Recent advances of black TiO₂ for production of hydrogen and other solar fuels

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Abstract: Abstract Text, 800-1000 characters.

1. Introduction

Pristine TiO₂ is characterised by a white color and a wide band gap (3.2 eV for the anatase phase) that limits its light absorption capacity to only a small part of solar energy, in the UV region. Therefore, pristine TiO₂ can efficiently absorb only ≈4-7% of the entire solar spectrum, limiting its photocatalytic applications. In addition, the efficiency of TiO₂ is further limited by the recombination of the photogenerated energy carriers, i.e. electrons and holes ^[1]. Already at this point, one would think that TiO₂ is not the material of choice for photocatalytic applications. Instead, it is the most studied semiconductor since Fujishima and Honda reported on the photoelectrochemical water splitting with TiO₂ as the anode photoelectrode ^[2]. TiO₂ is an abundant, non-toxic, chemically stable and low cost semiconductor and apart from its use as a photo(electro)catalyst for water splitting ^[3], it finds applications in photo-degradation of pollutants in water ^[4], air cleaning ^[5], CO₂ reduction ^[6], dye-sensitized solar cells ^[7], photocatalytic sensors ^[8], cosmetic, self-cleaning paints, antibacterial agents ^[9], and batteries ^[10].

Several strategies have been developed in order to tune the energy band structure of TiO₂ and expand the light absorption capacity towards the visible region ^[11]. The most common strategy is to incorporate non-metal and metal elements in the crystal lattice and create impurity levels in the band gap of TiO₂ ^[12]. This strategy was introduced by Asahi et al. when N-doped TiO₂ red-shifted its light absorption response ^[13]. An enormous amount of reports were generated afterwards including the incorporation of, among others, non-metal elements; N, C, F, S ^[14], transition-metal elements; Mo, Ni, Fe, Co, Cr ^[15], noble-metal elements; Au, Ag, Pt ^[16], as well as co-doping with metal and non-metal elements; Fe/N, Mo/S, Mo/C, N/S, La/N ^[17]. Vast is also the literature on theoretical studies employing density functional

theory (DFT), reporting on the mechanism of the enhanced visible light absorption ^[18]. On the other hand, the impurity energy states induced by the incorporation of foreign elements may as well serve as recombination centers, undermining the photocatalytic performance of the doped material ^[13]. Coupling with other semiconductors of lower band gap have also been tried, including CdS, WO₃, Fe₂O₃ and BiVO₄ ^[19].

Recently, the colorful chemistry of TiO₂ has been revealed and colored TiO₂ materials have been developed, including yellow, green, brown, red, blue and grey of different shades ^[20]. The colorful chemistry of TiO₂ have been assigned to structural and electronic changes, including the formation of oxygen vacancies, reduction of the Ti⁴⁺ states to Ti³⁺, incorporation of Ti-H and Ti-OH species, formation of disordered layers on the surface, as well as due to modification of the electron density and bandgap narrowing. It was in 2011, when Chen *et al.* reported the black TiO₂ by high pressure hydrogenation, that unprecedented interest was triggered for intense research in black titania ^[21]. The optical absorption of black TiO₂ nanoparticles is extended to the infra-red (IR) region (approx. 1150 nm), while a core/shell crystalline/disorder structure is obtained on its surface. Both the photocatalytic activity, as well as the electronic conductivity in black TiO₂ are heavily improved and the synthesis of black TiO₂ by various methods and for various applications have evolved as hot areas in the current research perspective of TiO₂. In the literature, several valuable reviews are available summarizing the different synthetic routes and applications of black TiO₂ ^[22].

Summarizing the findings in the literature, the synthetic routes developed for the preparation of black TiO₂ films and powders are given in Figure 1 and include; hydrogenation under low/high H₂ pressure, reduction by Al, Mg, NaBH₄, CaH₂, NaH, chemical partial oxidation of TiH₂, Ti, Ti(II), electrochemical reduction, ultrasonication, plasma treatment, laser modification, proton implantation, ionothermal synthesis, N doping, self doping via gel combustion, Si quantum dot assisted chemical etching and oxygen removal via UV-irradiation ^[23].

The diversity and importance of black TiO₂ is highlighted by the large number of applications in photodegradation of organic compounds, photocatalytic and photoelectrocatalytic water splitting, dye-sensitized solar cells, Li, Na, Al-ion batteries, supercapacitors, solar desalination, fuel cell, field emission, microwave absorption and cancer photothermal therapy. Recently, black and defective TiO₂ has been also used for the reduction of CO₂ to solar fuels, as well as photofixation of N₂ to NH₃. Additionally, hydrogen generation through water splitting can be performed on black TiO₂, free of any cocatalyst loading, implying that the intrinsic catalytic properties of TiO₂ have been significantly improved towards the reduction of protons to hydrogen. In many cases, cocatalyst-free hydrogen production can also be considered as the intermediate product for the

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generation of solar fuels, highlighting the importance of black TiO_2 as a universal photocatalyst.

Figure 1. A summary of the different routes for the synthesis of black TiO_2 nanomaterials. Reprinted with permission from [23]. Copyright 2018 Wiley VCH.

Given the promise of these new developments, this mini review focuses on the latter two aspects of cocatalyst-free hydrogen and solar fuels production. We hope that this article will stimulate and encourage further modifications and discoveries, in order to improve the efficiency towards important chemical transformations based on cheap and abundant elements.

2. Properties of black TiO_2

Typically, black TiO_2 is produced by exposing nanoparticles of anatase TiO_2 to high pressure and high temperature hydrogenation (20 bar H_2 atmosphere at 200–500 °C for various time ranges). This results in reduced nanoparticles with a crystalline core and an amorphous shell that absorbs visible light. The enhanced absorption range in black TiO_2 is related to the presence of surface defects such as hydroxyl groups, oxygen vacancies and Ti–H bonds, and the creation of mid-gap energy levels within the band gap. Several studies have been devoted to clarify the crystalline core–amorphous shell structure of TiO_2 nanoparticles with TEM/HRTEM. Xia et al. reported the crystal structure of white TiO_2 with uniform lattice fringe distance of 3.536 Å [24]. Instead, black TiO_2 nanocrystals showed a crystalline core (3.515 Å), and an amorphous outer layer with highly distorted adjacent lattice planes (e.g. 6.747 Å, 4.203 Å, 2.983 Å).

In white TiO_2 (Figure 2a) the band gap is the result of a valence band from O 2p orbitals and conduction bands formed by Ti 3d orbitals. The current explanation for the structure/property relations in black TiO_2 is that when TiO_2 is exposed to reducing agents (for instance H_2) a large number of defects (and surface lattice disorder) may form as oxygen vacancies in the valence band (VB) and localized Ti^{3+} sites at the conduction band (CB) (Figure 2b), instead of Ti^{4+} of the perfect anatase (Figure 2a) [18b]. The resulting unpaired electron (polaron, $\text{P}^\cdot$) are responsible for the substantial change in electrical conductivity of TiO_2 . The energy of the defect states will lie within the band gap E_{gap} (forming

additional mid-gap energy levels), leading to enhanced optical absorption, until the higher agglomeration of defects at the surface of black TiO_2 will pile-up the defects states in the band gap (Fig. c) and induce the absorption of all visible light [25].

Figure 2. Defects responsible for the formation of colored centers and charge carriers in TiO_2 . The upper row shows the structure of the perfect anatase crystal, oxygen vacancies formation and the agglomeration of the defects at the surface of the nanoparticle. The low row shows the density of states in each crystal structure. Reprinted with permission from [22a, 25]. Copyright 2018 Nature Publishing Group.

3. Cocatalyst free H_2 photogeneration

The term cocatalyst-free H_2 production was introduced by Liu et al. when they went back to Chen and Mao's work on synthesizing black TiO_2 under annealing at high H_2 pressure [26]. The difference in Liu's approach was to anneal TiO_2 nanotubes for 1 h at 500 °C, while Chen did the annealing of TiO_2 powders at 200 °C for 5 days.

The authors chose to work with TiO_2 nanotubes for increased surface area. The optimized sample showed a stable H_2 evolution rate of $7 \mu\text{mol h}^{-1} \text{cm}^{-2}$ for several days, which was maintained when the same electrodes were used after one and two months of storage. Samples reduced under atmospheric pressure showed very little hydrogen production, as it can be seen in Figure 3a. This improvement of the intrinsic catalytic activity of the material is assigned by the authors to the formation of distinct Ti^{3+} defect sites, which are induced by the atmospheric reduction in hydrogen. The light reflectivity spectra show also the improved light absorption in the visible region for the reduced nanotubes (Figure 3b). It should be noted though, that this H_2 may not purely come from water splitting, but also from the protons released by the methanol photodegradation. It is expected that the photogenerated hydroxyl radicals can easily oxidize methanol, as such a case is widely proven by classic photocatalytic degradation of organic compounds [27]. The authors did not discuss the mechanism nor they reported any O_2 evolution rates.

Figure 3. a) Photocatalytic H₂ production, under solar simulated light, in a 50/50 vol% methanol water solution with TiO₂ nanotubes treated under different conditions. air: heat treatment in air at 450 °C, Ar/H₂: heat treatment in H₂/Ar (5 vol%) at 500 °C, Ar: heat treatment in pure Ar at 500 °C, HP-H₂: heat treatment in H₂ at 20 bar at 500 °C, Sci ref: Conditions as in [21a]. The inset shows optical images of the different samples. b) Integrated light reflectance curves of the air, HP-H₂ and H₂/Ar treated TiO₂ nanotubes. Reprinted with permission from [26]. Copyright 2014 American Chemical Society.

The same group used the high-energy proton implantation technique with the aim to similarly activate the TiO₂ nanotubes (Figure 4a) [28]. They studied the effect of the nanotube length and compared the results with proton implantation in single crystal anatase wafers, with preferred crystal orientation towards the [001] plane (Figure 4b inset). In the case of the nanotubes, the implant zone extended to approx. 1.2 μm from the top surface and the lattice defects caused by the implantation to approx. 800 nm, while in the case of the single crystal these were 350 nm and 200 nm, respectively.

The results showed that the implantation process activated the top surface of the material and a maximum rate of H₂ evolution of approx. 14 μL h⁻¹ cm⁻² was achieved in the 12 μm long TiO₂ nanotubes (Figure 4b). Again the hydrogen production was from an aqueous solution of methanol and the O₂ production rate was not discussed. The change in the intrinsic properties of the material in this case is assigned to the structural disorder induced by the proton implantation, as well as to the formation of paramagnetically active recombination states close to the conduction band of anatase. These are again related to the formation of Ti³⁺ defects, which were also found in the high H₂ pressure treated material. A follow-up work of the same group, expanded the study on the effect of the ion implantation in relation to the preferred orientation of the TiO₂ crystal [29]. It is generally accepted that the [001] plane is more reactive than the [101] [30]. The main conclusion of this work supports the idea that structural disorder (defects, exposed high index planes) is crucial for the

intrinsic activation of the TiO_{2-x} surface for metal-free H₂ production. Simple hydrogenation, which changes the absorption spectra of TiO_{2-x} is not enough for photocatalytic H₂ production, therefore activation of the material does not necessarily coincide with the black color.

Figure 4. a) High-energy proton implantation strategy and activation of the surface of the TiO₂ nanotubes for photocatalytic metal-free H₂ production. b) Photocatalytic H₂ production, under solar simulated light, in a 50/50 vol% methanol water solution with TiO₂ nanotubes of different lengths. For comparison purposes the inset shows the photocatalytic H₂ production under similar conditions in a (001) anatase single crystal before and after ion implantation. Reprinted with permission from [28]. Copyright 2017 American Chemical Society.

Another way to introduce structural defects, as well as Ti³⁺ electronic states by lattice damaging, is by mechanochemical methods such as dry ball milling [31]. Such a well-established method has the advantage of low temperature synthesis and easiness in preparation and handling, compared to high temperature and pressure treatments. Zhou *et al.* studied the effect of ball-milled commercial TiO₂ nanopowders in the presence of TiH₂ as the H₂ source. The authors found that an optimum concentration of 2% TiH₂ and 15 min of ball milling gave an activated sample, which produced H₂ with a photocatalytic rate of 220 μmol h⁻¹ g⁻¹ (Figure 5a). The proposed mechanism is illustrated in Figure 5b. The authors proposed that the TiH₂ introduced OH-groups in the lattice of TiO₂, stabilizing such donor states close to the conduction band (approx. 0.2 eV below). The TEM analysis also indicated the presence of an amorphous shell layer, which is typical for black TiO₂ treated under H₂ atmosphere. Longer ball milling times increase the amorphous shell layer leading to reduced reactivity of the nanomaterial, due to extended growth of the amorphous phase (Figure 5c-e).

Figure 5. a) Photocatalytic H₂ production, under solar simulated light, in a 50/50 vol% methanol water solution with a commercial anatase TiO₂ nanopowder treated under different amounts of TiH₂. b) Charge transfer process mechanism under illumination of the defective nanopowder. c, d, e) TEM images of the untreated nanopowder, after 15 min of ball milling and after 4 h, respectively. Reprinted with permission from [31]. Copyright 2016 John Wiley & Sons, Ltd.

Liang *et al.* recently compared the photoelectrochemical performance for water splitting of pure and hydrogenated amorphous TiO₂ [32]. The main aim of this work was to study the effect on the optical and catalytic properties of the amorphous shell, which is a characteristic feature of black TiO₂. A 280 nm film of amorphous TiO₂ was prepared on fluorine-doped tin oxide (FTO) glass substrate by pulsed direct magnetron sputtering from an TiO₂ target. The hydrogenated film, which appeared blue, was prepared in one-go during the sputtering process by introducing a H₂/Ar gas mixture in the chamber. The amorphous nature of the TiO₂ films was confirmed by TEM analysis, as it can be seen in Figure 6a.

Figure 6. a) TEM images of the undoped and blue amorphous TiO₂ films. b) Absorption spectra of the undoped (a-TiO₂) and blue amorphous TiO₂ (a-TiO₂:H) films. The inset shows optical photos of the films. Reprinted with permission from [32]. Copyright 2017 Elsevier.

The authors proposed a model to explain the color change (Figure 6b), and according to it the extended mid-gap states have a band tail, which merges with valence band of the amorphous TiO₂ (Figure 7a). Regarding the improved photoelectrochemical activity the H-doping passivated the recombination centers, while at the same time it introduced shallow donors in the form of H substitutional for oxygen and H interstitial. The amorphous doped-TiO₂ film showed a photocurrent density of 0.67 mA cm⁻² at 1.23 V vs NHE under solar simulated illumination (Figure 7b). It should be mentioned that neither any hydrogen or oxygen production rates are given, nor the stability of the material under water splitting conditions.

Jiang *et al.* suggested an alternative route in order to stabilize oxygen vacancies in reduced TiO₂ by the presence of carbon layers [33]. In their synthetic strategy, Jiang *et al.* formed gray single-crystal TiO₂ nanorods and the appearance of carbon layers was induced by trace amounts of precursor solutions used for the synthesis of TiO₂ (butyl alcohol generated from the hydrolysis of tetrabutyl titanate).

Figure 7. a) Proposed electronic energy band diagrams of the undoped (a-TiO₂) and blue amorphous TiO₂ (a-TiO₂:H) materials. b) Photoelectrochemical performance of the undoped (a-TiO₂) and blue amorphous TiO₂ (a-TiO₂:H) films under solar simulated light. The photocurrent-potential curves were recorded in 1 M NaOH solution in a three-electrode configuration with Pt as the cathode and Ag/AgCl as the reference electrode. Reprinted with permission from [32]. Copyright 2017 Elsevier.

The authors argued that the carbon layers create a favorably reductive atmosphere for the stabilization and concentration increase of oxygen vacancies. The material rich in oxygen vacancies is confirmed by electron spin resonance (ESR) spectra, where the signal at $g = 1.995$ (proportionality factor) indicates the high concentration of oxygen vacancies (Figure 8a). TEM analysis revealed in this case also, the formation of an amorphous shell layer, which surrounds the single crystal TiO₂ nanorods. Diffuse reflectance measurements showed the red-shift in the light absorption behavior of the material by 0.23 eV (Figure 8b). Photocatalytic hydrogen production tests in a triethanolamine/water solution showed a maximum hydrogen evolution rate of 69.7 $\mu\text{mol h}^{-1}$ for the sample treated under H₂ atmosphere at 500 °C for 2 h, at normal pressure conditions (Figure 8c). The optimized material was stable when stored in air for at least six months, as it can be seen by the H₂ production test in Figure 8d. In this work the oxygen evolution rate, if any, is not reported, a fact that seems to be neglected in general.

Figure 8. a) ESR spectra measured at room temperature for the air-treated and reduced single-crystal TiO₂. b) Diffuse reflectance spectra of the air-treated and reduced single-crystal TiO₂. c) Photocatalytic H₂ production in a triethanolamine/water solution under solar simulated illumination of samples prepared at different annealing temperatures for 2 h. The variety of samples include hydrogenated P25 (Hy-P25), hydrogenated anatase (Hy-anatase), air-treated sample at 500 °C (Air-500) and firstly air-treated followed by hydrogenation sample (Air-Hy-500). d) Photocatalytic reuse of the Hy-500 sample including an experiment after 6 months. Reprinted with permission from [33]. Copyright 2018 Elsevier.

The following article discussed in this section, although not directly linked to black TiO₂, highlights the importance of the disorder layers in cocatalyst-free H₂ generation ability of TiO₂-based nanomaterials. Such a modification is directly linked to the amorphous shell layer found in black TiO₂. Cho *et al.* induced the selective positioning of a disordered layer between the anatase and rutile phases in P25. This heterojunction boosted by approx. 11 times the H₂ production compared to Pt-loaded conventional anatase and rutile single heterojunction TiO₂ systems [34].

Figure 9. a) Schematic presentation of the defect engineering process. b) XRD spectra of the different samples during the engineering process, highlighting the change in the rutile peak. c-e) TEM images of the different samples during the engineering process. Reprinted with permission from [34]. Copyright 2018 American Chemical Society.

The synthetic route followed by the authors is schematically given in Figure 9a. The P25 is treated in a solution of Li/ethylenediamine (Li/EDA), which induces the disordering of the rutile phase, selectively. The partial oxidation of the sample recrystallizes the bulk rutile phase, keeping the disordered outer layer (Figure 9b-e). Apparently, such a heterojunction activated the P25, which showed a cocatalyst-free photocatalytic H_2 production rate of approx. $4 \mu\text{mol cm}^{-2} \text{h}^{-1}$ in a methanol containing solution. The Pt-loaded P25 showed a rate of $0.35 \mu\text{mol cm}^{-2} \text{h}^{-1}$. This work further highlights that selective defect engineering in the same material can significantly alter the intrinsic properties and lead to improved photocatalytic activities.

Chatzidakis *et al.* developed an approach for the determination of the intrinsic catalytic activity of nanostructured semiconductors, by decoupling any effects due to surface area [35]. In this approach, the charge transfer resistance (R_{ct}) is multiplied by the double layer capacitance (C_{dl}), which is proportional to the surface area. Both parameters can be obtained by electrochemical impedance spectroscopy at the potentials of interest. The $R_{\text{ct}}C_{\text{dl}}$ product, with units ΩF , is an indicator of the intrinsic catalytic activity of the material and can be regarded as the time constant of the associated reaction. The lower the $R_{\text{ct}}C_{\text{dl}}$ value the faster the kinetics. We believe that such an analysis can shed light on defining a true catalytic boosting, excluding the effect of increased surface area.

4. CO_2 photoreduction and N_2 photofixation with black TiO_2

The reactivity of oxygen vacancies and Ti^{3+} species has been recently connected to process beyond H_2 generation that are even more energy demanding, such as CO_2 reduction [36] and NH_3 synthesis from activation of the N_2 molecule. This development is of great importance for systems of artificial photosynthesis and generation of solar fuels. In this chapter a few recent and among the first reports are presented. As mentioned in the introduction, H_2 can be regarded in many instances as an intermediate product for the formation of other energy-rich compounds, such as alcohols and biomass [37].

Fang *et al.* prepared a TiO_2 photocatalyst, which contained an increased amount of Ti^{3+} species that were “protected” from oxidation, due to contact with air and water, by an amorphous surface layer of about 1–2 nm as it can be seen in Figure 10a [38]. In addition, they had control over the orientation of the exposed planes, (001) and (101), by changing the concentration of the fluoride anions in their synthetic route (Figure 10b). The (001) and (101) planes are functioning as hole and electron collectors, improving their separation. Moreover, such tunable morphology led to the selective reduction of CO_2 to CO and CH_4 .

Figure 10. a-b) TEM images of the optimized sample, $\text{TiO}_{2-x}-0.50$. c) XRD spectra of TiO_{2-x} samples treated with different volumes of HF. d) Photocatalytic CO_2 reduction to CH_4 and CO over the optimized and non-optimized TiO_{2-x} samples, under solar simulated light. e) Corresponding photocatalytic selectivity for CH_4 and CO. Reprinted with permission from [38]. Copyright 2017 The Royal Society of Chemistry.

The optimized sample contained 20% of the (001) planes (8,5

c) and the photocatalytic selectivity towards CH_4 was improved from 51.7%, which was in the sample dominated by the (101), to 83.4% (Figure 10d-e). Overall, the enhanced light absorption, improved charge carriers separation and preferential plane exposure led to a noble-metal-free CO_2 photoreduction on the surface of TiO_{2-x} .

Another work relating the effect of fluorinated TiO_{2-x} on the selective metal-free CO_2 photoreduction towards methane was presented by Xing *et al.* [39]. In this work, TiO_{2-x} mesoporous single crystals (MSC) were doped with F atoms. According to DFT calculations, the F atoms substituted oxygen vacancies in the lattice interval of TiO_{2-x} and due to F atoms' strong electronegativity, they attracted the electrons from the Ti^{3+} species, regenerating Ti^{4+} . As a result, an internal strong electrical field appeared, leading to the upsweep of Ti^{3+} impurity level, and to a stronger reduction potential of the material (Figure 11a). The higher selectivity of the fluorinated material was explained in terms of better kinetics, which allowed the fast reduction of the intermediate CO to methane (Figure 11b and c). The stability of the material was excellent, but it was assessed under continuous illumination for only 16 h.

Figure 11. a) Schematic presentation of the impurity band up-sweep due to fluorination of the MSC. b) Photocatalytic CH_4 production over different samples under solar simulated light and in the presence of CO_2 and H_2O vapor. c) Selectivity of the fluorinated MSC over the unmodified one. Reprinted with permission from [39]. Copyright 2018 American Chemical Society.

Apart from CO_2 photoreduction towards energy-rich compounds, NH_3 is also an indispensable chemical in modern society for the production of fertilizers and fibers [40]. Industry has an experience in handling and producing ammonia through the Haber-Bosch process for over 100 years. This process is extremely energy demanding as high pressures (>200 bars) and temperatures (>673 K) are required. In addition, large amounts of CO_2 are emitted due to the coupled steam reforming process of fossil fuels for the production of the intermediate H_2 . The following reports are not directly related to black- TiO_2 as presented so far, but the common link is the increased amount of oxygen vacancies and Ti^{3+} species. In the case of N_2 activation, it is also evident that it happens on these sites, where the N_2 molecule can be strongly adsorbed. Hirakawa *et al.* reduced in H_2 atmosphere, at 673 K for 2 h, a commercially available TiO_2 powder, which is not explicitly presented as hydrogenated or black TiO_2 [41]. The large amount of oxygen vacancies and Ti^{3+} was confirmed by ESR measurements and their activity is compared to that of TiO_2 surface-modified by noble metals (Ru, Pt and Pd). The bare, reduced TiO_2 produced 20 μM of NH_3 after 24 h, while the noble-metal loaded one produced less than 6 μM after 24 h. The proposed mechanism for N_2 activation and NH_3 synthesis is schematically given in Figure 12. The surface Ti^{3+} species serve as active sites for the adsorption and reduction of N_2 to NH_3 . The authors reported a solar-to-chemical conversion efficiency of 0.02%, which is an order of magnitude lower than that of natural photosynthesis (0.1%).

Figure 12. Proposed mechanism for N_2 fixation on the rutile TiO_2 (110) surface around the oxygen vacancies. Reprinted with permission from [41]. Copyright 2017 American Chemical Society.

Another way to induce oxygen vacancies in the lattice of TiO_2 is by electrochemical reduction at sufficiently negative potentials [42]. Zhang *et al.* followed this strategy on TiO_2 nanosheets deposited on Ti substrate and they operated the electrode at -0.7 V vs. RHE in 0.1 M Na_2SO_4 [43]. The authors confirmed with XPS the presence of increased amount of oxygen vacancies, which remained unchanged after 2 h of operation at this potential. The catalyst achieved a NH_3 production rate of $9.16 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$ with a faradaic efficiency of 2.5%. This high activity in the nitrogen reduction reaction is attributed to the enhanced adsorption and activation in the in-situ generated oxygen vacancies in the TiO_2 nanosheets. A closely related work is published by Yang *et al.* [44]. TiO_2 nanosheets are again employed and here the authors induce oxygen vacancies by thermal annealing at 350 $^\circ\text{C}$ in Ar atmosphere, i.e. reducing atmosphere. Moreover, the authors exploited the surface plasmon resonance of Au nanoparticles, where highly energetic holes, known as hot electrons are formed.

Figure 13. a) Schematic presentation of the plasmonic hot electron generation and N_2 reduction pathway. b) Illustration of the whole process on the surface of the modified photocatalyst. Reprinted with permission from [44]. Copyright 2018 American Chemical Society.

In this system, the oxygen vacancies adsorb and activate the N_2 molecules and the hot electrons act as the reducing agents, converting N_2 to NH_3 (Figure 13a and b). The apparent quantum efficiency of N_2 photofixation was 0.82% at 550 nm, which corresponds to the plasmon resonance of the Au nanoparticles on the surface of the TiO_2 nanosheets.

5. Summary and outlook

In this mini review we presented some of the most important cutting-edge research and progress on black TiO_2 , which is among the most promising photocatalysts that have been recently

discovered. A number of other related review articles are cited and we hope to provide a good database for further information and research on black TiO₂.

A consensus exists regarding the reasons behind its high photocatalytic activity, which is related to the disordered structure and the large amount of oxygen vacancies and Ti³⁺ species. These active centers change the intrinsic catalytic activity of TiO₂ and metal-free proton reduction, CO₂ photoreduction and N₂ fixation have been realized. Main concern regarding the stability of black TiO₂ is the oxidation of the Ti³⁺ species, as well as oxygen uptake. Some of the authors seem to take this into account and apart from reusing the material months after its synthesis, other novel approaches have also been developed, such as protective carbon or amorphous layers. On the other hand, there are reports where the stability is assessed over only a few hours of operation and post-mortem analysis is not conducted.

The topic opens several questions. It is evident that the main interest is in the surface disorder and defects, but there is little attention paid to the bulk of the material. For example, why a fully amorphous blue TiO₂ [32] has similar activity and improvement of its intrinsic properties after hydrogenation, with a typical core/shell crystalline/disordered black TiO₂ [31]? In addition, there are some contradicting findings; when the amorphous layer extended towards the bulk the catalytic activity of black TiO₂ was heavily compromised, but a fully amorphous material was highly active. Is there any phase transition that should be considered? How important is the thickness of the amorphous shell? Another concern is related to the absence of reports on the oxygen evolution reaction during cocatalyst-free water splitting. It is common to use the concepts of "open-circuit" and "cocatalyst-free" water splitting, but in fact, sacrificial compounds, such as methanol, are present during the photocatalytic process. It is

known that such compounds can act as scavengers of the photogenerated carriers, but is it confirmed that the produced hydrogen comes from water splitting itself? We think that labelled experiments with the use of isotopes can shed a better understanding of the mechanism involved.

Overall, the highly defective TiO₂ with its unique optical and intrinsic catalytic properties is a very promising material for practical synthesis of solar fuels. There is abundant room for further research and understanding of the underlying mechanisms of light absorption and surface chemical transformation. This review provides a short introduction to black TiO₂ and serves as a database for further studies and research. It also provides the latest trends and findings in the production of solar fuels and we hope to trigger new thoughts and developments not only from experts in this field, but also from researchers from various backgrounds and levels of knowledge.

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Keywords: black TiO₂ • defects • photocatalysis • hydrogen • solar fuels

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