

Review

Recent Advancements in the Understanding of the Surface Chemistry in TiO₂ Photocatalysis

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Abstract: Surface chemistry plays a major role in photocatalytic and photoelectrochemical processes taking place with the participation of TiO_2 . The synthesis methods, surface characterizations, theoretical research methods, and hardware over the last decade generated opportunities for progress in the surface science of this photocatalyst. Very recently, attention was paid to the design of photocatalysts at the nanoscale level by adjusting the types of exposed surfaces and their ratio, the composition and the surface structure of nanoparticles, and that of individual surfaces. The current theoretical methods provide highly detailed designs that can be embodied experimentally. The present review article describes the progress in the surface science of TiO_2 and TiO_2 -based photocatalysts obtained over the last three years. Such aspects including the properties of macro- and nano-scale surfaces, noble-metal-loaded surfaces, doping with Mg and S, intrinsic defects (oxygen vacancies), adsorption, and photoreactions are considered. The main focus of the article is on the anatase phase of TiO_2 .

Keywords: anatase surfaces; aspect ratio; adsorption; surface heterogeneity; nanosheets; metal loading; doping; oxygen vacancies; photoreactions

1. Introduction

Titanium dioxide has multiple applications in the areas of catalysis, photocatalysis, electrocatalysis, adsorption, photovoltaics, and sensing [1,2], in addition to many others. Its annual production is around 10 million tons owing to its use as a white pigment. Its unique properties of high chemical stability and activity in photocatalytic processes made it a subject of intensive scientific research over the last half-century.

Titanium dioxide exists in its three main phases—rutile, anatase, and brookite. Furthermore, there are several other rarely obtained phases such as TiO_2 B. All the crystal phases of TiO_2 exhibit photochemical activity. However, the anatase phase usually possesses the best photocatalytic properties. Mixed phases, for example, the well-known rutile–anatase mixture P25 powder, have a high activity due to the existence of heterojunctions and the separation of photogenerated electron–hole pairs [3].

 TiO_2 drives all classes of photocatalytic and photoelectrocatalytic processes under proper conditions. When applied for the abatement of pollutants, both adsorption and photodegradation contribute to the media purification [4]. Due to the formation of very stable surface complexes with polyvalent anions, adsorption is an efficient water purification method from Cr(VI), V(V), Bi(III),



and As(V) [5]. For the purely adsorptive purification, TiO_2 should be preferably in amorphous hydrous form.

While rutile was the subject of surface science research for a long time, anatase became the subject of intensive interest only recently, following the developing of preparation methods that allowed the controlling of its shape. Anatase exposes mainly (101), (001), and (100) surfaces in its crystals. In relations between nanoparticles, shapes, and photocatalytic activity, there is a general consensus that nanoparticles with a large number of (001) facets have a higher activity than nanoparticles comprising (100) facets or (101) facets [6], whereas the photocurrent density is the highest for (100) facets. It seems that the effect of the surface structure on photoactivity is substrate- and reaction- sensitive. Therefore, it is desirable to develop understanding and prediction methods for selecting proper shapes and exposed facets for a given process and substrate. Recently, Peng and Tsang [7] summarized faceting effects in TiO_2 and ZnO in relation to photocatalysis. In light of the large number of published manuscripts, this review concentrates on the progress obtained over the last three years.

2. The Surface Structure of Bulk TiO₂

The structure and properties of different surfaces of TiO_2 are of great importance for designing highly active photocatalysts and solar cells. The development of means which enable the preparation of TiO_2 particles with controlled facets facilitated the integration of theory and experiments when studying the TiO_2 surfaces. The study of structures of the most often obtained surfaces, such as (101) and (001), also attracted significant interest. The (001) surface is regularly considered as the most reactive one for dark and photoreactions. Recently, its structure was investigated theoretically by Shi et al. [8] using a PBE GGA functional, with an emphasis on surface stress effects. The unreconstructed clean (001) surface shown in Figure 1a has a very high anisotropic stress, with the stress tensor component along (100) equal to -29.7 kbar and that along (010) equal to -35.6 kbar. In order to reduce this stress, the surface undergoes reconstruction with the formation of an additional ridge of atoms every fourth unit cell, as shown in Figure 1b,c. The reconstructed surface has just a -1.2-kbar stress tensor component in the (100) direction. However, the stress in the (010) direction was not reduced. Therefore, it was suggested that this stress can be released by creating vacancies in the ridge atoms. This approach was evaluated, but the effect of such defects on the stress in the ridge was found to be minor.



Figure 1. The structure of a pristine (**a**), (1×4) reconstructed (**b**), and (001) (**c**) anatase surface. Reprinted with permission from Reference [8]; copyright (2017) American Chemical Society.

Oxygen vacancies that are often present in the surfaces of TiO_2 and in the bulk give rise to states at approximately 1 eV below the Fermi level [9]. Theoretical methods resulted in a large scattering of values for the location of these states (from 0.1 to 1.8 eV below the conduction band), mostly reflecting differences in the applied computational methods. Therefore, additional experimental data are required for anatase and rutile surfaces for shedding light on the real state levels of oxygen vacancies.

A recent review by Fujishima et al. [10] summarized the literature data on defects in bulky TiO_2 surfaces such as oxygen vacancies, hydroxyl groups, interstitial Ti atoms, and Ti vacancies, as well as on the surface electron and hole polarons. Thus, we do not consider these questions in the present

review. Another comprehensive review of the role of defects in photocatalysis, which overviews not only titanium dioxide but also other photocatalysts such as ZnO, Co₃O₄, ZnS, BiO₂, WO₃, BiOCl, and many more, may assist readers whose interest extends beyond TiO₂ [11].

3. The Structure of the Surfaces of TiO₂ Nanoparticles

Nanoparticles are particles with typical sizes lower than 100 nm in one, two, or all three dimensions. As the typical size is reduced, the role of edges and vertices becomes more and more important in determining the properties of the particles. The properties of nanoparticles were the subject of research for quite a long time. However, only after modern computational methods and hardware were developed to the proper level did it become possible to investigate nanoparticles with a realistic size of 1 nm and larger in an accurate manner.

Among the nanoparticles of TiO_2 of all sizes, nanoparticles with one, two, or all three dimensions below 10 nm are of special interest since size effects are clearly present at such sizes. Prominently, computational models resulted in TiO_2 nanoparticle structures that were in agreement with experimental observations, i.e., the crystalline core was surrounded by a few layers of amorphous atoms [12]. Here, the PM6 semiempirical method was found to be advantageous for modeling TiO_2 compared to the newer method PM7.

Recently, the structure and locations of photogenerated charge carriers in decahedral anatase nanoparticles were the subject of intensive computational research. Fazio et al. [13] studied two decahedral nanoparticles and a spherical anatase nanoparticle, shown in Figure 2a, using the hybrid functionals B3LYP and HSE06. They obtained triplet excited states and the locations of electrons and holes in each of these nanoparticles. Figure 2b,c demonstrate the spin density of a hole and an electron, respectively. The hole tends to be localized over oxygen atoms in the middle layers and over oxygens around (101)/(101)/(101)/(101) corners. The electron is localized over titanium atoms in the central part.



Figure 2. (a) The structure of the anatase nanoparticles NC_S (TiO₂)₁₅₉(H₂O)₄, NC_L (TiO₂)₂₆₀(H₂O)₆, and NS (TiO₂)₂₂₃. (b) Spin density of an extra hole in the NC_S nanoparticle. (c) Spin density of an extra electron in this nanoparticle. Reprinted with permission from Reference [13]; copyright (2016) Elsevier.

These results are in a good accord with the results obtained for smaller decahedral anatase nanoparticles with exposed (001) and (101) facets [14]. Here, nanoparticles of different size and different content of surface hydroxyl groups at the (001)/(101) edges and vertices between the four adjacent

(101) surfaces were constructed. It was found that the positions of untrapped electrons and holes depended on the distribution of surface OH groups in such small nanoparticles. As in the previous example, holes tended to localize in the central parts of the particle and electrons localized over the whole nanoparticles or over (001) facets.

It was demonstrated recently that the surface of anatase TiO₂ nanoparticles smaller than 2 nm possesses inherent heterogeneity in the acidity strength of the adsorption sites [15]. A CO molecule was adsorbed on all possible Ti atoms in exposed (001), (100), and (010) facets of the anatase nanoparticles. A small increase in the area of the (001) surface resulted in average CO adsorption enthalpy decrease by about 10 kJ/mol. Adsorption over (100) and (010) surfaces was stronger ($\Delta H_{ads} = -131$ to -138 kJ/mol) than adsorption over the (001) surface ($\Delta H_{ads} = -76$ to -95 kJ/mol). It is interesting that adsorption over the edges between (100) or (010) surfaces and (001) was as strong as over (100) surfaces, while adsorption over the edges between (100) surfaces and (010) surfaces was somewhat weaker ($\Delta H_{ads} = -126$ kJ/mol). The energy of CO adsorption is known to correlate with the strength of surface Lewis sites and with the infrared band frequency of adsorbed CO. Stronger acid sites have larger adsorption energy and lower CO vibration frequency. Thus, the (100) and the (010) surfaces are the strongest Lewis acid catalysts. The sites over (100) or (010) surfaces near the vertices possess the highest CO adsorption energy and the strongest Lewis acidity.

Lamiel-Garcia et al. [16] theoretically studied anatase nanoparticles of octahedral and decahedral shapes exposing (101) and (001) surfaces, with size up to 6 nm and formulas of $(TiO_2)_{10}$ – $(TiO_2)_{455}$. The energy of formation per TiO₂ unit and the band gap, as well as variations of other parameters, were studied with PBE, PBEx, and PBE0 functionals. The presence of quantum-size effects was noted for all nanoparticles, and it was predicted that bulk-like properties would be obtained at typical dimensions larger than approximately 20 nm.

Selli et al. [17] modeled spherically shaped TiO₂ nanoparticles containing 300 to 4000 atoms. They compared the precision of computations carried out using the semiempirical method DFTB (matsci-0-3 parameters set) versus the traditionally used B3LYP hybrid functional. Similar results were obtained by all three methods (DFTB, PBE, and B3LYP). Simulating the annealing of the nanoparticles resulted in spherical shapes, 1.5 to 4.4 nm in diameter. The well-faceted decahedral nanoparticles expected according to the Wulff construction were not formed, probably because of the small duration of the annealing process (less than 45 ps).

Results obtained by the DFTB method indicated a quantum-size effect for particles, 1.5–3.0 nm in diameter. In contrast, DFT B3LYP computations yielded a steady decrease in the bandgap for all diameters. According to the results of this study, the DFTB method is recommended since it provides satisfactory precision and high computation speed. Investigation on photogenerated charges revealed that electrons and holes, trapped at the surface or at the subsurface of the photocatalyst, have considerably larger stability (-0.79 eV) compared with the vertical triplet state that can be considered as unbound exciton [18]. In another recent study [19], the optical band gap was theoretically investigated for nanoparticles containing 1-84 TiO2 units. It was found that the band gap was essentially the same for particles containing more than four TiO_2 units. This possibly reflects the fact that the band gap in these particles is determined by the surface states, which are size-independent in contrast to most cases where the bandgap is determined by the bulk and, hence, it is size-dependent. Another reason for the scattering in the results could be the use of particles that differed in their shapes. Both hypotheses were confirmed in another recent study [20], which considered decahedral anatase nanoparticles of different shape and with different surface groups. The quantum-size effect was present within each group of nanoparticles of specific shape but constant contribution of surface states. However, the locations of photogenerated holes and electrons were seldom in agreement with the experimental data.

Le and Schweigert investigated the interfaces between two decahedral anatase nanoparticles of $(TiO_2)_{70}(H_2O)_2$ connected together via their (001) facets or via (101) facets [21]. They found that the deep trap states could be localized at the interfaces between two nanoparticles due to local structure

deformations. Interestingly, they also found that some of (001)/(101) edges were hydroxylated in the course of geometry optimization; the result was consistent with the higher stability of such nanoparticles [14].

Oxygen vacancies (V_O) are inherent defects in titanium dioxide and exert influence on its properties. A number of recent theoretical studies were devoted to V_O in nanoparticles. A complete set of V_O was studied in Reference [22] for a decahedral anatase nanoparticle (TiO₂)₁₂₁(H₂O)₆ having OH groups at (001)/(101) edges. Vacancies were found to be more stable in (101) surface compared to (001) facet. The most stable vacancies were in the subsurface layer of atoms of (101) facet closer to the vertices between four adjacent (101) facets. Morales-García et al. [23] studied oxygen vacancies in an octahedral anatase (TiO₂)₈₄ nanoparticle with a length of 3 nm, exposing (101) facets only, as shown in Figure 3. The functionals PBE, PBEx, and PBE0 were used for the computations, and the relative stability of V_O was different for these functionals. The most easily formed vacancies were at the top vertex (T1) and possibly in the bulk (I-3-2) (Figure 3).



Figure 3. The $(TiO_2)_{84}$ anatase nanoparticle of 3 nm size with (101) facets (**a**) and oxygen vacancies in it (**b**). Reproduced from Reference [23] with permission; copyright (2018) American Chemical Society.

Morita and Yasuoka reported a thorough study on V_O and interstitial Ti in octahedral nanoparticles $(TiO_2)_{35}$ and $(TiO_2)_{165}$ using PBE + U (U_{eff} = 3.3 eV) and HSE06 approaches [24]. The most stable V_Os were found in the subsurface layer of atoms and at the tip, in agreement with previous study results. The oxygen vacancies correspond to deep traps of >1 eV below the conductance band. Using semiempirical computations, it was found that V_Os are easier to be formed in smaller anatase decahedral nanoparticles [25]. Three types of structures were found following the formation of V_O, namely, (1) repulsion of surrounding Ti atoms, (2) transfer of oxygen vacancy to a neighbor site, and (3) transformation of vacancy into Magneli phase.

Experimentally produced TiO₂ was found to have amorphous surface layers, 2–6 nm in thickness following hydrogenetaion. The amorphous layers were attributed to reduced and H-doped defective structures [26]. These layers are beneficial for the photocatalytic hydrogen production reaction.

The problems of finding the most stable shapes and sizes of TiO_2 nanoparticles, the effect of oxygen vacancies, and the presence of quantum-size effects were addressed in many theoretical studies, and the results were partially summarized in a recent review [27] covering research up to 2017. Surprisingly,

despite the expectation for a strong effect of the surface groups on these properties, such a strong effect was not echoed in the cumulative literature.

4. The Surface Structure of Two-Dimensional (2D) TiO₂

Nanoparticles having high predominance of just one facet are often called nanoblankets (nanosheets) since only one facet is actually present. Such nanoblankets can serve as very efficient materials for photocatalysis [28] and sensors since the fraction of the active surface is very high. Recently, it was demonstrated that the sensing properties of (001)-faceted anatase nanoblankets can be further improved by reductive treatment [29]. The resistivity response to vapors of ethanol, acetone, triethylamine, and formaldehyde increases dramatically, testifying for the adequacy of this treatment for sensing applications.

A special class of TiO₂ nanoblankets is represented by extremely thin sheets containing several layers of atoms. Such nanosheets are rarely prepared experimentally but could become of high interest in the near future. Intensive theoretical studies revealed some interesting properties of these very thin nanosheets. The thinnest nanosheets contain just a single layer of Ti and O atoms. However, such monolayer nanosheets are not stable, at least for (010) and (101) surfaces [30]. Their structure becomes strongly distorted, and they are converted into the same lepidocrocite structure. Such lepidocrocite titanates have an orthorhombic structure and formulas of H₂Ti₄O₉, H₂Ti₅O₁₁, and so on. These nanosheets have a thickness of 0.7 nm and demonstrate stable activity in hydrogen evolution [31]. Moreover, such "monolayer" nanosheets with a thickness of 1.2 nm were found to be more active under visible light in the oxidation of furfuryl alcohol to furfuraldehyde compared to more bulky sheets [32].

If a larger number of atomic layers are taken to construct a nanosheet, it becomes stable. Liu et al. [33] investigated (010) anatase nanosheets containing three to seven layers of atoms. There was a quantum-size effect, as the band gap increased when the thickness of the nanosheet decreased. The thinnest nanosheet possessed the highest conduction band minimum, which is considered beneficial for the photocatalytic reactions. Gao et al. [34] experimentally prepared very small nanoplates with 4–5 nm lateral size and 0.5 nm thickness (Figure 4). Their X-ray diffraction (XRD) pattern showed only the (002) peak attributed to anatase. Unfortunately, no further details on properties such as band-gap values and chemical composition were reported.



Figure 4. Experimentally prepared extremely small titania nanosheets: (**a**) high-resolution transmission electron microscopy (HR-TEM) image; The white circles indicate the presence of specific nanosheets (**b**) atomic force microscopy (AFM) thickness profile, showing the height of three particles. Reproduced from Reference [34] with permission; copyright (2017) Elsevier.

Hence, these properties were studied theoretically for the thinnest possible nanoblankets containing just two layers of Ti atoms of rectangular [35] and square shapes [36]. It turned out that the quantum-size effect was present in the square-shaped nanosheets but was obscured in the nanoribbons due to their smaller thickness. The surface of the nanosheet can be fully flat for small nanosheets having an even number of atomic layers, but it is curved for nanosheets with an odd number of layers. In any case, the extent of hydroxylation at the edges seems to be more important than the size effect in the value of the band gap.

Wang et al. [37] using DFT computations predicted four different phases of TiO₂ containing two layers of Ti atoms, named α -2D-TiO₂ to δ -2D-TiO₂, with the α -phase being the most stable. The anatase structure corresponds to the β -phase, which is slightly less stable. They also investigated oxygen vacancies in the most stable lepidocrocite-like phase and found that the unpaired electrons reside entirely over the Ti atoms adjacent to the vacancy in the ferromagnetic (triplet) state, a result in full agreement with recent semiempirical studies [22].

5. Metal-Loaded TiO₂ Surfaces

Loading of noble metals over the surfaces of titanium dioxide is an important method to improve photocatalytic activity via improvement of separation of photogenerated charges [38], decreasing energy barriers for reactions such as hydrogen production from water [39], spillover to the photocatalyst [40], and prevention of deactivation [41]. Experimentally, metal loading is carried out via a number of techniques including photodeposition [42,43], chemical reduction [44], and sputtering [45]. The first of these methods was suggested to result in selective loading of metal nanoparticles over (101) surfaces of decahedral anatase nanoparticles. However, careful consideration of transmission electron microscopy (TEM) and high-resolution (HR) TEM images of such loaded materials (Figure 5) does not lead to evident conclusion that only (101) surfaces are loaded and (001) surfaces are completely free from the metal nanoparticles. The latter method results in nonselective deposition of metal particles over TiO₂ surfaces.

Li et al. [46] constructed the simplest model of platinized TiO₂ by attaching a single Pt atom over the (001) surface. The Pt atom was bound to Ti and O atoms, forming 2.62 Å Pt–Ti and 2.05 Å Pt–O bonds. This structure undergoes strong changes as a result of chemisorption of molecular oxygen, hydroxyl group, or HCHO over the Pt atom or its surroundings. The strong changes might not be present in real Pt/TiO₂ catalysts because platinum is rarely loaded in the form of single atoms.

Schlexer et al. [47] used more advanced models containing 10 atoms of Ru or Cu attached to the (101) surface of anatase. The adsorption energy for the Ru₁₀ and Cu₁₀ clusters was found to be -735 and -350 kJ/mol, respectively, for stoichiometric TiO₂. Adsorption of CO₂ over the metal clusters resulted in some moderate changes in the structure of the metal clusters and their binding to the (101) surface. Adsorption results in CO₂ dissociation into adsorbed CO and O with a barrier of +76 kJ/mol for Ru₁₀/TiO₂. The presence of an oxygen vacancy at the periphery of the metal cluster leads to the stronger molecular adsorption of CO₂.

Schvval at el. [48] developed models consisting of Ag₄ clusters, attached to rutile (110) and to anatase (101) surfaces. Tetrahedral configuration of the cluster was found to be the most stable according to the DFT + U method used. The clusters were attached to oxygen atoms and injected charge into the TiO_2 surfaces.

A DFT + U-D3 investigation on the Pt₄/graphene and Pt₄/anatase (101) surfaces was reported recently and showed that the Pt₄/anatase material dissociates hydrogen almost without a barrier and there is spillover of formed hydrogen atoms onto the TiO₂ surface. The spillover results in the formation of surface OH groups.

Cu-loaded anatase particles are a good photocatalyst for CO₂ photoreduction with formation of CO [49]. A theoretical model was suggested for the photocatalytic cycle on Cu-loaded (101) surface of anatase, in which CO₂ adsorption at the Cu₄–TiO₂ interface is strong ($\Delta H_{ads} = -126$ kJ/mol) with

formation of carbonate. The most endothermic step is CO desorption ($\Delta H_r = +314 \text{ kJ/mol}$). Cu-loaded TiO₂ is a cost-efficient alternative to Pt-loaded TiO₂, which photoreduces CO₂ into CO and CH₄ [44].

Li et al. prepared anatase nanoparticles with a very high fraction of highly active (001) facets doped with fluoride anions [50]. After loading with Pt, these nanosheets demonstrated a quantum efficiency of 34% in hydrogen production, a rather high value. Introduction of oxygen vacancies (Vo) into the TiO₂ support improved the reductive properties of deposited Pd nanoparticles [51]. V_O were introduced into TiO₂ via calcination at 800 °C in Ar flow. As a result of the presence of V_O, the rate of electron transfer to adsorbed oxygen molecules increased significantly. The effect was attributed to the injection of electrons from the vacancies into the Pd nanoparticles, thus increasing the electron density required for the reaction. Similar effects were also applicable for photocatalytic reactions over metal-loaded TiO₂ having oxygen vacancies.



Figure 5. Microscopic images of anatase nanoparticles (**a**), of anatase nanoparticles loaded with Pt (**b**), with Ru (**c**), and with PtRu, and (**d**) using photodeposition. The insets in (**a**,**b**) represent the shape of the nanoparticles. The insets in (**c**,**d**) represent the size distribution. Reproduced from Reference [43] with permission; copyright (2018) Elsevier.

6. Adsorption over TiO₂ Surfaces

Adsorption is an important stage in catalytic and photocatalytic reactions, as well as in the operation of sensors. Important fundamental information about the adsorption complexes can be obtained experimentally, as well as by using quantum computations. Adsorption of organic compounds can modify the band structure of TiO_2 and induce visible-light adsorption. For example, a recent study by Barbierikova et al. [52] utilizing a small $(TiO_2)_8(H_2O)$ cluster showed that adsorption of 4-chlorophenol on TiO_2 P25 resulted in the formation of surface charge transfer complexes.

Currently, the majority of computational studies, including those on adsorption processes, utilize DFT functionals. However, semiempirical methods can also be used facilitating to work with much larger systems. A recent comparison of various DFT functionals, (CCSD(T), and the semiempirical methods PM6 and PM7), used to study adsorption of diethyl sulfide and thiophene over small TiO₂ clusters, showed that semiempirical methods provide correct but incomplete information, and the best method was found to be PBE0/6-31G(d) [53].

Geldof et al. studied the interaction of methylphosphonic acid with (101) and (001) surfaces of anatase [54]. This compound is of interest since it is one of the products of photocatalytic destruction

of organophosphorus toxic compounds. Adsorption can take place in mono- and bidentate forms over (101) surface and mono-, bi-, and tridentate forms over the (001) surface of anatase. The energy of adsorption over the (001) surface (-280 kJ/mol and -260 kJ/mol for bidentate and tridentate, respectively) was found to be much larger than for the (101) surface (-184 kJ/mol and -191 kJ/mol for monodentate and bidentate, respectively).

Quintero and Nagarajan [55] investigated the adsorption of the organophosphorus molecules dimethyl methylphosphonate (DMMP), sarin, and soman over rutile (110) surface in its clean, hydroxylated and hydrated forms, using a PBE functional. Figure 6 demonstrates the major findings of their study. In agreement with the results obtained for anatase surfaces [56], dissociative adsorption over clean rutile surface is thermodynamically unfavored. However, dissociative adsorption with cleavage of P–O bond over hydroxylated and hydrated surface is exothermic and does result in removal of the acute toxicity and volatility of such compounds.



Figure 6. Molecular and dissociative adsorption of dimethyl methylphosphonate (DMMP), sarin, and soman over (**a**) clean rutile TiO₂ (110) surface and (**b**) hydroxylated and hydrated rutile (110) surface. Reproduced from Reference [55] with permission; copyright (2018) Elsevier.

Rudshteyn et al. [57] considered adsorption of benzohydroxamic acid ($C_6H_5C(O)NCH_3(OH)$) over the (101) facet of anatase using DFT computations with a PBE GGA functional. The strongest adsorption was detected for monodentate binding, in which a dissociated OH group was connected to the surface Ti atom with adsorption energy of -53.5 kJ/mol. The highest occupied molecular orbital (HOMO) level in this adsorption complex was located in the organic adsorbate and, hence, the light absorption threshold was somewhat shifted to the visible-light region in comparison with TiO₂.

Setvin et al. [58] studied the adsorption of formaldehyde over a (101) surface of anatase using experimental and computational methods. Adsorption proceeds via the binding of the oxygen atom in formaldehyde to surface Ti_{5C} , and its energy was found to be -67 kJ/mol for the most stable configuration. Scanning tunneling microscopy (STM) was used for deducing the adsorption configurations experimentally. However, this value should be taken with some precaution since determining the positions of all atoms in adsorbed small molecules (such as HCHO) can be quite difficult.

A comprehensive study on the adsorption of acetone over adsorption sites on anatase nanoparticles with (001) and (010) exposed facets and on decahedral anatase nanoparticles with exposed (001) and (101) facets was undertaken recently [59]. The modern and precise semiempirical method DFTB, based

on DFT, was utilized to obtain the structure and energy of adsorption complexes. It was found that the adsorption energy over the (001) facet increased when the size of cubic anatase nanoparticles increased. A higher adsorption energy was found for the (101) facet compared to the (001) facet in the decahedral anatase nanoparticles. Interestingly, the adsorption energy also increased considerably when the (001) surface was hydroxylated by dissociative adsorption of water molecules. It was also discovered that, for the cubic nanoparticles, photogenerated holes were mainly localized over (001) surfaces, and electrons localized over (100) surfaces and in the bulk. For some of the adsorption complexes the electrons were localized over adsorbed acetone, while, for many others, they were not. The infrared (IR) spectra of the adsorption complexes were also studied. The DFTB method produced a very good agreement with the measured band gap and with the measured C=O IR peak (a theoretical value of 1784 cm⁻¹ versus experimental value of 1735 cm⁻¹). Adsorption of acetone resulted in spectral shift in the C=O peak from 1741 cm⁻¹ to 2027 cm⁻¹, i.e., both a downward and an upward shift were observed as a result of acetone adsorption. The shift was claimed to be related both to a strength change in the C=O bond and to a change in the reduced mass of the oscillator in different geometries of the adsorption complex.

Adsorption of NO and O₂ over a clean and hydrogenated (101) anatase surface was studied theoretically by Li et al. [60]. For the clean (101) surface, ΔE_{ads} was -47 kJ/mol and -19 kJ/mol for NO and O₂, respectively. Following hydrogenation, the adsorption was significantly stronger.

Oxygen vacancies play an important role in the processes of adsorption over TiO_2 surfaces, as was revealed in a recent study by Lang et al. [61]. While methanol tends to adsorb in a molecular form over intact (101) anatase surface, it adsorbs dissociatively and much more exothermically over oxygen vacancies. Adsorption was also found to stimulate migration of oxygen vacancies to subsurface atomic layers.

Nadeem et al. [62] reported that oxygen vacancies in the anatase (101) surface serve as sites for water dissociative adsorption. Here, the room-temperature formation of two hydroxyl groups over oxygen vacancies was confirmed by a theoretical study, as well as by STM.

Adsorption of heavy metals and other water contaminants is an important process for environment protection. Chen at al. [63] reported that adsorption of aqueous U(VI) at pH 5 was stronger over (001) facets compared to (100) facets and was the weakest for the (101) facets of anatase nanoparticles. Under UV irradiation, reduction of U(VI) into surface-bound compounds was observed. Adsorption of Pb(II) over a (101) surface of anatase was studied computationally by Zhang et al. [64]. The computed adsorption energy was -215 kJ/mol, which is very large, possibly due to the absence of any solvent in the computational model. Liao et al. [65] studied adsorption of Pb(II) and Cd(II) over (001) and (101) facets of anatase using experimental and computational DFT methods (PBE GGA functional). They found a higher adsorption energy of these cations upon adsorption on the (001) surface: -250 kJ/mol vs. -227 kJ/mol for Pb(II) and -46 vs. -13 kJ/mol for Cd(II). This theoretical result was confirmed by experimental results showing higher tendency for adsorption of metallic cations on nanoparticles having dominant (001) facets in comparison with nanoparticles having a high number of (101) surfaces.

Adsorption of dyes onto the surface of TiO_2 is a crucial stage in the fabrication of dye sensitized solar cells (DSSC). Gao et al. [66] recently studied the binding of retinoic acid to TiO_2 experimentally and computationally. They identified three anchoring modes via which the carboxyl group is attached to the TiO_2 surface: bidentate binding to two surface Ti cations, bidentate binding to Ti and to surface O, and bidentate binding to surface Ti and to a surface OH group. Analogously to many similar studies, a very small and amorphous $(TiO_2)_{16}$ cluster was used for the theoretical study, which undermines the accuracy of extrapolation of the electronic properties to real TiO_2 nanoparticles.

An interesting application of anatase TiO_2 films is in the fabrication of resistive gas sensors. Liang et al. [67] prepared two anatase samples: one containing predominantly (010) facets and a second containing predominantly (101) facets. It turned out (see Figure 7) that the drop in resistance upon exposure to acetone vapors was approximately twice as large for the sample containing (010) facets, an indication of more efficient charge injection into the (010) TiO_2 surface upon oxidation at the sensor working temperature (320 °C).



Figure 7. Resistive sensor response for anatase films containing crystallites with (010) and (101) surfaces (**a**) at 100 ppm acetone concentration and different sensor temperature, and (**b**) at 320 °C and different acetone concentration. Reproduced from Reference [67] with permission; copyright (2018) Elsevier.

7. Doping of TiO₂ and Its Effect on Adsorption

The introduction of dopants into the TiO_2 lattice and on the surface can dramatically change the properties of the photocatalyst [68]. A wide variety of elements are used as dopants for titanium dioxide, including N, Sn, V, and Pt. Some of these dopants induced visible-light photocatalytic activity. Nitrogen doping via substitution of oxygen atoms seems to be the most widely studied [69]. It leads to intraband states close to the valence band and stabilization of oxygen vacancies. The basic nature of Mg^{2+} cations makes adsorption of acidic molecules like CO_2 much stronger, and this can improve the efficiency of photoreactions. Mg atoms can also serve as sites for reactive adsorption. Sasani et al. [70] studied, with a PBE functional, the Mg doping in the (101) facet represented by a $Ti_{32}O_{64}$ slab. They found that surface Ti_{5C} sites are more stable after substitution with Mg^{2+} compared to Ti_{6C} sites. Mg^{2+} sites tend to be placed as far as possible from each other.

Hiremath et al. [71] synthesized MgO–TiO₂ composites with different ratios of Mg to Ti in the range of 0–5. Formation of different phases such as MgTiO₃, MgO–MgTi₂O₄, and MgO–Mg₂TiO₄ was detected. The best phase for CO₂ adsorption was found to be MgTiO₃.

Shakir at al. [72] prepared Mg-doped TiO_2 films and applied them for constructing DSSCs. They discovered that Mg doping induced visible-light absorption via introduction of intraband energy levels. DSSCs utilizing doped TiO_2 demonstrated improved efficiency compared to DSSCs utilizing undoped TiO_2 .

Mg doping for anatase TiO₂ was demonstrated beneficial for the photocatalytic reduction of CO₂ into CO, CH₃OH, and CH₄ [73]. The mechanism of the Mg effect was investigated computationally. It turned out that Mg surface sites were accompanied by oxygen vacancies that served as sites for strong CO₂ adsorption (Δ H_{ads} up to -163 kJ/mol compared to about -21 kJ/mol for pristine TiO₂). This study hints at the design of most active photocatalysts at atomic precision since only a few specific doping sites possessed very high adsorption enthalpy for CO₂.

Sulfur is a prominent and widely occurring dopant in TiO₂. It is inherently present as a result of utilization of sulfur-containing precursors in the preparation of titanium. It may exist at the surface and in inner layers of TiO₂ particles, either in an anionic form (S^{2–}) or in a cationic form (S⁴⁺ and S⁶⁺). The simplest method of preparing cationically S-doped TiO₂ consists of calcination of TiOSO₄ at a temperature of 700 °C or lower [74]. Doping with sulfur was demonstrated to have a positive influence on the stability during calcination, on porosity, on nanoparticle size, and on the visible-light photocatalytic activity of anatase TiO₂ [75].

Due to the positive effects of sulfur doping, S-doped anatase was a subject of intensive experimental and theoretical research. Cationic doping of anatase with sulfur proceeds via substitution of lattice

titanium atoms with sulfur atoms. Such a substitution can result in narrowing of the material band gap since S(IV) orbitals contribute to the valence band [76]. In a recent study [77], a close-to-reality model of S-doped TiO₂ was suggested in which the anatase was represented by a cluster having a highly hydroxylated surface. This model is reminiscent of the real anatase materials prepared from titanyl sulfate and containing residual sulfuric acid or multiple sulfate groups in its surface layers. Using a theoretical DFTB method, it was demonstrated that, after cationic substitution in TiO₂, sulfur retains its geometry characteristic for sulfates (for S(VI)) or sulfites (for S(IV)). All possible locations of sulfur in the decahedral anatase cluster were evaluated. It turned out that surface doping was preferable compared to bulk doping. Doping with S(VI) resulted only in a very small decrease in the band gap, from 3.22 eV to 2.96 eV, while S(IV) doping resulted in visible-light absorption with E_g = 2.65 eV.

8. Dark Reactions over TiO₂ Surfaces

The adsorption of reagents is the first stage in the majority of catalytic reactions. This is also true for photocatalytic transformations. The surface of TiO_2 under atmospheric conditions contains undercoordinated Ti^{4+} , hydroxyl groups, adsorbed water, and other species. Therefore, adsorption over TiO_2 can result in retaining the molecular structure of the adsorbate or its partial destruction as a consequence of surface reactions, i.e., adsorption can be molecular or reactive.

Air purification from toxic compounds that might be present in low concentrations is one of the most important applications of photocatalytic oxidation. It is desirable that the toxic pollutants become much less toxic right after their adsorption, i.e., already before the photoreaction. This is attained for a number of air pollutants including chemical warfare agents (CWAs) and their non-toxic simulants.

The possibility of reactive adsorption was recently studied for the malodorous compound and CWA stimulant diethyl sulfide (DES) using quantum computations [78]. A 2-nm anatase TiO_2 nanoparticle, exposing (001), (100), and (010) facets, was taken. All possible adsorption sites were considered. It was found that molecular adsorption proceeded via coordinating the sulfur atom of DES to surface oxygen atoms. The adsorption enthalpy varied in the range of -25 kJ/mol to -159 kJ/mol. Dissociative adsorption was found exothermic only for (100) surface and resulted in $-SCH_2CH_3$ and $-CH_2CH_3$ fragments adsorbed to Ti and O atoms. Thus, anatase TiO_2 with a large fraction of reactive (100) surface seems to be beneficial for air purification devices.

For photoelectrochemical processes, of importance are the electron transfer reactions at the photoelectrode–electrolyte interface. Zhou et al. [79] prepared TiO₂ specimens containing predominantly (001) surfaces and calcined them at different temperatures. Increasing concentrations of oxygen vacancies upon elevating the calcination temperature were registered using Raman spectroscopy. A concept of a reductive interaction of oxygen vacancies with O₂ to form O₂⁻ was suggested to explain the higher current density for reactions of Hg(II) at the electrode. However, the detection of V_O defects was not conclusive since their concentration was very low.

9. Surface Structure Effects in Photoreactions over TiO₂

9.1. Clean Anatase TiO₂

The ridge atoms over the (1×4) reconstructed anatase (001) surface were recently demonstrated to play a decisive role in methanol photooxidation over a single crystal sample [80]. These ridges contain Ti_{4C} atoms, in contrast to Ti_{5C} atoms over the intact (001) surface. Such coordinatively unsaturated Ti sites were suggested to be the active sites for methanol photooxidation.

Anatase crystallites typically have exposed (101) and (001) surfaces. With proper preparation methods, some other facets can be obtained. The presence of a larger fraction of (001) facets is generally reported to result in a higher photocatalytic activity [81]. The preparation typically utilizes HF to decrease the surface energy of the (001) facet due to the strong Ti–F interaction. Therefore, the increased activity of anatase catalysts with a large fraction of the (001) facet is attributed to the presence of fluoride anions over this surface. Indeed, Lei and Lu showed that decahedral anatase nanoparticles

washed with NaOH to remove the surface fluoride anions possessed higher photoactivity of (101) facets compared to (001) facets [82]. However, the question remains how the presence of fluoride anions can improve photocatalytic activity. Chen et al. suggested that adsorbed F^- ions formed a electrostatic field that attracted photogenerated holes to the (001) surface [83]. This explained the higher activity in the photooxidation of NH₃ on anatase containing 95% (001) surfaces in comparison with samples that did not contain F^- and surfaces with lower fraction of (001), as well as with fluorinated (101) facets. The (001) surface also demonstrated a higher efficiency in a DSSC solar cell, sensitized with N719 dye compared to the (100) surface [84].

Unfortunately, a discrepancy between experimental data and theory with respect to the localization of photogenerated electrons and holes still exists. Experimental data on photodeposition of Pt and PbO₂ revealed localization of electrons over the (101) surface and holes over the (001) surface. Theoretical calculations usually predict localization of both charge carriers in (101) facets. The computational results of Ma et al. [85] also confirmed the higher photocatalytic activity in CO₂ photoreduction of (101) facets of anatase compared to (001) facets due to more favorable energy levels of electrons in the (101) facet. No fluoride anions were added to the (001) facet in their study.

Setvin et al. [86] carried out a study on methanol photoactivation over (101) surface of anatase, using STM, TPD, XPS, and DFT. They found that dissociative adsorption of CH₃OH with the formation of surface bound methoxy groups was a prerequisite for further photocatalytic oxidation reaction. The DFT calculation, done using a PBE GGA functional and Hubbard repulsion correction with U_{eff} = +3.9 eV for the Ti 3d orbitals, revealed that dissociative adsorption was energetically unfavorable. If it proceeds near a surface OH group, the dissociation becomes allowed and results in the formation of H₂O that desorbs from the surface. Experimental data also showed dissociative adsorption and formation of HCHO under UV irradiation at low surface coverages. At high coverages, above 0.5 monolayer (ML), methyl formate was the photoreaction product. The DFT computation of the phototransformation of CH₃O into HCHO found only a small energy barrier of 0.2 eV.

9.2. Oxygen Vacancies

Introduction of a high concentration of intrinsic defects into the TiO₂ surface is a method for improvement of photocatalytic activity together with sensitivity toward visible light. Substoichiometric titanium dioxide (TiO_{2-x}) can be obtained, for example, via reduction of TiO₂ or via calcination of metatitanic acid. Introduction of V_O in the bulk and in the surface of TiO₂ resulted in strong improvements of CO₂ photoreduction into CH₄ under UV or visible light [87].

 V_O is an inherent component of TiO₂ material since titanium dioxide is known to be an n-type semiconductor and almost always has a deficit of oxygen in its structure. It turned out that surface oxygen vacancies have an important role in photocatalytic reactions. In particular, reduction of CO₂ proceeds in the adsorbed state at surface oxygen vacancies V_O . Ji and Luo investigated such a reduction into CO and CH₄ over V_O in the (101) facet [88]. It was found that V_O considerably reduces the reaction barrier compared to adsorption and reaction over surface Ti atoms. Oxygen vacancies play a key role in the reaction of dark and photocatalytic decomposition of N₂O over anatase (001) and (101) surfaces [89]. Figure 8 demonstrates that such reactions lead to filling the vacancy and, thus, its regeneration is an obligatory stage for the good and lasting photocatalytic activity. Moreover, photocatalytic hydrogen generation from water is possible over surface-reduced TiO₂ without the addition of co-catalysts [90].

In line with these observations are the recent studies on photocatalytic reactions employing reduced TiO_2 . One of the methods to produce partially reduced TiO_2 consists of calcination at 200–400 °C in vacuum [90]. An observed gray coloration indicated partial reduction of TiO_2 . Visible-light photocatalytic activity in the degradation of tetracycline and RhB increased significantly when the vacuum calcination temperature was increased to 300 °C. However, Hou et al. [91] suggested from their studies on photocatalytic hydrogen production that only surface oxygen vacancies have a positive effect on separation of electron–hole pairs while single-electron-trapped oxygen vacancies (SETOV) in the bulk induce recombination of charge carriers. Surface oxygen vacancies were suggested to be

produced in vacuum calcination, while calcination of nanotubes in air produced SETOV according to ESR data. This result is in agreement with enhanced photocurrent and photocatalytic activity in H_2 generation observed with anatase TiO₂ that was reduced by ethylene glycol at 180 °C [92].



Figure 8. Decomposition of N₂O over an anatase (001) surface containing an oxygen vacancy. Reproduced with permission from Reference [89]; copyright (2018) The Royal Society of Chemistry.

Various co-catalysts can be used in order to improve the photocatalytic activity of TiO_2 , and this is one of the most often used approaches. Graphene was a very popular object of research in recent years, and its combination with TiO_2 and Pt nanoparticles was found to be beneficial for reactions of photocatalytic oxidation of volatile organic compounds (VOCs) [93]. In graphene-containing heterojunctions, graphene can act as electron conductor to the active sites in another co-catalyst or can serve as a reduction or oxidation electrocatalyst [94]. Questions arise as to the nature of interactions between graphene (GR), graphene oxide (GO), and TiO_2 and the causes for the improved photocatalytic properties of TiO_2/GR or TiO_2/GO composites. Figure 9 shows the structure of anatase–GR and anatase–GO interfaces. Experimentally, it was found that GR and GO loading can decrease the anatase band gap [95]. This decrease can be related to the formation of additional states associated with the interaction of TiO_2 and graphene.



Figure 9. Interaction with the (101) surface of anatase of graphene (**a**) and graphene oxide (**b**). Reproduced with permission from Reference [95]; copyright (2018) Elsevier.

Indeed, analysis of orbitals and their energies in a cluster model involving a decahedral anatase nanoparticle and a fragment of graphene sheet showed that their interaction resulted in additional intraband states, and these states could participate in the photoexcitation of the composite under visible light [96]. Such new states caused visible-light-stimulated methanol production from CO_2 at a rate comparable to that under UV irradiation. The study of Piskorz et al. [97] performed by DFT and

TD DFTB also points to the electronic coupling between TiO_2 clusters and reduced graphene oxide (RGO) sheets, resulting in the photogeneration of electrons in the RGO.

The photocatalytic activity of decahedral anatase nanoparticles could be further improved by loading a Co_3O_4 oxidation co-catalyst on an F-doped (001) facet and a Pt reduction co-catalyst on (101) facets [98]. A decrease in ineffective reaction barriers was obviously the cause for the almost 10-fold increase in H₂ photocatalytic production rate on Pt/TiO₂/Co₃O₄ compared to hydrogen production with TiO₂/Co₃O₄.

10. Transient Phenomena in TiO₂ as a Tool for Understanding Its Photocatalytic Properties

From the early days of photocatalysis, it was understood that studying the whereabouts of photoinduced charge carriers could be the key for understanding the photocatalytic properties of titanium dioxide. Measuring transient phenomena following excitation may provide the essential knowledge required for designing efficient photoactive materials, especially if combined with appropriate theory. Accordingly, most of the manuscripts reporting on transient phenomena in TiO_2 were published prior to this decade, but they are still relevant. For example, electron paramagnetic resonance (EPR) spectroscopy provided valuable information on the trapping of photogenerated electrons within the bandgap of TiO_2 , suggesting localization on Ti^{3+} centers [99], while time-resolved photocharge (TRPC) measurements yielded the lifetime of the charge carriers [100]. Another technique for measuring transient phenomena is time-resolved microwave conductivity (TRMC), based on measuring changes in microwave power reflected from samples following photoexcitation, thus providing values for the lifetimes of photoexcited electrons in different types of TiO_2 of different phases, particle sizes, and modifications [101].

A common technique to study the dynamics of photoactive materials is UV-Vis absorption/ reflection. Based on this technique, evidence was found that the photogenerated electrons tend to be trapped at Ti^{4+} centers, forming Ti^{3+} , the lifetime of which was determined by following the recombination with the holes and by the interfacial transfer to molecules adsorbed at the surface. Of large importance are studies of sub-nanosecond relaxation dynamics in colloidal sols of titanium dioxide, where transient absorption spectra in the visible region yielded important information on the dependence of electron localization (Ti³⁺) and surface trapped holes on the particles' size [102]. The same technique was used to locate two different types of hole traps in TiO₂: deep traps containing unreactive holes that exhibit absorption at 450 nm, and shallow traps containing active holes having very high oxidation potential [103]. In a similar manner, spectral resolution enabled following trapped states on the surface of TiO₂ by taking advantage of the fact that the absorption peaks of free OH and free O^{2-} are around 260 nm [104]. A recent review, summarizing transient UV absorption measurements on the trapping dynamics of photogenerated electrons and holes in titanium dioxide, presented a large diversity in the measured decaying timescales, as $t_{1/2}$ ranged from 50 fs to 50 ps for trapping, 1 ps to more than 20 ns for recombination, and 300 ps to 0.1 ms for interfacial charge transfer [105]. In general, a correlation was found between longer decay times of Δabs in transient UV absorption/reflection measurements and higher activities. For example, time-resolved emission quenching studies comparing different forms of titanium dioxide found an average decay constant of 1.99 ns for anatase and 1.65 ns for the less active rutile phase [106]. Likewise, it was found that decorating titanium dioxide with Pt islands, acting as electron sinks, extended the life time of trapped holes from the picosecond to the millisecond time scale, in correlation with the observation of higher activity [107].

The presence of trapped charges, whether at the bulk or at the surface of a photocatalyst, affects the potential that the neighboring atoms experience. As a consequence, it is reasonable to assume that the trapped charges are likely to affect the localized modes of vibration of the atoms in the vicinity of the trapped charge. The effects may include a change in the location of the vibrational levels in the energy scale and a change in the derivative of the dipole moment with respect to displacement [101]. The former is expected to be manifested by a shift in the frequencies of specific IR/Raman peaks, whereas the

latter may be manifested by changes in the intensity of specific peaks, since the (frequency-dependent) extinction coefficient depends on the transition moment, which is strongly affected by the derivative of the dipole moment. In addition to that, a positive drift of the whole spectrum (i.e., regardless of wavenumber) may indicate that absorption of the IR photons excites charge carriers into a continuous band rather than to discrete levels. Transient changes in the IR spectrum of titanium dioxide were measured using a dispersive approach, following excitation by a laser pulse at 355 nm. A fast increase (faster than 50 ns) in the absorption of the whole IR spectrum (1000–4000 cm^{-1}), followed by a gradual decay back to the pre-excitation spectrum within 100 ms, was observed by Yamakata, Ishibashi, and Onishi [108]. The observation that the increase in the IR absorption was non-specific indicated that the transition of photogenerated electrons into the conduction band was either in an intra-band manner or from shallow midgap trap states. By monitoring the effect of electron scavengers and hole scavengers, it was concluded that trapped holes and electrons were localized on the surface of the photocatalyst, whereas free electrons were distributed in the bulk. A considerable body of research was performed on Pt/TiO₂, both under vacuum and in the presence of water vapor [109]. Development of means for measuring transient changes in the IR spectrum at the sub-nanosecond time domain enabled differentiating between trapping at shallow traps (typical time = 15 ps) and trapping at unreactive deeper traps (typical time = 150 ps) in TiO₂ aerogels [110]. Quite counter-intuitively, no correlation was found between the number of electron trapping sites and the decay rate to the deeper traps. Moreover, the quantitative relationship between the activity (as probed by the photocatalytic degradation rate of dichloroacetate) and the transient behavior at the sub-nanosecond timescale was reported to be unclear.

11. Conclusions

It can be concluded that investigations on surfaces of clean, doped, and impregnated titanium dioxide comprise a vigorously developing research field. Theoretical computational methods deliver surface and nanoparticle structure designs that correspond to improved photocatalysts. Moreover, many findings in the field of photocatalysis can be used for the preparation of very active thermally activated catalysts. This is especially true for the effects of surface structure and dopants on properties of individual surface sites.

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