Hydrogen induced trap states in TiO_2 probed by resonant X-ray photoemission

Emanuel Billeter[a,b], Andrea Sterzi[a], Abdessalem Aribia[c], Cesare Grazioli[d],
Marcello Coreno[e], Davide Bleiner[a,b], and Andreas Borgschulte[a,b]

[a]Laboratory for Advanced Analytical Technologies, Empa - Swiss Federal Laboratories for Material Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland
[b]Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland
[c]Laboratory for Thin Films and Photovoltaics, Empa – Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland
[d]IOM-CNR, Laboratorio TASC, Basovizza SS-14, km 163.5, 34149 Trieste, Italy
[e]ISM-CNR, Istituto di Struttura della Materia, LD2 Unit, 34149 Trieste, Italy

ABSTRACT

The standard approach to surface analysis is X-ray photoelectron spectroscopy (XPS), which is used to follow electronic structure changes of the catalyst material TiO_2 upon hydrogenation, however, without conclusion whether the effect can be traced back to the hydrogen treatment. Resonant photoemission experiments using a tunable synchrotron X-ray source yields further insights. The integration of the electron yield over all kinetic energies results in X-ray absorption spectra (XAS). Furthermore, in resonant conditions, electrons are excited from a core level to the conduction band and can subsequently be trapped by specific defect states. From this, the observed shallow trap states can be identified as Ti^{3+} states. We quantify the Ti^{3+}/Ti^{4+} ratio both from XPS and XAS and the oxygen to titanium elemental ratio. The correlation of the results from resonant and non-resonant photoemission reveals that hydrogen defects serve as trap centers, while defects associated with oxygen vacancies serve as recombination centers suppressing trap state emission. The main effect of hydrogen in TiO_2 is the increased disorder in the material.

Keywords: hydrogen, TiO_2, resonant photoemission, XAS, trap states, operando spectroscopy

1. INTRODUCTION

Hydrogen is ubiquitous in the technical as well natural environments and is thus involved in many reactions crucial for life and technology. Despite its relevance as well as abundance, its detection and chemical characterisation remains challenging particular, when studying surfaces, of, e.g., catalysts. The standard characterisation is X-ray photoelectron spectroscopy, capable of reliably detecting and quantifying all elements on a surface apart from hydrogen (and helium).[1] In this paper, we show that although photoemission spectroscopy reveals important information of hydrogen in the technically important catalyst support TiO_2. This output relies on the use of a special operando technique (Fig. 1), and the use of tunable soft X-rays from a synchrotron enabling resonant photoemission measurements.[2,3] The study showcases a methodology for hydrogen induced changes in matter with high potential, considering the progress in the development of table top tunable X-ray sources.[4]

A typical catalyst consists of metal nano-particles on oxide supports. Unlike the name may suggest, the oxide support is involved in the reaction. Since long, the so-called strong-metal support interaction is used to describe the affinity of a metal-support system for hydrogen[5] with Pt-TiO_2 as an archetypal example.[6] A recent publication highlights that the ability to chemisorb hydrogen and the hydrogen mobility on the oxide surface is a crucial property of the support,[7] which is defined by the reducibility of the corresponding oxide.[8, 9] A similar behavior is found in corrosion, where the inertness of an oxide layer on a metal against hydrogen is the

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Send correspondence to A. Borgschulte: E-mail: andreas.borgschulte@empa.ch, Telephone: +41 58 765 4639

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key parameter for achieving high corrosion resistance.[10] Finally, the efficiency of the production of renewable hydrogen depends on the electro-catalytic properties of the electrodes used, and in case of photocatalytic water splitting on the light absorbance of the photoanodes/cathodes. The photocathode is unavoidably in contact with highly reactive hydrogen. This hydrogen interaction may change materials properties markedly, which has been found to be detrimental in WO_3, but beneficial in NiO[11] and TiO_2.[12–14]

The modification of photocatalytically active materials such as TiO_2 by hydrogen is particularly interesting,[15] because both the optical properties as well as chemical properties change. The corresponding scientific questions are: with hydrogen exposure, are the changes confined to the surface, or is hydrogen migrating into the bulk of material? Does hydrogen react with the oxide forming water, and leave vacancies behind, or does it form hydroxyl groups? Although the questions are long known, and a multitude of studies were published tackling them, see, e.g., the excellent review of Rahimi et al.,[16] a concise picture is missing. This is partly due to the different preparation techniques. In this paper, we account for the latter uncertainty by following the changes induced by hydrogen operando with state-of-the-art resonant photoemission.[17] For this, we employ a membrane approach to high pressure surface science, which consists of a hydrogen permeable membrane (Pd), onto which a thin TiO_2 film is deposited (Fig. 1). Applying a hydrogen pressure up to one bar at the feed side results in the nearly equal chemical hydrogen potential at the TiO_2 thin film while keeping UHV conditions necessary for photoelectron spectroscopy experiments.[18] The initial defects such as vacancies and hydroxyl groups are unavoidable, but intercalating hydrogen in-situ reduces the number of undetermined parameters potentially introduced by subsequent ex-situ hydrogenation. Furthermore, TiO_2 does not dissociate hydrogen very well, which would pose a high barrier for hydrogen interaction, if the surface was simply exposed to molecular hydrogen at UHV-compatible pressures. In our experiment, hydrogen is from atomic hydrogen diffusion through the Pd membrane into the thin TiO_2 layer (Fig. 1).

2. EXPERIMENTALS

The high pressure X-ray photoelectron spectroscopy (XPS) study is based on the Pd membrane approach sketched in Fig. 1.[18–20] To maintain the pressure in the analysis chamber in the UHV-compatible range, the surface under investigation is not exposed directly to high pressure hydrogen, but hydrogen diffuses into the corresponding thin film from the backside. For this, the thin film is deposited onto a hydrogen selective Pd-membrane. If hydrogen permeation is rate-limiting, which is likely due to the low dissociation probability of hydrogen on TiO_2, the hydrogen chemical potential at the surface (in UHV) complies that of the feed side.[20]

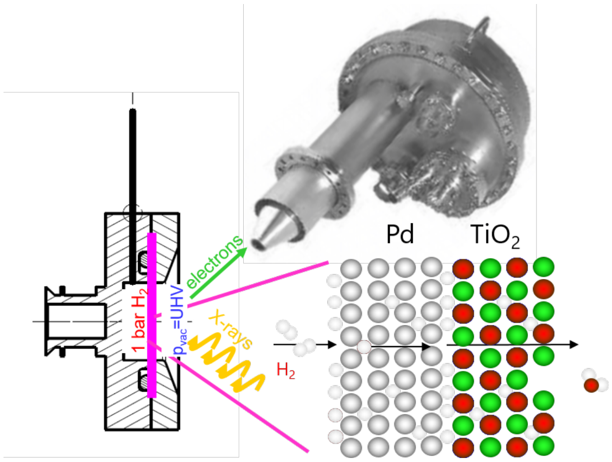

Figure 1. Sketch of the Pd-membrane approach for high pressure hydrogen photoemission spectroscopy.[18–20]

The Pd membranes were coated with a TiO_2 layer by atomic layer deposition (ALD) at a substrate temperature of 100°C with argon as carrier gas at a base pressure of 13 Pa in a Fiji G2 system (Veeco Instruments Inc.). The precursors were tetrakis(dimethylamino)titanium(IV) (TDMAT) (Sigma Aldrich) and H_2O. TDMAT was kept at 75°C while H_2O was unheated. The growth rate was determined by ellipsometry on Si(100) reference substrates and compared to SEM micrographs which showed a similar thickness with a larger uncertainty. For TiO_2 linear growth was observed with a growth rate of 0.053 nm/cycle.

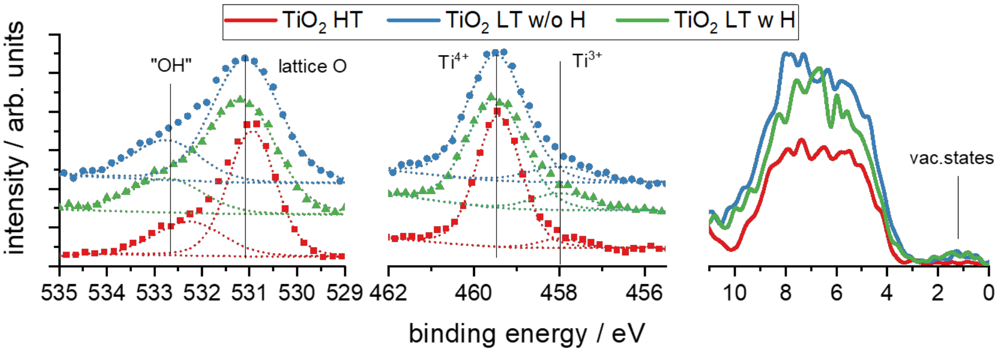

Figure 2. Synchrotron XPS spectra ($\hbar\omega = 650$ eV) O 1s, Ti 2p and valence band from TiO_2 on Pd membrane as grown (blue, $T = 120°C$, $p_{H_2} < 10^{-7}$ mbar), exposed to hydrogen (green, $T = 120°C$, $p_{H_2} = 1000$ mbar), and hydrogen removed at slightly higher temperature (red, $T = 210°C$, $p_{H_2} < 10^{-7}$ mbar). The color code is retained in the following figures. From the fitted intensities, we derive the Ti^{3+}/Ti^{4+} ratio, the ratio of OH to lattice oxygen, and the oxygen to titanium elemental ratio shown in Fig. 6.

The photoelectron spectroscopy measurements were carried out at the GasPhase beamline of the Elettra Synchrotron light source in Trieste (Italy). The beamline is equipped with a dedicated differential pumping system.[21] The combination of a high resolution monochromator with the high transmission of the electron analyzer allowed to collect spectra with a minimal energy resolution of 50 meV.[22]

The synchrotron measurements were recorded using 650 eV photon energy for the survey spectra and 160 eV for the valence band. During hydrogenation experiments, the photoemission spectra were recorded continuously in single sweep mode, with each spectrum taking approximately 120 s. The applied hydrogen pressure was measured by an external pressure gauge. As soon as the partial hydrogen pressure in the chamber was constant, the external hydrogen pressure was increased. This lead to approximately ten spectra being recorded for each external hydrogen pressure. These spectra were averaged for the subsequent data evaluation to improve signal to noise ratios. Data analysis was performed using the CasaXPS software. Due to the significant workfunction W_F shift during hydrogenation, the binding energy (and intial energy) were recalibrated using the Ti 2p and 3p peaks as given by Goepel et al.[23] Photoionization cross sections to estimate the oxygen titanium elemental concentrations assuming similar spectrometer transmission functions for the Ti2p and O1s transitions were taken from Yeh and Lindau.[24]

3. RESULTS

Figure 2 shows synchrotron XPS spectra ($\hbar\omega = 650$ eV) of TiO_2 on a Pd membrane at various conditions. The spectra are typical for ALD grown TiO_2 with a small amount of Ti^{3+},[17] as derived from fitting of the shoulder of the Ti $2p^{3/2}$ peak. The shoulder of the O 1s peak at 533.5 eV is attributed to OH species.[25] Minimum temperature was 120°C to remove most contaminants from air, in particular water. However, carbon contaminants could not fully be removed. The valence band spectra have a relatively high noise, but all main features such as the gap states are visible.

Both photoionization cross section and the photon flux of the beam line are higher at lower excitation energies, which give higher resolutions of the valence band as shown in Fig. 3. The valence bands of the ALD grown TiO_2 film correspond to TiO_2 with many defects. The character of these defects may be derived by comparison with literature. The reference spectra in Fig. 3 were measured on heavily Ar-sputtered crystalline TiO_2, i.e., TiO_2 with oxygen vacancies. However, in ALD-grown TiO_2, OH defects are more likely.[17,26] Strong indication of this assumption is the occurrence of band gap states. The corresponding shallow trap states (STS) near E_F

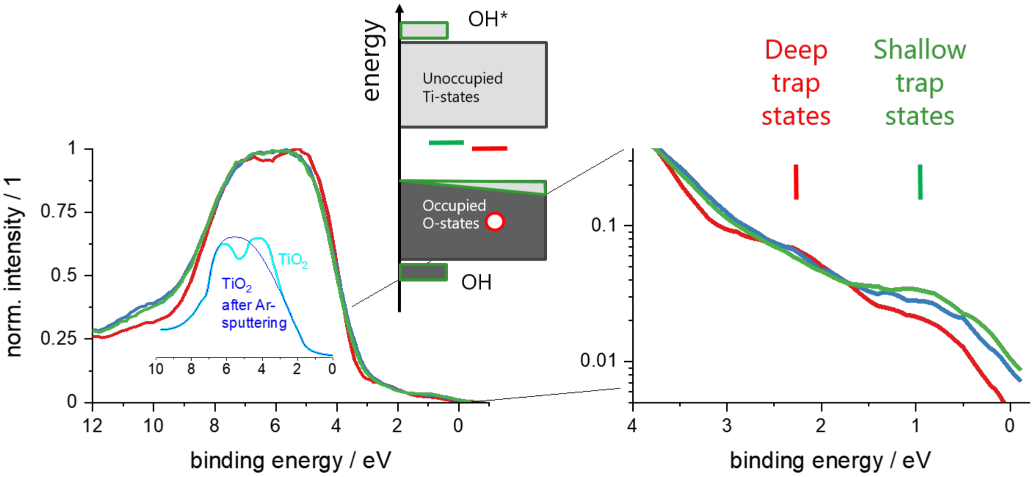

Figure 3. Synchrotron valence band spectra ($\hbar\omega$ = 98 eV). Sample conditions (color code) are the same as in Fig. 2. The small inset shows literature valence spectra.[23] The sketch visualizes the electronic structure of TiO_2 with hydrogen induced (OH) shallow trap states and oxygen vacancy induced deep trap states. The intensities are compared to Ti^{3+}/Ti^{4+} ratio and the oxygen to titanium elemental ratio in Fig. 6.

increase with applying hydrogen, but decrease with annealing at 200°C in vacuum. Annealing in vacuum and beam damage leads to deep trap states (DTS, see Fig. 3).[26]

The character of the band gap states are further analyzed using resonant photoemission (Fig. 4). A resonant photoemission experiment is the measurement of the kinetic energy of photoelectrons at a set of various excitation energies.[2,3] These are then plotted in a 2D map as shown in Fig. 4 for excitation energies around the Ti-L edge. Pioneering work with this techniques was performed by Das et al.[17] The authors demonstrated that the integration over all kinetic energies as a function of the excitation energy gives an X-ray absorption spectrum (electron yield XAS). Employing this on the 2D maps in Fig. 4 gives spectra (Fig. 5), which are very similar to XAS-spectra of anatase derived from total electron yield X-ray absorption spectroscopy.[27] The differences - in particular the broadening is due to the amorphous crystalline state in good agreement with literature.[17] In a simple view, the XAS-spectra represent the conduction band of TiO_2, which consists of (even more simplified) only unoccupied Ti 3d states. The formation of Ti^{3+} states will move some of these states to the valence band. This is visible particularly clearly at 458 eV, and may used to quantify the ratio of Ti^{3+} to Ti^{4+} ratio.[28] The changes of the ratio observed by XAS are in good agreement with ones determined by XPS, i.e., both techniques evidence a Ti^{3+} / Ti^{4+} ratio, which depends on the applied pressure and temperature.

However, the resonance spectra contain additional information. An extensive review on of the various effects is given by Das et al.,[17] but goes beyond the scope of this paper. We would like to focus on the band gap states, which can be assigned to the shallow trap states already found by XPS- and VB spectroscopy. These state vary strongly with excitation energy (Fig. 4), are either in or out-off resonance with Ti2p (L-edge) excitation.[3] This is very convincing evidence that the shallow trap states are Ti^{3+} states. Furthermore, the intensity of these states depend on the sample state also under resonance conditions, i.e., follow the same trend as found by XPS and VB spectroscopy: increasing with hydrogen exposure, but vanishing in vacuum at higher temperature (Fig. 5).

4. DISCUSSION

Before in-depth discussion of the photoemission results, it is worth reviewing some general facts about the hydrogen - oxygen - titanium system. The enthalpy of formation of solid TiO_2 and TiH_2 are -938.72 kJ/mol and -160 kJ/mol, respectively.[29,30] TiO_2 may thus considered to be a non-reducible oxide, as also titanium hydroxides do not exist in solid form. The surface may be covered with hydroxyl groups,[29,31] though. However, hydrogen causes defects in the bulk associated with marked materials changes.[8] In this respect it is more reducible than, e.g., Al_2O_3.[7,9] Some potential defects in TiO_2 are sketched in Fig. 6, such as oxygen vacancies, intercalated

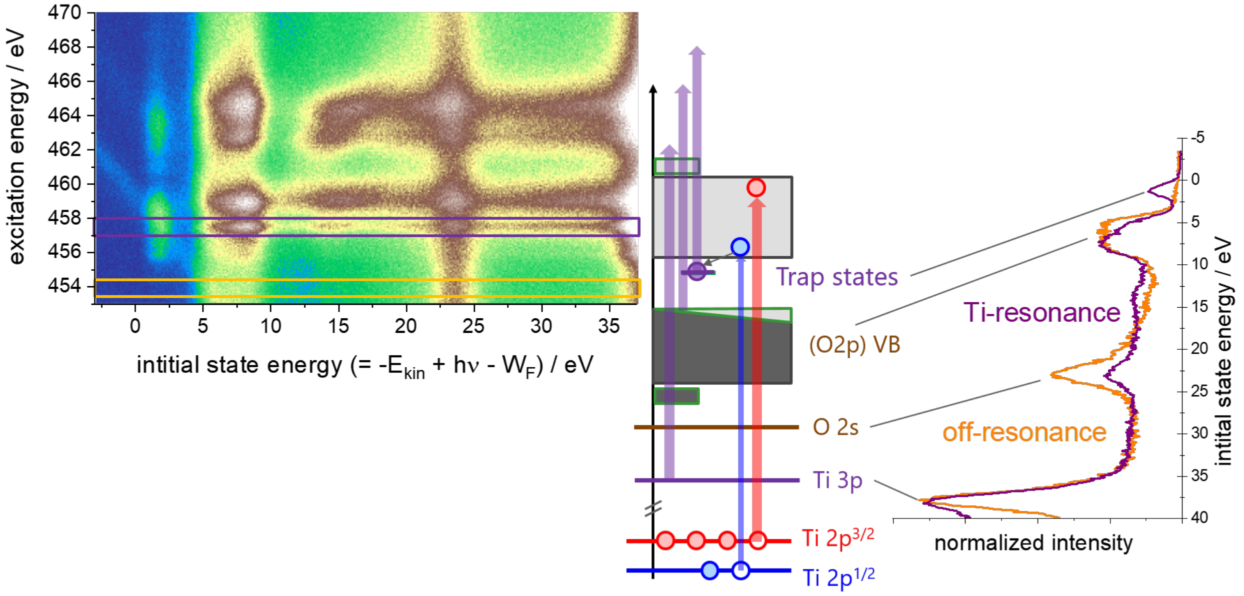

Figure 4. The color map (left panel) displays the number of photoelectrons excited from a TiO_2 sample as function of their kinetic energy (recalculated as initial state energy) and excitation energy. Although the initial state energy is defined as given in the figure, in practice the energy was aligned as described in the experimental section. The 2D map can be simplified by integrating over the full kinetic energy range yielding X-ray absorption spectrum (top right panel). More details are found plotting the initial state energies at constant excitation energy (right bottom and middle panels). The excitation energies used are indicated in the 2D map by colors. The sketch visualizes the electronic structure of TiO_2 and possible electronic transitions near the Ti L-edge. The shallow trap states are strongly enhanced in resonance conditions, i.e., Ti2p electrons are emitted to the conduction band and occupy subsequently trap states, in good agreement with the experiment.

hydrogen on an oxygen site, and OH in the bulk and at the surface of TiO_2. The number and character of these defects is debated, partly due to the very low concentration. From IR-absorption experiments,[32] a maximum hydrogen defect concentration of the order of 10^{15} to 10^{16} cm^{-3} was detected in plasma hydrogenated TiO_2, which corresponds to ppm concentrations (H per TiO_2).[32] Herklotz et al. found mainly OH defects, although this might be due to the limitation of the IR technique. However, calculations support this finding.[33]

Particular interest sparked so-called black TiO_2, usually nano-sized titania, prepared by exposing to hydrogen at pressures of several bar and elevated temperature ($> 200°C$).[34] Defects in TiO_2 are known to color titania crystals,[29] but black TiO_2 absorbs light particularly strong in the visible and infrared wavelength region.[34] Superior photocatalytic properties have been demonstrated on the material.[15] Mo et al. determined the hydrogen content of black titania as a function of the applied pressure, and found a particularly high hydrogen content of 100 ppm at 0.95 bar of hydrogen and an annealing temperature of 600°C using NMR, but simultaneously an oxygen loss of 300 ppm.[35] Similar to low hydrogen content TiO_2, the character of hydrogen induced defects/vacancies is debated. However, Chen et al. claim that Ti^{3+} defects or impurities are not responsible for the absorption in black TiO_2, in particular they found a contrary behavior of Ti^{3+} states as derived from Ti2p peaks and gap states being responsible for the absorption.[34] This is a verifiable observation. Figure 6 shows the dependence of the gap state intensity on the OH to lattice oxygen ratio, to the oxygen to titanium elemental ratio, and to Ti^{3+}/Ti^{4+} ratio. Clearly, the behavior is in sharp contrast to that described by Chen et al.[34] Furthermore, the on/off switching with and without Ti-resonance is evidence for the involvement of Ti-electrons.

Chen et al. put another idea into play: hydrogen induces a disordered phase on the surface (region) of titania.[34] This idea has charm, because the gap state intensity should not be regarded as the number of defects, but as the number of electrons present in the trap states, which depend more on their excitation and lifetime than

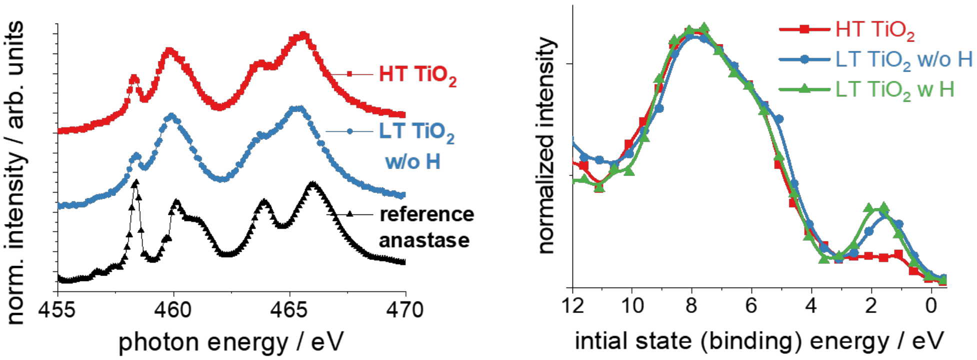

Figure 5. Left panel: XAS-spectra from integrating the resonant photoemission over the whole kinetic energy range. The anastase reference is from Ref.[27] Right panel: Ti-resonance valence band spectra of TiO_2 at different conditions. The sample conditions (color code) are the same as in Fig. 2. The intensity of the shallow trap states follow the same trend as found by XPS and VB spectroscopy.

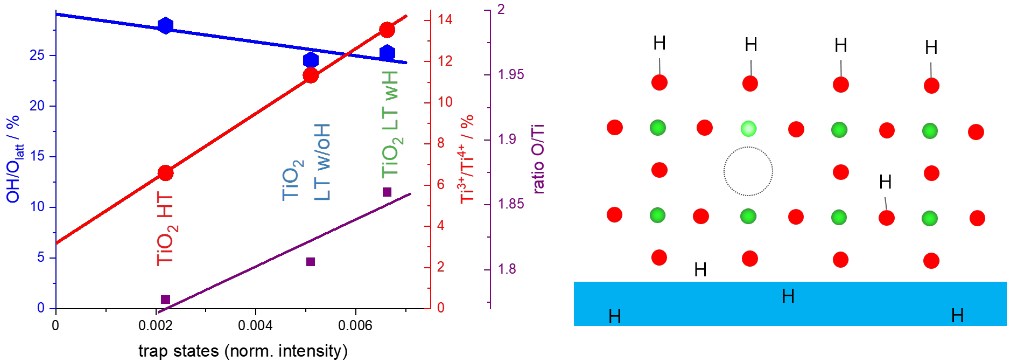

Figure 6. The left graph shows the dependence of the gap state intensity on the OH to lattice oxygen ratio, to the oxygen to titanium elemental ratio, and to Ti^{3+}/Ti^{4+} ratio, as derived from Figs. 2 and 3. The right sketch illustrate possible vacancies and defects in TiO_2 and Pd induced by hydrogen. See text for details.

on the intrinsic number of defects.[14] The ALD grown films in this publication (and others) have initially high disorder,[26] which is increased by hydrogenation, but cured upon annealing in vacuum. The lifetime of electrons in STS depends thus directly on the hydrogenation state. Furthermore, the formation of other trap states (DTS) will open additional decay channels further shortening the lifetime (recombination centers). The additional parameters are then only spectators indirectly indicating a change of the crystallinity / disorder of the TiO_2. The unexpected behavior of Ti^{3+} amount and O/Ti ratio can be understood that the removal of hydrogen defects by lowering pressure and/or annealing is a complex process, in which curing the crystal (reducing disorder) by hydrogen desorption without oxygen loss competes with the generation of oxygen vacancies by removing hydrogen *and* oxygen (water formation). The latter is enhanced by charge damage under UV/X-ray illumination.[26]

The results are representative for this topic in materials science: difficult to detect hydrogen at often low concentrations causes drastic materials changes, and the response of the systems depend on the specific materials preparation. Such research must rely on various at best simultaneously applied characterisation methods, and the repetitive and defined materials preparation. This is not limited to research associated with hydrogen,[36] but equally important in battery research,[37] and many other topics in materials science. The success of XPS, also coined ESCA (electron spectroscopy for chemical analysis)[1] is based on this demand. However, the paper at hand is one example that the standard XPS alone is not sufficient to detect hydrogen. The extension to resonant photoemission has potential to become a standard characterisation techniques, if reliable, small and cheap table top tunable X-ray sources are available. Various principles of such table top sources have been demonstrated,[4] and the advent of commercial system combined with photoemission is in sight. Furthermore, the utilisation of X-ray lasers may enable new techniques giving deeper insights into the materials science of hydrogen.

5. CONCLUSIONS

The use of the operando membrane approach allowed us to follow the complex behavior of hydrogen interaction with TiO_2 by resonant photoemission. Striking effect upon hydrogenation is the formation of defects in materials, which alter optical as well catalytic properties. We showed that the shallow trap states in ALD grown titania on Pd-membranes are Ti^{3+} electrons. The intensity of these states is related to the hydrogen treatment as well as Ti^{3+}/Ti^{4+} ratio evidence that STS are caused by hydrogen intercalation into TiO_2. However, the main effect of hydrogen seems not to alter the number of defects, but the disorder it creates in the material. This study offeres a perspective for future use of tabletop X-ray lasers (see also Sects. 1-4 [38])

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