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A mechanism for the hole-mediated water photooxidation on TiO₂ (1 0 1) surfaces

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Abstract

The mechanism of water photooxidation on TiO₂ surfaces is still controversial. Here we report a first-principles density functional study based on a hybrid functional method in which an adsorbed water molecule is found to directly interact with a self-trapped hole at a bridging oxygen site and to transform into an OH• radical species through a concerted proton/hole transfer. This study analyzes both the thermodynamics and kinetics of this step of the reaction, which is generally considered to be the rate determining one. The fate of the OH• radical is then investigated in terms of its reactivity with different surface species, with a second OH• radical, or with a second water molecule coming from the environment. We find that OH• radicals can either acquire a hydrogen from surrounding water molecules or, if they meet, couple to form hydrogen peroxide with highly associated energy gain.

Keywords: DFT, hybrid functionals, photocatalysis, water splitting, anatase

 Online supplementary data available from stacks.iop.org/JPhysCM/28/074002/mmedia

(Some figures may appear in colour only in the online journal)

Introduction

The photoinduced water splitting process can be conceptually and physically (in photoelectrochemical cells) divided into the water photoreduction to molecular hydrogen and the water photooxidation to molecular oxygen [1, 2]. Semiconductors, such as TiO₂ and WO₃, are often used as materials for the photoanode where the O₂ evolution takes place [3–5]. The molecular mechanism of the water photooxidation on an oxide surface is still undergoing debate. In the case of TiO₂, which can be considered the benchmark material for the investigation of this type of processes, there is not yet a general consensus whether the oxidation is initiated by a trapped hole at a surface hydroxyl (OH_s•) [6, 7] or by a nucleophilic attack of a water molecule to a surface trapped hole at a bridging O atom (O_{br}•) [8, 9]. In the following we propose, on the basis of density functional calculations with the hybrid B3LYP method, a possible reaction path for the water photooxidation on anatase (101) surface that is triggered by O_{br}• species but that produces OH• radicals intermediates. This proposed mechanism reconciles the apparent contradicting experimental literature. Evidence for OH• radicals formation is reported from spin

trapping [10, 11] or low temperature [12] electron spin resonance (ESR) and infrared (IR) spectroscopies [13]. However, evidence from photoluminescence, IR, and isotopic exchange studies support direct oxidation of water by the photogenerated holes [8, 9].

Water photoelectrolysis on both rutile (110) and anatase (101) surfaces has been the object of previous density functional theory investigations [14, 15]. For rutile, it was proposed that the water splitting process takes place at low coordinated sites and that OH• radicals are formed through oxidation of OH⁻ species [16]. More recently, the possibility of a direct hole transfer from regular rutile (110) or anatase (101) surfaces to water molecules has also been proposed [17–20].

Photoinduced holes must definitely play a fundamental role in any oxidation process when no molecular oxygen is present in the environment. On the contrary, in oxygenated environments, oxidation processes may be caused by oxidizing species that derive from O₂ reduction by photoexcited electrons, such as hydrogen superoxide or peroxide. However, the hole-mediated oxidation mechanism may not be the same for all photocatalytic reactions on the TiO₂ surface [21]. Holes can be generated in the TiO₂ bulk by UV irradiation and are

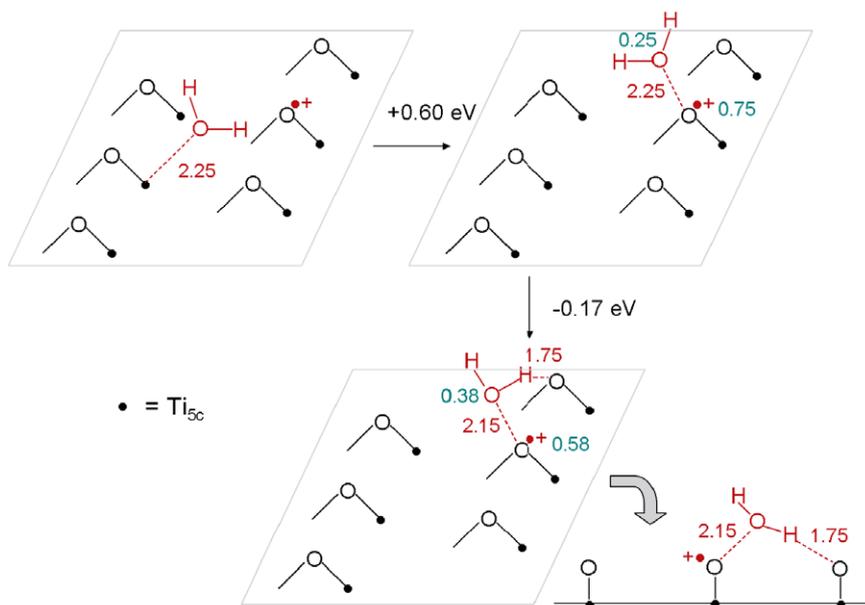


Figure 1. Schematic representation of the anatase 101 surface (a 1×3 supercell model with six Ti_{5c} sites and six bridging oxygens). Top left: one water molecule adsorbed on a Ti_{5c} site and a self-trapped hole (red dot) at a bridging oxygen site. Top right: one water molecule electrostatically bound to the self-trapped hole oxygen site. Bottom right: one water molecule electrostatically bound to the self-trapped hole oxygen site and through hydrogen bonding to a next-neighbouring bridging oxygen. Atomic distances are shown in Å (red text), spin density is shown in fraction of electron (light blue text), and energy changes are shown in eV (black text).

supposed to travel from the bulk to the surface if they do not recombine or are not trapped by bulk defects or impurities. Once at the surface, holes can be stabilized by surface traps. We have recently proven [22], on the basis of density functional calculations, that actually there is a driving force for holes to travel from the bulk to the surface and that surface bridging oxygens may allow for hole self-trapping, whereas terminal hydroxyl groups can behave as hole traps only if they are isolated, i.e. not involved in any hydrogen bonding with next-neighbouring bridging OH groups.

As introduced above, the purpose of the present first-principles density functional study is to investigate the interaction of a self-trapped hole at a bridging oxygen site on the anatase (101) TiO_2 surface with one water molecule. We observed, through a concerted proton/hole transfer, the formation of an OH^\bullet radical species whose fate is then investigated in terms of its further reactivity with (i) different surface species, (ii) a second OH^\bullet radical, or (iii) a second water molecule coming from the environment. We find that OH^\bullet radicals can either acquire a hydrogen from surrounding water molecules or, if they meet, couple to form hydrogen peroxide with highly associated energy gain.

Computational details

We use the CRYSTAL09 [23] package in which the Kohn–Sham orbitals are expanded in Gaussian type orbitals (the all-electron basis sets are O 8–411(d1), Ti 86–411 (d41), H 311(p1), and the hybrid functional B3LYP) [24, 25]. The anatase (101) TiO_2 surface was modeled by a slab of three triatomic layers with either 108-atoms and 1×3 periodicity or

144-atoms and 1×4 periodicity along the $[10\bar{1}]$ and $[010]$ directions; no periodic boundary condition was imposed in the direction perpendicular to the surface. The lattice parameters were optimized for the present computational setup. The k-space sampling for the geometry optimizations included four k-points. The presence of an electron hole in the slab has been simulated by introducing a positive charge in the periodic model, which was compensated by a uniform background of negative charge. Spin density numbers are presented in the following because they provide a quantitative evaluation of the fraction of the electron hole localized on a specific atom.

Results and discussion

In the following we elucidate the first steps of water photooxidation through the investigation of the interaction of a surface trapped hole first with one water molecule (0.17 monolayer coverage) and then with a second water molecule (0.25 or 0.33 monolayer coverage, see below). The binding energy of one water molecule on surface Ti_{5c} ions is estimated to be -0.64 eV with the present computational setup.

If one hole is present in the surface model and trapped at a bridging oxygen, far from the Ti_{5c} adsorption site, the water molecule binding energy (figure 1, top left) is found to increase up to -0.79 eV as a consequence of the increased electrophilicity of the surface. It is important to stress that despite the extensive search, it has not been possible to have the hole transferred neither to the undissociated adsorbed water molecule nor to a dissociated one with the proton on the next-neighbouring bridging oxygen (intrapair dissociative adsorption) [22]. As a next step we consider the possibility of

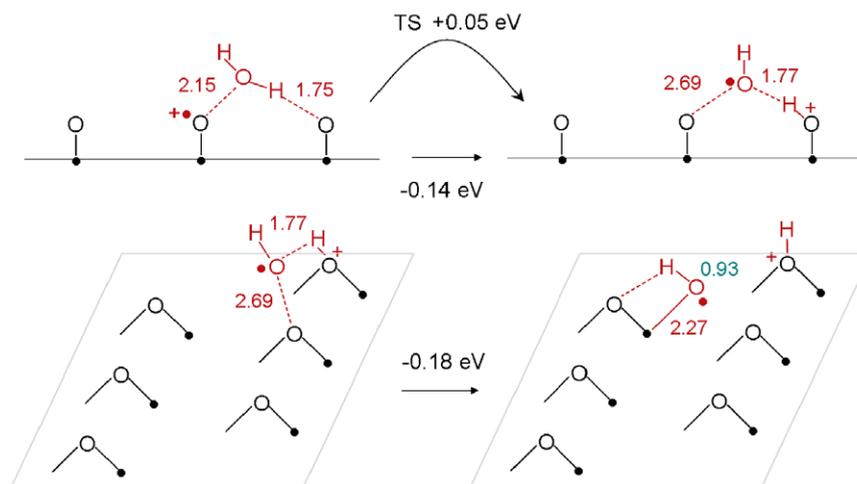
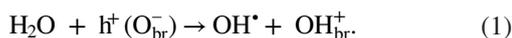


Figure 2. Top panel: schematic representation of the proton transfer from the adsorbed water molecule (see figure 1) to a bridging oxygen atom leading to the formation of an OH^\bullet radical species. Bottom panel: schematic representation of the OH^\bullet radical transfer to a Ti_{5c} site. Atomic distances are shown in Å (red text), spin density is shown in fraction of electron (light blue text), and energy changes are shown in eV (black text). TS = transition state.

a water molecule being attracted by a self-trapped hole (figure 1, top right) and undergoing a nucleophilic attack of the trapping bridging oxygen. Actually, we found that the water molecule can be bound to such surface oxygen by -0.19 eV, which can increase up to -0.36 eV if the water adjusts in a way to maximize one hydrogen bonding with the next bridging oxygen along a $[010]$ row (figure 1, bottom right). In both configurations we observed that the hole is partially delocalized on the water O atom (0.25 and 0.38, respectively, in the two configurations).

To totally transfer the hole to the water fragment we forced the transfer of the hydrogen bonded H to the next bridging oxygen (figure 2, top panel) and allowed for the system relaxation, according to the following equation:



The process is exothermic by -0.10 eV. The result is the formation of an OH^\bullet radical that is still somehow bound to the transferred H and it is rather far from the originally trapping bridging oxygen, which is now fully reduced back to an O^{2-} species. The thermodynamics suggests that this new situation is still preferable to having an unbound water molecule far from or detached from the surface. This is a crucial reaction step for water photooxidation, because we start from a water molecule adsorbed on a hole trapping bridging oxygen and end up with a dissociated OH^\bullet radical.

This is commonly considered to be the rate determining step for water photooxidation [14, 15]. Interestingly, the proton transfer to the surface is accompanied by the hole transfer from the surface to the forming hydroxyl species. The key question is whether this is a concerted or a sequential proton/hole transfer. A recent theoretical investigation of water photooxidation on the anatase (101) surface [17], based on constrained minimization from selected snapshots of a first principles molecular dynamics run, proposed a sequential process that is initiated by a proton transfer followed by an electron (or hole) transfer.

Table 1. Relative energies of the optimized structures at several (eight) fixed $\text{O}_{\text{br}}\text{-H}$ distances along the reaction path of equation (1). Spin density values on the water O atom are also reported.

Structure	Relative energy (eV)	$\text{O}_{\text{br}}\text{-H}$ distance (Å)	Spin density on O
1 $\text{H}_2\text{O}\cdots\text{O}_{\text{br}}^\bullet$	0.0	1.80	0.39
2	-0.02	1.685	0.44
3	-0.02	1.570	0.48
4	+0.0	1.455	0.54
5	+0.03	1.340	0.61
6	+0.05	1.227	0.72
7	-0.07	1.114	0.92
8 $\text{OH}^\bullet\cdots\text{HO}_{\text{br}}^+$	-0.14	0.99	0.986

Here we apply a different approach to investigate this very delicate issue. We have performed a series of constrained optimizations scanning the potential energy surface at different $\text{O}_{\text{br}}\text{-H}$ bond length values (from 1.80 to 0.99 Å) and allowing full relaxation of all other degrees of freedom. We clearly observed a continuous hole transfer taking place in parallel with the decrease in the $\text{O}_{\text{br}}\text{-H}$ distance (see table 1), as clearly indicated by the spin density values on the water O atom. The amount of localized spin density has not been imposed in the calculations but results from the self-consistent optimization of the electron density at a given geometry along the scanned reaction profile. The highest energy value is computed for a distance of 1.23 Å corresponding to a spin density of 0.72 on the forming OH species (table 1). The resulting activation barrier for the coupled proton/hole transfer is rather low at 0.05 eV (figure 2, top panel, and table 1). If the produced OH^\bullet radical is then transferred to adsorb on a Ti_{5c} adsorption site to form a TiOH_i^\bullet , there is an additional energy gain of -0.18 eV (figure 2, bottom panel).

When two of these events, described in equation (1), take place on the anatase surface, there will be two OH^\bullet radicals

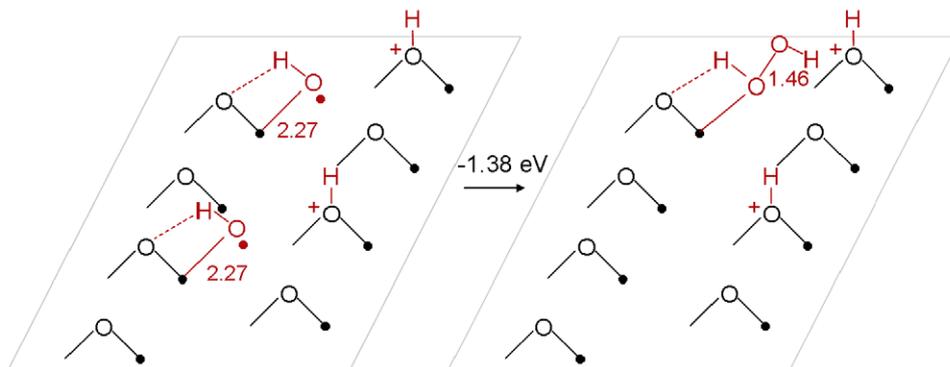


Figure 3. Schematic representation of the coupling of two OH• radical species to form one H₂O₂ molecule. Atomic distances in Å (red text) and energy changes in eV (black text).

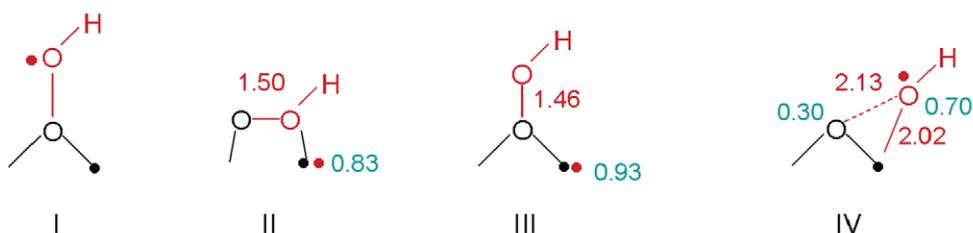


Figure 4. Schematic representation of the four configurations considered for the OH• radical, produced in reaction (1), adsorption on the surface.

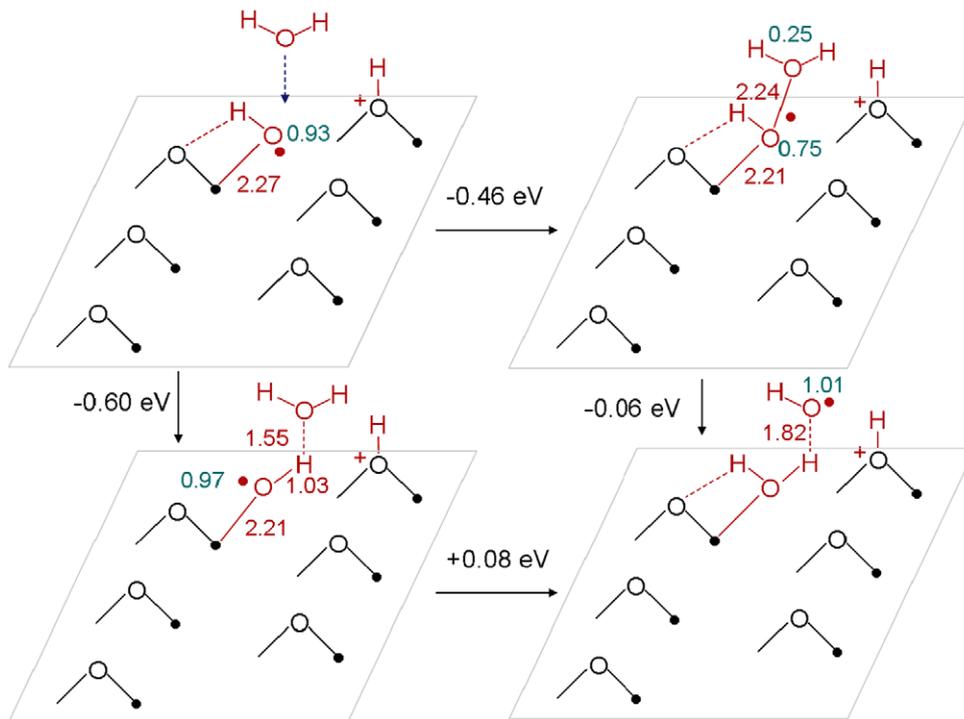


Figure 5. Schematic representation of OH• radical reactivity with a second water molecule, as discussed in the text. Atomic distances are shown in Å (red text), spin density is shown in fraction of electron (light blue text), and energy changes are shown in eV (black text).

formed, which are expected to couple, forming one hydrogen peroxide molecule (H₂O₂), adsorbing on a Ti_{5c} site (figure 3). The latter process (2 OH• → H₂O₂) is found to be highly

exothermic by -1.38 eV, which is probably the driving force toward the water photooxidation, in excellent agreement with early experiments [26].

We have also investigated the possibility that the OH^\bullet radical formed in reaction (1), before finding a second OH^\bullet radical on the surface and collapsing into a H_2O_2 molecule, binds to the nearby bridging O atom to form a TiOOH species, as suggested by the experimental literature [8, 9]. We have considered four possible situations as described in figure 4.

The first configuration (I in figure 4)) does not exist and the system spontaneously evolves back to the starting situation where the OH^\bullet radical has just been formed and is weakly bound to the OH_{br} species. The second and third configurations (II and III in figure 4) exist but are much higher in energy by approximately 2 and 1.5 eV, respectively. The fourth one (IV in figure 4) is the most relevant because it is approximately isoenergetic (+0.07 eV) to the starting situation resulting from reaction (1) and is most probably the intermediate to proceed to a rather stable TiOH_i^\bullet final configuration. These results seem to indicate that it is not easy to form a TiOOH species involving a regular lattice oxygen atom, even if undercoordinated (bridging) at the surface. Therefore, we may conclude that the chance for an OH^\bullet radical to meet a second OH^\bullet radical on the surface before reacting with any regular surface species is rather high.

Finally, there is also the possibility that other water molecules could interact or react with the newly formed terminal OH^\bullet radical, preventing or delaying the hydrogen peroxide formation. To investigate this hypothesis, we introduced a second water molecule in our model system (figure 5). This additional water molecule can bind the OH^\bullet radical through its H or O atoms. If the water H atom is hydrogen bonded to the O atom of the terminal OH species, then the interaction is negligible, causing the hole transfer from the terminal hydroxyl to a surface bridging O atom. If the water O atom is involved, then it can bind to the H or O atoms of the terminal OH^\bullet radical. When it binds to the hydroxyl H, the distance between the water O and the hydroxyl H is 1.55 Å (figure 5, bottom left). The spin density is still highly localized (0.97) on the hydroxyl O atom as in the case of an isolated Ti-OH^\bullet species. The interaction energy with respect to a gas phase water molecule amounts to -0.60 eV. On the contrary, when it binds to the hydroxyl O atom, the $\text{O}_{\text{OH}}-\text{O}_{\text{H}_2\text{O}}$ distance is 2.24 Å. The spin density is now delocalized between the two O atoms: 0.75 on the hydroxyl O and 0.25 on the water O atom (figure 5, top right). The interaction energy with respect to a gas phase water molecule amounts to -0.46 eV. The question now is whether the water molecule is willing to transfer an H atom to the OH^\bullet radical to form a new water molecule adsorbed at the surface and transform itself into an OH^\bullet radical (figure 5, bottom right). This process would transfer the radical entity from an adsorbed species to an interface one. If we could have a large number of molecules, then this new radical species would be in the interfacing liquid phase. Such a process is not so unfeasible because it costs only 0.08 eV if starting from the situation in which the second water molecule interacts with the hydroxyl H atom, whereas it releases -0.06 eV if starting from the situation in which the second water molecule interacts with the hydroxyl O atom.

Conclusions

The present density functional study indicates that hole-induced water dissociation, resulting in an OH^\bullet radical and a surface bridging OH species, is conceivable. This process is proposed to be a concerted proton/hole transfer. We observed that the hole transfer is from a surface bridging oxygen to the dissociating water molecule, whereas the concomitant proton transfer is from the water molecule to a different surface bridging oxygen.

On the basis of this mechanism, OH^\bullet radicals are formed through the oxidation of water molecules and not as a result of hole trapping by surface OH. This means that the degree of surface hydroxylation is not a determinant for the formation of the OH^\bullet radicals during the water photooxidation process. Such a conclusion could be generalized to the photooxidation of other species (e.g. organic molecules) when these processes take place in a water environment.

Once the surface OH^\bullet radicals are formed they can easily interact with other water molecules at the interface (we have investigated the interaction with one more molecule) and this triggers successive hole/proton transfers forming OH^\bullet radicals in the liquid phase where they might pair into hydrogen peroxide molecules. If two OH^\bullet radicals happen to meet, then the H_2O_2 formation is energetically highly favourable.

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