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Review of functional titanium oxides. II: Hydrogen-modified TiO₂

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Abstract

Band gap engineering of TiO₂ has attracted many researchers looking to extend its applicability as a functional material. Although TiO₂ has been commercialised in applications that utilise its special properties, its band gap should be modified to improve its performance, especially as an active photo catalyst. Reduction of TiO₂ under a hydrogen atmosphere is a promising method which can increase the visible-light absorption efficiency of TiO₂ and enhance its electrochemical and other properties related to electronic band structure. In this second review paper, the production and influence of O vacancies (V_O) and other defects, such as interstitial cations, under vacuum and hydrogen are reviewed for the common phases of TiO₂. The particular modification TiO_{2-x} in which O is randomly removed from the crystal structure is considered in detail. Despite early evidence that hydrogen is absorbed into the bulk of TiO₂, the action of hydrogen has become controversial in recent years, with claims that surface disorder is responsible for the enhanced photoactivity induced by exposure to hydrogen. The many published experimental and density-functional-theory modelling studies are surveyed with the aims of determining what is agreed or contested, and relating defect structure to band structure. It is concluded that further work is needed to clarify the mechanisms of defect production and defect diffusion, as well as the origins of the numerous sample colours observed following treatment in vacuum or hydrogen.

Keywords: TiO₂, Defects, Hydrogen, Oxygen vacancy, Interstitials

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LIST OF ABBREVIATIONS

a-TiO ₂	anatase TiO ₂
r-TiO ₂	rutile TiO ₂
a-TiO ₂ :H	Hydrogen-modified anatase TiO ₂
r-TiO ₂ :H	Hydrogen-modified rutile TiO ₂
AFM	Atomic Force Microscopy
CBM	Conduction Band Minimum
DFT	Density Functional Theory
DOS	Density of States
CSP	Crystallographic shear plane
EPR	Electron Paramagnetic Resonance
GGA	Generalized Gradient Approximation
HF	Hartree-Fock
HSE	Heyd-Scuseria-Ernzerhof
IPCE	Incident-photon-to-current-conversion efficiency
LMTO	Linear Muffin-Tin Orbital
NHE	Normal Hydrogen Electrode
PBE	Perdew-Burke-Ernzerhof
PECs	Photo Electrochemical Cells
STM	Scanning Tunneling Microscopy
TEM	Transmission Electron Microscopy
VBM	Valence Band Maximum
WBS	Wide Band-gap Semiconductor

XPS X-ray Photoelectron Spectroscopy

XRD X-Ray Diffraction

1 Introduction

Titanium dioxide (TiO_2) has been used in applications taking advantage of its optical properties, which depend on its electronic structure. TiO_2 has often been studied as a photo anode in photo electrochemical cells since Fujishima and Honda [1] used a rutile photo anode to convert absorbed UV light into a charge flow for water splitting. Rutile TiO_2 serves as a well-characterized and much-studied model for studying fundamental processes in a reducible oxide, and specifically the interplay between surface properties and defects present at the surface and in the bulk of the crystal [2, 3].

The efficiency of conversion of solar energy to hydrogen was very low because UV photon energies were required to excite carriers across the band gap of more than 3.0 eV. Many researchers have since pursued improvements by modifying the pristine oxide. Experiments and theory have confirmed that the reactivity and photo reactivity of oxide semiconductors depend strongly on crystal imperfections or point defects [4-8]. Furthermore, it appears that defect disorder also influences these properties. Point defects including oxygen vacancies and Ti^{3+} interstitials (both considered to be electron donors) and two-dimensional planar defects (crystallographic shear planes) are two probable defects in the reduced-rutile and -anatase structures [9-11]. Defect disorder is in fact proposed to be the determining factor in the modification of semiconducting properties, reactivity and photo reactivity of TiO_2 [12-14]. Reduced TiO_2 , which contains Ti^{3+} , has been demonstrated to exhibit visible light absorption [15-18]. Among the available reduction techniques, exposure to hydrogen gas is one of the most effective.

The first paper in this series [19] reviewed the structures and properties of pristine (or nearly pristine) TiO_2 . In this second paper, the focus is on TiO_2 containing randomly distributed point defects introduced by partial reduction in a hydrogen atmosphere, since this treatment has been found to influence the optical and electrical properties strongly [14, 17, 20-38]. From the perspective of chemical composition, the principal expected defect is the oxygen vacancy. This modification is usually represented as TiO_{2-x} where $x < 0.1$ approximately. The creation of oxygen vacancies is quite sensitive to the conditions of reduction such as temperature, nature of the reducing agent, duration of experiment, etc. It is essential to have a comprehensive understanding of the methods and techniques for generating oxygen vacancies, the mechanism

by which oxygen vacancies lead to Ti^{3+} interstitials and their influence on physical, chemical and optical properties.

The ordered Magnéli phases, Ti_nO_{2n-1} where $n \geq 10$, will be discussed elsewhere. In this more extreme modification of TiO_2 , crystallographic shear planes (CSP) characterise the crystal structure [22]. The relationship between the notations used for the stoichiometries of the ordered and disordered phases is $n \equiv 1/x$.

2 Defects in TiO_2

2.1 Classification of defects

From the perspective of electronic properties, defects can be classified as donors, acceptors, isovalent or isoelectronic centres, amphoteric, vacancies and interstitials [39]. The chemical nature and size of a defect or impurity affect the electronic properties of the material via its band structure. Defects involving dangling bonds (e.g. vacancies) tend to induce lattice relaxation and come into thermodynamic equilibrium with their surroundings by making new bonds. Host atoms also have to change their equilibrium position to accommodate defects when the size of impurity atoms is much bigger or smaller than their size [40].

Lattice charge neutrality should be applied incorporating the concentration of defects so that, for example (in Kröger-Vink notation [41], Table 1)

$$2[V_O^{\bullet\bullet}] + 3[Ti_i^{\bullet\bullet\bullet}] + 4[Ti_i^{\bullet\bullet\bullet\bullet}] + [D^{\bullet}] + p = n + 4[V_{Ti}^{\bullet\bullet\bullet\bullet}] + [A'] \quad (1)$$

where n and p are the concentrations of electrons and holes respectively, and $[D^{\bullet}]$ and $[A']$ are the concentrations of singly ionised donor- and acceptor-type foreign ions as dopants and impurities respectively.

Table.1. Kröger-Vink notation.

		Kröger-Vink notation
Ti_{Ti}^{4+}	Ti^{4+} ion in the titanium lattice site	$Ti_{Ti}^{\times}$
Ti_{Ti}^{3+}	Ti^{3+} ion in the titanium lattice site (quasi-free electron)	e'
V_{Ti}	Titanium vacancy	$V_{Ti}^{''''}$
Ti_i^{3+}	Ti^{3+} ion in the interstitial site	$Ti_i^{\bullet\bullet}$
Ti_i^{4+}	Ti^{4+} ion in the interstitial site	$Ti_i^{\bullet\bullet\bullet}$
O_o^{2-}	O^{2-} ion in oxygen lattice site	$O_o^{\times}$
V_o	Oxygen vacancy	$V_o^{\bullet\bullet}$
O_o^-	O^- ion in the oxygen lattice site (quasi-free hole)	$h^{\bullet}$

Possible point defects in metal oxides are shown schematically in Figure 1 [12]. The first (a) is a stoichiometric oxide where the Fermi level is located in the middle of the band gap; the second (b) contains the cation vacancies, which are electron acceptors; the third and fourth (c and d) contain oxygen vacancies and cation interstitials, which are electron donor-type defects.

Figure 1. Schematic representation of point defects in a binary oxide, MO, including defect free crystal (a), doubly ionised cation vacancy (b), doubly ionised oxygen vacancy (C), and doubly ionised interstitial cation (d), (left) and the related band models (right) [12]. The filled and empty circles represent electrons and holes, respectively.

Electronic impurities in semiconductors are generally grouped into two large categories comprising shallow impurities and deep-level defects [42]. The binding energy of a shallow impurity is typically less than 100 meV, which is much less than the band gap of TiO_2 and comparable to the characteristic thermal energy $k_B T$. In contrast, the energy required to excite an electron or hole from a deep-level defect is much larger than $k_B T$ [43].

Defects can be also classified as localised and delocalised. Localised states are close to the conduction or valence band [44]. The electronic states of deep defects are energetically positioned within the band gap and spatially localised; i.e. the wave function related to deep defect states is spatially confined, extending typically over only a few neighbouring atomic lattice sites. It is also worth mentioning that localization is directly related to the chemical nature of the defect. For example, it depends on the existence of any dangling or broken bonds, or it can

originate from atomic states that are largely decoupled from the host electronic structure [42, 44].

By heating titania (rutile or anatase) to temperatures above about 500 °C in vacuum or under reducing agents (H₂, CO, CH₄ etc.), point defects (interstitials, surface and bulk oxygen vacancies) are created. The oxide is reduced until the surface has a steady-state concentration of oxygen vacancies (V_O) in equilibrium with the bulk, forming TiO_{2-x} ($0 < x < 0.1$). At temperatures above about 1000 °C the oxygen vacancies order and Magnéli phases Ti_nO_{2n-1} ($3 \leq n \leq 10$) form.

V_O is more likely be created on under-coordinated surface sites, which are energetically favourable. In contrast, Ti_i are mostly found in the bulk of a sample due to a higher coordination number [45]. Cheng et al. [45] compared the relative stabilities of surface and subsurface sites of r-TiO₂ and a-TiO₂. DFT calculations have shown that defects on the surface of a-TiO₂(101) and a-TiO₂(001) are much more stable in the subsurface than at the surface. In contrast, bridging oxygen sites are favoured for r-TiO₂(110) [9].

Aono et al. [46] studied the atomic and electronic structures of defects in TiO_{2-x} by electron-paramagnetic-resonance (EPR) measurements. They concluded that the main lattice defects in TiO_{2-x} are Ti interstitials with a single paramagnetic electron ($S = 1/2$) where as x increases, S changes to 1. Bowen et al. [47] proposed that Ti^{3+} and Ti^{4+} interstitials and V_O are the dominant point defects.

2.2 Formation of oxygen vacancies

The formation of oxygen vacancies can be expressed as the following equilibrium [13]:

Empty sites in the oxygen sub-lattice are formed when oxygen ions are removed. Figure 2 shows that the removal of a neutral oxygen atom leaves behind two electrons that had been engaged in two Ti–O bonds which were broken when the vacancy was formed.

Figure 2. Schematic representation of the formation of doubly ionised oxygen vacancy [10].

There are two types of oxygen vacancies: oxygen vacancies below five-coordinate Ti ions, and those below bridging-oxygen-row Ti ions [48-51].

2.3 Formation of Ti^{3+} interstitials

“ Ti^{3+} ” species are produced by transferring the excess electrons of the defect to adjacent Ti^{4+} lattice ions [52, 53]. Figure 3 (a) shows a structural model of the parallel ($R_{\parallel}^0$) and vertical ($R_{\perp}^0$) $Ti^{4+}-O^{2-}$ bonding lengths, which are 1.988 and 1.944 Å respectively [11, 54, 55]. Figure 3 (b) shows that when reduction happens the two electrons of the V_O change two Ti^{4+} to Ti^{3+} ions.

Figure 3. (a) Model of central Ti^{3+} ion associated with an oxygen vacancy at its nearest location in the parallel direction. (b) Schematic of a flaw on partly reduced TiO_2 [54, 55].

Formation of titanium interstitials and vacancies is expressed as the following equilibria [13]:

Ti^{3+} surface defects can be generated by reduction of Ti^{4+} ions. There are two types of processes for Ti^{4+} reduction. The first one happens where Ti^{4+} ion receives a photoelectron which is usually generated due to UV irradiation on TiO_2 . Figure 4 shows how photo-generated electrons and holes are produced in TiO_2 by UV irradiation. The electrons can be trapped and reduce Ti^{4+} cations to Ti^{3+} , and the holes oxidise O^{2-} anions for the formation of O^- trapped holes or even oxygen gas. The second process is usually accompanied by the loss of oxygen from the TiO_2 surface [11, 56].

Figure 4. Scheme of UV-induced charge separation in TiO_2 . Electrons from the valence band can either be trapped (a) in the conduction band where they produce absorption in the IR region, or (b) by defect states, which are located close to the conduction band (shallow traps). Electron paramagnetic resonance spectroscopy detects both electrons in shallow traps, Ti^{3+} , and hole centres, $O^{\cdot -}$ [56].

Figure 5 shows a schematic diagram for the diffusion of Ti^{3+} interstitials to the $TiO_2(110)$ surface. An interstitial depletion layer is thus formed in the near-surface region upon annealing [57].

Figure 5. Schematic diagrams showing the Ti^{3+} depletion layer in the near-surface region and the activated bulk diffusion of Ti^{3+} interstitials toward the surface they react with O_t adatoms [57].

2.4 Computational studies

2.4.1 Defect structure

Density functional theory (DFT) has become a promising calculation method for studying the

electronic structure of point defects in semiconductors and isolators [16, 58, 59]. Using the HSE (Heyd-Scuseria-Ernzerhof) functional [60-63] helps to calculate formation energies and charge transition levels of point defects in semiconductors. HSE also has been used to separate the effects of structural relaxations in the various charge states on V_O . In recent research, the oxygen vacancy has been found to act as a shallow donor which is stable in the V_O^{2+} configuration for all Fermi-level positions within the band gap. The formation energy of V_O^{2+} in n-type TiO_2 (Fermi level at CBM) is about 1.0 eV under extremely oxygen-poor conditions. This formation energy of V_O^{2+} is low enough to account in principle for the observed n-type conductivity in TiO_2 single crystals annealed under Ti-rich (O-poor) conditions, and its dependence on the oxygen chemical potential is also consistent with the observed variation in the electrical conductivity with oxygen partial pressure [58, 64].

DFT with GGA (Generalized Gradient Approximation) and LDA (Local Density Approximation) have some difficulties in calculating the band-gaps of oxides such as TiO_2 and result in the overestimation of electron delocalisation for systems with localized d- and f-electrons. In TiO_2 , it has been shown that when oxygen vacancies are created, two electrons become localised on the Ti atoms which then create mid-gap states. However, GGA-DFT cannot calculate these expectations due to the electron self-interaction error in DFT [65-67]. One approach to compensate this failure is applying an additional Hubbard term to the GGA Hamiltonian. GGA-U adds a term to describe the strength of the on-site Coulomb interactions when two d- or f-electrons are located on the same cation [68-70]. A DFT+U study of defects in bulk rutile was made by Stausholm-Møller et al. [16]. Ti interstitials, O vacancies and H dopants were considered as defects. They found that the excess electrons localise spatially around Ti^{4+} ions to create Ti^{3+} ions. The average energy of the created band gap states is within a few hundredths of an electron volt from 0.94 eV below the conduction band minimum. Figures 6 and 7 show the DOSs of the plain DFT calculations ($U = 0$) and DFT+U calculations with $U = 2.5$ eV, respectively. Figure 6 shows the configuration of the three defects under study (Ti interstitial, O vacancy, and H dopant) and the DOSs obtained from plain DFT calculations ($U = 0$). Figure 7 shows that the gap states arising from V_O and the H dopant are largely Ti-3d in nature. Stausholm-Møller et al. [16] also concluded that the electrons donated to the host TiO_2 are fully localised. Plain DFT calculations show that electrons coming from V_O reside at the bottom of the

conduction band. By applying $U = 2.5$ eV, electrons will be localised on Ti atoms and create states in the band gap which show large Ti-3d character. For the H dopant situated near a bulk oxygen atom, the corresponding electron moved into the band gap after applying $U = 2.5$ eV.

Figure 6. Configurations of the three defects under study: Ti-interstitial (a), O-vacancy (b), and H dopant (c). Shown alongside the configurations are the DOSs obtained from plain DFT calculations ($U=0$). Spin-up and spin-down states are shown above and below DOS = 0, respectively [16].

Figure 7. DOS for the three defects obtained from a DFT-U calculation with $U=2.5$ eV. The coloured area corresponds to the contribution from the Ti-3d states from the atom [16].

Chrétien et al. [59] studied the electronic structure of the partially reduced TiO_2 (110) surface. DFT-U calculations with $U \leq 2.5$ eV suggested that two electrons on Ti atoms below the surface are delocalised and for $3.0 \leq U \leq 6.0$ eV the two electrons are localised on different Ti atoms to reduce them. Figure 8 shows the side and top view of the top stoichiometric layer of partially reduced rutile. An unpaired electron can be localised on a Ti atom by formation of a polaron in which the Ti atom is reduced to Ti^{3+} and the O atoms near the newly formed Ti^{3+} atom move

away. from it.

Figure 8. (a) Side view and (b) top view of the top stoichiometric layer of a partially reduced rutile $\text{TiO}_2(110)$ surface showing a $[3 \times 2]$ supercell. The green sphere indicates the position of a bridging oxygen vacancy created by removing one of the protruding bridging oxygen atoms. The atoms are labelled as follows: (1) bridging oxygen; (2) in plane oxygen; (3) 5-fold-coordinated Ti (5c-Ti); (4) 6-fold-coordinated Ti (6c-Ti*) at the vacancy site (6c-Ti*) [59].

2.4.2 Electron localization – polarons

When an oxygen atom is removed from the TiO_2 structure, it leaves behind two electrons. The fate of these electrons is highly controversial and complicated. Although some researchers propose the localization of the excess electrons [71-74], others suggest that excess electrons are delocalised over several Ti lattice sites [50, 52, 53, 75, 76].

A complex formed by reduced Ti ion which contains the unpaired electron and the displaced oxygen atoms is called a polaron. Each polaronic state is formed by an excess electron localised at an empty Ti-3d orbital with a locally distorted lattice structure. DFT calculations [59], predict that the unpaired electrons are localized (“self-trapped”) on two different Ti atoms, reducing them. Polaronic Ti^{3+} states are located at about 1 eV below the CB-edge. Photo-generated small polarons have been observed by EPR in commercial rutile [77].

Applying hybrid functionals within DFT showed that excess electrons can either occupy an extended state at the bottom of the conduction band or a localized state centred on an individual Ti site, producing a Ti^{3+} centre [78]. This electron and the surrounding polarization field forms a

small polaron, which is a distinct local lattice distortion around the Ti^{3+} ion. Figures 9(a) and (b) show charge distributions of a small polaron and a delocalized conduction-band electron in TiO_2 . Figure 9(a) demonstrates that the existence of the small polaron results in an optically detected deep level at 0.77 eV below the conduction band, while Figure 9(b) shows the equally distributed electron density over all Ti atoms of the TiO_2 lattice. The configuration coordinate diagram of the small polaron and a delocalized electron is shown in Figure 9 (c). According to this figure, there is an energy barrier that confines an electron to its delocalized, metastable state which prevents the delocalized electron from collapsing into the polaronic state. It also shows that small polarons are energetically more favourable, 0.15 eV, which results in shallow-donor behaviour of the vacancy [78]. In the recent report by Shibuya et al. [79], the surface reactivity of rutile TiO_2 (110) surfaces was ascribed to excess electrons introduced by donor defects. Polaronic Ti^{3+} states in the second layer below five-fold coordinated Ti row play the main role in surface reactivity of TiO_2 . They suggested that the existence of the maximum polaron concentration in the second layer is a prerequisite for having shallow donor sites.

Figure 9. Charge distribution and potential energy of a small polaron and a delocalized conduction-band electron in TiO_2 . (a) Spin density of a self-trapped electron (small polaron) corresponding to a single-particle level at 0.77 eV below the conduction band in rutile TiO_2 . (b) Charge distribution of a delocalized electron in the conduction band in TiO_2 . In both cases, the isosurfaces correspond to 10% of the maximum charge density. The corresponding band structures are shown underneath, where CB and VB refer to valence band and conduction band, respectively. (c) Calculated configuration coordinate diagram depicting the energy as a function of lattice distortion for a polaron (left) and a delocalized electron (right), with an energy difference between the ground-state configurations of 0.15 eV. Absorption of a photon with energy 0.61 eV causes an optical transition from a polaron to a delocalized electron [78].

2.5 Thermodynamics and kinetics

In addition, creation of a single point defect increases the internal energy, enthalpy and configurational entropy of a system. The equilibrium concentration of point defects is greater than zero owing to their relatively high configurational entropy, which leads to a minimum in the free energy at non-zero concentration. Different types and systems of defects can have different free energies of formation, and certain defects predominate in a particular solid [41, 80].

The relative stability of a charge state is determined by the formation energy:

$$E^f(V_O^q) = E_t(V_O^q) - E_t(\text{TiO}_2) + 1/2E_t(\text{O}_2) + \mu_O + qE_F \quad (9)$$

where $E_t(V_O^q)$ is the total energy of a supercell with a vacancy in charge state q , and $E_t(\text{TiO}_2)$ is the total energy of a perfect crystal in the same supercell and μ_O is a reservoir where the removed O atom is placed. The stability condition of TiO_2 is related to the chemical potential, namely, $\mu_{\text{Ti}} + 2\mu_O = \Delta H_f(\text{TiO}_2)$, where μ_{Ti} is the Ti chemical potential. The Fermi level E_F is also the energy of the electron reservoir, referenced to the valence-band maximum (VBM) [58].

Mass transport occurring between the surface and bulk depends on the diffusion of oxygen vacancies (V_O) and Ti interstitials (Ti_i). The rutile structure has open channels along the c-axis consisting of chains of voids with ~ 0.25 Å minimum radius [81]. Ti_i diffuse through these channels, while oxygen ions cannot pass through owing to their larger ionic radius (~ 1.46 Å). Therefore, oxygen ions diffuse by the vacancy mechanism from the bulk to the surface. Figure 10 shows sectional views of open channels in rutile and anatase, where the channels are represented by dots.

Figure 10. Projection of the rutile (001) and anatase (100) planes and positions of titanium and oxygen atoms in the tetragonal units of rutile and anatase. Large circles represent oxygen atoms and small ones titanium atoms. (a) Rutile (001) plane: Open channels along the [001] direction are expressed by dotted points. (b) Anatase (100) plane, open channels developing along the [100] direction which is parallel to the (001) cleavage plane [82].

The properties of nonstoichiometric rutile versus temperature and oxygen partial pressure p_{O_2} have been studied extensively. Measurements of self-diffusion as a function of p_{O_2} and temperature provided detailed information about the defect structure. Hoshino et al. [83] measured the tracer diffusion of Ti parallel and perpendicular to the c -axis as a function of temperature and p_{O_2} . They suggested an interstitial-type mechanism [84] for Ti diffusion. Henderson [85] reported that Ti interstitials are the major diffusive defects rather than O atoms or vacancies in rutile.

The diffusion mechanisms of Ti_i parallel and perpendicular to the crystal c -axis are found to be different. If the ionic radius of the transition metal is significantly less than the ionic radius of an oxygen ion, it can pass through the crystal along the c -axis. On the other hand, oxygen ions diffuse by the vacancy mechanism because of their large ionic radius of approximately 1.46 Å, so the open channels do not contribute to the diffusion of oxygen vacancies. Therefore, when the oxygen vacancy is a dominant defect, there is not much anisotropy in the activation energies and diffusion coefficient, unlike the Ti_i case [19, 81].

Iddir et al. [86] studied the structural energies and diffusion mechanisms of V_O and Ti_i in r-TiO₂. It was proposed that Ti_i is the major diffusive species due to its low migration barrier, which is ca. 1eV smaller than V_O . The energy barriers to migration of V_O^{2+} along three possible paths are compared in Figure 11. It was found that a larger barrier to Ti_i^{4+} migration along the [001] channels parallel to the c -axis than the [110] channels perpendicular to the c -axis [86].

Figure 11. A ball and stick model of the TiO₆ octahedron in rutile. The “atom” labelled by V is the oxygen vacancy in the equatorial plane. Its diffusion is considered along the paths A, B, and C. (b) Migration barriers of V_O^{2+} along the three paths shown in (a). The points (stars, circles, and squares) correspond to actual calculations to which smooth curves have been fitted [86].

Diffusion can occur through interstitial and interstitialcy mechanisms. The interstitial mechanism corresponds to the interstitial atom diffusing along the open [001] channels, so the lattice atoms relax around the defect to accommodate the induced stress (Figure 12). However, diffusion of Ti_i^{4+} is through the interstitialcy mechanism in which the diffusing atom takes the place of a bulk Ti (Figure 13). The interstitialcy configuration is somewhat favoured compared to the interstitial configuration [86].

Figure 12. (a) Diffusion profile of Ti_i^{4+} along [001]. The squares correspond to the actual calculations, which have been fitted by a smooth curve. Due to the symmetry of rutile, only a path of length $c/2$ is considered. (b)-(d) Snapshots of the diffusing Ti_i^{4+} and a portion of the surrounding bulk at the positions 1, 2, and 3 given in (a). Position 3 is the interstitial Ti configuration discussed in the text. Ti and O atoms are represented by gray (red) and white circles, respectively [86].

Figure 13. A diffusion profile of Ti_i^{4+} along a [110]. Due to the symmetry of rutile, only a path of length $a/2\sqrt{2}$ is considered. (b)-(d) Snapshots of the diffusing Ti_i^{4+} and a portion of the surrounding bulk at the positions 1, 2, and 3 given in (a) interstitialcy mechanism of Ti_i^{4+} along [110]. Position 1 is another view of position 3 in Fig. 12. Position 2 is the (slightly lower-energy) interstitialcy configuration. The diffusing Ti_i and the bulk Ti which gets

kicked out are shown by light gray (gold) circles. The rest of the Ti and O atoms are represented by gray (red) and white circles, respectively [86].

2.6 Reactivity

The physical and chemical properties of TiO_2 are highly affected by its surface conditions and number of Ti^{3+} surface defects [87-89]. Xiong et al. [11] studied Ti^{3+} surface defects and their effects on the photocatalytic activity of reduced TiO_2 . As mentioned, Ti^{3+} works as an active site for visible light absorption. The presence of Ti^{3+} on the TiO_2 surface shows the acidic and reducing properties of oxygen-deficient titanium oxide.

Point defects are very influential in governing the behaviour of reduced TiO_2 surfaces because of their ability to act as electron donors and oxygen acceptors in reductive processes. Two unpaired electrons are produced when an oxygen vacancy is created, which makes the reduced oxide a very strong Lewis base. The more vacancies are created, the stronger the Lewis basicity, i.e. ability of the surface to donate electrons of the surface. Therefore, the reactivity of the compound will also increase [90-92]. The result of lattice changes due to the presence of the defects is stabilization of the adsorbates, which cause partial loss of coordination of the surface atoms, particularly at the $Ti(5)$ (Figure 14) sites, which leads to stronger molecule-surface interactions.

Figure 14. Ball-and-stick model of $r-TiO_2(110)-(1 \times 1)$ surface. Large light balls, oxygen; small black balls, titanium. Vacancies in bridging oxygen rows are common on vacuum-annealed surfaces. The two types of bulk defects that are prevalent in reduced TiO_2 crystals, i.e. oxygen vacancies and titanium interstitials, are also indicated. Such bulk defects can often affect surface chemistry [92].

In addition, the presence of a subsurface defect leads to a substantial increase of the outward relaxation that further enhances the adsorption bonding through stronger interaction energy (Figure 15).

Figure 15. Atomic structure of anatase TiO_2 with co-existence of V_{Ti} and Ti_i [4].

Recently, Janotti et al. [78] reported a mechanism for the coexistence of the localised and delocalised excess electrons, polaronic Ti^{3+} states and shallow donor states, using hybrid DFT calculations in bulk TiO_2 [79]. For all tested surface defects, it was clear that reaction intermediates and activation barriers will be affected strongly by the presence of defects. Thus, even if the point defects remain static and do not participate directly in surface reactions, they may lead to major changes in the surface reactivity. As demonstrated in Figure 16, polaronic and shallow donor states created under the CB lower the ionization energy for electrons to escape from the surface to adsorbates [93, 94].

Figure 16. A proposed schematic of density of states for (a) pristine TiO_2 Degussa P25 and (b) reduced TiO_2 [94].

Schaub et al. [95] combined experiment and theory to study water dissociation on oxygen vacancies. The results showed that oxygen vacancies in the surface layer act as the active sites for water dissociation and the formation of two hydroxyl groups for every vacancy. Based on scanning tunnelling microscopy (STM) and DFT calculations, it was concluded that the water dissociation rate depends on the density of oxygen vacancies. The dissociation process occurs as soon as molecular water is able to diffuse to the active site (Figures 17 and 18).

Figure 17. Ball-and-stick model and corresponding simulated STM image at 1 V showing the appearance of (a) vacancy-free surface, (b) bridging oxygen vacancy, (c) bridging OH group, and (d) water molecule on top of a five-fold coordinated Ti atom. Red atoms: O; yellow atoms: Ti; blue atoms: H. In (c) the OH bond is tilted $\sim 47.9^\circ$ with respect to the surface normal. Another equivalent configuration exists with a tilt of -47.9° , which would make the simulated STM image symmetric [91].

Figure 18. Ball model of the $\text{TiO}_2(110)$ surface. (I) oxygen vacancy, (II) bridging hydroxyl group, (III) terminal hydroxyl group, and (IV) water molecule. Red atoms: O; yellow atoms: Ti; blue atoms: H [91].

Benz et al. [96, 97] attributed the sustained reductive $\text{C}=\text{C}$ coupling of benzaldehyde to migration of Ti interstitials to the surface. It is generally accepted that surface point defects, especially bridging oxygen vacancies, play a significant role in the reactivity of reduced $\text{TiO}_2(110)$ [69, 73, 81, 91]. There is also another possibility, namely that subsurface defects such as Ti interstitials and bulk oxygen vacancies affect their surface reactivity [16, 59]. STM observations have shown that oxygen interacts with subsurface interstitials even at room temperature [98, 99]. It was concluded that Ti interstitials dictate the surface reactivity of benzaldehyde over vacuum-reduced $\text{TiO}_2(110)$. Well-ordered $\text{TiO}_2(110)$ islands were formed by annealing the sample at 900 K, which is the evidence for Ti migration from the subsurface region [96]. Figure 19 shows the overall reactive process of monomeric benzaldehyde which comprises diffusion of monomeric benzaldehyde and subsequent formation of a diolate intermediate above a Ti interstitial site [97]. It is crucial to study how subsurface and bulk defects affect the chemical behaviour of reduced TiO_2 prepared for surface science. The migration of titanium interstitials is known to promote surface regrowth under both reducing and oxidizing conditions at elevated temperatures, and has recently been observed to occur at temperatures as low as $\sim 300\text{--}400$ K [96].

Figure 19. Schematic of benzaldehyde adsorption followed by pairing to form a diolate above a Ti interstitial site. Heating to 400 K produces gaseous stilbene and two oxygen atoms. The oxygen atoms form new nanoscale islands of TiO_x from reaction with titanium interstitials [97].

Furthermore, Lewis acid sites, either Ti^{4+} on crystalline or Ti^{3+} (Ti^{2+}) on reduced TiO_2 , play an important role in studying surface properties of reduced TiO_2 [100]. Reactive chemisorption occurs through interaction with Lewis acid sites (Ti^{4+}) and Lewis base centres (Ti^{3+}) of the reduced surface, which are generated upon the introduction of an oxygen vacancy [101]. As shown in Figure 20, Panayotov et al. [100] supposed that thermally-activated bridging lattice oxygen leaves behind $\text{Ti}^{3+}\text{-Vo-Ti}^{3+}$ donors and moves to the surface (as a highly reactive O atom) where it reacts with a methoxy group that is bound to Ti^{4+} , which is a coordinatively unsaturated Lewis acid site. Although oxygen vacancies had been proposed as the coupling site of aldehydes to olefins, recent experiments point to Ti interstitials as the main active point defect for reductive coupling [96, 102].

Figure 20. Schematic diagram illustrating thermally activated bridging lattice oxygen leaving behind $\text{Ti}^{3+}\text{-Vo-Ti}^{3+}$ donors. The oxygen atom diffuses to the particle surface where it burns a methoxy group that is bound to a coordinatively unsaturated Ti^{4+} Lewis acid site. Electrons trapped at shallow donor states are detected in our experiments when they are excited into the conduction band via absorption of IR radiation [100].

It was reported that hydrogenation of a- and r-TiO₂ results in black and bluish colours as oxygen is removed from the crystal and colour centres are produced [18, 103]. Yellow defective a-TiO₂ nanoparticles were also observed where a white suspension slowly turns to obviously yellow colloidal solution (Figure 21) [4]. UV-VIS absorption spectra of the white and yellow colloidal solutions of a-TiO₂ were recorded to investigate the nature of the defects in the as-synthesised materials. A steep increase of light absorption at ~400 nm for normal TiO₂ colloidal solution became less steep for the yellowish solution. It was proposed that the shift in the light adsorption edge of yellowish solution was due to the creation of other defects than Ti³⁺ defects, since otherwise a bluish colloidal solution should have been produced. A combination of V_{Ti} (titanium vacancies) and Ti_i (titanium interstitials) was suggested.

Figure 21. UV-vis absorption spectra of normal and yellow TiO₂ colloidal particles [4].

3 Hydrogen–TiO₂ interactions

Following dissociation of H₂ at the surface, atomic Hydrogen can penetrate into the bulk. Due to its small size and high reactivity, atomic H diffuses through channels in the semiconductor lattice and interacts with host atoms, impurities and defects, creating hydroxyl groups in particular. Early experiment on hydrogen reduction of rutile and anatase confirmed that structural changes

caused by exposure to hydrogen occurred within the bulk, not only at the surface.

In 1983 Iwaki [82] studied the hydrogen desorption behaviour of anatase and rutile samples using temperature-programmed desorption (TPD) in the temperature range of 298–1073 K. Following the introduction of 51 kPa of hydrogen to the sample at various temperatures (between 573 and 773 K for 2 hrs), TPD measurements were done. It was reported that the colour of the sample changed to bluish grey when the temperature was raised above 673 K. TPD spectra of hydrogen absorbed by anatase and rutile samples are shown in Figure 22 [82]. It was found that the onset temperatures of hydrogen desorption from anatase and rutile differed, and anatase yielded two H_2 desorption peaks (623–673K and 773–823K) while rutile yielded a single broad peak at 923–973 K. The TPD spectra for anatase also exhibited higher peaks, because of the larger open channels in the anatase structure compared to rutile. The results suggested strongly that the hydrogen taken up by rutile was bonded to the bulk, with most of the hydrogen desorbed via the open channels in the TiO_2 lattice.

Figure 22. TPD spectra of hydrogen desorbed from titanium dioxide. Hydrogen was introduced at (a) 573, (b) 623, (c) 673, (d) 723 and (e) 773 K. Anatase: The broken line (f) was obtained by gas chromatography after introduction of hydrogen at 773 K (arb. units). Rutile: The dotted line (f) is for the original untreated rutile sample. The broken line (g) corresponds to curve (e) in the Anatase panel (arb. units) [82].

Iwaki [82] also proposed models for the description of the hydrogen adsorption behaviour of TiO_2 as follows [82]:

where V_O is an oxygen vacancy which traps an electron. Hydrogen is also adsorbed on neighbouring oxygen to form a hydroxyl group [82]:

In 1993 Khader et al. [22] reported experiments on the electrical conductivity of sintered rutile pellets as a means to investigate the mechanism of reduction by hydrogen. According to their results, reduction leads to the loss of oxygen according to the following overall reaction:

and this leads to the formation of oxygen vacancies according to the following overall reaction:

where V_r^{2-} is a reactive oxygen vacancy at which H_2 can be adsorbed quickly.

The kinetics of reduction of rutile was studied at times up to 2 hours and temperatures of 300 to 500 °C. Doubly ionised oxygen vacancies are predominant under such conditions [104-107].

According to Khader et al. [22], rutile reduction by hydrogen proceeds in three stages (Figure 23):

1. Slow adsorption of H_2 on deactivated sites, V_d^{2-} .
2. Exponential increase of the electrical conductivity with time, during which the autocatalytic reactions were observed which means that the product of the reaction at a certain time accelerates the reaction at later times. The resulting V_r^{2-} offer more sites for H_2 adsorption, so leading to a greater degree of hydrogen coverage.
3. At long reduction times and high conductivities, the conductivity increases slowly with time which suggests that reduction is a diffusion-controlled process. This implies that, as the reduction proceeds, more vacancies are generated within the bulk of the pellet.

Figure 23. Variation of the electrical conductivity vs time of reduction at various temperatures [22].

The conductivity increase in the second region was attributed to the production of surface oxygen vacancies. Outward diffusion of oxygen ions leaves behind oxygen vacancies and the oxygen ions react with the adsorbed H_2 on the surface to produce H_2O . As the reduction reaction penetrates deeper, the diffusion path lengthens, causing a slower increase of the conductivity in stage 3. Based on the experimental evidence, Khader et al. concluded that the concentration of O^{2-} (solid) was constant. The relationship between the conductivity and the time of reduction was modelled by

$$\sigma = \sigma^0 \exp(k_i t) \quad (9)$$

where σ^0 is the conductivity at $t = 0$ and k_i is the rate constant which relates to the concentration of O^{2-} . The Arrhenius plot of $\ln k_i$ versus $1/T$ based on Figure 23 is shown in Figure 24 and yields an activation energy of TiO_2 reduction is 15 kcal mol^{-1} .

Figure 24. Arrhenius plot of $\ln k_i$ vs $1/T$ [22].

Haerudin et al. [108] studied the reduction of Degussa P25 TiO_2 (80% anatase-20% rutile) under a hydrogen atmosphere. The colour of the sample changed to blue during the reduction process. They concluded that the number of oxygen vacancies was strongly controlled by thermodynamics rather than kinetics. After introducing oxygen to the system at room temperature, the colour changed to grey-white, suggesting surface re-oxidation of the reduced titania. According to the Mars-van Krevelen mechanism [109] adsorbed molecules will be reduced by removal of oxygen from the catalyst surface, leaving an oxygen vacancy behind that may in turn be re-oxidised by dioxygen. The concentration of oxygen vacancies is controlled by thermodynamics, with a non-zero equilibrium concentration owing to the relatively high configurational entropy of a point defect. For treatment temperatures of 400 °C and below, the following equilibrium reaction was proposed [108]:

Upon hydrogen treatment above 400 °C, the density of surface vacancies seemed to reach saturation and simultaneously vacancies were formed in the bulk.

Liu et al. [30] treated 30 nm anatase nanoparticles under hydrogen and found that the optimum temperature for the H_2 treatment was ca. 500–600 °C. The photocatalytic performance of H_2 -treated a- TiO_2 was maximized by exposure to H_2 at 560 °C. They studied hydrogen and a- TiO_2 interactions through in-situ EPR spectroscopy. The EPR signal intensities for the H_2 -treated TiO_2

sample showed that both V_O and Ti^{3+} affect the photocatalytic activity properties of H-modified TiO_2 (Figure 25). The peaks with g factors of 1.955 and 2.002 were assigned to Ti^{3+} and adsorbed oxygen, respectively, for H_2 treatment temperatures lower than 400 °C.

Figure 25. The EPR spectra of V_O ("OV") and Ti^{3+} during the H_2 treatment at different temperatures [30].

An evolution profile of V_O and Ti^{3+} intensity versus the treatment temperature is shown in Figure 26. When the H_2 treatment temperature was increased to 450 °C, the Ti^{3+} signal intensity increased smoothly and reached its maximum value at 600 °C. The V_O signal intensity reached a maximum at 450–520 °C and declined at over 560 °C, because electrons in the V_O were transferred out to form Ti^{3+} as more energy was supplied by hydrogen. At 700 °C, the signal intensities of both V_O and Ti^{3+} were very weak, due to the phase transition reaction of anatase to rutile. Liu et al. proposed the following mechanism for H_2 and TiO_2 interactions during the H_2 treatment. Firstly, hydrogen interacts physically with the adsorbed oxygen at temperatures below 300 °C. This phenomenon was demonstrated by the absence of the EPR signals associated with adsorbed oxygen (Fig. 25) and the significant H_2 consumption. Secondly, at temperatures higher than 300 °C, electrons move from the H atoms to the O atoms in the TiO_2 lattice. Thus, the V_O forms, when the O atom leaves the surface with the H atom in the form of H_2O . Thirdly, the interaction between H_2 and TiO_2 proceeds more rapidly at temperatures higher than 450 °C,

when electrons are transferred to Ti^{4+} to form Ti^{3+} cations. The H_2 consumption rate appeared to be even higher at temperatures higher than 450 °C.

Figure 26. The EPR intensity of Ti^{3+} and V_O vs. H_2 treatment temperature during the H_2 treatment [30].

Shin et al. [110] found that hydrogen-treated nanosized (20 nm) a-TiO₂ had a better electronic conductivity as an anode in Li-ion batteries compared to pristine and vacuum annealed TiO₂.

The photocatalytic activity of TiO₂:H in the visible region has been associated with an upward shift of the VBM. However, the extent of hydrogen incorporated and the undesirable formation of certain bulk/interfacial defects affect the visible light activity of TiO₂:H.

Wang et al. [111] reported that H-modified rutile TiO₂ nanowires and nanotubes performed better in photo-electrochemical water splitting than pristine ones. The nanowire diameters and length were in the range of 100–200 nm and 2–3 μm, respectively. Incident-photon-to-current-conversion efficiency (IPCE) was used to characterise the photo-conversion efficiency of the prepared photo anodes (Figure 27) via

$$IPCE = \frac{(1240 I)}{(\lambda J_{light})}$$

where I is the measured photocurrent density at wavelength, λ , and J_{light} is the measured irradiance at that wavelength. The IPCE measurements confirmed that r-TiO₂:H nanowires had higher photo activity than pristine ones. Figure 27(b) shows the energy diagram of the hydrogen-

modified TiO_2 versus NHE. E_{10} and E_{20} are the oxygen vacancy energy levels at about 0.75 and 1.18 eV and $E_{\text{Ti-OH}}$ and $E_{\text{Ti-OH-Ti}}$ are the energy levels of surface hydroxyl groups. Examining Figure 27(a), the visible and near-IR light absorption could be attributed to transitions from the oxygen vacancy levels to the TiO_2 conduction band. However, the photo-excited electrons located at oxygen vacancies are not involved in water splitting because their energy levels are well below the $\text{H}_2\text{O}/\text{H}_2$ reduction potential. This explains the observation of weak photo activity in the visible region for H- TiO_2 nanowires and the negligible contribution to the photocurrent. Additionally, the electronic transition between the localised oxygen vacancy states and the delocalised conduction band is not expected to be significant because the coupling between the localised and the delocalised energy states should be weak.

Figure 27. (a) IPCE spectra of pristine TiO_2 and H- TiO_2 nanowires prepared at 350, 400, and 450 °C, collected at the incident wavelength range from 300 to 650 nm at a potential of -0.6 V vs Ag/AgCl. Inset: Magnified IPCE spectra that highlighted in the dashed box, at the incident wavelength range from 440 to 650 nm. (b) A simplified energy diagram of H- TiO_2 nanowires. E_{10} and E_{20} are referred to the oxygen vacancies (red dashed lines) located at 0.73 and 1.18 eV below the TiO_2 conduction band; $E_{\text{Ti-OH}}$ and $E_{\text{Ti-OH-Ti}}$ (blue dashed lines) located at 0.7 and 2.6 eV below the TiO_2 valence band represent the energy levels of surface hydroxyl group. The black dashed lines indicate the $\text{H}_2\text{O}/\text{H}_2$ and $\text{O}_2/\text{H}_2\text{O}$ potentials. Arrows highlight the possible electronic transitions between the different energy levels in H- TiO_2 [111].

Hydrogen modification of r- TiO_2 nanowires at 450 °C or above caused a gradual colour change to black (Figure 28(a) [111]), which demonstrates the visible light absorption activity of the sample resulting from treatment with hydrogen. Figure 28(b) [111] shows the XRD patterns of

pristine and treated r-TiO₂ nanowires. The XRD pattern showed no phase change after hydrogenation.

Figure 28. (a) Pictures of TiO₂ nanowire arrays at different temperatures. (b) XRD patterns of pristine r-TiO₂ and r-TiO₂:H nanowires annealed in hydrogen at various temperatures (300, 350, 400, 450, 500, and 550 °C). (Arrows show the diffraction peaks corresponding to Sn metal) [111].

The black colour observed by Wang et al. is in contrast to the observation by Qui et al. [18] that exposure of r-TiO₂ nanorods to hydrogen at temperatures below 500 °C caused a colour change to strong blue (Figure 29(a)). Subsequent exposure to air induced a grey colour.

Figure 29. (a) Synchrotron XRD patterns (b) UV-vis spectra and (c) XPS spectra of blue and white r-TiO₂ nanorods. Hydrogenation modification was carried out in-situ at approx. 35 bar H₂ pressure [18].

Rietveld refinement of the synchrotron diffraction patterns (Figure 29(a)) of the blue and white r-TiO₂ nanorods revealed a significant expansion in the *c* direction. The synchrotron patterns confirmed that the hydrogenation of r-TiO₂ nanorods is a bulk phenomenon. According to Figure 29(b) white, grey and blue TiO₂ samples behaved differently in the visible light region. The blue r-TiO₂ showed the highest visible light absorption which can be related to the creation of the mid-band gap states. There was no significant difference between the XPS spectra of blue and white TiO₂, which is evidence that the bluish colour of TiO₂ after hydrogenation is not because of surface distortions and most likely results from defects created in the sub-surface or bulk of the r-TiO₂ nanoparticles.

Zheng et al. [112] studied the effects of hydrogenation on the photocatalytic activity of 8 nm diameter a-TiO₂:H nanowires. They proposed an economical method to produce surface-modified and morphology-improved a-TiO₂ nanowires. They synthesised a-TiO₂:H nanowire-microspheres by converting protonated titanate nanotubes (H-TiNT) to a-TiO₂:H under a hydrogen atmosphere. It was shown that a-TiO₂:H nanowire-microspheres have Ti-H and O-H bonds on their surface which caused the improvement of their visible-light absorption and photocatalytic activities. The colour of the TiO₂ nanowire-microspheres changed to brown during the hydrogenation process while that of TiO₂-air microspheres was white (inset to Figure 30(a)). The XRD patterns of a-TiO₂:H and a-TiO₂:air (Figure 30(b)) demonstrate that there is no major change in the crystal structure owing to hydrogenation, although their quality is not sufficient to reveal subtle changes in crystallography without analysis by profile refinement.

Figure 30. (a) UV-vis absorption spectra, (b) XRD patterns for a- $\text{TiO}_2\text{:H}$ and a- $\text{TiO}_2\text{:air}$ anatase 8 nm diameter nanowires [83].

Chen et al. [103] enhanced the visible-light absorption of 8 nm a- TiO_2 nanoparticles, where the colour changed to black (inset to Figure 31(a)) when exposed to 20 bar of H_2 at 200 °C for 5 days. The onset of optical absorption of the black a- $\text{TiO}_2\text{:H}$ nanocrystals was lowered to about 1.0 eV (~ 1200 nm) compared to ~ 300 nm for white a- TiO_2 . The XRD patterns (Figure 31(b)) did not reveal any obvious structural changes during the reduction process, and it was proposed that hydrogen introduced surface disorder in the surface layers of a- $\text{TiO}_2\text{:H}$. The black colour of the a- $\text{TiO}_2\text{:H}$ is in contrast with the brown colour of Zhang et al.'s [112] a- $\text{TiO}_2\text{:H}$ sample.

Figure 31. (a) XRD patterns of the white and black TiO_2 nanocrystals (shown in inset). (b) Spectral absorption of the white and black a- TiO_2 nanocrystals [103].

Yu et al. [17] synthesised a-TiO₂:H nanosheets and tested them as a photocatalyst. They reported that the photoactivity properties of the prepared a-TiO₂:H depended on the concentration and distribution of defects such as Ti^{3+} interstitials and V_O . They found that a-TiO₂:H nanosheets hydrogenated at 600 °C for longer than 10 h showed 10 times higher photoactivity than pristine a-TiO₂. It was claimed that the samples which were hydrogenated at 500 °C for 0.5–1 h changed to strong blue, which is in contrast to the reports that pristine white a-TiO₂ nanocrystals turn to black by hydrogenation at elevated temperature [8, 18, 31, 113, 114] (Figure 32).

Figure 32. a-TiO₂:H samples prepared with a 50 sccm H₂ gas flow at temperature range of 500–700 °C. Gradual changes in colour from blue to grey were seen which depends on annealing temperatures and time [17].

In a 2016 study by Wu et al. [4], ultra-small (~3 nm) yellow TiO₂ nanoparticles were produced by a sol-gel method and UV light pretreatment. Fitting the (101) XRD peak revealed an expanded (101) interplanar spacing, which was interpreted as indicating the presence of Ti_i defects, Figures 33(a) and (b). We remark that the small shift in the peak position of 0.01° is within the stated uncertainty, is comparable to the effect of changing samples and would require whole-pattern fitting to be reliably measured.

The photocatalytic activity of yellow a-TiO₂ was studied by decomposing formaldehyde in aqueous solution for H₂ production. As Figure 34(a) shows H₂ was produced by yellow a-TiO₂ during visible light irradiation without using any co-catalyst. Figure 34(b) shows the XPS spectra of the white and yellow a-TiO₂. There was no obvious peak for Ti³⁺ in Ti-2p spectra for the yellow sample (Figure 34(b)) which was explained by oxidation of Ti³⁺ to Ti⁴⁺ in air after turning off the UV light.

Figure 33. XRD patterns of normal and yellow a-TiO₂ (Blue dot lines represent standard pdf card (21-1272) for a-TiO₂); (b) XRD peak fitting of the a-TiO₂(101) peak using a pseudo-Voigt function [4].

Figure 34. (a) Visible light driven ($\lambda > 420$ nm) hydrogen production via decomposition of formaldehyde in aqueous solution without using any co-catalyst. (b) XPS spectra of Ti-2p for normal and yellow a-TiO₂ powders [4].

Figure 35 shows EPR spectra of white and yellow TiO_2 . The presence of V_{Ti} is evidenced by the line at $g = 1.998$ in yellow a- TiO_2 . The small additional signals in the EPR spectra were attributed to dopants present in the sample [4].

Figure 35. EPR spectra of white and yellow TiO_2 powders measured at room temperature [4].

Table 1. Summary of literature reports on hydrogenation of different structures of TiO_2 .

Year	Author	Material	Environment	Conclusion
1983	Iwaki et al. [82]	A- and r- TiO_2	53 kPa H_2 at temperatures between 573–773 K for 2 h.	The interaction of hydrogen with titanium dioxide was attributed to the formation of surface hydroxyl groups.
1998	Haerudin et al. [108]	TiO_2 -P25	1 bar H_2 at temperatures between 200–475 °C.	The number of vacancies increases with increasing treatment time and with increasing hydrogen flow rate. Blue under hydrogenation and turned to grey-white in oxygen atmosphere.
2003	Liu et al. [30]	30 nm a- TiO_2	H_2/Ar mixture gas at temperatures between 500–600 °C	EPR results showed that during the hydrogen treatment, V_{O} was first produced and Ti^{3+} was then generated.
2011	Shin et al. [110]	20 nm a- TiO_2 nanopowders	5% $\text{H}_2/95\%$ Ar mixture at 500 °C	H-treated TiO_2 has better electrode properties than vacuum annealed TiO_2 .

2011	Chen et al. [103]	a-TiO ₂ nanocrystals-8 nm in diameter	hydrogenated in a 20 bar H ₂ at about 200 °C for 5 days	Black- Disordered outer layer surrounding a crystalline core was around 1nm and the core crystallised a-TiO ₂ nanocrystals.
2011	Wang et al. [111]	nanowire arrays r-TiO ₂ nanotube arrays and a-TiO ₂ nanowire diameter: 100-200 nm and length: 2-3µm	annealed in air at 550 °C for 3 h – finally to black (450 °C or above)	The dark colour suggests that the TiO ₂ has visible light absorption as a result of hydrogen treatment.
2012	Zheng et al. [112]	8 nm a-TiO ₂ nanowire	TiO ₂ :H nanowire-microspheres is dark brown	They found that TiO ₂ :H nanowire-microspheres have Ti-H and O-H bonds on their surface.
2014	Qiu et al. [18]	40 nm r-TiO ₂	35 bar H ₂ at 450 °C for 1 h. Sample colour changed to blue	Blue-TiO ₂ based Li-ion batteries have higher energy capacity and better rate performance.
2015	Nandasiri et al. [36]	r-TiO ₂ (110) single crystals (10 × 10 × 1 mm ³)	H ₂ implantation into r-TiO ₂ (110)	Rapid stability of TiO ₂ :H due to rapid bulk diffusion of H to its interfaces, followed by desorption (as H ₂ O or H ₂) and surface reduction.
2016	Mehta et al. [34]	Nanostructured a-TiO ₂	5% H ₂ /95% Ar mixture at 300 °C	The enhancement of photocatalytic activity depends on the duration of hydrogen treatment.

In a 2015 study bringing fresh insight to the problem, Nandasiri et al. [36] reported, based on Rutherford back-scattering measurements, that hydrogen implanted into rutile TiO₂(110) diffused to the surface at low temperatures (~373 K) and was completely depleted from the near-surface region (≤ 800 nm) by 523 K. This reduction most likely resulted from the reaction of H with surface oxygen, followed by formation and desorption of water. The presence of surface Ti^{3+} persisted until the thermally induced surface-to-bulk diffusion of Ti^{3+} interstitials was initiated above 550 K. Nuclear reaction analysis (NRA) was performed on H-implanted samples to determine the hydrogen depth profiles as a function of annealing temperatures (Figure 36) [36]. The hydrogen profile was significantly altered by annealing at 373 K, with the peak becoming a uniform concentration gradient. Little or no hydrogen was lost from the crystal (into the vacuum) during the 373 K annealing. Interestingly, although the H profile broadened toward the surface during heating, there was no significant broadening toward the bulk. A significant

amount of hydrogen was lost into the vacuum during annealing at 473 K. The signal at 473 K may be due to H trapped at structural defects generated during the implantation process. Further annealing at 523 K completely removed all of the implanted H. We remark that the effective heating rate corresponding to the stated annealing time of 30 min. at each temperature is much lower than the typical 5 K/min heating rate applied by Iwaki [82], consistent with the complete desorption of implanted H at relatively low temperatures observed by Nandasiri et al.

Figure 36. Hydrogen depth profiles measured by the resonant $1\text{H}(19\text{F}, \alpha\gamma)16\text{O}$ nuclear reaction analysis for the hydrogen-implanted $\text{TiO}_2(110)$ single-crystal sample after annealing in vacuum. Inset displays the integrated area in the profile as a function of annealing [36].

Colour change is one of the most obvious consequences of the reduction of both anatase and rutile, and accompanies the changed electrochemical behaviour. It has been proposed that the changed sample colour resulting from exposure to hydrogen corresponds to the formation of a disordered TiO_{2-x} surface layer, resulting in a crystalline core/amorphous shell structure with enhanced visible light absorptance [22, 36, 115]. This structural model was used by Chen et al. [84] as the basis of a proposal that shallow mid-band gap states appear just below the conduction band in hydrogen-modified (black) anatase. For anatase, there is strong evidence from electron microscopy of a disordered surface layer [8, 116]. However, the evidence presented here for rutile is consistent with a structural modification taking place throughout the rutile particle.

We remark that the creation of a surface layer of disordered material should produce readily detectable changes in the x-ray diffraction pattern from TiO_2 nanoparticles, because the number

of atoms in the near surface region is comparable to the number of atoms within the bulk: (i) the integrated intensities of the diffraction peaks should decrease significantly; (ii) the peaks should broaden visibly owing to the reduction in the coherently diffracting crystallite size; (iii) the diffuse/isotropic background should increase as the lost Bragg intensity is redistributed through reciprocal space. There is no evidence for such changes in the high-quality synchrotron x-ray diffraction patterns of Qiu et al. [18] for rutile nanorods, which were obtained on a single sample during in-situ exposure to hydrogen. There is also no indication of such changes in the laboratory XRD patterns of Chen et al. [84], although the strength of any conclusions is limited by the low statistical quality of the data. It therefore appears that the explanation of enhanced electrical properties of hydrogen-modified anatase owing to surface-only processes requires further investigation and does not apply to rutile.

4 Summary

Oxygen deficient titanium dioxide has attracted a lot of attention due to its different behaviour compared to pristine titanium oxide. Despite the enormous amount of experimental work and numerous DFT calculations that have been done, understanding of the surface and bulk properties of TiO_{2-x} is still incomplete. Zhang et al. [117] mentioned in their recent paper on black TiO_2 that despite various efforts to study defective TiO_2 , controversy persists about the exact effect of mid-gap states in TiO_{2-x} and how the presence of structural disorder narrows the band gap. In the view of Diebold [118], whether disorder modifies only the surface properties or affects the bulk properties has not been addressed. This review paper has summarised many experimental and theoretical results obtained for r- $\text{TiO}_2\text{:H}$ and a- $\text{TiO}_2\text{:H}$ and highlighted the contradictions between them. It should form the basis for further research to clarify the effects of hydrogen on generating defects in the bulk of r- TiO_2 , their role in the optical and electrochemical properties relative to surface distortions, and also the diffusion mechanism of H and V_O in hydrogenated samples. The effects of different environmental conditions on the sample's colour were surveyed and it was found that here too there are inconsistencies between literature reports, with no basis as yet apparent on which to reconcile them.

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