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Full Length Article

Dissociation behavior of water molecules on defect-free and defective rutile TiO_2 (1 0 1) surfaces

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ABSTRACT

In the current investigation, reactive molecular dynamics simulation has been used to study and compare the dissociation behavior of water molecules on defect-free and defective rutile TiO_2 (1 0 1) surface. According to the contour map for a water molecule on the TiO_2 (1 0 1) surface, water molecules have proven to dissociate around 20 times faster in the defective surface rather than defect-free surface. In the presence of defects, the oxygen atoms near the defects have lower electrostatic potentials and therefore higher reactivity which adsorption of molecules to the defects and their vicinity increases while for the defect-free surface, water molecules are adsorbed like clusters and exhibit lower dispersion. Also investigation of the density profile has proven water molecules have better dispersion through the defective surface. Namely, presence of defects leads water molecules to be adsorbed at different spots through the surface. In addition to the density profile, dissociation of water molecules to hydroxyl groups and respective diffusion of hydrogen atoms into the surface (down to the second sub-layer) has been undertaken through inspection of contours for water molecules in the defective surface throughout the simulations.

1. Introduction

Recently, titanium dioxide has attracted great attention as a promising semiconductor for experimental and theoretical researchers. Potential applications for TiO_2 vary from applications in removal of organic pollutants [1], heterogeneous degradation [2] and applications in solar cells [3] to Photo-catalytic applications [1,4–7]. Through all these applications, TiO_2 is used in humid environments or aqueous medium conditions which make investigations on water-TiO_2 interactions necessary. Adsorption and dissociation of water molecules on diverse TiO_2 surfaces are the identifying characteristic for photocatalytic properties of the semiconductor and has attracted experimental and theoretical investigations [8–14]. Molecular dynamics simulations have also been used to get insights into water-TiO_2 interactions, most frequent water-metal oxide investigations [15–28]. Also quantum simulations in this regard, have proven water molecules have a layered structure over TiO_2 surfaces [8]. Dynamic heterogeneity has been observed for adjacent layers of water molecules to the surface, the mobility of water molecules in the first layer, the layer in contact with the surface, is very low and the water molecules move more freely in the next layer. Such a freedom of movement for the second layer molecules causes a change in the orientation of water molecules in the first layer. Furthermore, exchange of molecules and hydrogen bonds have been observed between the two layers. Through the developments and improvements of Reax force field, van Duin et al. have performed molecular dynamics simulations towards better understandings of TiO_2 and its behavior in aqueous and non-aqueous environments [8–13]. Recently, some investigations on adsorption and dissociation of water molecules on different anatase and rutile species have proven that Reax simulation results are in agreement with quantum calculations and experimental works [13,14].

Recent Reax force field molecular dynamics investigations on anatase and rutile TiO_2 crystals covered with water molecules have proven dissociation of water molecules and creation of hydroxyl groups. As with the different percentages of coverage with water molecules, the fraction of hydroxyl groups near the surface of each crystal can be variant, the percentage of hydroxyl groups present in the system, can be a measure of dissociation and adsorption strength of water molecules to the crystals. It has been observed that the higher number of water molecules in monolayers upper than the one adsorbed to the surface, will lead to higher water dissociation and consequently the higher number of hydroxyl groups in the near-bed layer.

Further molecular dynamics investigations on interactions of water molecules on the anatase and rutile TiO_2 surfaces have proven water molecules dissociate and turn to Ti-OH and O-H functional groups on the surfaces. Since the role of each surface functional groups differs,

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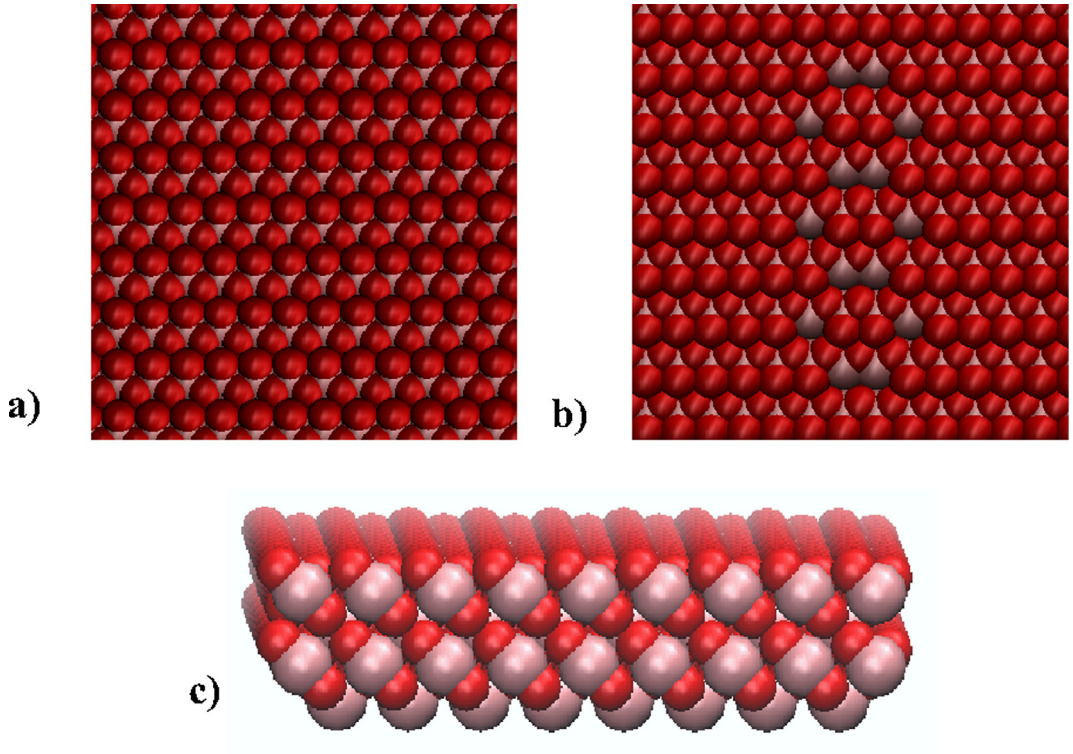

Fig. 1. (a) Defect-free TiO_2 surface (b) defective TiO_2 surface (c) side-view of TiO_2 surface. Color code: oxygen atom, red color; titanium atom, pink color. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

distinct orientations of water molecules and consequently diverse dissociation frequencies are observable. On the inactive (0 0 1) anatase surface, no considerable adsorption and dissociation are observed. The mean H-bond length for water molecule-surface oxygen is much larger than the one measured for (0 1 1) rutile, while on the (0 1 1) rutile surface, the first water sub-layer is separated from the bulk creates improved water-surface interactions through functional groups on the surface and keeps the 2nd sublayer closer to the surface [15]. Interestingly, TiO_2 substarte is often found with defective structure in the nature. As so, experiments have proven the defective structures cause improved photo-catalytic efficiency [16,17]. Investigations on the defective TiO_2 structures have proven that defects act as an active sites for adsorption and dissociation of water molecules [9,18–31]. Respective investigations on (1 1 0) rutile surface, have shown water dissociation happen through bridge-bonded oxygen (BBO) vacancies in the structure of TiO_2 surface. Investigations of the behavior of water molecules on the defective TiO_2 surface have shown that water molecules approach the surface and tend to place into the vacancies through their Oxygen atoms, then they lose a hydrogen atom and leave a hydroxyl group in the defect. On the other hand, releasing of H atom tends to move forward through the BBO row by an intrinsic diffusion process and separate the adjacent hydroxyl groups. The complex intrinsic diffusion observed for H atoms in which different H-diffusions are observable for adjacent OH groups, are accompanied with the probability for transfer of a hydrogen atom from a BBO row to the next one [25,26]. In addition to the experimental studies, quantum mechanical investigations have also been devoted to the role of such defects in the function of the surface through diverse TiO_2 crystals. The coordination number for the bulk rutile crystal is measured to be six, while five and six for (1 1 0) rutile surface and five for (1 0 1) rutile surface. Surfaces with coordination numbers lower than 6, correspondingly, are more reactive and exhibit potentials for more surface reactions due to the vacancies present on their surface.

For rutile (1 0 1), where all titanium atoms have five coordination numbers, water molecules adsorb to the surface and dissociate into OH groups and lead TiO_2 surface covered with hydroxyl groups. Such a surface modification (hydroxylation) further stabilizes reaction conditions. It has also been observed that, through removal of the oxygen atom and consequent unsymmetrical surrounding Ti atoms, surface reactivity is enhanced [27]. In the current investigation, reactive molecular dynamic simulation has been used to study water-titnium dioxide system and compare the dissociation behavior of water molecules on defect-free and defective rutile (1 0 1) surfaces. The coordination number for the rutile (1 0 1) is five with 14 oxygen vacancies that the surface is more reactive and exhibit potentials for more surface reactions due to vacancies present on their surface and the effect of oxygen vacancies on the dissociation and the adsorption water molecule is investigated. Also for analyzing of the behavior of two systems is shown some figures for example; total energy, mean square displacement, number density, radial distribution function and trajectories of water molecules.

2. Simulation details

In the ReaxFF method, the forces are derived from a general energy expression,

$$E_{system} = E_{bond} + E_{over} + E_{under} + E_{lp} + E_{val} + E_{vdWaals} + E_{coulomb} \quad (1)$$

The partial contributions in Eq. (1) include bond energies ($E_{coulomb}$), energy contributions to penalize overcoordination and (optionally) stabilize under-coordination of atoms (E_{over} and E_{under}), lone-pair energies (E_{lp}), valence angle energies (E_{val}), and terms to handle non-bonded Coulomb ($E_{coulomb}$) and van der Waals ($E_{vdWaals}$) interaction energies. All terms, except the last two, include bond-order dependence and depend on the local environment of each atom. The Coulomb energy ($E_{coulomb}$ and $E_{vdWaals}$) of the system is calculated using a geometry-dependent charge distribution determined using the electronegativity equalization method (EEM) [28] in which individual atomic charges vary in time. This feature allows ReaxFF to describe charge transfer in chemical reactions. For a more detailed description of the