Water on TiO$_2$ studied by work function change: adsorption in cycles

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Abstract

The nature of water adsorption on TiO$_2$(110) rutile surface attracts a lot of attention for quite some time. In spite of the considerable experimental and theoretical efforts a lot of details remain unclear. We have been using work function study to follow the adsorption of water on TiO$_2$ at room temperature, and interpreted the results in terms of fast dissociative adsorption on bridging oxygen vacancies (BOV) and much slower non-dissociative adsorption on Ti$_{5f}$ rows. Additionally, we concluded that water from Ti$_{5f}$ rows efficiently desorbs at room temperature which is not the case for BOV adsorption sites. Here we propose a novel experimental approach which consists of monitoring in real-time the work function change during cycles of water adsorption. Since desorption at BOVs does not take place at room temperature, this method allows us to resolve the adsorption dynamics on the two adsorption sites. The first results changed our understanding of the phenomenon: we show that both, adsorption on BOVs and Ti$_{5f}$ are both very fast. Additionally, slow exponential decay of the work function is observed, which is not directly related to water adsorption. The possible explanation of the third slow contribution could be related to the migration of hydrogen atoms along the bridging oxygen rows.

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Introduction

TiO$_2$ is one of the most studied metallic oxides due to the possible applications in photo-catalysis, heterogeneous catalysis, as gas sensors, solar cells, bio-compatible materials among other applications. Besides, it is investigated as a model metallic oxide surface. In addition, rutile TiO$_2$ (110) has attracted particular attention as the most stable TiO$_2$ surface. The chemical activity of this surface is mainly governed by the bridging oxygen vacancies (BOV), which act as the adsorption sites for different molecules. Water adsorption on TiO$_2$ (110) is thoroughly investigated using various surface sensitive experimental techniques among which STM particularly shed light to this very complex system [1,2].

Concerning the water adsorption on TiO$_2$ (110)-(1x1) surface, two sites have been mainly identified: BOVs on which the dissociative adsorption takes place yielding in formation of two hydroxyls with hydrogen atoms facing the vacuum, and the non-dissociative adsorption on titanium rows with two hydrogen atoms facing the vacuum [3]. Knowing that both hydroxyl and water molecules are polar, work function change should be proportional to the dipole concentrations. Work Function Study (WF) has been employed to monitor the water adsorption dynamics on reduced rutile TiO$_2$ (110) surfaces [4-6]. Recently, we showed that water adsorption on non-reconstructed TiO$_2$(110) could be also monitored this way in spite of the quite small signal intensity due to the small concentration of BOVs [7, 8].

It is well-known that there will be no desorption from BOVs at room temperature in contrast to Ti rows from which the desorption is efficient [1-3]. Here we use this fact to resolve the two different contributions to the WF change: if the sample is exposed to water exposing/pumping cycles the desorption will take place on both adsorption sites in the first cycle but only on Ti rows in subsiding cycles. This novel approach in WF study will allow us to resolve adsorption dynamics’ related to different adsorption sites.

Experimental details

The experiments were performed in the multipurpose surface analysis apparatus described elsewhere [9] with the base pressure in low 10$^{-10}$ mbar region. The water used in the experiments has been purified using several freeze-pump-thaw cycles. Its partial pressure has been followed using an ionization gauge while the purity of the introduced gas has been checked by a residual gas analyzer. WF was monitored as an onset of the secondary electron energy distribution. Secondary electron emission was stimulated by non-monochromatic X-rays emitted from the Mg K$_\alpha$ (1.2536 keV) anode of an X-ray source, routinely used for XPS. In that way we avoid formation of BOVs which can be created even by low energy electrons [5]. The TiO$_2$ sample was biased to -30 V to improve the detection of electrons with low kinetic energies. The secondary electron energy spectra have been taken in time intervals of about 20 s in fixed analyzer transmission mode with the pass energy of 10 eV. The sample was cleaned through several Ar$^+$ sputtering (3 keV, at oblique incidence) and annealing cycles, at 773 K for 10 min, until only Ti and O peaks were observed in X-ray photoelectron spectroscopy (XPS) survey spectra. Just before the true experiments the sample is annealed for short time at 773 K in order to suppress the contamination from the residual gas water vapour.
Results and Discussion

In previous WF measurements during the water adsorption on non-reconstructed TiO$_2$ (110) rutile we were observing an initial steep drop of the work function followed by the much slower linear decrease and finally, after turning off the water introduction valve, partial recovery of the work function up to the level close to the elbow defined by the two slopes. The steep drop was considered to be due to the water adsorption on BOVs while the lower slope and the later work function recovery were addressed to adsorption/desorption on/from Ti rows. According to the basic adsorption models [10] slower decrease of the WF signal should be part of an exponential decay. In order to check that we were repeating our measurements with much longer exposing times. The typical result is presented in Figure 1.

![Figure 1. WF change due to the water exposure; water partial pressure is about 2 $\times$ 10$^{-8}$ mbar.](image)

Although we indeed observe exponential decay for the slower contribution, the recovery of the work function after closing the valve is much lower than expected. Since this result challenges our previous assumption, we decided to perform WF study during the water adsorption in cycles in order two resolve the two contributions corresponding to water adsorption on BOVs and on Ti rows. The result of such an experiment is given in Figure 2. In the frame of the first cycle WF signal should correspond to adsorption on both sites while in other cycles only adsorption on Ti rows should be relevant. The striking result of this experiment is that introduction of water provokes steep drop of the WF signal at the beginning of each cycle. This is clear proof that adsorption dynamics' on BOVs and on Ti rows are both very fast. Therefore, a new question concerning the origin of the slow WF decrease is open.

The slow decrease of the work function is not affected by fast and huge changes of the water partial pressure i.e. it is not directly related to the water adsorption: although the valve is closed and the water partial pressure is low, further decrease of the work function is clearly observed between the first and second exposure cycle. On the other hand, this signal can be observed only after the initial water exposure. Since the water molecules are assumed to be efficiently desorbed from Ti rows at the end of each cycle, the signal is somehow related to water adsorption on BOVs.
Figure 2. WF change due to the water exposure in two cycles. Steep drop is present after each cycle indicating that adsorption on Ti rows is also fast.

The result of water adsorption on BOVs is creation of hydroxy l pairs i.e. two neighboring dipoles are formed. Due to their Coulomb interaction they are partially depolarized so that the total dipole moment of the pair is smaller that the sum of two hydroxyl dipole moments far from each other. This effect is taken into account in the frame of the Topping model [11] describing the work function change dependence on dipole concentration

\[ \Delta WF = -\frac{e}{\varepsilon_0} \cdot \frac{n_{BOV} \cdot 2 \cdot \mu_0}{1 + \frac{\alpha}{4\pi\varepsilon_0 \langle r \rangle^3}} , \]  

(1)

where \( \mu_0 \) is the moment of a dipole placed far from other dipoles, \( \langle r \rangle \) is the average distance between the dipoles, \( \alpha \) is the dipole polarizability and \( n_{BOV} \) is the concentration of bridging oxygen vacancies.

Migration of hydrogen atoms along bridging oxygen rows, which is equivalent to migration of hydroxyl dipoles, has been observed at room temperature, when the average time between two hops is about 5000 s [12]. Since considerable number of dipole pairs will become separated during the measurement, slow decrease of the work function could indeed be related to the migration of hydrogen atoms along bridging oxygen rows.

In order to test this assumption we model the hydrogen migration using 1D ‘random walks’ model by Ehrlich [13] according to which the mean distance between two atoms equals

\[ \langle r \rangle = \Delta r \cdot \left\{ 1 + \sum_n w(n,t) \cdot n \right\} , \]  

(2)

where \( \Delta r \) is the distance between the two bridging oxygen atoms, \( w(n,t) \) is the probability to migrate to distance \( n \cdot \Delta r \) in the time interval \( t \). This probability equals...
\[ w(n,t) = \exp\left(-\frac{t}{\tau}\right) \cdot I_n\left(\frac{t}{\tau}\right), \]  

(3)

where \(\tau\) is averaging time between two hops and \(I_n\) is the modified Bessel function of the first kind and order \(n\). Time evolution of the work function change due to hydrogen migration is given in Figure 3. The obtained result is both, qualitatively and quantitatively similar to the experimental ones however, not all parameters used are realistic. Namely, the problem is with the polarizability taken to be 15 Å\(^3\) which is few times higher than the expected value for the water molecule. Although hydrogen migration has relevance in describing the slow work function change, it is either not considered properly by this simplified approach or it could be that some other effects are dominantly responsible for this signal.

Figure 3. Work function change due to the migration of the hydrogen atoms calculated for the following parameters:

\[ n_{BOV} = 5 \cdot 10^{13} \text{ cm}^2, \mu_0 = 0.75 \text{ D}, \tau = 5000 \text{ s}, \alpha = 15 \text{ Å}^3. \]

Conclusion

WF study is an efficient tool to monitor adsorption of water on TiO\(_2\) in real time. However, the interpretation of experimental results is not straightforward. Usually it is considered that the work function change is directly related to the dipole surface concentration, which was also our starting assumption. By performing water adsorption in cycles we managed to resolve the contributions of two different adsorption sites and identify an additional contribution with slow dynamics which is not directly related to water adsorption. We discussed the possibility of addressing this contribution to migration of hydrogen atoms. It was shown the migration can explain the time evolution of this contribution qualitatively, although there are some difficulties concerning the quantitative description. The observed discrepancy may be due to the inappropriate model, but also due to the presence of other effects which are not yet taken into account.
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