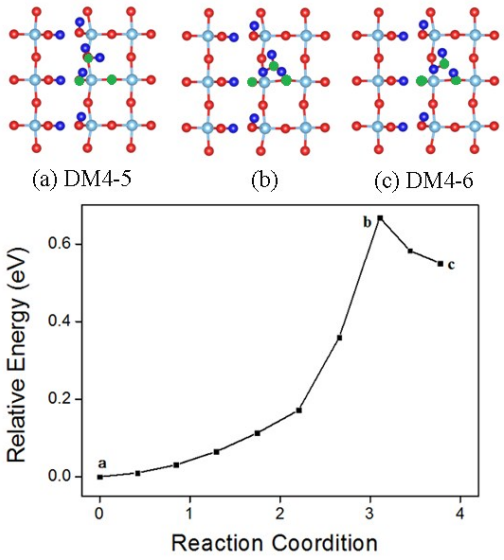

Fig. S7. Potential energy profile for water-assisted hydrogen transfer from surface hydroxyl to the surface Ti_{5c} atom on the TiO_2(001)-(1×1) *surface. Corresponding atomic configurations of a-c labeled in the potential energy profile are separately shown in (a)-(c) for the initial, the transition and the final states in the pathway. The H, O and Ti atoms in water and (001) surface are represented by blue, red and light blue spheres, respectively. Especially, the O atoms participated in the reaction are represented by green spheres.*

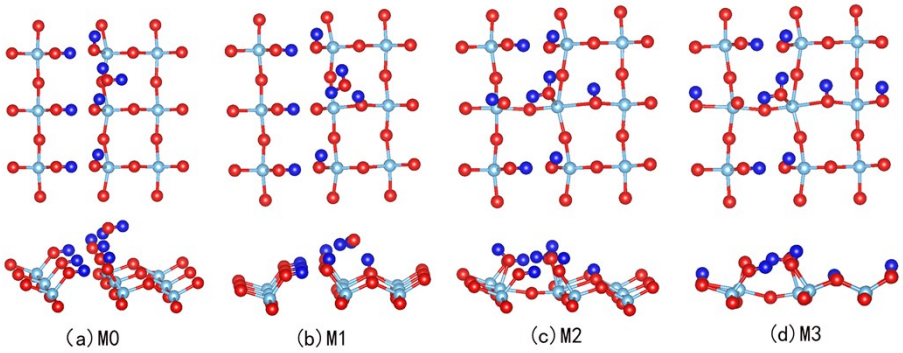

Fig. S8. (a)-(d) show top and side views of the configurations in the initial state and three intermediate states involved in the OER pathway on TiO_2(001)-(1×1) surface, respectively. H The representation for H, Ti and O atoms is the same as that in Figure S1.

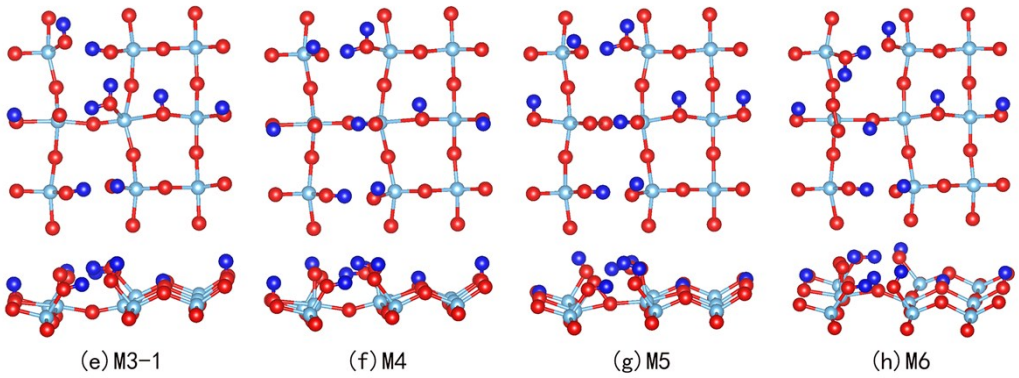

Fig. S9. (a)-(d) show top and side views of the configurations in three intermediate states and the final state involved in the OER pathway on TiO_2(001)-(1×1) surface, respectively. The representation for H, Ti and O atoms is the same as that in Figure S1.

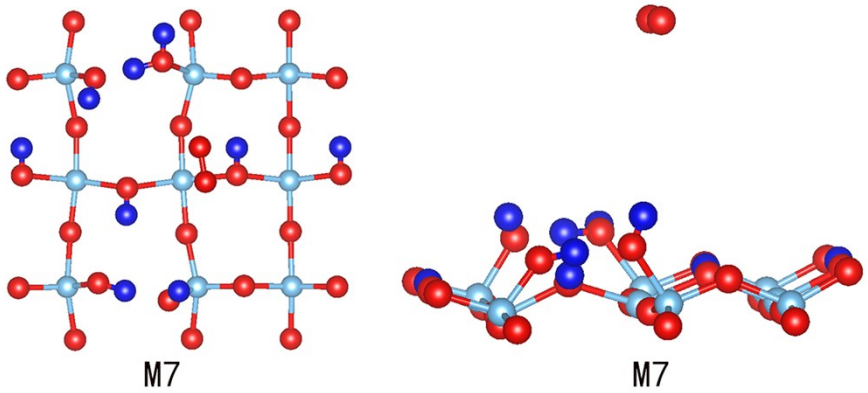

Fig. S10. top and side views of the O_2 desorption configurations on the TiO_2(001)-(1×1) surface. The representation for H, Ti and O atoms is the same as that in Figure S1.

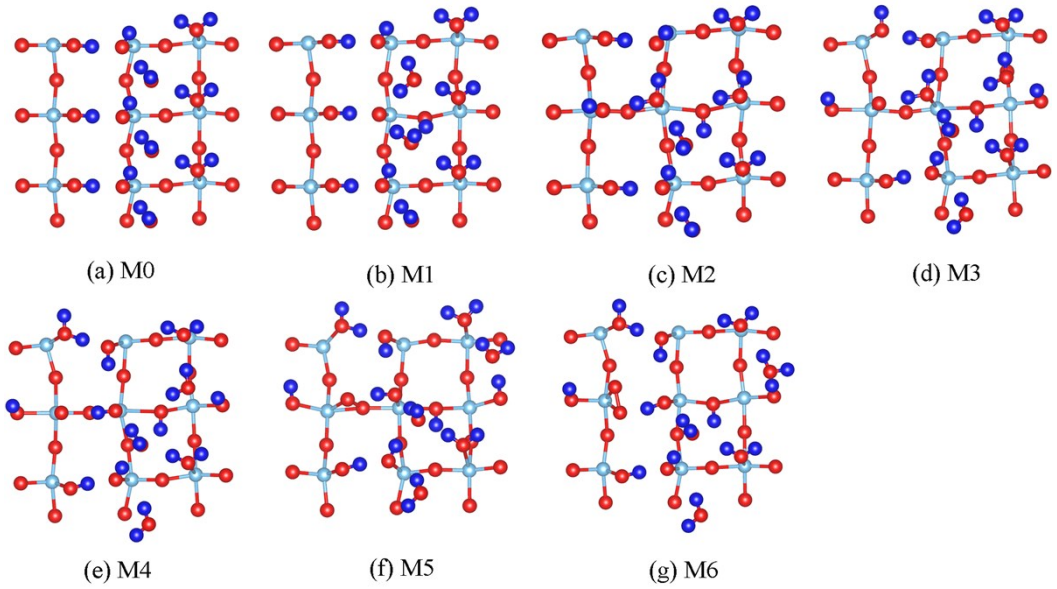

Fig. S11. *Top views of structures of the initial, intermediate and final states involved in the OER process on the unreconstructed TiO_2(001) surface. The representation for H, Ti and O atoms is the same as that in Fig. S1. Note that the initial sate M0 is the same as the DM9 structure.*

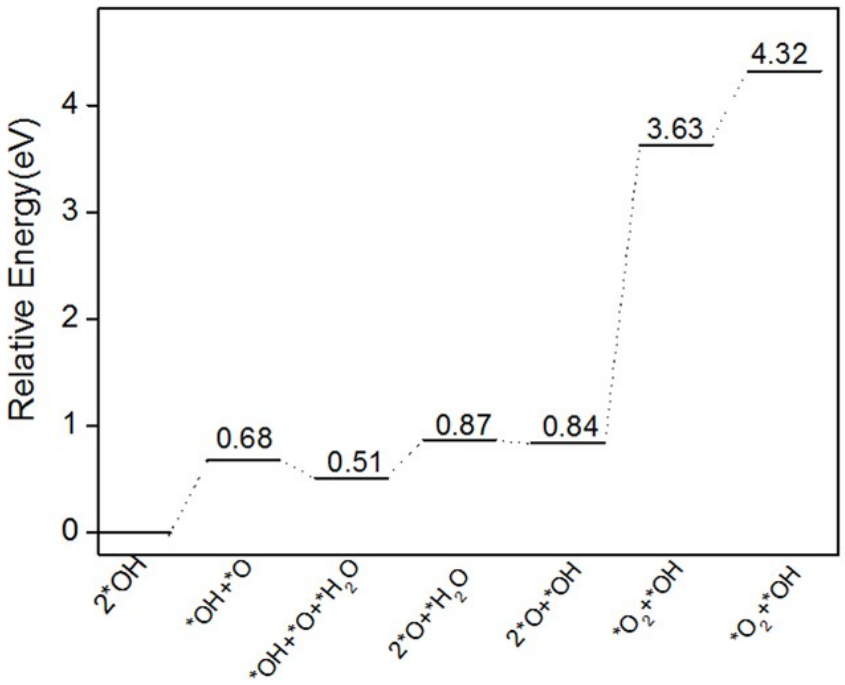

Fig. S12. Calculated potential energy profiles of the initial, intermediate and final species during water-assisted OER pathway on the unreconstructed TiO_2(001) surface.

*Table S1. Relative adsorption energies (E_{ads}) of the initial, intermediate and final states during the OER pathway on the TiO_2(001)-(*1×1*) surface*

	M0	M1	M2	M3	M3-1	M4	M5	M6
E_{ads}（eV）	0	0.14	0.13	0.28	0.24	0.35	0.99	1.11