Formation of OH groups and Hydrogen Peroxide Molecules on the TiO$_2$ Anatase Surface: Pseudopotential Calculations

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Abstract

The density functional pseudopotential simulation was carried out to study dissociation of the H$_2$O molecule on the TiO$_2$ anatase surface (pure and W doped). Formation and desorption of the OH groups were studied, and it was shown that the adding of tungsten into titanium dioxide leads to reduction of the desorption energy of OH groups from 6.06 eV to 4.74 eV. Creation of the hydrogen peroxide H$_2$O$_2$ molecules was also investigated. Substitution of Ti with W on the TiO$_2$ anatase surface decreases the formation energy of hydrogen peroxide molecules and moves it up to the range of visible sun light. Decrease of the formation energy of free OH groups and H$_2$O$_2$ molecules, which are fissile oxidizers, increases their quantity in water and promotes increase in effectiveness of organic pollutants decomposition.

Introduction

Titanium dioxide (TiO$_2$) in the form of anatase has a wide range of the functional properties. It is one of the most often used semiconductors for cleaning of sewage and air, for solar elements and generators of hydrogen. The effectiveness of TiO$_2$ anatase in these applications is caused by combination of its unique properties: a biological indifference (not toxicity), low cost and high resistance to photocorrosion in aqueous solutions[1-5]. The high photocatalytic activity of TiO$_2$ anatase usually is explained by the fact that it has the suitable width of the forbidden region (from 2.4 eV to 2.8 eV) and the considerable positive potential of a valence band (+3.1 eV) which allow it efficiently to photolise water to such strong oxidizers as OH radicals and H$_2$O$_2$ molecules, which are capable to deep oxidation of organic molecules into CO$_2$ and H$_2$O [3].

However, pure TiO$_2$ anatase possesses a small quantum yield because of the fast electron-hole recombination; it is not stable because its structure is inclined to transform into a more stable but not photo-active TiO$_2$ rutile phase; the edge of characteristic absorption of anatase lies at the efge of the UF range, thus it is not capable to use efficiently solar energy.

Addition of some transitional metals is used to eliminate these shortcomings. It is known that introduction of Nb, Mo, and especially W leads to improvement of photocatalytic activity[6-9]. Authors of those works connect this fact with large valences and oxygen attraction of above metals in comparison with Ti.

As it is noted by many authors[3,10-13], main factors of photocatalytic effect of the titanium dioxide on decomposition of organic pollutants in water are following ones:

1.   formation of hydroxyl OH groups;
2.   formation of molecules of hydrogen peroxide H_2O_2.

The hydroxyl OH group is a strong oxidant; thus it is important to study mechanisms of dissociation of the H_2O molecule to an OH group and an H atom, and to make clear how W affects desorption the OH group from the surface of TiO_2. Hydrogen peroxide H_2O_2 also is a rather strong oxidant, and formation of its molecules at the TiO_2 surface in water has to be studied too.

As it is noted above, usually at the descriptions of photocatalytic activity of TiO_2 anatase the main attention is directed on electronic transitions under the influence of light; however we consider that these transitions serve only as the mechanism for absorption of energy, which can come to the system in different ways. Therefore, we build our research of mechanisms of the water decomposition near the anatase surface (pure and doped) only through study of energy of the system, without the direct consideration of electron transitions. As a doping element we chose tungsten because it is the most efficient dopant.

Methods and Models

The present investigation was carried out in the framework of the density functional theory[14,5] with using the well-known computer code FHI96md[16]. Exchange-correlation effects were calculated in the general gradient approach GGA [17]; the plane wave energy cutoff was taken of 50 Ry; pseudopotentials were constructed using the FHI98pp code[18]. Studied surfaces were modeled by slabs placed into a supercell with a size of 14.5248×14.5248×40.0 a.u.3 (a.u.=0.529 Å). The pure TiO_2 slab contained 16 Ti atoms and 32 O atoms. To study the dopant influence one of the surface Ti atoms was replaced with a W atom; an additional O atom was placed near the W atom to saturate its large valence. Figure 1 demonstrates a placement of atoms in the slabs $Ti_{16}O_{32}$ и $Ti_{15}W_1O_{33}$ and on their surfaces.

Results and Discussions

Formation of OH groups

First of all we studied water adsorption on the pure TiO_2 surface. We have found that positions just above metal atoms are the most favorable places for the molecule H_2O. This result agrees with data of the known works[19-21]. The H_2O molecule adsorption energy on the pure TiO_2 has been found equal to 1.2 eV. Ti and W atoms situated on the doped surface have approximately the same adsorption activity and the H_2O adsorption energy above them is about 2.0 eV. There are published data only for pure TiO_2. It was reported [19] that the H_2O adsorption energy on the TiO_2 rutile depends on the water covering and lies in the range of 0.95-1.08 eV. The H_2O adsorption energy on the TiO_2 anatase surface was found of 0.73 eV [20].
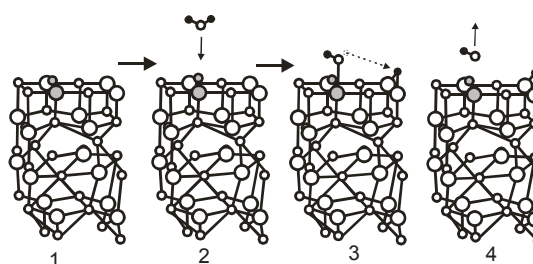

Fig. 1. A scheme of study the behavior of the H_2O molecule on the TiO_2 surface. Ti atoms are presented as big white balls; O atoms are shown as small white balls; H atoms are imagined as small black balls. The grey colored balls present Ti atoms replaced with W atoms and an addition O atom. The reaction path for the H_2O molecule dissociation is demonstrated by a dotted line. The numbers 1, 2, 3, 4 correspond to: (1) the clear surface; (2) the adsorption of the H_2O molecule; (3) the H_2O dissociation to OH and H; (4) the desorption of the OH group.

Increase of the adsorption energy of a water molecule under the influence of impurity demonstrates that binding energy of the molecule atoms with atoms of the surface increases. As the change of binding energy happens due to "flowing" of the electronic density, a qualitative conclusion follows: this increase in bonding with a surface has to decrease in bonding within the H_2O molecule.

Our second step is to investigate dissociation of the H_2O molecule to the OH group and the H atom. This process was studied recently for the H_2O molecule adsorbed above the Ti adatom placed upon the TiO_2 rutile surface[21]. Authors have found that the OH the group remains to be bound with the Ti atom while hydrogen atom moves to other metal atom. The reaction path is characterized by a small barrier (about 0.2 eV) and the energy gain of 1.2 eV.

In our case the final state of the dissociation reaction is practically the same. The OH group remains connected with atom of metal (W), however the H atom goes to the bridge position between two Ti atoms (Fig. 1). The barrier height is 0.3 eV for the pure TiO_2 and 0.8 eV for the doped with W (Fig. 2). The energy gain of this reaction is 2.5 eV for the pure TiO_2 anatase and 0.9 eV for the doped one.

We see that the W atom accompanied by the additional atom of oxygen increases the barrier height of the H_2O dissociation reaction (0.8 eV instead of 0.3 eV). However, the energy spent for overcoming the barrier (0.8 eV) is compensated by

the final energy gain of 0.9 eV; thus this reaction can happen without additional inflow of energy.

The aim of our investigation is to find the energy needed for desorption of the OH group. Let us pay an attention to the fact that the energy gain of the reaction in the doped system is much less than in the pure one. It means that products of the reaction in the doped system are in less bound state than in pure one. Our calculations confirm this conclusion. The energy for desorption of an OH group has been found to be 6.06 eV for the pure system and 4.74 eV for the W doped one.

Therefore, the presence of W atoms really stimulates the emergence in water of free OH radicals and thereby promotes more intensive decomposition of organic substances which are present in aqueous solutions.

Formation of Hydrogen Peroxide
Hydrogen peroxide is a rather stable substance, in which atoms of hydrogen are weakly bound. Owing to this fact this substance acts as a strong oxidizer. In usual conditions it may be produced through reaction of oxygen with water:

$$O_2 + 2 H_2O => H_2O_2.$$
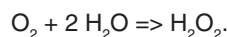
The energy scheme of this reaction is shown in Figure 3. The energy barrier of the reaction is caused by requirement of some additional energy for dissociation of the oxygen molecule. The reaction
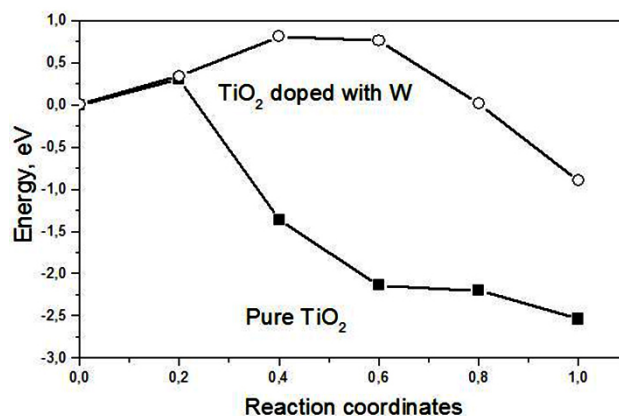

Fig. 2. The energy barrier for the H_2O dissociation on the TiO_2 anataze surface: pure and doped with W.

$$E_{\text{barrier}} = 5.1 \text{ eV}$$

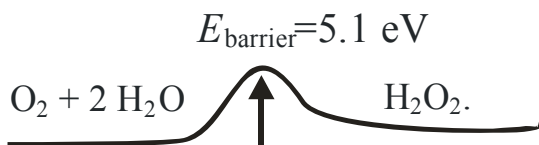$$O_2 + 2\,H_2O \qquad \qquad H_2O_2.$$

Fig. 3: Scheme of the reaction of the hydrogen peroxide formation.

product (a hydrogen peroxide molecule) is less favorable than initial products (molecules of oxygen and water) therefore, this reaction goes with energy absorption.

Our calculations show that dissociation of oxygen molecules on the surface of titanium dioxide happens spontaneously, without any barrier. However the both atoms of oxygen are bound with the TiO_2 surface, taking so-called "bridge" positions between atoms of titanium (Fig. 4).

If titanium dioxide is within water, single atoms of oxygen can interact with water molecules. The scheme of such reactions is presented in Fig. 5.

The calculation procedure consisted in the following steps. A molecule of water was located above the TiO_2 surface at the distance of 10 a.e., what provided its weak interaction with surface atoms; the oxygen atom of this molecule was fixed, i.e. its coordinates remained invariable in the course of this study. The initial system represented on the left panel of Fig. 5 was brought to the equilibrium state, the equilibrium energy was calculated. Then the O_1 oxygen atom marked with an arrow was moved step-by-step in the direction of the water molecule, and the equilibrium energy of the whole system was again found in the every step. When the atom O_1 approached the
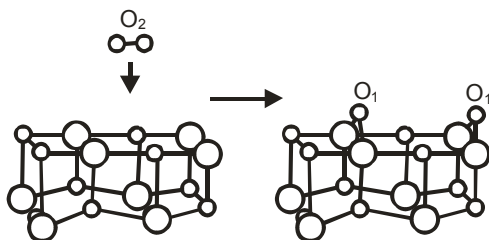
oxygen atom of the H_2O molecule on such distance, at which the total energy of the system corresponded to a certain minimum, the O_1 atom remained in this situation, and we began to shift the closest atom of hydrogen towards the O_1 atom until a new minimum of total energy was obtained.

The energy scheme of these calculations for the pure (not doped) TiO_2 is presented in Fig. 6. We see that the total value of the energy needed for formation of a molecule of hydrogen peroxide near the surface of the pure titanium dioxide, consists of energies needed for overcoming two barriers. First, the barrier (ΔE_O) for the oxygen atom separation from the surface of pure TiO_2 and its accession to the H_2O water molecule; second, the barrier (ΔE_H) for the hydrogen atom separation from the oxygen atom of the water molecule and its joining with the already associated oxygen atom with final formation of the hydrogen peroxide H_2O_2 molecule. As a summary result we obtained: ΔE(pure TiO_2)= 9.88 eV. This is a very big value even for the ultra-violet radiation! Thus formation of hydrogen peroxide acts very slowly at the sun light using pure TiO_2 as a catalyst.

We have done the same calculations for the case when titanium dioxide was doped with tungsten. In this case spontaneous dissociation of the oxygen molecule was also observed on the titanium dioxide surface near the W atom (Fig. 7).

The geometrical formation scheme of a hydrogen peroxide molecule near the surface of TiO_2 doped with tungsten is presented in Fig. 8. The energy scheme is plotted in Fig. 9.

Our calculations show that the total value of the energy needed for formation of a hydrogen peroxide molecule near the surface of titanium dioxide doped
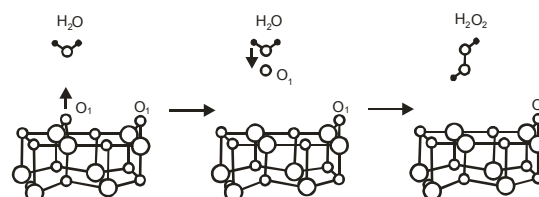

Fig. 4. The scheme of dissociation of a molecule of oxygen on the TiO_2 surface. Hereinafter, only two atomic layers of the TiO_2 slab are shown for simplicity.

Fig. 5: The scheme of interaction of single atoms of oxygen with a water molecule near the surface of the pure titanium dioxide.

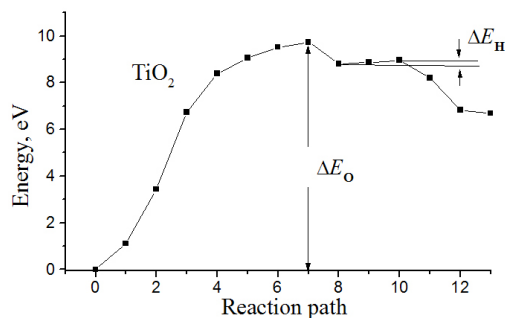**Fig. 6. Change of the total energy of the TiO$_2$ system + H$_2$O + O$_1$ + O$_1$ in the course of formation of the molecule H$_2$O$_2$. ΔE_O is a barrier for the oxygen atom separation from the surface of pure TiO$_2$ and its accession to the H$_2$O water molecule; ΔE_H is a barrier for the hydrogen atom separation from the oxygen atom in the molecule of water and its accession to already joined oxygen atom with final formation of the hydrogen peroxide H$_2$O$_2$ molecule.**
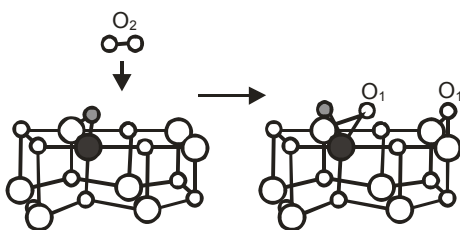
Fig. 7: The scheme of dissociation of the oxygen molecule on the surface of TiO$_2$ alloyed by tungsten.
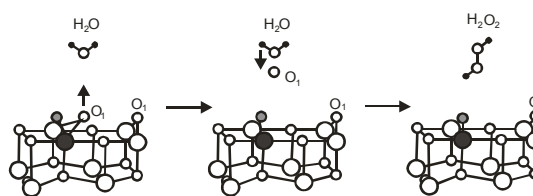
Fig. 8. The scheme of interaction of single atoms of oxygen with water molecule near the surface of titanium dioxide alloyed by tungsten.
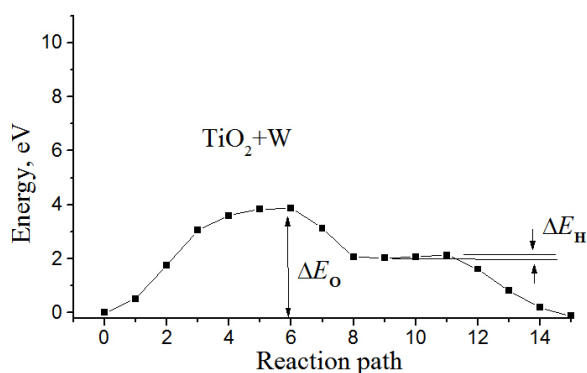
Fig. 9. Change of the total energy of the TiO$_2$ system + H$_2$O + O$_1$ + O$_1$ in the course of formation of the molecule H$_2$O$_2$. ΔE_O is a barrier for the oxygen atom separation from the surface of TiO$_2$ doped with tungsten and its accession to the H$_2$O water molecule; ΔE_H is a barrier for the hydrogen atom separation from the oxygen atom in the molecule of water and its accession to already joined oxygen atom with final formation of the hydrogen peroxide H$_2$O$_2$ molecule.

with tungsten is equal to 4.0 eV. This value is much less than the barrier energy for the case of pure titanium dioxide (9.88 eV) and corresponds to the conventional demarcation between ultra-violet radiation and visible light.

Conclusion

The density functional pseudopotential simulation shows that the barrier height for dissociation of the H_2O molecule to the OH group and atomic H on the W doped surface of TiO_2 anatase is 0.8 eV. The energy gain of this reaction is 0.9 eV for the doped one. The energy spent for overcoming the barrier of 0.8 eV is compensated by the final energy gain of 0.9 eV; thus this reaction can happen without additional inflow of energy.

The calculated energy for desorption of an OH group is 6.06 eV for the pure TiO_2 anatase and 4.74 eV for the W doped system.

The energy needed for formation of a hydrogen peroxide H_2O_2 molecule near the surface of titanium dioxide doped with tungsten is 4.0 eV. This value is much less than the barrier energy for the case of pure titanium dioxide (9.88 eV) and corresponds to the conventional demarcation between ultra-violet radiation and visible light.

Summarizing results, we can say that at the same conditions the number of OH radicals and hydrogen peroxide molecules near the W/TiO_2 catalyst has to be much larger than near the surface of pure TiO_2. As the value of energy necessary for creation of OH radicals and hydrogen peroxide molecules approaches the range of visible light, the effectiveness of decomposition of organic pollutants in aqueous solutions significantly increases in accordance to experiments. We believe that results of this work will be useful as to understanding of fundamental mechanisms of reactions on the surfaces of catalysts, and to concrete industrial applications.

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