



Article

Supplementary information for "Chlorine adsorption on TiO₂(110)/water interface: Nonadiabatic molecular dynamics simulations for photocatalytic water splitting"

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S1. Comparison of $d_{\text{O-H}}$ between $U_{\text{Ti}(d)} = 0 \text{ eV}$ and $U_{\text{Ti}(d)} = 4.2 \text{ eV}$

The predicted $d_{\text{O-H}}$ with different concentrations of H_2O adsorbate on the surface could be also affected by Hubbard correction, but investigation of the relation between varied $U_{\text{Ti}(d)}$ and concentration of H_2O is beyond the scope of our research. To simplify the discussions, one and four H_2O s adsorbate on the slab being non-optimized initial models are only considered in this section. The detailed difference of $d_{\text{O-H}}$ between $U_{\text{Ti}(d)} = 0 \text{ eV}$ and $U_{\text{Ti}(d)} = 4.2 \text{ eV}$ are presented for Cl adatom atop the TiO_2 surface with one H_2O adsorbate and four H_2O adsorbate during the AIMD in Figure S1. The $d_{\text{O-H}}$ for $\text{H}_2\text{O}_{\text{Cl}}$ (green dashed-line ellipse), being the nearest water molecule around the deposited Cl adatom, are monitored by each 10 fs within 300 fs summation. After the AIMD running is done, the trajectories of all the cases are colored in yellow. The thermalized $d_{\text{O-H}}$ at 300 fs are illustrated by pink circles, which are not fully dissociated ($d_{\text{O-H}} < 2 \text{ \AA}$). To provide insights into the trajectories for non-dissociated results, the confidence ellipses based on the Gaussian distributions are utilized to express the oscillation area during the AIMD. The blue ellipses mean that the region contains 98.9 % of each monitored $d_{\text{O-H}}$ from 0 fs to 300 fs of AIMD. The added $U_{\text{Ti}(d)}$ increases the adsorption energy and decrease the bond lengths between adsorbate and surface. In Figure S1, the distributions of $d_{\text{O-H}}$ and thermalized bond length (pink circles) with DFT+U are more concentrated. As a consequence, the $U_{\text{Ti}(d)}$ actually cause the variations of $d_{\text{O-H}}$; it is controversial to directly apply the $R_{\text{O-H}}^{\text{C}}$ predicted by $U_{\text{Ti}(d)} = 0 \text{ eV}$ to the structures simulated by $U_{\text{Ti}(d)} = 4.2 \text{ eV}$.

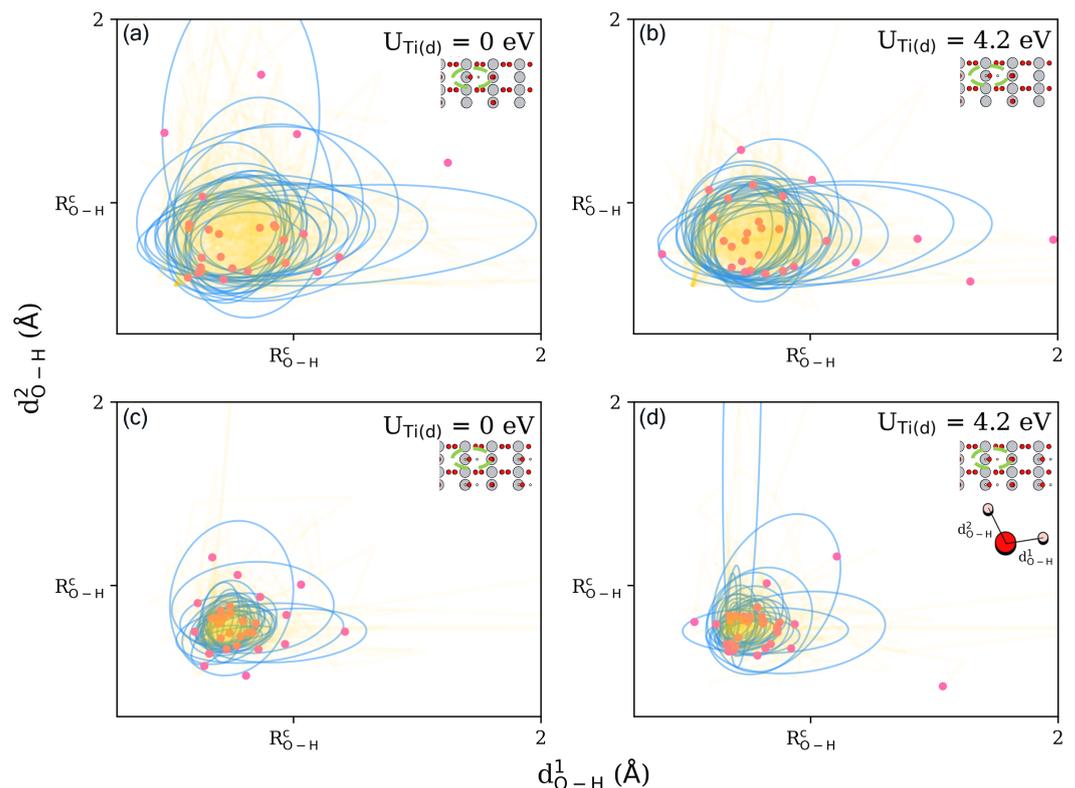


Figure S1. Distributions of $d_{\text{O-H}}$ for the nearest water molecule around the deposited Cl adatom during AIMD. A scatter illustration of two $d_{\text{O-H}}$ for $\text{H}_2\text{O}_{\text{Cl}}$ are presented with (a) $U_{\text{Ti}(d)}$ equal to 0 eV for one H_2O adsorbate, (b) $U_{\text{Ti}(d)}$ equal to 4.2 eV for one H_2O adsorbate, (c) $U_{\text{Ti}(d)}$ equal to 0 eV for four H_2O adsorbate and (d) $U_{\text{Ti}(d)}$ equal to 4.2 eV for four H_2O adsorbate on the surface. The insets are the top view of the surface in (a-d). The green dashed line is the initial position of the monitored $\text{H}_2\text{O}_{\text{Cl}}$. The draw in (d) is the comic structure to illustrate the definition of $d_{\text{O-H}}$. The yellow trajectories are the all paths of $d_{\text{O-H}}$; the pink circles are the thermalized $d_{\text{O-H}}$ below 2 Å. The blue ellipses are the covariance confidence ellipse of $d_{\text{O-H}}^1$ and $d_{\text{O-H}}^2$; the number of standard deviations to determine the ellipse's radius is equal to 3.

S2. Comparison of optimized and non-optimized TiO₂ surface models

In this section, the geometric structure between optimized and non-optimized TiO₂ surface models are discussed. The optimized bond length of each hydroxyl is illustrated in Figure S2(a) to study whether the optimization would trigger the water dissociation. Each water molecule consists of 2 bond lengths of hydroxyl which are expressed to d_{O-H}^1 and d_{O-H}^2 in Figure S2(b). It is clearly shown that the optimization process would not cause the water dissociation for both H₂O_{Cl} and H₂O_{Other}. Meanwhile, most relaxed structures are more stable than the initial models. Figures S2(c-j) are the optimized Cl adatom positions, which are classified to the statistical results in Figure 1(k). It is worth mentioning that the optimal height (h) of Cl adatom is at least larger than 2.5 Å. Besides, most the cases present that the Cl adatom is tend to cus sites of the surface and locations with more water molecules.

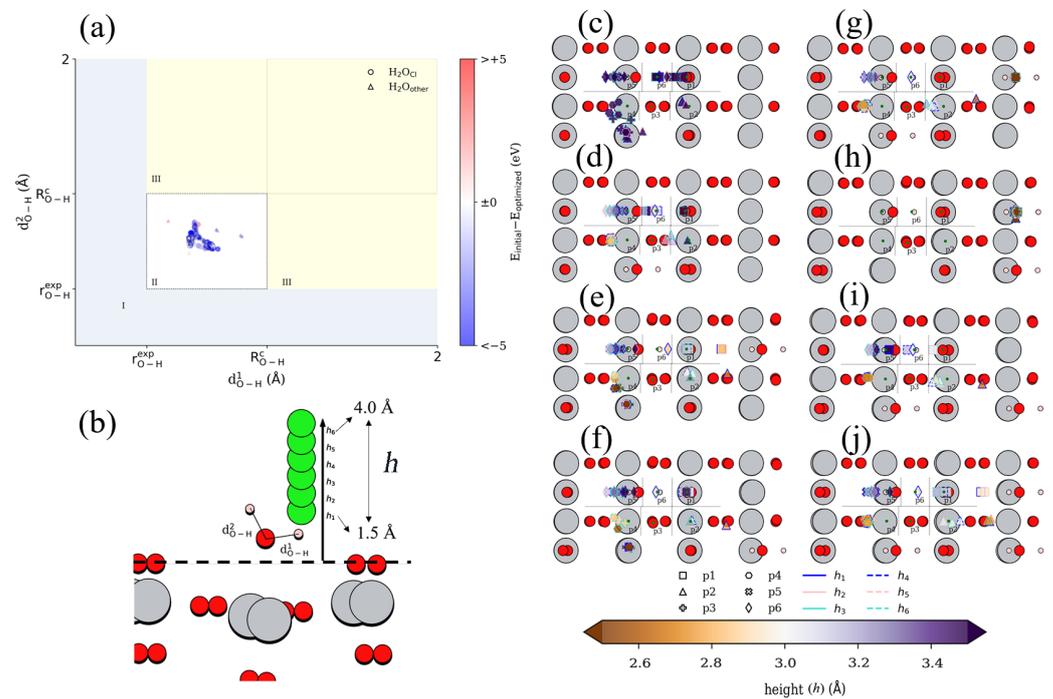


Figure S2. Relations of the geometric structure between optimized and non-optimized TiO₂ surface models.

S3. Relation between kinetic energy, energy barrier and energy difference during AIMD runs

To demonstrate the unreasonable equilibrated configurations during AIMD, the diagrams between kinetic energy, energy barrier and energy difference are applied in Figure S3. During the simulated time, the total energies, kinetic and potential are recorded at each monitored time steps; the total energy is composed of kinetic and potential. In Figure S3, the x-coordinate represents the energy difference between total energy at 0 fs (E_{initial}) and at 300 fs (E_{final}). The y-coordinate is the maximal potential difference in comparison with the initial potential (at 0 fs). If the initial potential is the maximum, the energy barrier (E_{barrier}) is equal to zero. Regarding to kinetic, the magnitude of each dot is the kinetic energy (E_{kinetic}) at 300 fs. The idea of energy difference and energy barrier are inspired by Nudged Elastic Band (NEB) method which is a common technique for discovering transition paths. NEB method utilizes the assigned states (images) of system to find the minimum energy along the reaction path through a static potential built upon the DFT. However, it is emphasized that the results in this section would not further relaxed again by NBE method for the minimum energy. The trajectories of non-optimized TiO_2 surface models are used to discuss in this section because the optimized TiO_2 surface models cannot construct the cases of Cl adatom below 2.5 Å. Besides, the tendency for other types of surface models with two and three H_2O s adsorbate are similar. Therefore, only 4 types of surface models are shown on the top panels in Figure S3. First of all, the shorter distance between the initial Cl adatom and surface (or H_2O adsorbate) would trigger the larger E_{kinetic} at 300 fs due to the repulsion. Meanwhile, the E_{barrier} is tend to zero because of the larger E_{kinetic} . It is obvious for the height of Cl adatom at 1.5 Å (h_1). Besides, the some of the cases in Figure S3(e) and S3(f) are out of the axis range due to the initial Cl adatom too close the H_2O adsorbate, which would destroy the TiO_2 surface structures. In general, the distance between the initial Cl adatom and surface (or H_2O adsorbate) would highly determine the suitability of equilibrated configurations during AIMD. Unfortunately, there is no an uncomplicated regulation between the initial structures with as well as without optimization and thermalized structure after AIMD. Therefore, all cases after AIMD are individually examined for the rationality, including initial structures (576 cases) of optimized and non-optimized TiO_2 surface models.

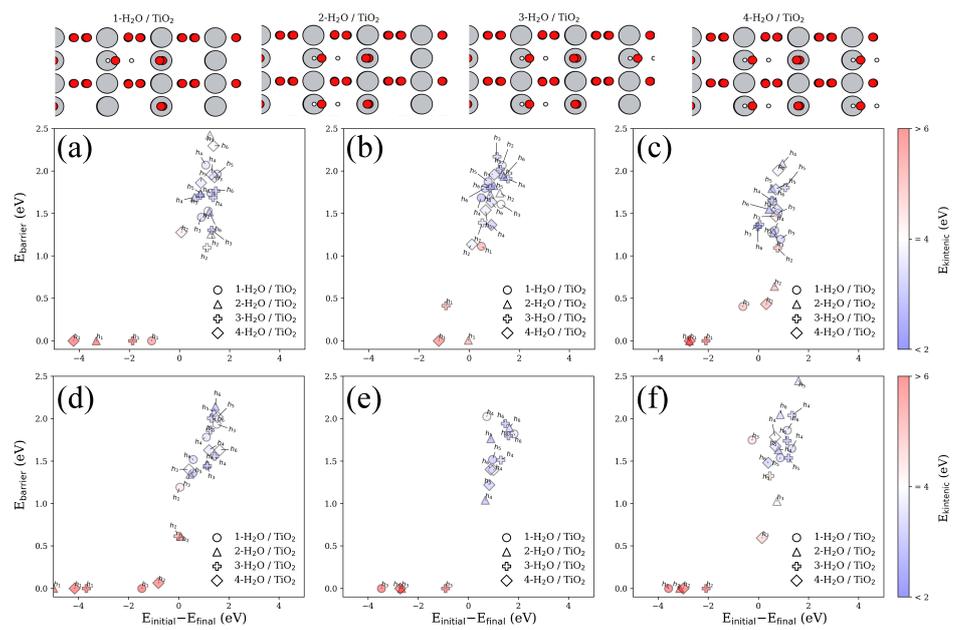


Figure S3. Relation between kinetic energy (E_{barrier}) (E_{final}), energy barrier and energy difference for the total systems of TiO_2 surface models ($E_{\text{final}} - E_{\text{initial}}$). The legends of 1- $\text{H}_2\text{O}/\text{TiO}_2$ (circle), 2- $\text{H}_2\text{O}/\text{TiO}_2$ (triangle), 3- $\text{H}_2\text{O}/\text{TiO}_2$ (cross) and 4- $\text{H}_2\text{O}/\text{TiO}_2$ (diamond) are corresponding to the figures on the top panels from the left to right direction.

S4. Inappropriate initial position of Cl adatom causing destroy the surface during AIMD

Due to the inappropriate initial position of Cl adatom, the surface is totally destructed during AIMD runs in Figure S4. No matter which types of surfaces are considered from one to four H₂O adsorbates, it can be found that the Cl adatom destructs the surface due to the Cl adatom being too close to surface or H₂O adsorbate. From the Figure S4, the huge repulsion causes the large momentum for total structure which trigger the unreasonable kinetic energy. The final positions of Cl and water are far away from the surface, which are up to ten or hundreds of angstroms. Generally, the initial position of Cl adatom is highly depended on the rationality of thermalized configurations. Therefore, all these types of inappropriate initial guesses are excluded after undergoing AIMD calculations.

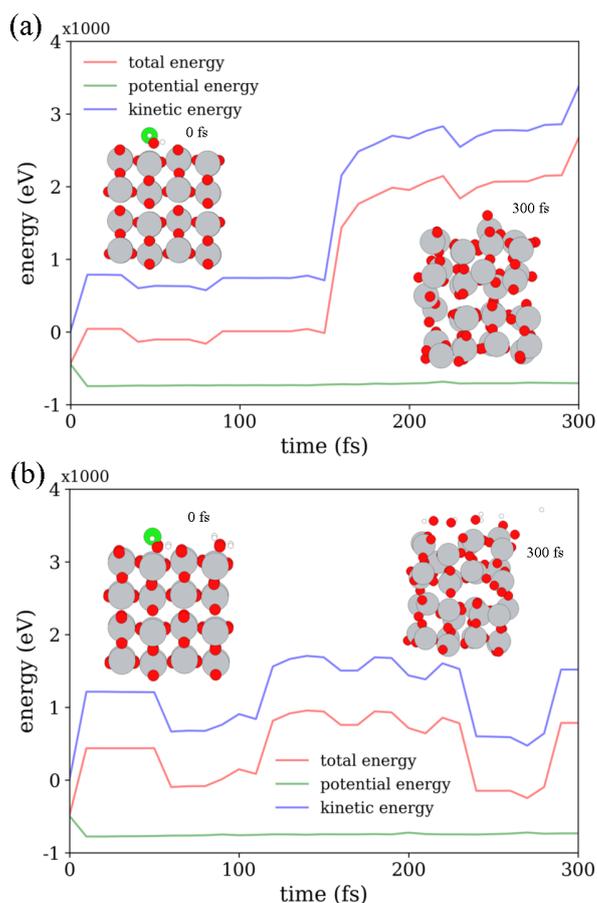


Figure S4. Inappropriate initial guesses induced the failure of molecule dynamics. The time-dependent relation of total energy (red line), potential energy (green line) and kinetic energy (blue line) are shown for (a) single and (b) four water molecules on the surface. The insets are the initial (0 fs) and final (300 fs) structures.

S5. Water splitting reaction induced by thermal equilibrium

Two of those cases are shown in Figure S5. The extra Cl atom provides a variety of intermediate states, and could trigger either hydroxyl or hydronium to occur during the process. The final configurations present the reaction following to the Eq. 1 in Figure S5(a). Yet, the dissociated hydrogen of water is oscillated between the oxygen of water and the oxygen of bridge site. The dissociated process repeats many times and shows two illustrative insets in Figure S5(a) for the period of 60 to 70 fs and 220 to 230 fs. As for the case of hydronium, the insets in Figure S5(b) reveal that the adsorbed waters on titanium at cus site form an intermediate state of hydronium at 230 fs and further donate one hydrogen to the oxygen of bridge site at 260 fs. Though, the final configuration still can be found in a hydronium not the phenomenon of dissociation at 300 fs. Compared to Figure S5(a), the reaction process of hydronium is much steadier. Specifically, these two examples don't mean that the process involved in hydronium must be more stable than the reaction of hydroxyl. Both reaction pathways could explore the kindred phenomena. The purpose of thermalization is utilized to determine the possibility of structures for undergoing the ED-TDDFT. Although there's considerable uncertainty in those dissociated cases when the time period was enlarged to the picosecond scale, preparing the thermalized interface for the moment of photoexcitation was still tolerable at hundreds femtoseconds.

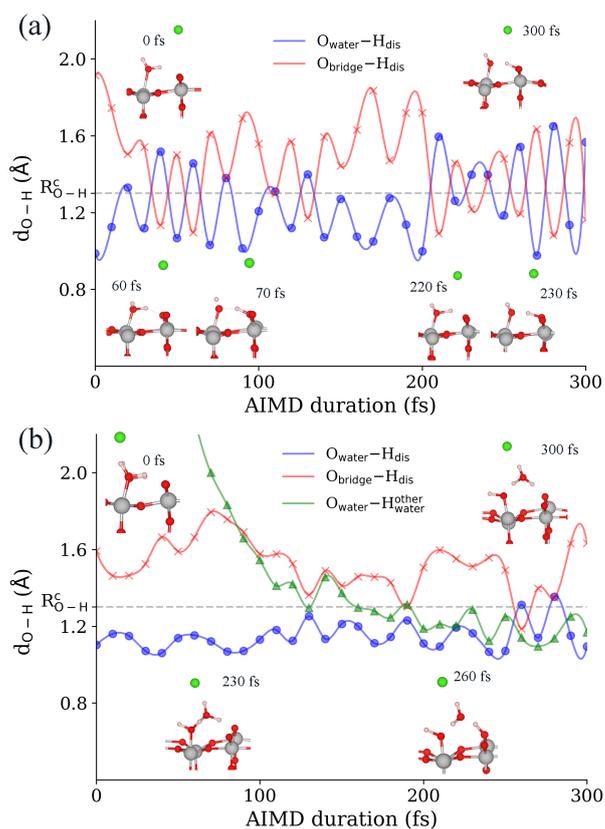


Figure S5. Dynamics O-H bond length (d_{O-H}) as a function of the simulation time. (a) The reaction pathway involves in Eq. 1 for the intermediate state of hydroxyl. (b) The reaction pathway involves in Eq. 2 for the intermediate state of hydronium. The oxygen atom of water molecule, oxygen atom of bridge site, dissociated hydrogen atom, and hydrogen from another water molecule are O_{water} , O_{bridge} , H_{dis} and $H_{\text{other water}}$, respectively. The blue circles (red crosses) are the d_{O-H} corresponding to O_{water} and H_{dis} (O_{bridge} and H_{dis}); the green triangles are the donor of the $H_{\text{other water}}$ for forming the hydronium. The solid lines are the fitting curves based on each 10 fs sampling results; the dashed lines indicate the criteria of OH-bond breaking. The insets are the geometric structures at the numbered times.

