



Defective Dopant-Free TiO₂ as an Efficient Visible Light-Active Photocatalyst

Marcin Janczarek ^{1,*} and Ewa Kowalska ^{2,*}

- ¹ Faculty of Chemical Technology, Institute of Chemical Technology and Engineering, Poznan University of Technology, Berdychowo 4, 60-965 Poznan, Poland
- ² Institute for Catalysis, Hokkaido University, N21 W20, Sapporo 001-0021, Japan
- * Correspondence: marcin.janczarek@put.poznan.pl (M.J.); kowalska@cat.hokudai.ac.jp (E.K.)

Abstract: Pristine and modified/doped titania are still some of the most widely investigated photocatalysts due to its high activity, stability, abundance and proper redox properties to carry out various reactions. However, modifiers and/or dopants resulting in visible-light activity might be expensive or work as recombination centers under UV irradiation. It seems that defective titania, known as "self-doped" TiO₂, might be the best solution since it can be obtained under mild conditions without the addition of expensive materials and methods. This review discusses various methods of defective titania preparation, characterization of defect types, their localization (surface vs. bulk) and their function, as well as proposed mechanisms of photocatalytic reactions in the presence of self-doped titania. Although many kinds of defective titania samples have already been prepared with different colors, color intensities and defect kinds (mainly Ti³⁺ and oxygen vacancies), it is difficult to conclude which of them are the most recommended as the preparation conditions and activity testing used by authors differ. Furthermore, activity testing under solar radiation and for dyes does not clarify the mechanism since bare titania can also be excited and sensitized, respectively, in these conditions. In many reports, authors have not considered the possible influence of some impurities originated from the synthesis method (e.g., H, Al, Zn, Cl, F) that could co-participate in the overall mechanism of photocatalytic reactions. Moreover, some reports indicate that defective titania, especially black ones, might decrease activity since the defects might work as recombination centers. Despite some unproven/unclear findings and unanswered questions, there are many well-conducted studies confirmed by both experimental and theoretical studies that defective titania might be a promising material for various photocatalytic reactions under both UV and visible-light irradiation. Based on available literature, it could be proposed that optimal defects' concentration, the preferential role of surface defects, a higher surface-to-bulk ratio of defects in rutile than in anatase, and the beneficial impact of disordered surface are the most important aspects to be considered during the preparation of defective titania.

Keywords: defective titania; vis-response; heterogeneous photocatalysis; hydrogenated titania; oxygen vacancy; Ti³⁺; disordered titania

1. Introduction

Over the past 40 years, titanium(IV) oxide (TiO₂; titania) has been of great interest because of its exceptional properties as an efficient photocatalyst in the different types of reactions. Its important advantages are its good stability toward photocorrosion, positions of conduction (CB) and valence bands (VB) corresponding to redox potentials of various crucial chemical transformations (e.g., photooxidation of organic compounds, photocatalytic hydrogen generation and CO₂ photoreduction), low cost, and relative nontoxicity, which are the main factors contributing to its wide research interest [1–8]. However, the overall efficiency of photocatalytic processes based on titania can be hampered by the recombination of photogenerated charge carriers (electrons and holes) and the intrinsic



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). photoabsorption properties of TiO₂. The relatively wide bandgap of titania (3.0-3.2 eV) corresponds only to UV light absorption and, as a result leads to very small utilization of solar radiation (3-4%). Many attempts to improve the photocatalytic performance of titania by overcoming the above-mentioned functional limitations have been proposed. Most of these methods concern metal or non-metal modification/doping of TiO₂, and preparation of titania-containing heterojunction systems [9-20].

The introduction of external species to titania structure and the interaction between modifier/dopant and titania brings many challenges, such as intrinsic stability problems and the real possibility of commercialization of designed visible-light active photocatalysts. The development of semiconductors such as titania with structural defect disorders to introduce visible-light photoabsorption properties and subsequently provide corresponding photocatalytic efficiency in this irradiation range has been shown as a promising strategy. Numerous studies have shown that the introduction of defects such as oxygen vacancies or Ti³⁺ species might be responsible for the resultant properties of such prepared materials also described as a 'self-modified/doped titania' [21–82]. Furthermore, the presence of defects can also affect charge transport [83] and surface properties of semiconductor [25]. However, many studies have shown that the modification of photo-absorption properties (most often towards visible light) does not correspond in every case to photocatalytic activity improvement in the considered range of irradiation (the debatable example of black titania). Therefore, the origin of the enhancement of photocatalytic performance of titania-containing defects is still under discussion and requires clarification. In this review, a brief overview of defective TiO_2 has been carried out in relation to the abovementioned fundamental issues to provide the current knowledge and perspectives of defective materials.

2. The Types of Defect Disorders in Titania

The crystal imperfections, characteristic for solids, might be divided concerning the dimensionality of the crystal lattice: (i) zero-dimensional defects (known as point defects), (ii) one-dimensional defects (line defects), (iii) two-dimensional defects (planar defects), and (iv) three-dimensional defects (volume defects) [84]. The point defects are places where an atom is missing or irregularly placed in the crystal array. One-dimensional defects are recognized as dislocations (edge or screw). Planar defects can be divided into three groups: grain boundaries, twin boundaries, and stacking faults. In turn, 3D-defects can be described as aggregates of atoms or vacancies (precipitates, dispersants, and voids/cracks).

The point defects are present in any titania nanocrystal involving the following types: (i) oxygen vacancies, (ii) titanium interstitials, (iii) titanium vacancies, (iv) interstitial (e.g., hydrogen or nonmetal dopants), and (v) substitutional impurity (e.g., metal or nonmetal dopants) [25,66,85]. The formation of intrinsic defects (i)–(ii) can be described using the Kröger–Vink notation by the following example of defect equilibria (1) and (2) [26,85]:

$$O_O^x \leftrightarrow V_O^{\bullet \bullet} + 2e' + \frac{1}{2}O_2 \tag{1}$$

$$Ti_{Ti}^{x} + 2O_{O}^{x} \leftrightarrow Ti_{i}^{\bullet\bullet\bullet} + 3e' + O_{2}$$
 (2)

where:

 O_0^{x} — O^{2-} ion in the oxygen lattice site,

 $V_{O}^{\bullet\bullet}$ —oxygen vacancy,

e'—Ti³⁺ ion in the titanium lattice site (quasi-free electron),

 Ti_{Ti}^{x} —Ti⁴⁺ ion in the titanium lattice site,

 $Ti_i^{\bullet\bullet\bullet}$ —Ti³⁺ in the interstitial site.

As shown in Figure 1a, the removal of surface oxygen ion results in the formation of oxygen vacancy, whereas the consequence of the removal of two oxygen ions from the lattice is the formation of titanium interstitial, as presented in Figure 1b. Both formations

occur in reducing conditions. Taking into consideration the oxidizing conditions, oxygen adsorption triggers the formation of titanium vacancies (Equation (3)) [85].

$$O_2 \leftrightarrow V_{Ti}^{\prime\prime\prime\prime} + 4h^{\bullet} + 2O_O^x \tag{3}$$

where: $V_{Ti}^{'''}$ titanium vacancy,

 h^{\bullet} —O⁻ ion in the oxygen lattice site (quasi-free electron hole).



Figure 1. Formation of doubly ionized oxygen vacancy (**a**) and trivalent titanium interstitial (**b**): large and small circles represent lattice oxygen and titanium ions, respectively; black circles denote electrons and the square represents an empty lattice site. Reprinted with permission from [28]. Copyright 2011, American Chemical Society.

The existence of point defects is responsible for the formulation of structural rearrangements, which might cause distortions in the local symmetry of Ti octahedra, influencing the charge carriers' transport, thus affecting the efficiency of the photocatalytic process [66].

It must be emphasized that the correlation between oxygen vacancies and Ti^{3+} is complex. One can distinguish three cases of these relations: (i) the electric charges of Ti^{3+} species in TiO_2 can be balanced by oxygen vacancies $\rightarrow Ti^{3+}$ and oxygen vacancies appear/disappear simultaneously, (ii) besides Ti^{3+} and oxygen vacancies, a certain amount of structural defects are present \rightarrow inequalities between Ti^{3+} and oxygen vacancies occur, (iii) electric charges of Ti^{3+} species in TiO_2 are balanced by protons $\rightarrow Ti^{3+}$ has no direct connection with oxygen vacancies [86]. Furthermore, it is necessary to underline that the ionic defects are responsible for the formation of donor and acceptor levels in the electronic structure of TiO_2 (Figure 2) [26]. As one can see, the type of intrinsic defects determines the band configuration.

An important issue influencing the electronic properties of titania is the location of point defects. There are three main locations: (i) at the surface (first atomic layer), (ii) at the subsurface (crystal slab), and (iii) in the bulk of crystal [66]. Furthermore, an interesting and challenging point is the parallel formation of different types of defects, described as *defects pairing*. Its role in the explanation of photocatalytic mechanisms is often overlooked, mainly because of the difficulties in their proper characterization [66,87].



Figure 2. Band model of TiO₂ with the indication of the energy levels of intrinsic lattice defects: oxygen vacancies, titanium interstitials and titanium vacancies. Reprinted with permission from [26]. Copyright 2008, American Chemical Society.

3. Dopant-Free Defective Titania Nanomaterials—Preparation Strategies and Properties

The incorporation of defects into titania structure can be conducted by: (i) changes of the titanium-to-oxygen ratio and related concentration of point defects (self-modified titania), (ii) incorporation of higher- and lower-valence ions, forming donors and acceptors, respectively [28]. This review focuses on the first approach described as a dopant-free defective or self-modified titania.

3.1. Thermal Treatment in the Presence of Hydrogen Gas

The application of hydrogen to prepare the reduced, defective form of titania was introduced in the early works of Cronemeyer and Breckenridge [88,89]. Cronemeyer performed hydrogen reduction of rutile single crystals at high temperatures (e.g., 800 °C), obtaining blue-color samples. In the next work, the increased electrical conductivity in the reduced rutile crystals was described as the consequence of the ionization of trapped electrons in oxygen vacancies [90]. For the first time, in the case of hydrogen-reduced rutile, Chester found that lines in the electron spin resonance spectrum might be attributable to Ti³⁺ interstitials or oxygen vacancies [91]. Hasiguti and Yagi have proposed that electrical conductivity is connected with the presence of Ti³⁺ interstitials defects [92]. However, Sekiya et al. have suggested the dominant role of oxygen vacancies for hydrogen-reduced anatase [93].

It has been proposed that during hydrogenation, hydrogen reacts with the lattice oxygen to form oxygen vacancies and simultaneously one oxygen vacancy leaves behind two excess electrons [86]. The mentioned electrons can locate at titanium positions, and thus Ti³⁺ formation can also occur. Therefore, the type of defects (including their coexistence) is strictly dependent on the preparation conditions. As shown in the work of Liu et al., the setting of hydrogen-treatment temperature below 450 °C results in the appearance of only oxygen vacancies, whereas an increase in the temperature to the higher values is responsible for the coexistence of both oxygen vacancies and Ti³⁺ interstitials [94].

Yu et al. discussed the relation between types of defects, their distribution and hydrogenation conditions [95]. During the preparation of hydrogenated samples at 600 °C, a high concentration of Ti^{3+} was detected in the bulk at early stage of the process, and subsequently, their gradual transformation into surface oxygen vacancies has been observed with reaction progress. Therefore, the longer duration of thermal treatment under hydrogen causes the attenuation of Ti^{3+} and the increase of oxygen vacancies which produced O⁻ species as a result of oxygen presence at ambient conditions. Figure 3 shows the color changes of hydrogenated samples depending on the time of the thermal treatment.





Chen et al. prepared the novel black hydrogenated titania exhibiting solar-induced photocatalytic activity (related to methylene blue and phenol degradation, and hydrogen generation with Pt-particles presence as co-catalyst) [96]. They applied H₂-thermal treatment in high-pressure system (20 bar) at 200 °C for five days. In this case, the presence of mid-gap electronic states in the lattice of disordered titania structure was indicated as the main reason for observed photocatalytic behavior [96,97]. Wei et al. synthesized hydrogenated {001}-facets-dominated anatase nanosheets [98]. These materials showed higher UV/vis and vis irradiation-induced photocatalytic activity than pristine TiO₂. The presence of both oxygen vacancies and Ti³⁺ was detected, resulting in a significant bandgap narrowing [98]. Similarly, Naldoni et al. prepared black TiO₂ nanoparticles with specific crystalline core/disordered shell morphology and the significant bandgap narrowing (Figure 4) [30]. Oxygen vacancies were present in the bulk anatase crystalline phase, whereas the disordered surface was nearly stoichiometric.

In the other work, Lu et al. prepared defective titania nanomaterials by hydrogenation at room temperature under hydrogen with a pressure of 35 bar [99]. They used P25 as a staring material and found that titania powders treated under hydrogen for more than 15 days had a dark color and a crystalline-disordered core–shell structure. Liu et al. utilized titania nanotubes to prepare black, photocatalytically active material [100]. The hydrogen treatment was applied using different preparation conditions, e.g., under atmospheric conditions or high pressure. It has been stated that the high H₂-pressure annealing results in the temperature stable, Ti^{3+} -defect structure of anatase nanotubes with good photocatalytic properties towards hydrogen generation under solar radiation.

In contrast, Leshuk et al. obtained contradictory photocatalytic results for black TiO₂ prepared by high-temperature hydrogenation (up to 450 °C) under 20-bar H₂ for 24 h [101]. The deterioration of photocatalytic activity under sunlight irradiation of methylene blue solution for hydrogenated samples with an increase in H₂-treatment temperature was observed despite strong visible-light absorption. It has been proposed that the presence of vacancy defects is confined rather to the core of TiO₂ crystals than their surface, and, in this case, they behave as trap sites and charge recombination centers [101]. Similar conclusions were drawn by Liu et al. for the black and grey-colored titania samples prepared by hydrogenation [49]. The better photocatalytic effects were achieved for gray-colored titania, which means that photocatalytic activity (H₂ evolution) is not related to the optical absorption of TiO₂. It has been suggested that black titania obtained at higher temperature contains a higher concentration of Ti³⁺ defects that might act as recombination centers.

Therefore, the proper conditions for hydrogenation of titania (temperature, H_2 pressure, time of treatment) are very important to adjust the best ratio between different types

of defects. Though the presence of defects has been confirmed by experimental approaches in most of these studies, there is no information on the possible role of adsorbed/bound hydrogen. An unanswered question is how and if hydrogen participates in the overall mechanism, and thus the observed visible-light activity of these "hydrogenated" samples. Additionally, the use of dyes for visible-light activity testing does not guarantee the real vis response due to the competitive mechanism of titania sensitization by dyes. Moreover, in many cases the mechanism of visible-light activity of "self-doped" titania has not been discussed in detail. It should be pointed out that the bandgap narrowing also means lower redox properties, and thus inability to reduce oxygen by one-electron mechanism.



Figure 4. The comparison between the structure and density of states (DOS) of (**a**) P25 TiO₂ and (**b**) black TiO₂. Reprinted with permission from [30]. Copyright 2012, American Chemical Society.

3.2. Application of Other Reductants

Another approach to preparing self-doped TiO_2 without application of high temperature/pressure conditions, and thus with less energy consumption than H₂-gas hydrogenation, is to apply mild sources of hydrogen such as NaBH₄ [102]. The respective reactions are as follows [36]:

$$NaBH_4 + 8OH^- \rightarrow NaBO_2 + 8e^- + 6H_2O \tag{4}$$

$$\mathrm{Ti}^{4+} + \mathrm{e}^{-} \to \mathrm{Ti}^{3+} \tag{5}$$

Xing et al. successfully prepared self-doped titania nanoparticles by a simple onestep solvothermal method with NaBH₄ added as a reductant [32]. Self-modified titania samples had a good visible light photocatalytic activity in phenol degradation. The authors found the positive correlation between the activity and the concentration of Ti^{3+} and oxygen vacancies. Similarly, Fang et al. obtained self-doped TiO_2 samples through NaBH₄ reduction step with visible-light induced activity for Rhodamine B degradation [73]. It has been proposed that under visible-light irradiation of photocatalyst, electrons are excited to the impurity levels resulting from the presence of Ti^{3+} and oxygen vacancies. Moreover, it has been suggested that the life of the photoinduced electron in the oxygen vacancy trap is longer than that in the conduction band, which favorably reduces oxygen and produces a superoxide radical, thus enhancing photocatalytic activity [32]. An interesting approach has been proposed by Zuo et al., who developed the preparation method with in situ generated reducing gases (CO and NO) [27]. By the combustion of ethanol solution of titanium(IV) isopropoxide and 2-ethylimidazole at 500 °C in the air the blue powders are obtained. During combustion, the imidazole reacts with oxygen to form reducing gases that cause the reduction of Ti^{4+} to Ti^{3+} . Theoretical calculations and experimental results have confirmed the presence of Ti^{3+} defects and improvement of photocatalytic activity in the visible-light region.

Apart from gases, solid materials have also been proposed as a reductant. For example, Wang et al. prepared oxygen-deficient TiO_{2-x} by the application of aluminium [103]. The mechanism of reduction by alumina is attributed to sustaining low oxygen partial pressure from melting aluminum and releasing oxygen from TiO₂. TiO_{2-x} nanocrystals possess a unique core-shell structure of $TiO_2@TiO_{2-x}$, inducing significant enhancement of visible and near-infrared photoabsorption. In the other work, Cui et al. prepared black anatase TiO₂ nanotubes by the melted aluminum reduction of pristine anodized and air-annealed TiO₂ nanotube arrays [104]. In the reduction process, TiO₂ nanotubes and aluminum powder were heated to 500 °C and 850 °C for 4 h, respectively. The black anatase TiO₂ nanotubes have strong absorption ability from visible-light to near-infrared regions. Apart from aluminum also zinc has been used as a reducing agent. For example, Zhao et al. obtained gray-colored rutile by reduction with Zn in a solvothermal process, i.e., TiCl₃ aqueous solution in the presence of isopropanol and Zn is heated at 180 °C for 6 h [105]. The excess of zinc is removed by aqueous solution of hydrochloric acid. It has been observed that an increase in Zn amount applied to the solvothermal synthesis results in a stronger visible-light absorption of prepared powders.

3.3. Oxidative Treatment

In contrast to reduction methods, an oxidative treatment has also been proposed to obtain defective titania samples, e.g., oxidation of TiH₂. Liu et al. performed the oxidation of TiH₂ by H₂O₂ during hydrothermal treatment at 160 °C for 20–27 h, resulting in the preparation of titania powders with blue and light blue colors [31]. It has been proposed that the rice-shaped Ti³⁺ self-doped titania nanoparticles have been obtained, according to the surface oxide–interface diffusion–redox reaction mechanism (Figure 5).



Figure 5. (**A**) Scheme of the formation mechanisms for the rice-shaped Ti³⁺ self-doped titania nanoparticles. (**B**,**C**) The interface diffusion–redox diagram. Reprinted with permission from [31] Copyright 2013, The Royal Society of Chemistry.

Similarly, a successful approach was achieved by Grabstanowicz et al. for Ti^{3+} -self-doped rutile (black powders) prepared via solution-based oxidation of TiH_2 in H_2O_2 , followed by calcinations in Ar. [106]. The prepared samples possess high stability in the

air up to 180 °C and exhibit strong visible-light photocatalytic activity in the degradation of organic compounds in water. Another oxidative approach has been proposed by Pei et al. [107]. TiO₂ of grey color was prepared by facile hydrothermal treatment of titanium monoxide in HCl solution at 160 °C for 24 h. The presence of both Ti^{3+} and oxygen vacancies was reported.

Interesting method based on oxidation has been proposed by Kako et al., in which colorful (mostly yellow and pale yellow) rutile samples are prepared by heating Ti_2O_3 at 550–900 °C [35]. It has been proposed that the formation of Ti^{3+} -interstitial (Ti_i^{3+}) sites is mainly responsible for visible-light absorption.

3.4. Other Methods

Considering low-temperature plasma treatment, it is possible to reduce the surface layer of titania owing to the presence of high-energy electrons and atoms. Indeed, Nakamura et al. have obtained hydrogen plasma-treated TiO₂ containing oxygen vacancies with visible-light activity [22]. In the other study, Teng et al. prepared black TiO₂ by hydrogen plasma treatment, and band gap narrowing has been explained as a result of the synergistic presence of oxygen vacancies and Ti-H bonds [108]. Wang et al. proposed the black core–shell structure of TiO₂@TiO_{2-x}H_x, prepared also by hydrogen plasma method [109]. The enhanced solar light absorption of prepared samples has been explained by the existence of the amorphous shell inducing the localized surface plasmon resonance. It has been proposed that hydrogen treatment is responsible for the reduction of titanium (Ti³⁺ localized states), and thus improved photocatalytic activity.

It should be mentioned that most methods described above are based on the addition of other chemical species, e.g., hydrogen, chloride, zinc, alumina, etc., and thus their possible presence in the final product should be also considered. To avoid this problem, physical methods of titania modification have also been proposed. For example, Xiang et al. prepared defect-containing and highly air-stable titania samples using a low-temperature vacuum-activated method [75]. The obtained photocatalysts possess higher visible light activity in degradation of methyl orange and phenol than commercially available unmodified Degussa P25 titania. By EPR analysis, it was confirmed that three types of oxygen-vacancy states exist in the bandgap of vacuum-activated titania, i.e., O_v^{++} , $[O_v \cdot Ti^{3+}]^+$ and $[O_v \cdot Ti^{3+}]^0$ (Figure 6). It was found that neutral $[O_v \cdot Ti^{3+}]^0$ readily transforms to $[O_v \cdot Ti^{3+}]^+$ in the presence of O_2 and light irradiation. This transformation can move up the oxygen vacancy color center, resulting in a decrease in the visible-light response and decay of color [75].

In the other work, Xia et al. prepared vacuum-treated titania nanocrystals, which displayed long-wavelength optical absorption due to the existence of oxygen vacancies and Ti³⁺ defects, as well as possible surface structural disorders [110]. It has been proposed that both oxygen vacancies and Ti³⁺ defects might influence the photocatalytic activities in methylene blue decomposition and hydrogen generation. Interestingly, it has been concluded that oxygen vacancies positively influence the decomposition of methylene blue while harming the photocatalytic generation of hydrogen.

Dong et al. confirmed by the analysis of vacuum-activated P25 samples that their enhanced photocatalytic activity is attributed to the high separation efficiency of photogenerated electron-hole, caused by decreasing the ratio of bulk to surface oxygen vacancies [72]. Different strategy to apply vacuum to generate surface oxygen vacancies in titania has been proposed by Katal et al. [58]. Degussa P25 titania pellets were transformed by sintering at different temperatures (500–800 °C) under vacuum conditions. The color of pellets has changed from white to black, and the presence of oxygen vacancies and Ti³⁺ was confirmed. It was found that the density of oxygen vacancy influences the solar light-induced photocatalytic activity for acetaminophen degradation. Furthermore, it was stated that this density might be optimized for a sample, i.e., the higher density than the optimum value has a negative effect on the photocatalytic activity [58].

A promising approach is to combine the defect engineering with the facets' control, e.g., by the application of hydrothermal methods. Liu et al. obtained anatase nanosheets

with controlled defect locations exclusively in the bulk or on the surface by adjusting temperatures and HF amount during hydrothermal synthesis [111]. It has been proven that photocatalytic performance has a strong correlation with charges-participated surface reactions with the relation to the controlled defect locations. The TiO₂ {001} nanosheets exclusively with surface defects are more photocatalytic active than other photocatalysts with bulk defects.

The innovative strategy to obtain defective titania material is the application of γ -ray radiation [112]. The γ -ray reduction has interesting advantages over traditional reduction methods, i.e., no required strict controlled experimental conditions, mostly independent on temperature, no need to require the addition of reductant substances. The γ -ray radiation at room temperature has been applied by Zhao et al., who obtained defective titania with both oxygen vacancies and Ti³⁺ defects, and good visible light-induced photocatalytic properties [112]. Another "green" approach to generate structural disorders in titania is to apply mechanochemical synthesis. For example, Wang et al. have used planetary ball milling apparatus to provide the milling in air or argon atmosphere [61]. It was proposed that the generated defects (V_O and Ti³⁺) are responsible for color change (yellow–milling at air atmosphere or gray–argon atmosphere) and visible-light photocatalytic activity.



Figure 6. Band structure model and color changing for vacuum activated TiO₂ and the illustration of its photosensitive property in the air. Reprinted with permission from [75]. Copyright 2011, The Royal Society of Chemistry.

4. Defect-Depending Photocatalytic Activity of Self-Doped TiO₂

As stated for the visible light-induced photocatalysis, the semiconductor materials utilized in this process should provide photoabsorption properties connected with the corresponding range of irradiation [9]. In the case of UV-active TiO_2 , the extension of the absorption into visible-light region can be achieved through different methods of modification by addition of modifier/dopant (e.g., metal or non-metal elements). Other approach is to focus on the modification of defect disorder that determines the related semiconducting properties of TiO_2 such as electronic structure and charge transport [28]. Among methods based on defect engineering; it has been proposed that the preparation

of modifier/dopant-free titania is a promising direction to obtain efficient visible-light active photocatalysts.

In the preliminary works on reduced titania, it was shown that a slight reduction of TiO_2 could modify an absorption spectrum towards visible-light region, including also infrared part of irradiation [89,90]. This statement was firstly correlated with photocatalytic activity by Nakamura et al. in 2000 [22]. They applied plasma treatment to prepare reduced TiO_2 with defective structure. The presence of oxygen vacancies was confirmed, and the electrons trapped on oxygen vacancies were detected under visible light irradiation. Interestingly, the clear correlation between the number of trapped electrons on oxygen vacancies and the removal rate of NO_x (the photocatalytic oxidation of NO to NO_3^-) was presented, as shown in Figure 7. Authors have postulated that the formation of the oxygen-vacancy states located between the VB and CB is crucial for the visible-light-induced photocatalytic activity (as shown in Figure 2).



Figure 7. The removal of NOx as a function of the saturated intensity of ESR signal at different wavelengths from the visible light region. Reprinted with permission from [22]. Copyright 2000, Elsevier.

In the important work by Kuznetsov and Serpone, the correlation between the occurrence of spectral bands in the absorption spectra of visible-light-active TiO_2 was discussed [21]. They concluded that the presence of absorption bands in the visible-spectra region of doped titania results from the reduction of TiO_2 , causing the formation of oxygen vacancies in the presence of an effective electron acceptors, which competes with Ti-related sites in the capture of electrons. Furthermore, it was stated that visible-light activity originates from the color centers associated with oxygen vacancies, while the spectral bands detected at longer wavelengths correspond to Ti-related color centers [21].

Zuo et al. prepared self-doped titania by the combustion method using ethanolic solution of titanium(IV) isopropoxide and 2-ethylimidazole [27]. Ti³⁺ centers were recognized by EPR analysis. The authors stated that the Ti³⁺ inside the bulk is responsible for the bandgap narrowing. Additional presence of oxygen vacancies has been described as an extra benefit for visible-light absorption. Moreover, the high concentration of V_O can break a selection rule for indirect transitions, causing an enhanced absorption for photon energy below the direct bandgap. The visible-light activity of prepared materials was confirmed in the reaction of hydrogen evolution [27].

The breakthrough research on defective titania was performed by Chen et al. in 2011 [96]. For the first time, black titania nanoparticles were prepared by thermal treatment under high pressure of hydrogen. The significant color change from white to black has involved the absorption in the near-infrared region. The exceptional visible-light activity for black titania is mainly connected with the presence of defects such as oxygen

vacancies [30,48,113,114]. However, in the case of black TiO₂, there is an important role of modified light absorption properties, which results from the introduction of lattice disorder and hydrogen impurities, causing bandgap narrowing to 1.54 eV by the incorporation of electronic states [96].

It should be pointed out that this findings by Chen et al., i.e., that introduction of a disordered surface layer in titania crystal has been beneficial for photocatalytic activity, was not entirely consistent with the accepted knowledge. The mostly considered statement was that the high crystallinity was the basic condition to avoid detrimental recombination effects [115]. It has been known that titania disordering occurs by reduction methods from the surface to the core. Therefore only a disordered outer shell was in contact with water (interface). It is in agreement with the work by Naldoni et al. [30] mentioned before, stated that oxygen vacancies are present in the bulk anatase crystalline phase (core), whereas the disordered surface (shell) is nearly stoichiometric (Figure 4).

The concept of the order/disorder junction system for the defective titania system was also studied by Zhang et al. [116]. They prepared selectively reduced/disordered photocatalyst based on Degussa P25. The strong reducing agent in superbase consisting of lithium in ethylenediamine was applied at the room temperature. The anatase phase was unchanged remaining white color, but the rutile one was fully converted into black titania. In consequence, the overall color of transformed P25 turned to blue. In opposition to anatase phase, the atomic arrangement of black rutile was strongly disordered. They tested blue P25 in a simulated solar light-induced photocatalytic generation of hydrogen. The following reaction rates of H₂ evolution were reported: 13.89 mmol $h^{-1} g^{-1}$ using 0.5 wt% of Pt (co-catalyst) and 3.46 mmol h^{-1} g⁻¹ without using any co-catalyst. The exceptional efficiency without Pt was ascribed to the internally separated electrons/hole through type-II heterojunction. Figure 8 shows the mechanistic differences between conventional black titania (core-shell) and the three-phase interfaces composed of ordered white anatase and disordered black rutile with open structures for electrolyte access. In the case of conventional black titania, the photogenerated electrons migrate out from the ordered core to the disordered shell via a tunneling process to achieve contact with water. When there is no electron acceptor (e.g., Pt) on the shell surface, the probability of charge recombination increases. A different situation is considered for blue P25 with water/order/disorder/water junction, where the efficient separation of redox sites for oxidative and reductive processes occurs (Figure 8) [116].



Figure 8. Proposed mechanism for charge separation and H₂ generation in conventional black TiO₂ (**top**) and blue P25 (**bottom**); green part: ordered TiO₂, gray part: disordered TiO₂. Reprinted with permission from [116]. Copyright 2016, Royal Society of Chemistry.

Liu et al. prepared different types of defective titania by hydrogenation procedure, resulting in gray, black-gray and black titania samples [49]. They found that gray-colored titania is more active than the black (H_2 production), concluding that the additional optical absorption in the visible range, induced by the reductive reaction conditions, does not correlate with the photocatalytic efficiency. Black titania shows several magnitudes higher concentration of paramagnetic Ti³⁺ states, which might act as recombination centers for charge carriers, mainly in the sub-band-gap range, and therefore might suppress visible-light photocatalytic activity [49]. These results confirm the statement that the photocatalytic performance of defective titania materials relies on the concentration and distribution of defects: oxygen vacancies or Ti^{3+} . In another research project, Tan et al. prepared colored (from light blue to black) defective titania nanoparticles by using NaBH₄ as a reductant [117]. Their results have shown that an optimum concentration of oxygen vacancies gives a maximum improvement of photocatalytic activity, beyond which the photocatalytic efficiency decreases. The darkest sample does not have the highest photocatalytic performance. The experimental results, together with theoretical calculations, indicated that the energy level of defective TiO₂ consists of two categories: first one is the conduction band tail owing to the presence of vacancy bands, and the second one is the valence band tail contributed from the crystalline phase transformation. Both categories imply a bandgap narrowing, a broad visible light absorption and the presence of disordered layer [117].

Kong et al. focused their efforts on an explanation of the influence of surface/bulk defects ratio on the photocatalytic activity [118]. They prepared titania samples with tunable bulk/surface defects by vapor-induced hydrothermal hydrolysis at different temperatures. It was experimentally confirmed that both surface and bulk defects are important for the efficiency of photocatalytic processes. A decrease in the relative concentration ratio of bulk defects to surface defects significantly improves the charge carrier separation and simultaneously enhances the photocatalytic performance. Similar observations were obtained by Yu et al. [95]. As mentioned in the previous section, they also analyzed the types and distribution of defects. The remarkable improvement of photocatalytic activity for TiO₂ sample hydrogenated at 600 °C has been reported. It was concluded that this phenomenon occurs because of a diffusion of bulk defects to the surface.

The role of surface defects such as oxygen vacancies has also been confirmed by Jiang et al. [119]. The V_O on the titania surface plays an important role in the adsorption of oxygen molecules interacting with Ti^{3+} sites or acts as electron scavengers (charge carrier trapping and prevention of recombination). In the study by Amano et al., the role of defects in the photocatalytic activity of rutile was discussed [45]. The most suitable temperature for hydrogen treatment to achieve the best photocatalytic efficiencies was found to be at 600–800 °C. The H₂ treatment at 500 °C created Ti^{3+} ions, whereas the annealing at 700 °C has increased the density of electrons in the conduction band, resulting in an improvement of the electrical conductivity of titania, which might play an important role in suppressing the fast recombination. Therefore, the hampering of the recombination effect in the defective TiO_2 might be caused by a high electrical conductivity and high degree of band bending [45].

In the other work, Sinhamahapatra et al. prepared black titania samples with good photocatalytic properties for visible-light assisted hydrogen production by magnesiothermic reduction [42]. They postulated that the balance combination of different factors such as the content of Ti^{3+} and V_O defects (surface/bulk) and recombination centers exist simultaneously with an optimized bandgap and band positions. The correlation between surface V_O and photocatalytic performance was also determined in the study by Chen et al. [81].

Different observation were performed by Leshuk et al. [101]. As shown in Figure 9, pristine, non-hydrogenated titania had better photocatalytic activity than all hydrogenated samples. With an increase in hydrogenation temperature the photocatalytic efficiency decreases. Furthermore, with a higher temperature of hydrogenation, stronger photoabsorption in the visible-light region was observed, i.e., from light yellow color for the sample

prepared at 250 °C to black color for that at 450 °C. Authors attributed this activity decrease mainly to the presence of oxygen vacancies in the bulk as a result of hydrogenation—the higher temperature, the higher is the content of V_O bulk defects. This localization of V_O defects means that the vacancies behave as trap states and charge recombination centers [101]. This is in agreement with the previous study by Kong et al. [118].



Figure 9. Photocatalytic oxidation of methylene blue under simulated solar light for nonhydrogenated ("Unhydrog.") and hydrogenated titania samples at different temperatures. Reprinted with permission from [101]. Copyright 2013, American Chemical Society.

An important aspect of the photocatalytic properties of defective TiO_2 is the role of the crystal phase. It has been shown, owing to theoretical calculations, that oxygen vacancies are more stable on the surface of rutile than anatase [120]. Furthermore, it was confirmed that defects introduce a gap state near the conduction band. In other work, based on first-principles density-functional theory calculations, the subsurface dominance of oxygen vacancies in anatase was found [121]. The latest paper of Wagstaffe et al. distinguishes the differences between the reduced rutile {110} and anatase {101} in relation to the photooxidation of carbon monoxide reaction [122]. The defective rutile possesses higher photocatalytic activity than the defective anatase due to the different locations of defects within the crystal structure, as shown in Figure 10. These results are in agreement with the above-mentioned theoretical works. In the case of anatase, the surface-to-bulk ratio is small, therefore the bulk defects are more important acting as charge traps. Then, a recombination rate increases and photocatalytic efficiency decreases.



Figure 10. Photocatalytic oxidation of CO on anatase (green) and rutile (black). The graphs for the reduced surface are shown by dotted lines, whereas the graphs for the stoichiometric surface are indicated as solid lines. Reprinted with permission from [122]. Copyright 2020, American Chemical Society.

A different situation is observed for defective rutile, where a significant defect concentration is on the surface. Therefore, any charge trapped by these defects will be held at the surface and made available to participate in the reaction, which influences the inhibition of the recombination effect. Furthermore, some of the surface defects will immediately be eliminated by exposure to oxygen and will no longer act as charge traps [122].

Another factor influencing the photocatalytic efficiency of defective TiO_2 might be the titania structure arrangement. Lan et al. prepared black TiO_2 samples based on ordered mesoporous microspheres [60]. They utilized a compatible reducing agent (2ethylimidazole) to introduce it into the mono-micelle assembly process. Such type of reductant also plays the role of a building block of mesostructured frameworks and, in situ, reduces Ti^{4+} to generate defects during calcination.

Finally, the coexistence of bulk Ti³⁺ defects and ordered mesostructured has been found. Interestingly, the optimal amount of reductant influencing Ti³⁺ defects concentration were established to prepare the most active sample for solar-induced hydrogen production and dye degradation. It was stated that the 3D has opened mesoporous alignment comprehensively access to the reactive solution and provided an effective transport pathway, while the stable Ti³⁺ defects enable narrowing the bandgap for extended light absorption simultaneously, improving charge carriers separation [60]. Another interesting approach was performed by Xin and Liu [74]. They combined the well-ordered inverse opal structure of titania and chemical hydrogenation to prepare black TiO₂ inverse opals. It was found that after hydrogenation, the inverse opal morphology had not changed (Figure 11), but the visible-light-induced photocatalytic activity improved significantly in comparison to white inverse opal titania and P25 [74].



Figure 11. (**A**,**B**) FE-SEM, (**C**) TEM, (**D**) HR-TEM images of black TiO₂ inverse opals. Reprinted with permission from [74]. Copyright 2015, Royal Society of Chemistry.

The promising direction of the design of defective TiO_2 for many photocatalytic applications is the combination of defect design with crystal facets' engineering. Single-crystalline titania with exposed crystal facets have been described in many research reports as a semiconducting material with an exceptional photocatalytic activity [123–128]. In the study of Liu et al. titania nanocrystals with exposed {001} and {101} facets, and {001}) or {101} dominated facets were prepared by a hydrothermal method with the usage of HF as a morphology controlling agent [47]. Subsequently, faceted nanocrystals with

defects were prepared by a solid-state method through NaBH₄ reduction. Taking into consideration the samples without introduced defects, the efficiency of photocatalytic CO_2 reduction was highest for the sample with co-exposed {001} and {101} facets due to the enhanced charge transfer separation between {001} and {101} interfaces. Comparing samples with defects and without defects, in each case, better photocatalytic activity was reported for defective samples. Authors have found that the applied reduction method (NaBH₄) have induced the formation of both surface and subsurface Ti^{3+} on the TiO_{2-x} {101} and surface/subsurface/bulk Ti^{3+} on the $TiO_{2-x}\{001\}$)- $\{101\}$) but only surface Ti^{3+} on the TiO_{2-x} {001). It was concluded that the presence of co-exposed {001} and {001} facets and point defects could provide more active sites, better charge separation efficiency by the existence of {101}-{001} surface junction, and finally, the extension of visible-light response due to the presence of defects [47]. In the latest work, Liu et al. synthesized self-doped anatase nanosheets with co-exposed {001} and {101} facets, with different percentage of exposed {001} facets by hydrothermal method [111]. The obtained samples have possessed different locations of defects. A sample with 70% content of exposed {001} facets is the most active in the photocatalytic H_2 evolution under solar-light simulated irradiation.

It has been suggested that the presence of only surface defects could be responsible for the highest activity of this sample. Different from bulk defects, surface defects might play the role not only as charge-carrier traps but also adsorption sites. Simultaneous trapping of charges and adsorbed species at the same surface defects might enhance the efficiency of photocatalytic processes. The reaction mechanism of photocatalytic generation of hydrogen over self-doped faceted anatase nanosheets is shown in Figure 12. The existence of {001}-{101} surface heterojunctions causes the migration of photogenerated electrons to {101} surfaces to mediate the surface reduction reactions to produce hydrogen, whereas the photogenerated holes tend to migrate to {001} facets to initiate the surface oxidation reactions of methanol. A high density of surface defects might improve the dissociative adsorption of water into surface OH groups, facilitating the formation of surface H-bonding network and, subsequently, the hydrogen production rate [111].



Figure 12. Photocatalytic reaction mechanism of photocatalytic H₂ generation in methanol/water solution over self-doped anatase nanosheets with exposed {101} and {001} facets. Reprinted with permission from [111]. Copyright 2021, Elsevier.

5. Summary and Conclusions

The concept of visible-light-induced photocatalysis is still mainly based on modified or doped titania. Modification usually means the use of metal or non-metal elements or preparation of heterojunctions with different materials. However, so-called 'self-doping' is also promising option. This approach is equated with defect engineering. With proper design, it is possible to prepare photocatalysts with exceptional visible-light activity, even driving co-catalyst-free hydrogen evolution (without the use of noble metals). However, there are also research reports about defective titania-based materials without beneficial photocatalytic properties, also suggesting a detrimental effect of defects on the overall performance. These discrepancies are due to the application of different methods of introducing defects (e.g., hydrogenation, chemical reduction, or vacuum treatment), including various modification parameters (e.g., the temperature of annealing or H₂ pressure). The application of different defects' introduction conditions results in dissimilar defects' configurations including various types of defects and variety of their distribution. At this point, it is important to emphasize the role of proper characterization of defects using techniques such as EPR and XPS. There are also some papers, in which this characterization and the corresponding discussion are incomplete, and thus the drawn conclusions do not fully support the research hypothesis. Moreover, it should be pointed out that the modification methods and chemical species used for the preparation of defective titania, e.g., H, Cl, F, Al, Zn, etc., could also influence the final product (e.g., impurities as additional dopants/modifiers), and thus influencing the overall activity and the mechanism of photocatalytic reactions.

However, there are only several studies that consider this aspect. Moreover, dyes (commonly tested in these studies) are not recommended to be used for photocatalytic activity measurements under visible-light irradiation because of competitive titania sensitization by dyes. Additionally, the activity testing under natural or simulated solar radiation does not allow to discuss the mechanism of photocatalytic reactions on defective titania samples since unmodified titania is also excited under these conditions. Furthermore, in many cases, the mechanism of photocatalytic reactions under visible-light irradiation has not been discussed in detail. Many authors have not considered that the bandgap narrowing also means lower redox properties, and thus, the inability to perform some reactions, e.g., one-electron reduction of oxygen in the case of titania excitation from VB to defective sites (below CB).

Despite some unproven/unclear reports/findings and unanswered questions, there are many well-conducted studies indicating that defective titania might be promising materials for various photocatalytic reactions under overall solar radiation. Based on the available literature, one can formulate the following guidelines relevant to prepare visible-light active photocatalysts based on defective titania:

- The existence of optimal defects' concentration—stronger photoabsorption properties in the visible-light range does not directly mean higher photocatalytic activity, as charge carriers' recombination effect on defect sites exists;
- The preferential role of surface defects in comparison to bulk defects was shown;
- The surface-to-bulk ratio is higher for rutile than anatase (the role of crystal phase);
- The beneficial impact of the disordered surface layer of titania should be clarified.

Furthermore, the promising direction to design self-doped TiO₂ with extended potential of application is the combination of defect architecture with crystal facets engineering.

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