

Review

A Review on Oxygen-Deficient Titanium Oxide for Photocatalytic Hydrogen Production

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Abstract: Photocatalytic technology based on the specific band structure of semiconductors offers a promising way to solve the urgent energy and environmental issues in modern society. In particular, hydrogen production from water splitting over semiconductor photocatalysts attracts great attention owing to the clean source and application of energy, which highly depends on the performance of photocatalysts. Among the various photocatalysts, TiO₂ has been intensively investigated and used extensively due to its outstanding photocatalytic activity, high chemical stability, non-toxicity, and low cost. However, pure TiO₂ has a wide band gap of approximately 3.2 eV, which limits its photocatalytic activity for water splitting to generate hydrogen only under ultraviolet light, excluding most of the inexhaustible sunlight for human beings. Fortunately, the band gap of semiconductors can be manipulated, in which introducing oxygen defects is one of the most effective measures to narrow the band gap of titanium oxides. This review considers the fundamentals of photocatalytic water splitting for hydrogen production over TiO₂, discusses the latest progress in this field, and summarizes the various methods and strategies to induce oxygen defects in TiO₂ crystals. Then, the next section outlines the modification approaches of oxygen-deficient titanium oxide (TiO_{2-δ}) to further improve its photocatalytic performance. Finally, a brief summary and outlook of the studies on TiO_{2-δ} photocatalysts for water splitting to produce hydrogen are presented.

Keywords: TiO₂ crystals; oxygen defects; photocatalysis; water splitting; hydrogen production



Citation: Chen, Y.; Fu, X.; Peng, Z. A Review on Oxygen-Deficient Titanium Oxide for Photocatalytic Hydrogen Production. *Metals* **2023**, *13*, 1163. <https://doi.org/10.3390/met13071163>

Academic Editors: José Gerardo Cabañas-Moreno, Alberto Moreira Jorge Junior and Karina Suarez Alcantara

Received: 18 May 2023

Revised: 15 June 2023

Accepted: 20 June 2023

Published: 22 June 2023



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1. Introduction

The exploitation and utilization of fossil fuels, such as coal, oil, and natural gas, facilitates the development of industrialization and urbanization. However, fossil fuels are non-renewable resources with limited reserves, which will certainly become scarce. In addition, the use of fossil fuels has dramatically induced negative effects on the ecological environment. For instance, carbon dioxide emitted during fossil fuel burning is one of the main greenhouse gases. The industrial by-products and wastes cause severe pollution to the environment. Some pollutants even harm human health by accumulating through the food chain [1,2]. Hence, it is necessary and urgent to develop sustainable energy to replace fossil fuels. Renewable energy sources, such as solar energy, wind power, and geothermal power, are being developed and widely used. However, the replacement of fossil fuels still remains elusive due to the restriction on techniques and the economy [3–5].

Among the many candidates, hydrogen energy is considered as one of the most promising energy carriers. Hydrogen is one of the most abundant elements on earth, and hydrogen energy can be obtained from a variety of natural resources. Moreover, hydrogen has superb combustibility, a high ignition point (585 °C), and a high heat of combustion ($1.42 \times 10^5 \text{ kJ} \cdot \text{kg}^{-1}$). Compared with most of the common fuels, it has unparalleled superiority (see Table 1). Additionally, the combustion product of hydrogen contains only water (see Equation (1)), while the burning of fossil fuels will produce a large quantity of carbon dioxide, sulfur oxide, nitrogen oxide, and so on, which are associated with a

series of severe environmental issues, including greenhouse effects, photochemical smog, and acid rain [6,7]. Comparatively, hydrogen is certainly a clean, efficient, and sustainable energy source with tremendous prospects for development. Nowadays, more than 95% of hydrogen in industry is produced from fossil energy, such as natural gas, petroleum, and coal. However, these traditional processes for hydrogen production have low efficiency and emit a large amount of exhaust gases such as carbon dioxide [7–9]. Producing hydrogen by water electrolysis is also an important method to prepare hydrogen on a large scale, but it will consume a large amount of electric energy [10,11]. Fortunately, the emergence of photocatalytic technology provides a new option for hydrogen production: producing hydrogen by photocatalytic water splitting. The abundant water resources and inexhaustible solar energy on Earth provide significant advantages for hydrogen production methods [12].

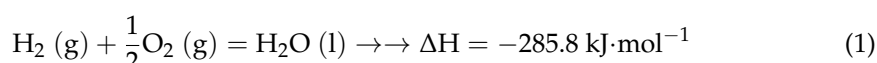


Table 1. Heat of combustion and ignition points of some commonly used fuels [13].

Fuels	Heat of Combustion (kJ·mol ^{−1})	Heat of Combustion (kJ·kg ^{−1})	Ignition Point (°C)
hydrogen	285.8	1.42×10^5	585
coal	-	$8.36 \times 10^3 \sim 3.06 \times 10^4$	300~700
gasoline	-	4.31×10^4	427
diesel	-	4.26×10^4	220
kerosene	-	4.31×10^4	80
natural gas	-	$3.89 \times 10^4 \text{ kJ} \cdot \text{m}^{-3}$	650
wood	-	1.2×10^4	200~290
ethanol	1366.8	2.97×10^4	12
methane	890.3	5.55×10^4	538
butane	2653	4.56×10^4	365
acetone	1788.7	3.08×10^4	465
graphite	393.7	3.28×10^4	~650

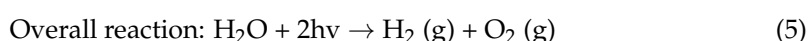
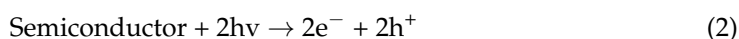
Photocatalysts are the key for producing hydrogen efficiently from the photolysis of water. In literature, TiO₂ was the first reported photocatalyst, which has been studied extensively and already applied in some specific areas due to its high photocatalytic activity, non-toxicity, good stability, low cost, and so on. Since the 1990s, the TiO₂ photocatalyst has made great progress in the fields of photodegradation of environmental pollutants and photocatalytic water splitting to produce hydrogen [14–16]. However, the utilization rate of solar energy by TiO₂ photocatalyst is very low due to the fact that TiO₂ can be excited only by short-wavelength ultraviolet light, which accounts for only approximately 5% of solar light. This drawback urges scientists to develop methods to modify TiO₂ photocatalysts which can be driven by visible light. Among them, ion doping, constructing heterojunctions, noble or transition metals decoration, dye sensitization, structural designing, and construction of oxygen defects have proven effective strategies [17–20]. In particular, the construction of oxygen defects is one of the most efficient ways to manipulate the band gap of titanium oxides. Literature surveys indicate that oxygen-deficient titanium oxide (TiO_{2−δ}) can absorb more visible light than stoichiometric TiO₂, and the formation of oxygen defects in titanium oxide could also enhance its electrical conductivity, thus facilitating the transfer of photogenerated electrons [21,22]. As a result, many TiO_{2−δ}-based photocatalysts with superb performance have been developed to generate hydrogen from water splitting [23,24]. In fact, oxygen defects are often consciously or unconsciously introduced into TiO₂ in various modifying processes. Hence, some approaches, including but not limited to ion doping, deposition of noble metals, and loading on supports, are often adopted to enhance the photocatalytic activity of TiO₂ jointly with introducing oxygen defects [25–29].

Therefore, in this review, the mechanism of photocatalytic hydrogen production by water splitting over TiO_2 is firstly discussed in detail. Then, the effect of introducing oxygen defects on the photocatalytic activity of TiO_2 is analyzed. The last part of this section provides a brief overview of the research progress in photocatalytic water splitting to generate hydrogen over $\text{TiO}_{2-\delta}$ -based photocatalysts. In Section 2, a variety of methods to introduce oxygen defects into TiO_2 are summarized, and their merits and shortcomings are analyzed. This will guide proper techniques to develop $\text{TiO}_{2-\delta}$ based materials. In the following Section 3, we will discuss the modification methods of TiO_2 photocatalysts in addition to the introduction of oxygen defects, such as ion doping, deposition of noble metals, dye sensitization, and so on, which are helpful for further enhancing the photocatalytic activity of $\text{TiO}_{2-\delta}$. Finally, the perspectives and existing challenges of photocatalytic water splitting into hydrogen over $\text{TiO}_{2-\delta}$ based photocatalysts are presented in the short section of Conclusions and Outlook.

2. Fundamentals of Producing H_2 by Photocatalytic Water Splitting over TiO_2

2.1. Mechanism of Photocatalytic Water Splitting to Generate H_2

Photocatalysis technology is based on the special energy band structure of semiconductors. In ground state, the valence band (VB) of a semiconductor is fully occupied by electrons and the conduction band (CB) is empty. There is a quantized and discontinuous band gap between the low energy VB and high energy CB. The band gap energy (E_g) of semiconductors is narrower than that of insulators (>5 eV). Therefore, the electrons in VB of a semiconductor can be excited and leap into CB when it is stimulated by photons with certain energy (higher than E_g), leaving the same number of holes in VB (Figure 1). Photogenerated electrons (e_{CB}^-) and holes (h_{VB}^+) possess strong reducing and oxidizing abilities, respectively, and will migrate quickly to the surface of photocatalysts to participate in redox reactions [30]. The photocatalysts can directly decompose water when they are suspended in water, which does not require a complex reaction system. Photocatalytic water splitting over semiconductors generally involves the following five steps: (i) water molecules are adsorbed on the surface of a photocatalyst; (ii) the electrons in VB leap into CB, producing e_{CB}^- and h_{VB}^+ under the irradiation by light; (iii) the photogenerated e_{CB}^- and h_{VB}^+ transfer to the surface of the photocatalyst; (iv) the e_{CB}^- reduces H^+ into hydrogen and h_{VB}^+ oxidizes H_2O to oxygen, which are commonly referred to as the hydrogen evolution reaction and oxygen evolution reaction; and (v) the produced hydrogen and oxygen are desorbed from the surface of the photocatalyst. Among them, steps II–IV are the rate-determining steps on the photocatalytic water splitting (see Equations (2)–(5)). As the O_2 dissolved in water will markedly compete e_{CB}^- with the hydrogen evolution reaction, sacrificial agent is added into the system to improve the photocatalytic efficiency. The commonly used sacrificial agents include EDTA-2Na, methanol, and so on. In those cases, h_{VB}^+ will be quickly captured by sacrificial agents instead of reacting with H_2O because a single-electron process usually is faster than an O_2 evolution reaction.



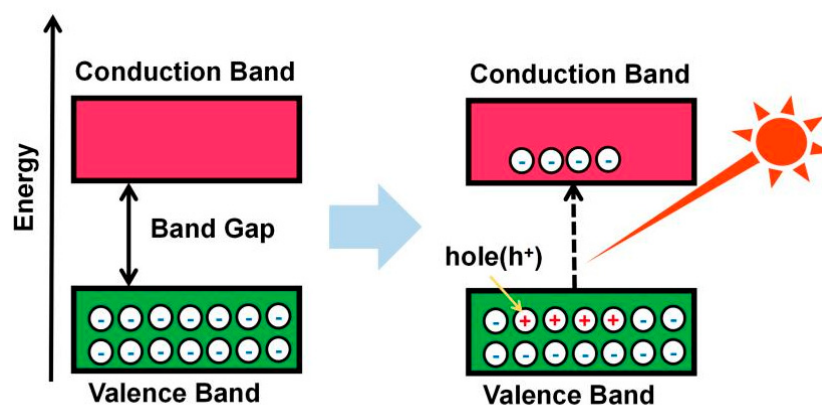


Figure 1. Schematic illustration of the energy band structure of semiconductors.

During photocatalytic water splitting, only the photons carrying energy greater than the E_g value of a semiconductor can excite the valence electrons into CB. As the E_g value of TiO_2 is approximately 3.2 eV, only ultraviolet light with a wavelength less than 380 nm can excite its valence electrons. Next, apart from moving to the surface of the semiconductor to participate in redox reactions, those excited electrons will also recombine with the holes, releasing light and/or heat energy. The recombination of e_{CB}^- and h_{VB}^+ is the deactivation process of the photogenerated carriers, which does not contribute to the photocatalytic water splitting and should be avoided as much as possible (Figure 2a). Moreover, the reducing ability of e_{CB}^- depends on the bottom of CB (CB minimum) and the oxidizing ability of h_{VB}^+ relies on the top of VB (VB maximum). The necessary conditions for photocatalytic water splitting are that the CB minimum is more negative than the reduction potential of H^+/H_2 (0 V vs. NHE at pH = 0) and the VB maximum is more positive than the oxidation potential of $\text{H}_2\text{O}/\text{O}_2$ (1.23 V vs. NHE at pH = 0). This requires an E_g value of no less than 1.23 eV, covering the oxidation-reduction potential of H_2O . In fact, the E_g value of photocatalysts for photocatalytic water splitting is generally required to be more than 1.9 eV due to the influence of mechanical and thermodynamic losses. Specifically, the CB minimum and VB maximum of TiO_2 are approximately -0.2 and 3 eV, respectively [31]. Therefore, TiO_2 can split water into hydrogen and oxygen efficiently through photocatalysis (Figure 2b).

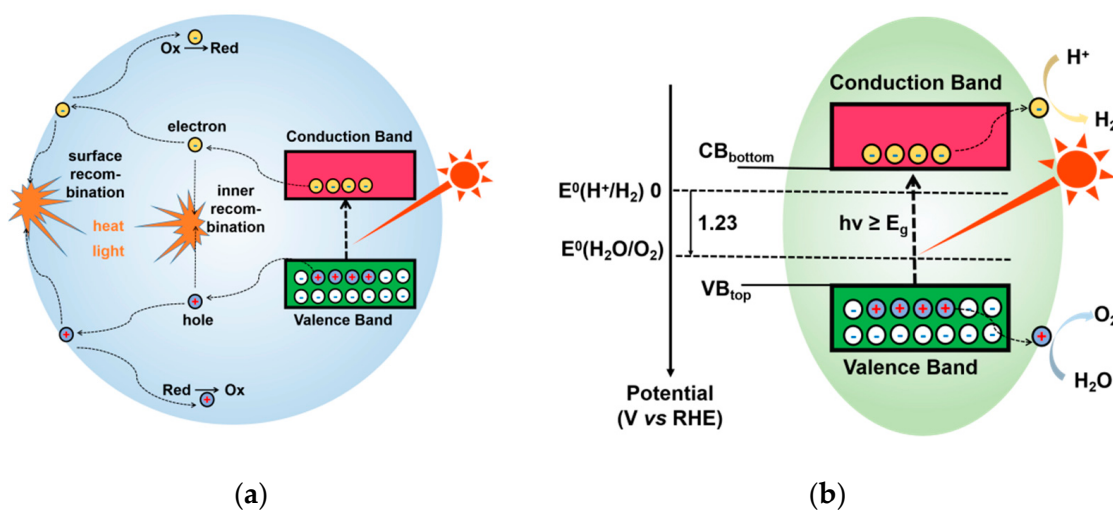


Figure 2. (a) Behavior of photogenerated carriers in a semiconductor. (b) Schematic illustration of the mechanism during photocatalytic water splitting over a semiconductor.

2.2. Impact of Oxygen Defects on the Photocatalytic Activity of TiO_2

As mentioned above, TiO_2 can only absorb ultraviolet light because of its wide band gap. However, a large proportion (about 50%) of the solar spectrum is visible light. Thus, enhancing the capability of harvesting visible light is an effective way to improve the photocatalytic performance of TiO_2 . In the literature, it was reported that the original white TiO_2 would be turned black after it was thermally treated with H_2 , indicating that the light absorption capability of the reduced TiO_2 (actually $\text{TiO}_{2-\delta}$) was significantly enhanced. Moreover, it has been proven that the light absorption spectrum edge of $\text{TiO}_{2-\delta}$ will shift to a long wavelength as the density of oxygen defects increases (Figure 3a) and the corresponding E_g decreases (Figure 3b) [21,32,33]. When there is an oxygen vacancy, one atom of oxygen in TiO_2 is bonded with three Ti atoms, and two redundant electrons are shared by the surrounding three Ti atoms (see Figure 3c). A portion of Ti^{4+} will be converted into Ti^{3+} after trapping the redundant electrons. The appearance of Ti^{3+} species in the nonstoichiometric $\text{TiO}_{2-\delta}$ is generally considered as the main reason that causes its absorption to visible light. Ti^{3+} species caused by oxygen defects can introduce new intermediate defect states (shallow donor) below the bottom of CB and modify the band gap structure of TiO_2 (Figure 3d), which means that $\text{TiO}_{2-\delta}$ has a narrower band gap and thus can absorb visible light [34–37].

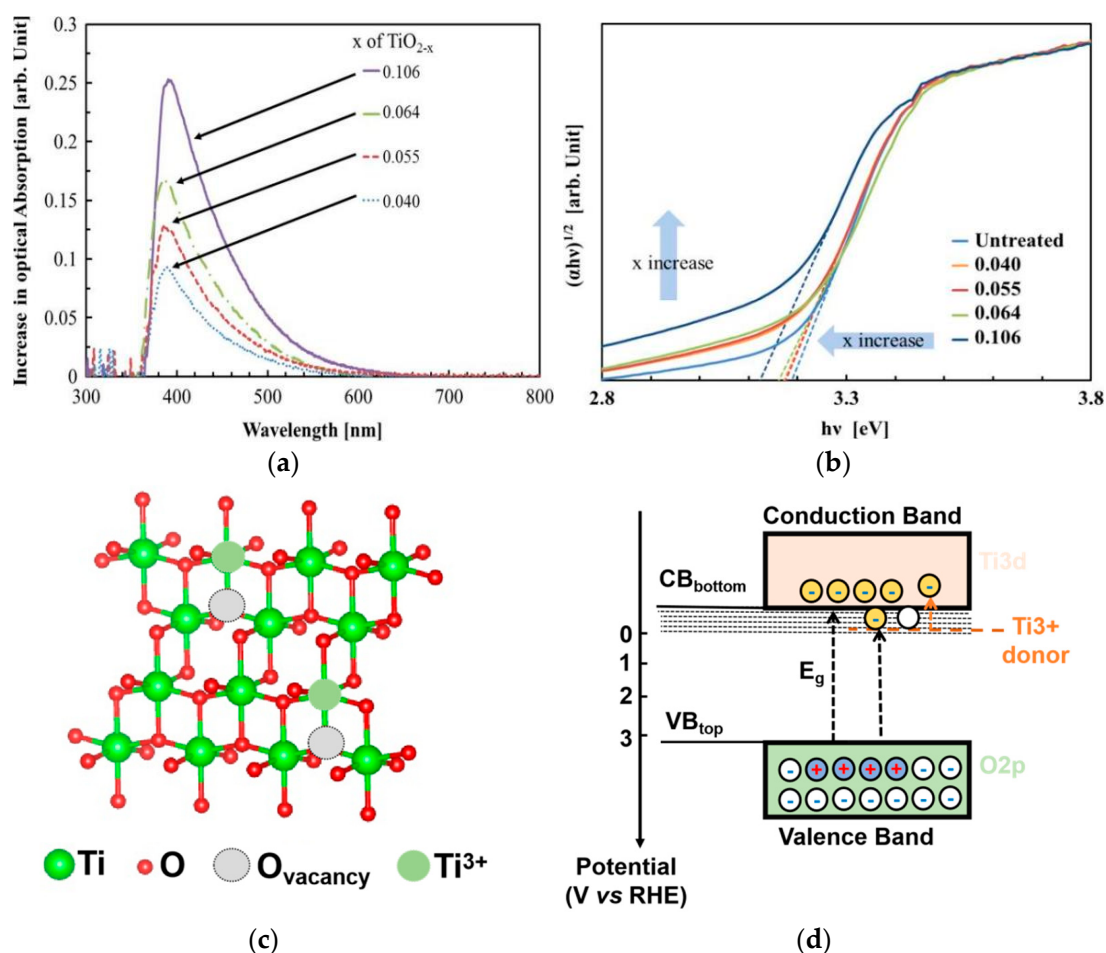


Figure 3. (a) Optical absorption of various TiO_{2-x} samples and (b) their corresponding band gaps [32]. (c) Illustrations on oxygen vacancy and (d) donor states owing to Ti^{3+} .

On the other hand, the presence of oxygen vacancies enlarges the lattice spaces of TiO_2 . As a result, the resistance to electron transfer will decrease. A low resistance for electron transfer is beneficial for the quick transfer of photogenerated electrons, thus suppressing the recombination of photogenerated e_{CB}^- and $h\nu_{\text{VB}}^+$ [38]. For example, Hao et al. [39]

prepared an oxygen-deficient blue titanium oxide, reporting that the prepared $\text{TiO}_{2-\delta}$ electrode would present a much lower charge transfer resistance (87 Ω) compared with its TiO_2 counterpart (356 Ω) [39]. Additionally, the bridging oxygen vacancies tend to cause the Ti 3d defect state in the band gap of TiO_2 . The Ti interstitials in the near-surface region can provide the electronic charges that the photocatalytic reactions need [40]. As a result, $\text{TiO}_{2-\delta}$ will present a higher photocatalytic performance than TiO_2 .

2.3. Brief Overview on Photocatalytic Water Splitting to Generate H_2 over $\text{TiO}_{2-\delta}$

Since the earliest report on light-driven water splitting by Fujishima and Honda in 1972 [41], semiconductor photocatalysis has attracted great attention in the field of catalysis. However, for quite a long period, semiconductor photocatalysis developed at a mild speed and many studies were focused on the photodegradation of pollutants [42,43]. After entering the 21st century, studies on semiconductor photocatalysis have grown explosively and quite a lot of photocatalysts with excellent performance have been developed [25,44]. In particular, although oxygen vacancy was reported to generate a defect state in the band gap of TiO_2 leading to a narrower band gap of $\text{TiO}_{2-\delta}$ in 1980s, $\text{TiO}_{2-\delta}$ -based photocatalysts were promptly developed and applied to water splitting until recently [45–47].

In earlier times, oxygen defects were often introduced into TiO_2 unconsciously during the modifying process, and it was then discovered that those titanium oxides with oxygen defects perform better on photocatalysis than those without oxygen defects. Therefore, researchers began to develop oxygen-deficient titania photocatalysts and explored the detailed mechanisms of how oxygen defects influence the photocatalytic performance of titanium oxides [37,48]. In 2008, Sasikala et al. [49] synthesized a series of Sn- and Eu-doped TiO_2 ($\text{Ti}_{1-(x+0.001)}\text{Eu}_{0.001}\text{Sn}_x\text{O}_{2-\delta}$, where $0.05 < x < 0.3$) nanoparticles, which showed an onset of light absorption at approximately 450 nm and high activity for hydrogen generation. Liu et al. [50] subsequently reported an oxygen-deficient anatase TiO_2 nanosheet with a dominant (001) crystalline plane, indicating that a special electron transfer process on the reconstructed surface of TiO_2 substantially enhanced the hydrogen evolution rate from photocatalytic water splitting. TiO_2 treated by H_2 at high temperatures also presented enhanced photocatalytic activity for water oxidation and high apparent quantum efficiency for O_2 evolution (41% under light irradiation at 365 nm) [51]. An electron-beam irradiated titania film shows a wider range of absorbed light and higher efficiency of hydrogen production owing to the oxygen vacancies or defects enhancing mobility and separation of electrons and holes [52]. Other oxygen-deficient TiO_2 samples can be obtained by using the ion layer gas reaction (Spray-ILGAR) technique, microwave induced reduction, and the solution plasma process. They show high photocatalytic hydrogen evolution activity [53,54]. In summary, many $\text{TiO}_{2-\delta}$ -based photocatalysts have been developed, but most of them are used to degrade pollutants and only a limited number of them are used to split water [22,23,27,55–57]. Among these limited reports, thermal treatment in hydrogen is the most widely used method of introducing oxygen defects in TiO_2 [22]. The introduced oxygen defects in TiO_2 are generally combined with other strategies, such as ion doping and composition with other semiconductors, to achieve high hydrogen evolution activity, which has been the focus of recent studies [47,58–61].

3. Methods of Introducing Oxygen Defects in TiO_2

3.1. Reductive Treatment

Reductive treatment is the most direct way to introduce oxygen defects in TiO_2 . TiO_2 can be reduced into $\text{TiO}_{2-\delta}$ by adding a proper reducing agent. Among the many reductants, H_2 is the most widely used option because of its strong reducing ability without introducing impurities [22,62–65]. However, H_2 treatment is usually carried out at high temperatures and the explosion limit of H_2 falls in a very wide range of 4.0–75.6 vol.%. In other words, the operation of H_2 treatment on TiO_2 is quite dangerous and requires very accurate processes. Moreover, treating TiO_2 with H_2 is usually a time-consuming task. For example, Xu et al. [66] reported black TiO_2 through H_2 treatment in a 20.0 bar of H_2

atmosphere at approximately 200 °C for 5 days. Zhang et al. [67] prepared defective $\text{TiO}_{2-\delta}$ hollow microspheres also by high-temperature H_2 reduction for 3 h at 550 °C. Wierzbicka et al. [68] synthesized a reduced “grey” brookite TiO_2 photocatalyst by hydrogenating it at 500 °C, showing a remarkable noble metal free photocatalytic H_2 evolution performance, substantially higher than that of hydrogenated anatase or rutile TiO_2 . The density of defects can be adjusted by tuning the H_2 treatment temperature, soaking time, and H_2 concentration. For instance, Samsudin et al. [69] put TiO_2 into a continuous flow of 1 atm of pure H_2 at 500 °C for different times, finally obtaining $\text{TiO}_{2-\delta}$ with different densities of oxygen defects. They indicated that with time of H_2 treatment, the density of oxygen defects increased, the color of the products becomes deeper from white to dark gray and to bluish gray (Figure 4a), and the light absorption ability of the resultant $\text{TiO}_{2-\delta}$ was significantly enhanced (Figure 4b). However, more defects do not always guarantee better photocatalytic performance. Here, the photocatalytic performance of TiO_2 hydrogen treated for 24 h is inferior to that of the sample treated for 12 h. This might be due to more defects acting as recombination centers of photogenerated carriers. Thus, the control of oxygen defect density in TiO_2 is also important. In addition, because treating TiO_2 with H_2 will not introduce other impurities, the shallow donor levels of Ti^{3+} are the major factor narrowing the band gap of titanium oxides. The increased electron density on the catalyst surface led by Ti^{3+} and oxygen vacancies is also beneficial for improving photocatalytic performance.

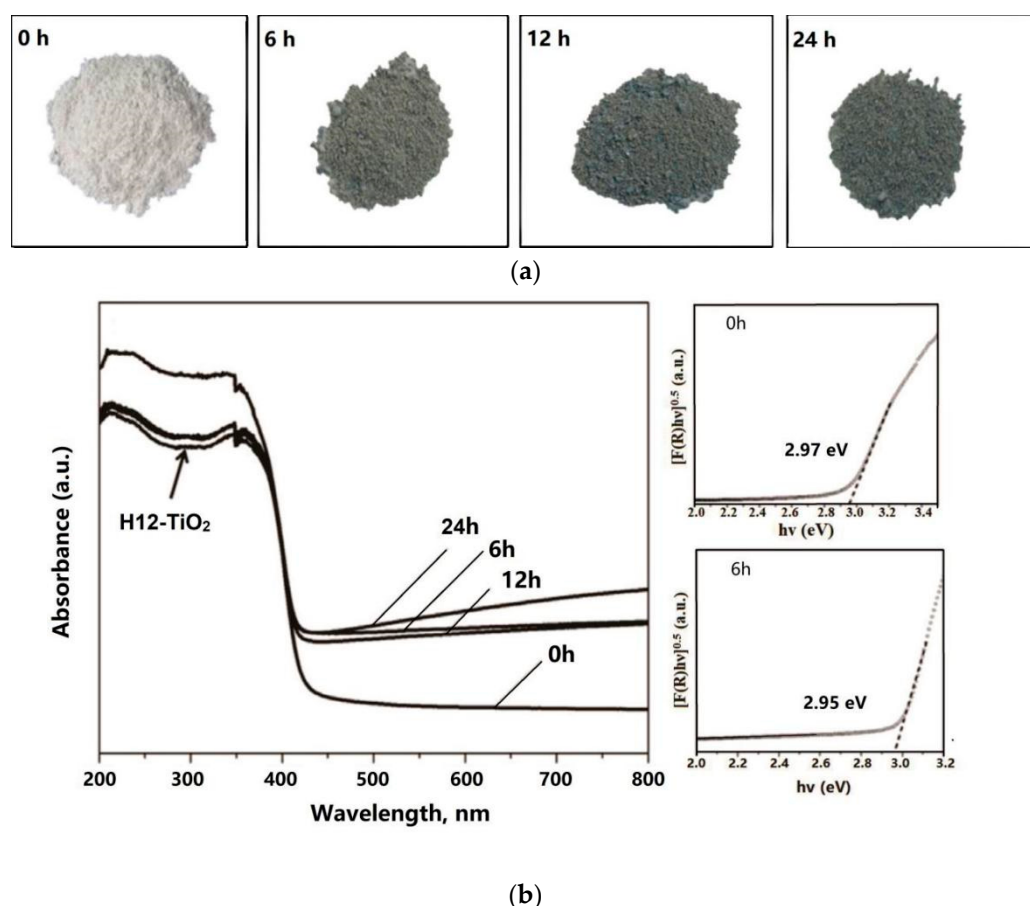


Figure 4. (a) Digital images and (b) absorption spectra together with K-M functions showing the calculated band gap interpolation for TiO_2 hydrogenated at different times [69].

Apart from H_2 , some other gases have been also used as reductants. For example, NH_3 is also often used to reduce TiO_2 . Chen et al. [56] synthesized a N-doped and oxygen-deficient TiO_2 photocatalyst by heating the commercially available pure TiO_2 in a NH_3 atmosphere at 550 °C for 5 h. It is easy to introduce N into TiO_2 (N doping) when using NH_3 as the reducing agent. Similarly, Ihara et al. [70] prepared a N-doped oxygen-deficient

titanium oxide by calcinating the hydrolytic product of $\text{Ti}(\text{SO}_4)_2$ with ammonia in dry air at 400 °C for 1 h. Additionally, some familiar reducing substances such as carbon, NaBH_4 , and Li can be also used to prepare oxygen-deficient TiO_2 [71]. Guan et al. [72] prepared a product of oxygen-deficient TiO_2 by a three-step process, which showed strong absorbance over the whole visible-light region. In their process, a Ti coating was first pretreated in carbon powder at 1073 K for 2 h, which was then oxidized at 1073 K for 15 h in air. Next, the obtained samples were treated in carbon powder again at 973 K for 30 min, finally obtaining the product of oxygen-deficient TiO_2 . Zhao et al. [73] first prepared TiO_2 anatase nanorods by a two-step hydrothermal method. Then, the obtained sample was mixed with NaBH_4 (1:1 in mole) in a mortar and thermally treated in Ar at 300 °C for 30 min, finally acquiring the reduced anatase nanorods. Interestingly, Martinze et al. [74] prepared a reduced blue TiO_2 by using Li foil and TiO_2 which were solved in ethylene diamine, stirring in anhydrous and dark conditions for 1440 h. Treating with these non-hydrogen reductants avoids the risk of explosion compared with hydrogen treatment.

In addition, providing an anoxic environment in the treatment process of TiO_2 can also result in the same effect as adding reducing agents. For example, Pereira et al. [75] obtained oxygen-deficient TiO_2 films with enhanced visible and near-infrared optical absorption by periodically interrupting the O_2 gas supply in the process of magnetron sputtering. Dhumal et al. [76] synthesized oxygen-deficient titanium suboxide (TiO_x with $x < 2$) nanoparticles by using a diffusion flame aerosol reactor under an oxygen lean environment in the formation zone of particles. Xiao et al. [77] reported the formation of oxygen vacancies in TiO_2 during the process of calcining TiO_2 in Ar or N_2 atmospheres. Kushwaha et al. [78] prepared a black oxygen-deficient TiO_2 -graphite nanocomposite by calcining Ti-EDTA complex under hypoxic conditions. Singh et al. [36] investigated the effect of thermal treatment on TiO_2 thin films under an oxygen anoxic environment, reporting a reduction in the band gap of 0.36 eV.

3.2. Pulsed Laser Irradiation

The excimer laser is a powerful tool and is often used to manipulate the composition and structure of material surfaces. Pulsed laser irradiation is a simple process for producing black, oxygen-deficient TiO_2 . A photochemical reduction reaction will take place during the pulsed laser absorption, thereby resulting in the evolution of oxygen deficiencies. The absorption of focused laser irradiation accompanied by fast heating/cooling processes will promote the formation of a porous surface [79–81]. As mentioned before, the dangers involved in hydrogenation operation greatly limit its application, while hydrogen plasma irradiation overcomes this shortcoming well [82,83]. For example, Wang et al. [82] synthesized a black titania with a core/shell structure ($\text{TiO}_2@\text{TiO}_{2-x}\text{H}_x$) assisted by hydrogen plasma and its photocatalytic activity for water splitting and cleaning pollutants was much better than that of TiO_2 . In addition, Nd:YAG, ArF, KrF, and XeCl excimer lasers are also frequently used methods besides hydrogen plasma [84,85]. Nakajima et al. [85] indicated that the TiO_2 crystal surface would be successfully reduced through ArF, KrF, and XeCl excimer laser irradiation, forming an oxygen-deficient $\text{TiO}_{2-\delta}$ layer with a thickness of 160 nm. Moreover, as shown in Figure 5a, the resistance of TiO_2 decreased after laser irradiation. Significant diffuse scattering around the (220) reflection for a wide range of Q_x (0.04~0.04) over the irradiated sample (Figure 5b) indicated a strong local lattice distortion near the surface of the sample. Pulsed laser irradiation is very suitable for surface treatment. It is simple to get high reductive efficiency based on photochemical reactions due to high-power laser irradiation. Meanwhile, the resultant surface of photocatalysts generally has a large specific surface area which is beneficial for improving photocatalytic performance.

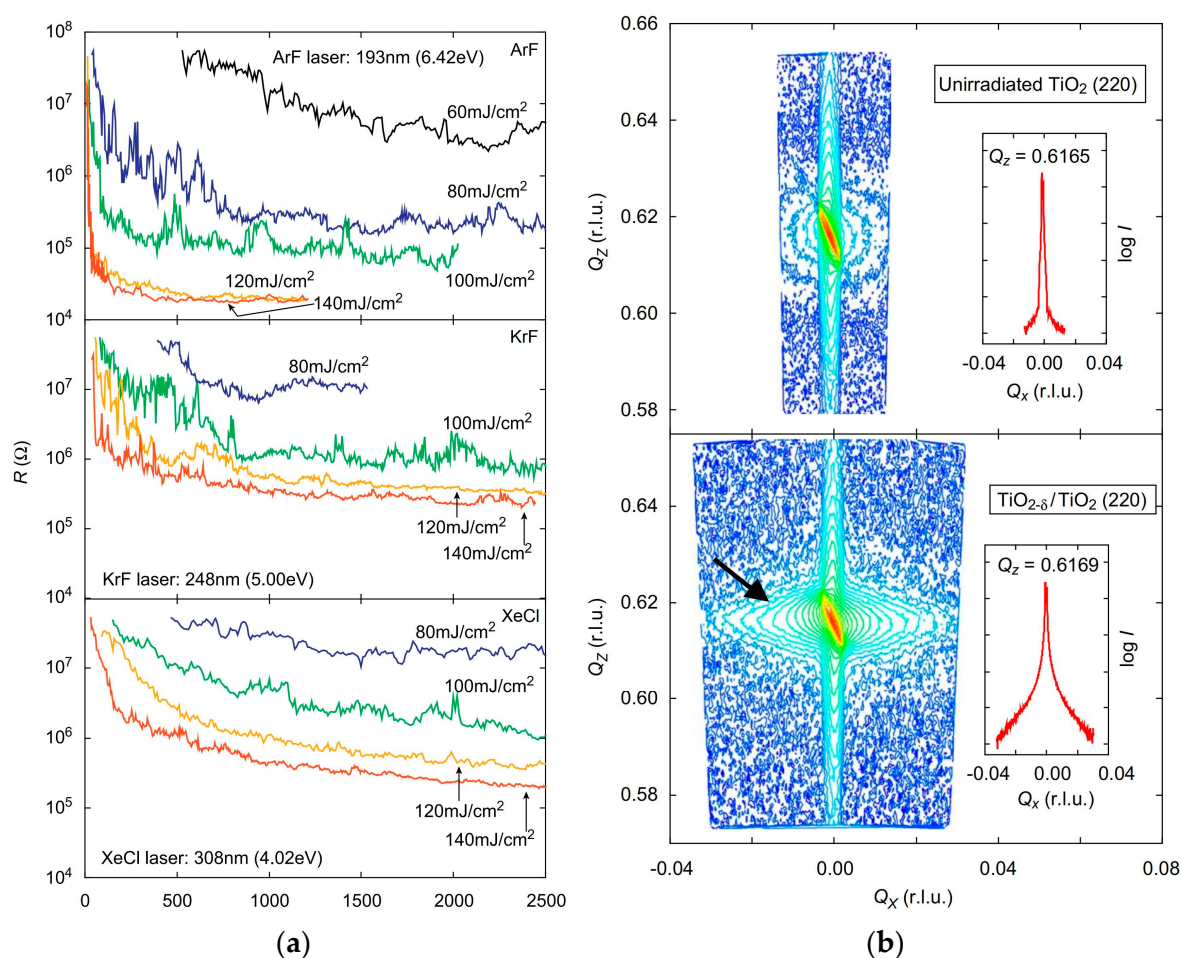


Figure 5. (a) Surface resistance of TiO₂ (100) substrates as a function of pulse number irradiated by ArF, KrF, and XeCl lasers. (b) Reciprocal space mappings around the (220) reflection for the unirradiated TiO₂ (100) substrate and laser-irradiated TiO_{2-δ}/TiO₂ (100) substrate. The insets show the Q_x profiles at the (220) reflection [85].

3.3. Pulsed Laser Deposition

Pulsed laser deposition (PLD) is a good technique to prepare functional thin films by depositing the ablated substances on a substrate. The oxygen deficiency in the film can be adjusted by controlling the partial pressure of O₂ and laser power density. For instance, Leichtweiss et al. [86] prepared oxygen-deficient titanium oxide films with an average composition of TiO_{1.6} by PLD at room temperature, which presented high efficiency for the water-splitting reaction. Kunti et al. [87] deposited TiO₂-SiO₂ composite films on amorphous quartz substrates at different partial pressures of O₂ by PLD technique, revealing the generation of oxygen defects and Ti³⁺ states in the films. Moreover, ion-doped, oxygen-deficient TiO₂ films can be obtained by changing the humidity of the environment, atmosphere, and ion implantation [88–90]. For instance, Socol et al. [90] fabricated N-doped crystalline TiO₂ thin films by PLD in N₂ or N₂-O₂ mixtures. Nath et al. [91] synthesized TiO_{1.5} nanoparticles by varying the focusing conditions of pulsed laser ablation. Rahman et al. [92] prepared TiO₂ nanostructures with different morphologies and incorporation of oxygen vacancy defects on a Si substrate by a single-step, catalyst-assisted PLD method (Figure 6). The morphology can be controlled by adjusting the deposition temperature and template. The film materials with special morphological structures can be prepared by PLD, thus adjusting the specific surface area of the catalysts. Ion doping can also be achieved by changing the reacting atmosphere. Thus, the band gap of titanium oxides can be reduced jointly by oxygen defects and ion doping.

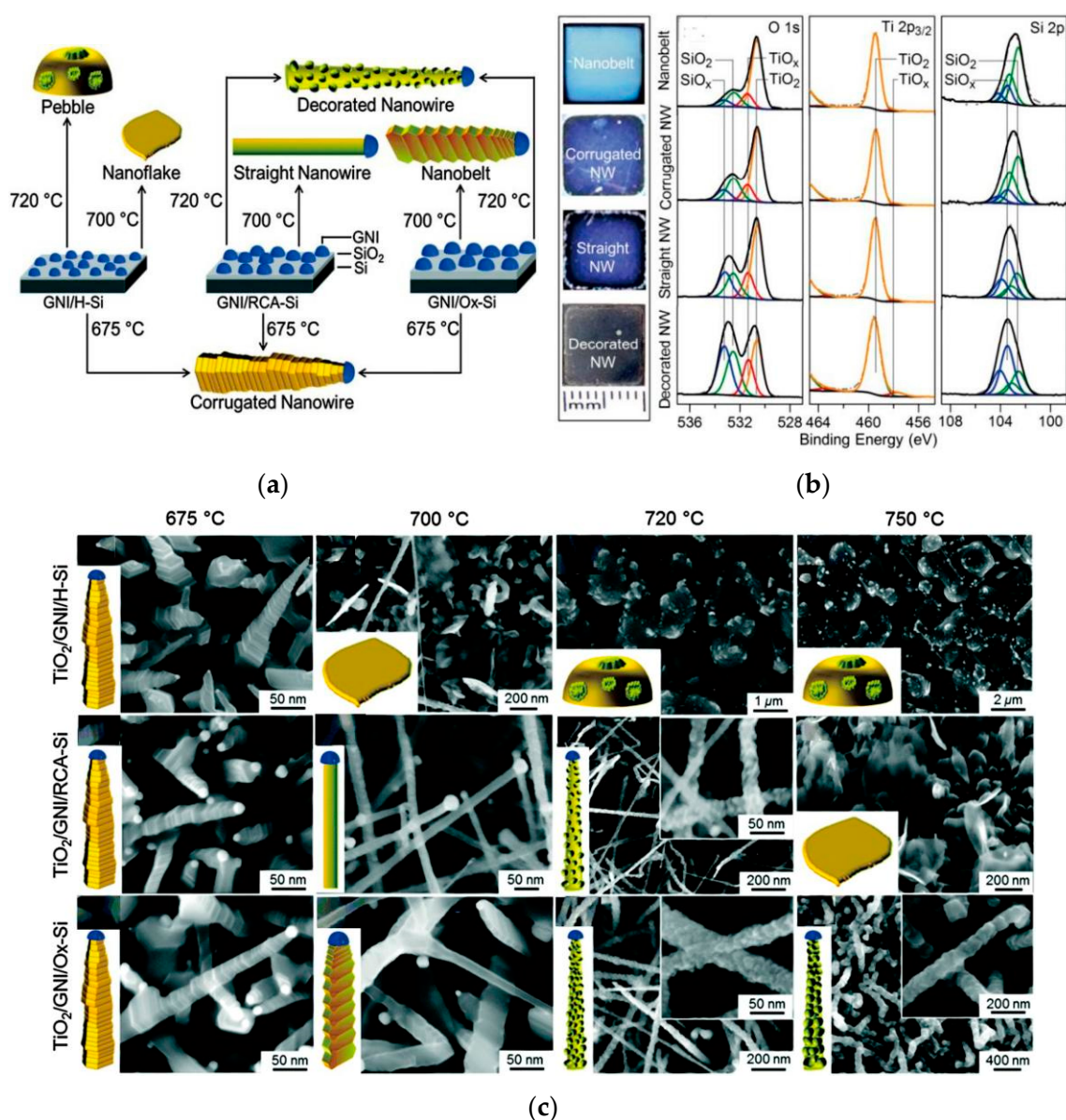


Figure 6. (a) Schematic models of TiO_2 nanostructures grown on gold nanoisland (GNI)-modified Si (100) templates at 675, 700, and 720 °C. (b) Photographs and XPS spectra of O 1s, Ti 2p_{3/2}, and Si 2p regions of TiO_2 films consisting of nanobelts, corrugated nanowires (NWs), straight NWs, and decorated NWs. (c) SEM images of TiO_2 nanostructures grown in 20 mTorr Ar at 675–750 °C on GNI-modified, H-terminated Si (GNI/H-Si), GNI-modified, RCA-cleaned Si (GNI/RCA-Si), and GNI-modified, thermally-oxidized (GNI/O_x-Si) templates. The corresponding lower left insets show schematic models of the as-grown nanostructures, and the upper right ones display the magnified SEM images of the selected nanostructures [92].

3.4. Ion Doping

Due to the difference in electronegativity between various elements, the introduction of impurity atoms into TiO_2 will change the partial concentration of electrons in TiO_2 , thus producing oxygen defects in it. For instance, Ti^{4+} will be converted into Ti^{3+} when the oxygen atoms in TiO_2 are replaced by highly electronegative F atoms due to the increased electron density around Ti^{4+} caused by the doped F atoms [93]. As shown in Figure 7a, clear Ti^{3+} signals can be observed in the EPR spectrum of fluorine-treated anatase. The corresponding Raman spectra also display a slight shift to a higher frequency at the peak of 144 cm^{-1} , which is attributed to the presence of oxygen vacancies and Ti^{3+} . The oxygen

vacancies are spontaneously introduced during N doping [94]. Pu et al. [95] successfully prepared N-doped, oxygen-deficient TiO_2 microspheres through a two-step synthesis method. Firstly, TiO_2 microspheres are synthesized by solvothermal synthesis. Then, the final oxygen-deficient titanium oxide products were obtained by electron beam irradiation using urea as the nitrogen source, and the concentration of Ti^{3+} increased with an increasing dose of the electron beam irradiation. Wang et al. [26] reported a N-doped TiO_2 ($\text{TiO}_{2-x}\text{N}_x$) by a simple wet method: hydrolyzing acidic tetra-butyl titanate in ammonia solution followed by calcination at 350°C for 1 h. Of course, the nitrogen source for doping generally directly or indirectly originates from reducing NH_3 , which can also promote the reduction of TiO_2 . Moreover, the doping of some metal ions, such as Eu^{3+} , La^{3+} , and Gd^{3+} , can introduce oxygen defects in TiO_2 as well. Those ions with a lower valence than Ti^{4+} can generate anion vacancies in TiO_2 [96–98], thereby forming Ti^{3+} . Zhang et al. [99] proved that the formation energy of a vacancy on the La-doped TiO_2 surface was lower than that formed on the pure TiO_2 surface treated in reducing conditions or oxidizing conditions by calculation (Figure 7b). Wang et al. [96] synthesized 0.4 mol% Gd and 2.0 mol% La co-doped TiO_2 microspheres via a hydrothermal method, which exhibited enhanced visible-light absorption. The doped La^{3+} and Gd^{3+} create abundant oxygen deficiencies and surface defects in the sample, decreasing the excitation energy of TiO_2 . Doping TiO_2 with highly electronegative elements will inevitably result in oxygen defects. Thus, introducing oxygen defects during the ion-doping process usually occurs unconsciously and controlling the density of oxygen defects is a great challenge. However, scientists can combine the advantages of ion doping and oxygen defects to improve the photocatalytic performance of TiO_2 [100,101].

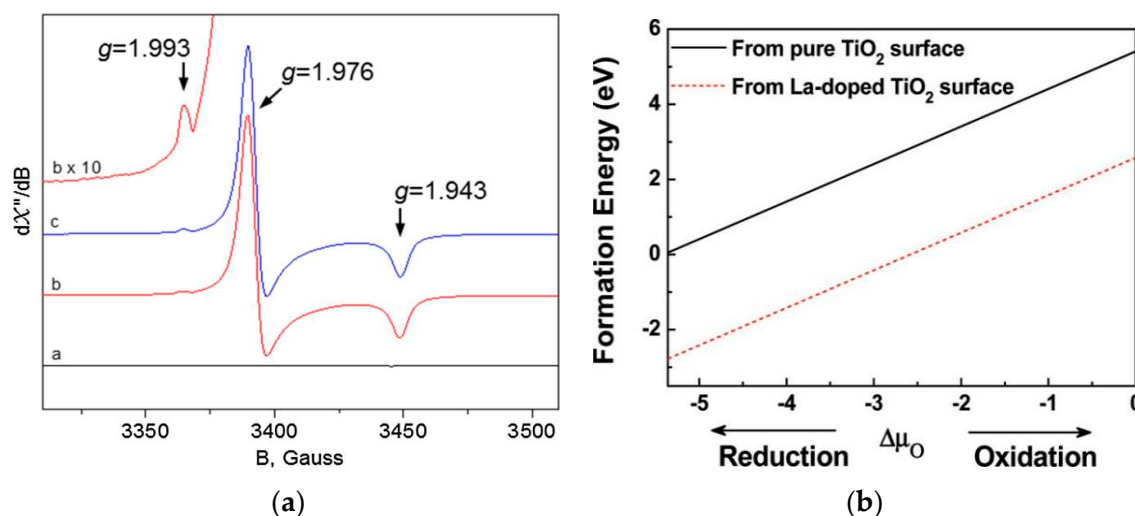


Figure 7. (a) EPR spectra of the anatase samples synthesized by a hydrothermal treatment with different HF amounts [93]. (b) Formation energies of oxygen vacancies as a function of $\Delta\mu\text{O}$ (the difference in oxygen chemical potentials [99]).

3.5. Plasma-Assisted Deposition

Plasma-enhanced chemical vapor deposition (PECVD) has the features of low deposition temperature, high purity, uniform thickness and composition of films, as well as easy control of reaction parameters. It can be used to prepare various metal films, inorganic films, and organic films. The structure and properties of films can be adjusted by controlling reaction conditions. Specifically, highly active species can be produced by plasma treatment under mild conditions. For example, Hatanaka et al. [102] prepared $\text{TiO}_x\text{:OH}$ films using a remote PECVD technique, which showed high photoconductivity. Sakai et al. [103] obtained oxygen-deficient TiO_2 anatase films by using oxygen plasma-assisted reactive evaporation by increasing the supply of titanium atoms, and the resultant oxygen-deficient TiO_2 films showed excellent hydrophilicity, which was conducive to thorough contact with

water and facilitated its splitting reaction. Li et al. [104] introduced numerous oxygen deficiencies and Ti^{3+} defects on the surface of TiO_2 nanoparticles via Ar plasma. Similarly, Hojo et al. [105] also successfully introduced oxygen defects in a $\text{TiO}_2\text{:Nb}$ film by annealing the sample with Ar plasma irradiation. Recently, Kawakami et al. [106] reported a kind of anatase/rutile mixed phase TiO_2 nanoparticle with many oxygen deficiencies, which were obtained by annealing the sample with low-temperature O_2 plasma. There are also excited species, such as ozone and OH generated during the plasma discharge in water. Thus, the plasma-liquid interaction has been widely applied to prepare nanomaterials. For instance, An et al. [107] prepared gray hydrogenated TiO_2 spheres using a plasma-modified sol-gel system. Mizukoshi et al. [108] obtained a blue TiO_2 containing oxygen defects by generating discharge plasma in an aqueous ammonia solution containing TiO_2 powder. TiO_2 was reduced by a reducing species, such as hydrogen radicals generated during the plasma discharge process in aqueous ammonia. The color of TiO_2 was gradually deepened with treating time and the capacity of light absorption was enhanced simultaneously, mainly because of the increasing amount of oxygen defects in the samples. Apart from introducing oxygen defects, plasma-assisted treating also leads to more bridging/terminal oxygen groups adsorbed on the surface of the samples, thus facilitating the charge transfer and suppressing the recombination of electrons and holes.

3.6. Ultrasonic-Assisted Techniques

Ultrasonic spray pyrolysis is a simple, low-cost, and scalable technique [54,109–112]. In the literature, Nakaruk et al. [110] successfully prepared fully dense TiO_2 films with oxygen deficiencies by using ultrasonic spray pyrolysis and proved that the concentration of oxygen deficiencies could be controlled by changing the annealing temperature. Oxygen vacancies can also be directly induced in TiO_2 by low-frequency ultrasound (LFUS) treating because the high-speed particle collisions and shock waves from LFUS can impact the atomic arrangement in the TiO_2 lattice. For instance, Osorio-Vargas et al. [113] prepared visible-light responsive TiO_2 -based photocatalysts by dispersing P25 powder into water and exposed this to a LFUS environment for 6 h. Bellardita et al. [114] reported that ultrasonic treating P25 powder dispersed in water induced oxygen deficiency in TiO_2 , thus narrowing the bandgap of TiO_2 from 3.18 to 3.04 eV.

3.7. Calcination under Anoxic Conditions

Thermal treatment atmosphere exerts an important influence on the formation of oxygen deficiencies [115–118]. The ratio of O and Ti in the resultant titanium oxides will be less than 2 when there is not enough oxygen in the preparation process. For instance, Albetran et al. [119] revealed that the color of titania changed from white to gray and black as the ratio of Ar/air of the thermal treating atmosphere increased (Figure 8a), and the light absorption of the corresponding products was also improved (Figure 8b). Sang et al. [120] fabricated oxygen-deficient TiO_2 nanotube arrays by calcining in nitrogen, or a mixture gas of 5% hydrogen in nitrogen, which exhibited higher photocurrent density and smaller charge transfer resistance than that of the samples calcined in air (Figure 8c,d). This is because the large lattice spaces caused by oxygen vacancies decreases the electrical resistance for electron transfer. Qi et al. [121] prepared a defective TiO_2 sample with oxygen deficiencies by thermally treating TiO_2 at 200 °C under vacuum conditions. The defect concentration in the sample is positively proportional to the thermal treatment time. Li et al. [122] reported an oxygen-deficient dumbbell-shaped anatase TiO_{2-x} product. In detail, a TiCl_3 -HAc mixed solution was solvothermally treated at 180 °C for 5 h and the solvothermally synthesized product was calcined under vacuum at 400 °C for 1 h.

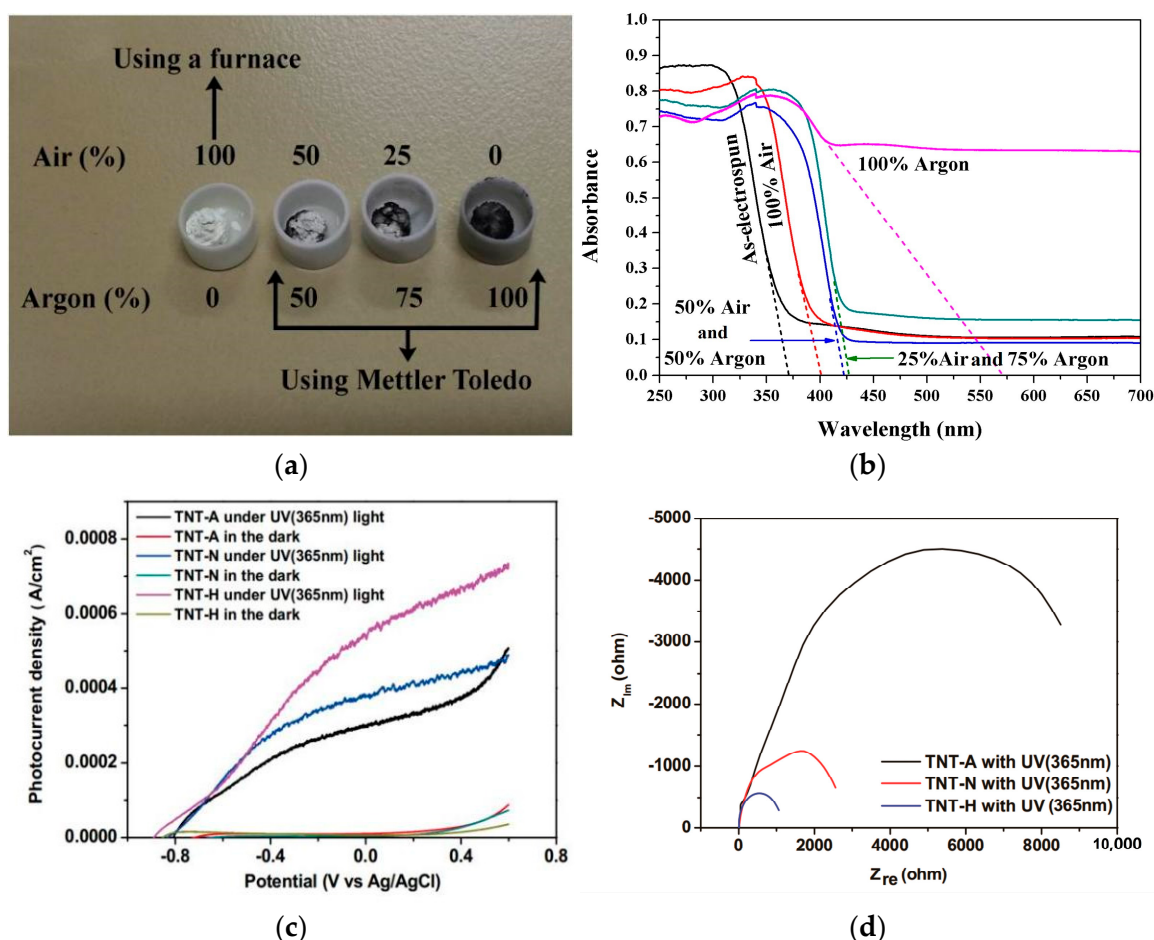


Figure 8. (a) Digital photograph and (b) band gaps of the electrospun TiO₂ nanofibers prepared by non-isothermally heating from 25 to 900 °C at 10 °C/min in argon–air mixtures [119]. (c) Photocurrent density vs. the applied potential of the TiO₂ nanotube arrays annealed in air (TNT-A), N₂ (TNT-N), and 5% H₂/N₂ mixture gas (TNT-H) under ultraviolet light (365 ± 15 nm) irradiation and the control tests in the dark [120]. (d) Electrochemical impedance spectroscopy plots of the anodized TiO₂ nanotubes annealed in air (TNT-A), N₂ (TNT-N) and 5% H₂/N₂ mixture gas (TNT-H) under ultraviolet light illumination [120].

3.8. Molten Salt Calcination

Du et al. [118] reported a facile strategy based on molten salt calcination to construct oxygen deficiencies in TiO₂. A flower-like TiO₂ precursor was synthesized via a solvothermal method using tetrabutyl titanate and acetic acid (HAc)/N,N-dimethyl formamide (DMF) as the titanium source and solvent, respectively. The as-prepared precursor was mixed with eutectic salts of LiCl/KCl (45/55 by weight) and calcined in a muffle furnace at 400 °C for 2 h. The lattice oxygen of TiO₂ was consumed during the calcination because of the low partial pressure of O₂ in the molten salt, thereby introducing numerous oxygen deficiencies and Ti³⁺ in the final product.

In summary, up to now, hydrogen reduction is still the most extensively used method to prepare oxygen-deficient TiO₂ owing to the strong deoxidizing ability and purity. However, it is time consuming and has high energy consumption and a high explosion risk. Thus, some other reductants such as carbon, NH₃, and Li are also used to reduce TiO₂ in the literature. Synthesizing titanium oxide in an anoxic environment is widely used because it is easily implemented. Pulsed laser irradiation is a simple process for producing oxygen-deficient TiO₂; however, this is more suitable for treating films because the radiation response mainly happens in the surface layer. Similarly, oxygen-deficient TiO₂ films can be easily obtained through adjusting the partial pressure of O₂ and the laser power density of

PLD. Introducing oxygen defects through ion doping is a natural process and the density of oxygen defects mainly depends on the doped species of ions and their concentration. Plasma discharge in water will provide reductively excited species, which can easily reduce TiO_2 . However, it is currently not widely applied. Oxygen-deficient TiO_2 can be prepared by ultrasonic spray pyrolysis or by calcinating under anoxic conditions, and the density of oxygen deficiencies can be controlled by controlling the experimental temperature. Molten salt calcination is simple and easily operated. Introducing oxygen defects improves the photocatalytic performance of TiO_2 in 2 major ways: one is narrowing band gap to absorb more light, and the other is changing the lattice structure to decrease resistance to electron transfer. Table 2 compares the different methods of introducing oxygen defects in TiO_2 .

Table 2. Comparison of different methods of introducing oxygen defects in TiO_2 .

Methods	Advantages	Disadvantages	Ref.
Reduced by H_2	Strong reducing ability, no impurities introduced, and easy control on the density of oxygen defects by adjusting reaction time.	High temperature, high energy consumption, time-consuming, and high risk.	[65,67–69]
Reduced by chemical reductants such as NH_3 , NaBH_4 , and carbon	Mild reaction conditions and low energy consumption.	Difficult control on the density of oxygen defects and easy introduction of impurities.	[56,70–72]
Prepared in anoxic environment	Convenient operation and can easily obtain products in large quantities.	High temperature, high energy consumption, and time consuming.	[78,79,82]
Pulsed laser irradiation	High reactivity and reducing efficiency and convenient operation.	Special equipment needed.	[88,91,92]
Pulsed laser deposition	Convenient operation, easy control on the density of oxygen defects by adjusting the partial pressure of O_2 and laser power density, and easily obtains special morphological structures of products.	Special equipment needed.	[80,81]
Ion doping	Mild reaction conditions and wide selection of approaches.	Unconsciously introduces oxygen defects without controlling their density and easily introduces impurities.	[95,97,98,100,101,107]
Plasma-assisted deposition	Mild and controllable reaction conditions which is suitable for preparing films.	Special equipment needed and low productivity.	[104,106]
Ultrasonic-assisted techniques	Convenient operation, low cost, and scalable.	The density of oxygen defects is not easily controlled.	[54,109,112,114]
Calcination under anoxic conditions	Convenient operation and easy to control the density of oxygen defects by adjusting the partial pressure of O_2 .	High temperature, high energy consumption, and time consuming.	[117,120,121]
Molten salt calcination	Convenient operation and easily obtains products in large quantities.	Special TiO_2 precursor needed.	[118]

4. Modification Methods of $\text{TiO}_{2-\delta}$ Photocatalysts

$\text{TiO}_{2-\delta}$ has been proven to perform better than stoichiometric TiO_2 in the process of photocatalytic water splitting. Many strategies such as ion doping, constructing heterojunction and deposition of noble metals have been proved to effectively improve the photocatalytic activity of TiO_2 . Thus, the photocatalytic activity of $\text{TiO}_{2-\delta}$ should be enhanced further by these strategies.

4.1. Ion Doping

Ion doping can introduce defects into TiO_2 which could act as the capture traps of photo-generated carriers, thereby suppressing the recombination of photogenerated e_{CB}^- and h_{VB}^+ . The lattice distortion caused by the doped atoms with different ionic sizes would increase the asymmetry of the crystal structure, which could promote the separation of photogenerated e_{CB}^- and h_{VB}^+ . Additionally, the energy band structure of TiO_2 can be effectively manipulated by ion doping. The narrowed band gap can extend the light absorption and enhance the utilization efficiency on solar energy of the resultant photocatalysts.

4.1.1. Metal Ion Doping

The doping of transition metals has been proven an effective method for regulating the band positions of TiO_2 . The main principle is to insert an additional energy level between the original conduction band and valence band. For example, Sheng et al. [123] reported a Pd-doped TiO_2 , revealing that the photogenerated e_{CB}^- and h_{VB}^+ were efficiently separated after Pd doping. Sasirekha et al. [124] prepared a Ru-doped anatase TiO_2 supported on silica by a solid-state dispersion method, which performed well in the photocatalytic reduction of carbon dioxide. Gao et al. [125] indicated that the doping of Mo, Pd, Ru, and Rh could narrow the band gap of TiO_2 , thus enhancing the probability of activation by visible light. Their theoretically calculated results through density functional theory revealed that the impurity states of 4d electrons would form new degenerate energy levels, thus narrowing the band gap of TiO_2 . Thalgaspitiya et al. [126] synthesized mesoporous composites of M-doped titanium dioxide (M = Mn, Co, Ni, Mo, and W) with reduced graphene oxide (rGO), indicating that the indirect band gap of the composites could be adjusted into the range of 2.20–2.48 eV.

Rare earth ions have rich energy levels and unique features of 4f electronic transitions, providing unique opportunities for manipulating the band gap of semiconductors by elemental doping. For instance, Wang et al. [127] fabricated samples of La^{3+} - or Yb^{3+} -doped TiO_2 supported on r-GO, reporting that the anionic vacancies in the TiO_2 lattice caused by La^{3+} and Yb^{3+} would generate Ti^{3+} , thus enhancing the visible-light response of the samples. Stengl et al. [128] prepared several samples of rare earth (La, Ce, Pr, Nd, Sm, Eu, Dy, Gd)-doped TiO_2 , which were all visible-light sensitive. Fang et al. [129] synthesized rare earth ion (Er^{3+} and/or Yb^{3+})-doped TiO_2 photocatalysts by a hydrothermal method, indicating that the doping of Er^{3+} and/or Yb^{3+} could decrease the recombination rate of photogenerated electron-hole pairs, finally leading to a higher photocatalytic efficiency of TiO_2 . In addition, the phase transition from anatase to rutile can be significantly delayed by the doping of rare earth ions [130,131].

Alkali metal and alkali earth metal ions were also used to improve the photocatalytic activity of TiO_2 . Liu et al. [132] prepared a mesoporous Na-doped titanium dioxide with a band gap of 3.08 eV. The doped Na ions could enter into the (004) crystalline plane of anatase TiO_2 , finally leading to the dislocation defects in TiO_2 . Lv et al. [133] successfully fabricated AM- TiO_{2-x} samples (AM = Mg, Ca, Sr, and Ba), revealing that the CB position of TiO_2 became more negative after AM doping, thus improving the hydrogen production ability of TiO_2 . The separation of carriers and transfer efficiency were also dramatically promoted (Figure 9a–c).

4.1.2. Nonmetallic Ion Doping

The doping of nonmetallic ions can expand the light-absorption region of TiO_2 and suppress the recombination of photogenerated e_{CB}^- and h_{VB}^+ . Normally, the p orbital in the most outer electronic layer of the doped ions would hybridize with the 2p orbital of O in TiO_2 , forming new shallow levels near the top of the valence band. For example, N doping is widely studied because the ion radius of N is closest to that of O [134,136–138]. Li et al. [136] prepared a N-doped TiO_2 which performed better in photocatalytic hydrogen evolution than the undoped TiO_2 under the same conditions (Figure 9d). Yuan et al. [139] prepared a N-doped TiO_2 with a high specific surface area by heating a mixture of urea and TiO_2 .

The absorption spectrum of the N-doped TiO_2 shifted to the wavelength of 600 nm and the sample showed high photocatalytic activity on hydrogen evolution. Momeni et al. [140] prepared S-doped TiO_2 nanostructure photocatalyst films which performed well in the removal of RhB and hydrogen generation under visible-light radiation. Carmichael et al. [141] reported B-doped titanium dioxide films with a hydrogen evolution rate of $24 \mu\text{L}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$, which far exceeded the undoped TiO_2 at $2.6 \mu\text{L}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$. Wu et al. [142] fabricated F-doped TiO_2 particulate thin films, which could be applied in the photodegradation of organic pollutants and photoinduced splitting of water into hydrogen under the irradiation of either UV or visible light.

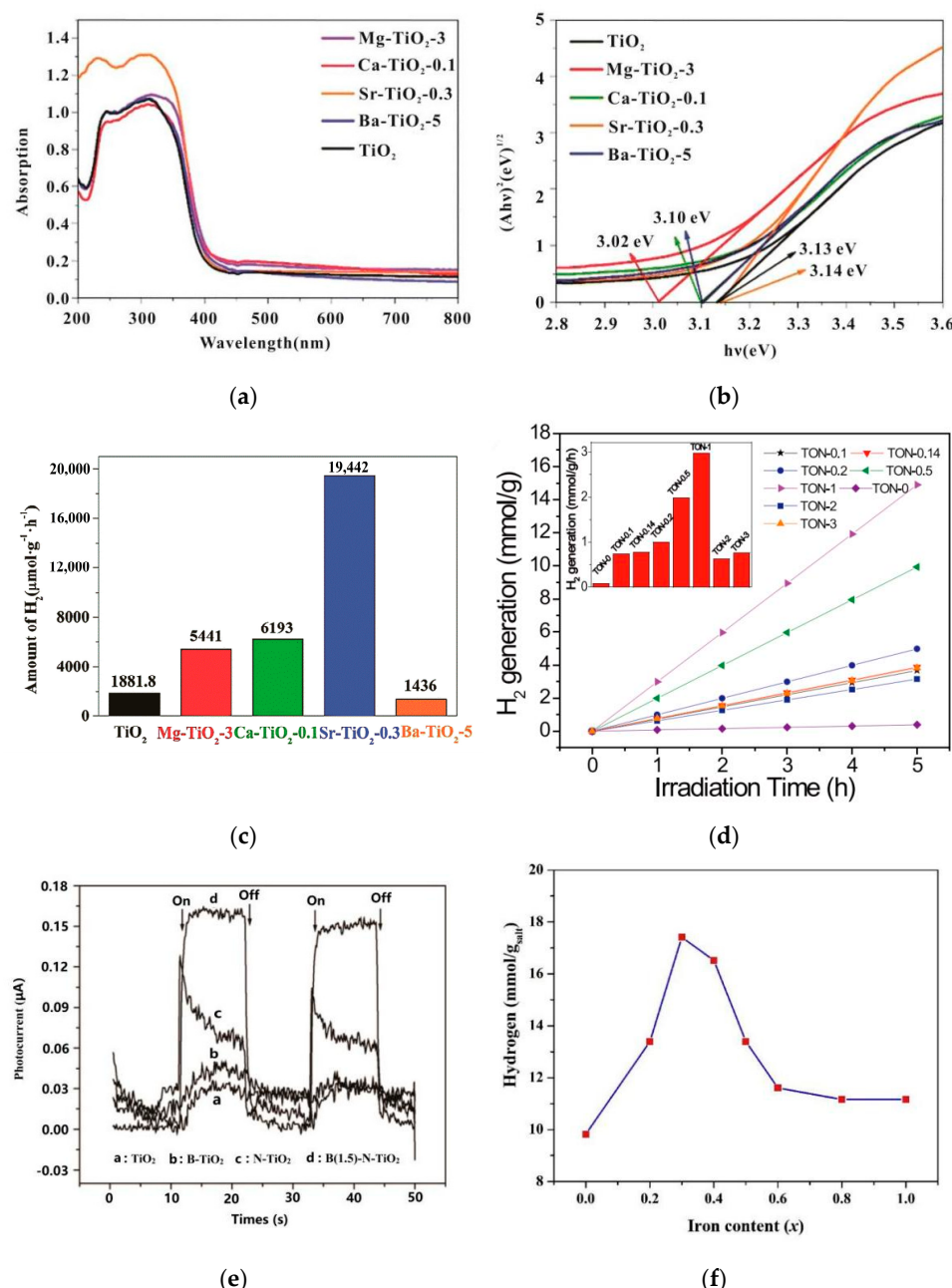


Figure 9. (a) UV-Vis diffuse reflectance spectra of TiO_2 and alkaline earth metal-doped TiO_2 [133] and (b) gaps in TiO_2 and alkaline earth metal-doped TiO_2 [133]. (c) Photocatalytic H_2 production from water splitting over TiO_2 and alkaline earth metal-doped TiO_2 under the condition of adding Pt as a co-catalyst [133]. (d) Photocatalytic H_2 generation over TiO_2 doped with different amounts of N [129]. (e) Photocurrent response curves of TiO_2 , B-doped TiO_2 , N-doped TiO_2 , and (B,N)-co-doped TiO_2 to visible light [134]. (f) Photocatalytic H_2 generation over $(\text{Fe}_x\text{Co}_{1-x})$ -co-doped TiO_2 [135].

4.1.3. Multiple Ion Co-Doping

Different ions have different impacts on TiO_2 ; thus, the co-doping of multiple ions is an effective method to obtain higher photocatalytic activity. In the literature, Zhu et al. [143] studied the electronic and optical properties of C-, Mo-, and (Mo,C)-co-doped anatase TiO_2 using the first principle calculations. The results show that the optical absorption edges of the (Mo,C)-co-doped TiO_2 will shift towards the visible-light region. Diao et al. [144] reported K, Na, and Cl co-doped rutile TiO_2 , exhibiting good photocatalytic degradation of gaseous formaldehyde under visible-light irradiation. Li et al. [134] reported the photocatalytic activity for hydrogen production over (B,N)-co-doped TiO_2 under visible-light irradiation. N doping extends the absorption edge to the visible-light region and B doping acts as the shallow trap for photogenerated electrons to prolong the life of the electrons and holes. Consequently, stronger photocurrents were observed on (B,N)-co-doped TiO_2 than those of N-doped TiO_2 , B-doped TiO_2 , and undoped TiO_2 (Figure 9e). Barakat et al. [135] prepared $\text{Fe}_x\text{Co}_{1-x}$ -co-doped titanium oxide nanotubes, achieving distinct enhancement of the visible-light absorption capacity (Figure 9f). Filippatos et al. [145] even reported a photocatalyst of H, F, and Cl co-doped titanium dioxide with a high hydrogen production rate.

In short, improving the photocatalytic performance of TiO_2 by ion doping is mainly based on introducing defects, changing the lattice structure, and adjusting the band gap. Metal ion doping also affects the electron distribution and lattice size. Nonmetallic ions, such as N-, S-, and P-doping, generates new shallow levels by the hybridization of Ti 2p orbital with O 2p, thus narrowing the band gap of TiO_2 . Ion doping can be achieved through lots of ways, so it is easy to carry out in various experimental environments. However, the results may be quite different when using different doping methods.

4.2. Composite

The heterostructure formed by the recombination of two or more semiconductors with matched energy band structures can effectively improve the separation efficiency of photogenerated e_{CB}^- and h_{VB}^+ . As shown in Figure 10, there are usually four types of heterostructures based on different relative positions of the energy band, including type I, type II, type III, and the Z-scheme system [146,147]. The built-in electric field formed along the interface will promote the transfer of electrons. Additionally, the combination with narrow band semiconductors could allow TiO_2 to respond to visible light.

For instance, Smith et al. [148] synthesized a nanotubular composite of TiO_2 - WO_3 . This composite demonstrated an increase of 46% in water-splitting efficiency compared to TiO_2 nanotubes prepared under similar conditions. Choudhury et al. [149] prepared ultra-thin PdO-TiO_2 composite films which could be used to photogenerate hydrogen efficiently from methanol/water for a long period of time. Navarrete et al. [150] synthesized $\beta\text{-Ga}_2\text{O}_3/\text{TiO}_2$ composite photocatalysts for H_2 production from a water/methanol mixture (Figure 11a). The high activity is attributed to the slow charge recombination of the photogenerated e_{CB}^- and h_{VB}^+ (Figure 11b). Gholami et al. [151] confirmed that the activity of the ZnO-TiO_2 composite for photodegradation of bentazon was better than that of ZnO and TiO_2 separately. Chen et al. [152] constructed a NiO/TiO_2 heterojunction on the surface of TiO_2 film. The strong inner electrical field effectively separates the photogenerated electron-hole pairs, and thus the composite exhibited much better photocatalytic activity than the original TiO_2 film (Figure 11c,d). The graphene- TiO_2 composite has been widely studied because of its excellent mobility of charge carriers, large specific surface area, flexible structure, high transparency, and good electrical and thermal conduction [153–159]. Zhang et al. [157] prepared a $\text{TiO}_2/\text{graphene}$ sheet composite by a sol-gel method, exhibiting a hydrogen evolution rate of $8.6 \mu\text{mol}\cdot\text{h}^{-1}$ which was nearly two times that over the commercially available Degussa P25 ($4.5 \mu\text{mol}\cdot\text{h}^{-1}$). Fu et al. [159] constructed a $\text{g-C}_3\text{N}_4/\text{graphene-CNTs/TiO}_2$ Z-scheme photocatalytic system, in which the graphene CNTs effectively promoted the transfer of photogenerated carriers, thereby generating a stronger photocurrent (Figure 11e,f). The built-in electric field along the interface of the composite can promote the transfer of electrons, thus suppressing the recombination

of photogenerated e_{CB}^- and h_{VB}^+ . Therefore, scientists could purposefully design the structure of composites according to the band structure of semiconductors, which can reduce the uncertainty of experiments.

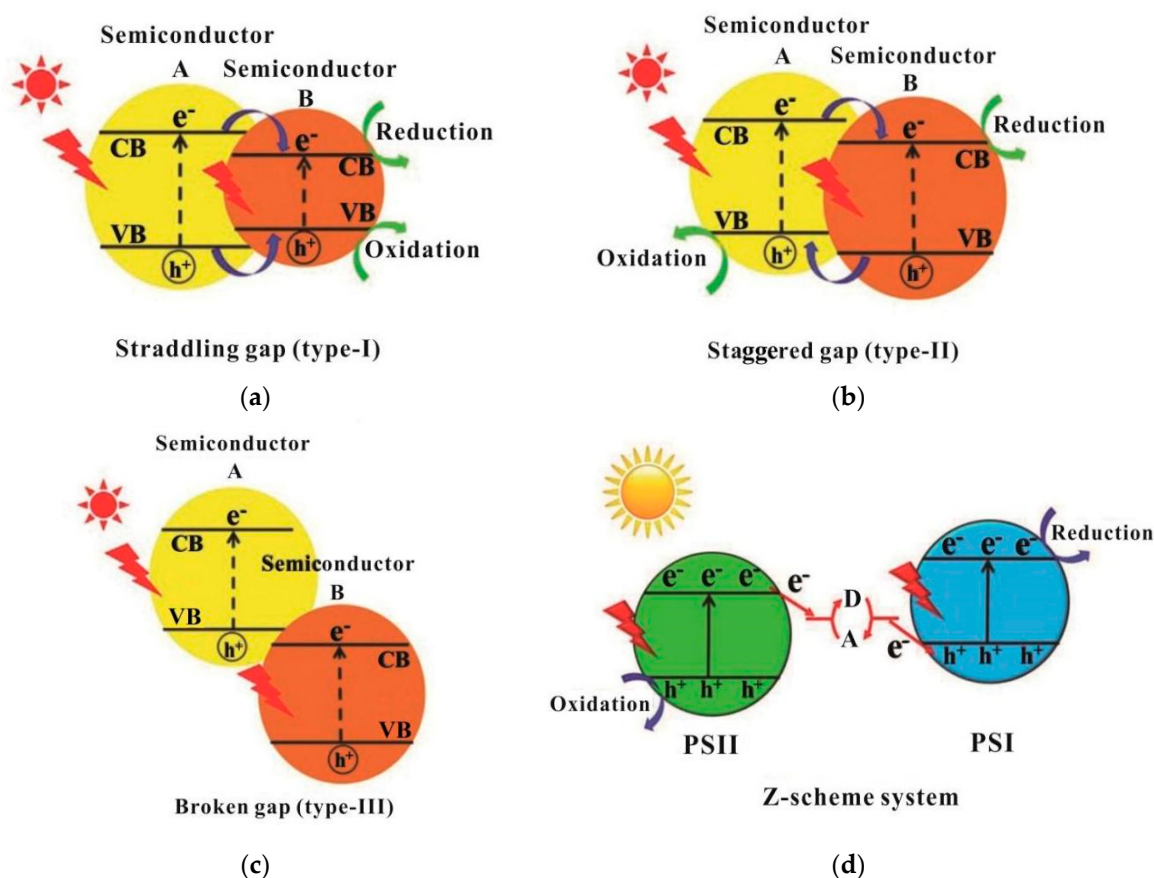


Figure 10. Schematic illustration on the separation ways of photogenerated electron-hole pairs over heterojunction photocatalysts: (a) type-I, (b) type-II, (c) type-III, and (d) Z-scheme [147].

4.3. Surface Noble Metal Deposition

The photogenerated carriers will be redistributed when the surface semiconductor comes into contact with metal. The electrons will transfer from the n-type semiconductor to metals because of the lower Fermi levels of metals. Moreover, the surface plasmon polaritons can enhance the light response of TiO_2 [160–163]. In the literature, Zheng et al. [164] investigated the photocatalytic performance of TiO_2 deposited with Au, Ag, and AuAg bimetallic nanoparticles. The results showed that the local surface plasmon resonance of noble metals improved the photocatalytic activity TiO_2 under visible-light irradiation. Luo et al. [165] reported a visible-light-driven responsive Au/rGO/hydrogenated TiO_2 nanotube array ternary composite with a high hydrogen evolution rate of $45 \text{ mmol} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$. The visible-light harvesting was significantly improved by the Au nanoparticles due to the localized surface plasmon resonance effect. Ag, Pd, and Rh have also been used to modify TiO_2 by depositing them on its surface [61,166–169]. For example, Ge et al. [167] decorated Ag nanoparticles onto vertically aligned TiO_2 nanotube arrays. The Ag-decorated TiO_2 can efficiently drive photocatalytic water splitting under visible-light irradiation owing to the surface plasmon resonance of Ag. Due to the local surface plasmon resonance, the photocatalytic performance of noble-metal-modified TiO_2 is significantly greater than that of the modified TiO_2 by other methods such as ion doping and composites. However, the high cost incurred by expensive noble metals restricts the application of this strategy.

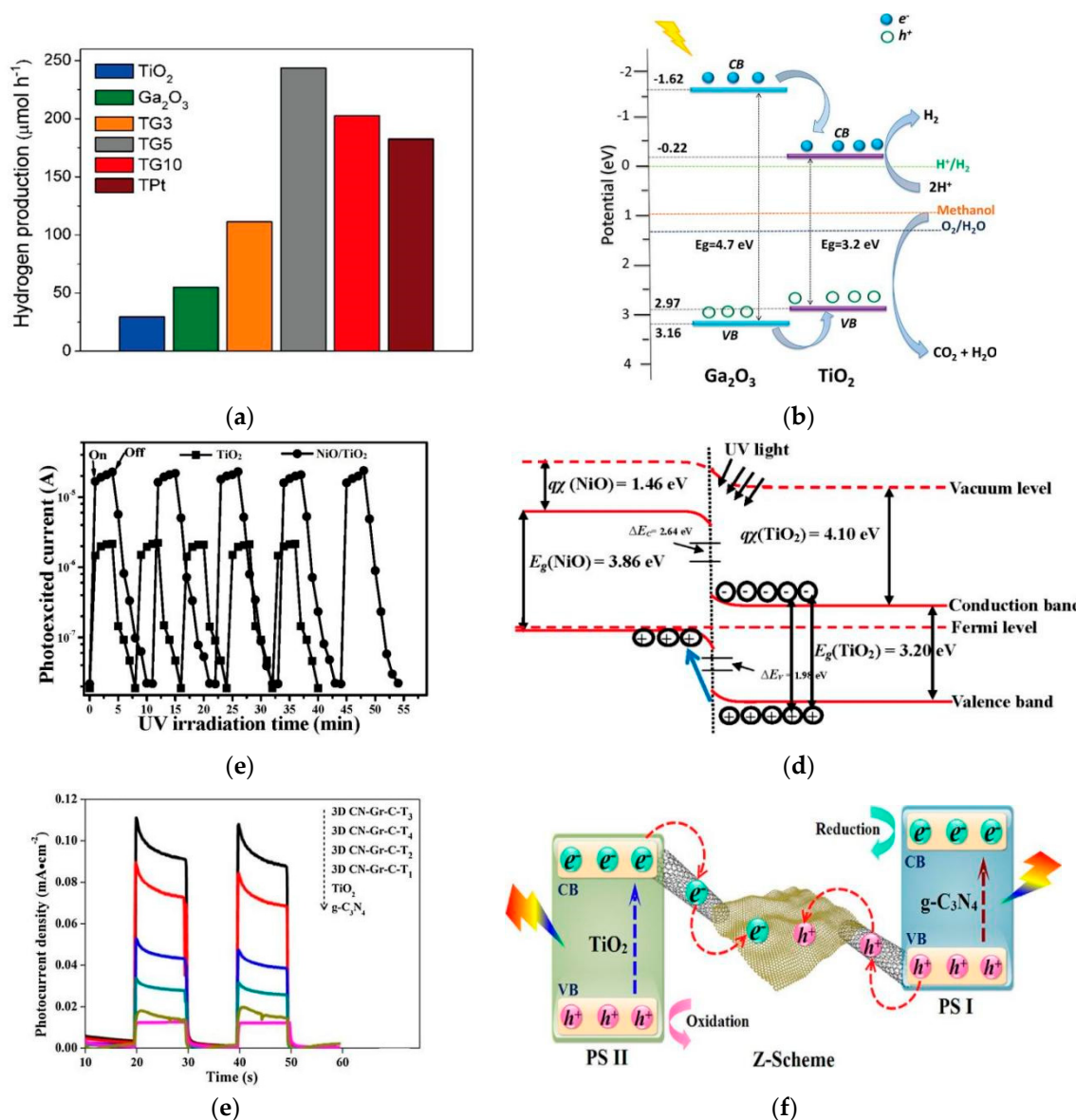


Figure 11. (a) Average hydrogen evolution rates of TiO₂, Ga₂O₃, TG3 (3% Ga₂O₃/TiO₂), TG5 (5% Ga₂O₃/TiO₂), TG10 (10% Ga₂O₃/TiO₂) photocatalysts, and TPt reference (Pt modified TiO₂) [150]. (b) Mechanism for H₂ production over the TG5 photocatalyst [150]. (c) Transient current response curves of TiO₂ and NiO/TiO₂ nanocomposite under ultraviolet light irradiation [152]. (d) Schematic diagram on the energy band of a p-NiO/n-TiO₂ heterojunction structure [152]. (e) Transient current response curves of 3D g-C₃N₄/graphene-CNTs/TiO₂ samples with different amounts of TiO₂ under an Xe lamp [159]. (f) Schematic diagram of the photocatalytic processes over 3D g-C₃N₄/graphene-CNTs/TiO₂ [159].

4.4. Dye Sensitization

The excitation potential of some dyes is more negative than the CB potential of TiO₂. Thus, the light response range of TiO₂ can be effectively expanded by dye sensitization. Dye molecules can deliver photogenerated electrons to the CB of TiO₂ and then the electrons transfer further to participate in reactions [170–172]. For example, Shi et al. [171] prepared Eosin Y-sensitized nanosheet-stacked hollow-sphere TiO₂ for efficient photocatalytic H₂ production under visible-light irradiation. Vallejo et al. [170] reported the enhancement on light absorption and photocatalytic activity over rGO-TiO₂ thin films after they were sensitized by natural dyes extracted from *Bactris guineensis* (Figure 12). In fact, lots of dyes have been used to sensitize TiO₂, such as complexes of Fe (II) and

polypyridyl, quinacridone, hydroxoaluminum-tricarboxymonoamide phthalocyanine, and so on [173–175]. Dye sensitization is easy to realize and has a low cost. Although many natural dyes can be used as raw materials for the sensitization of TiO_2 , sensitized TiO_2 is not always stable which limits its wide application.

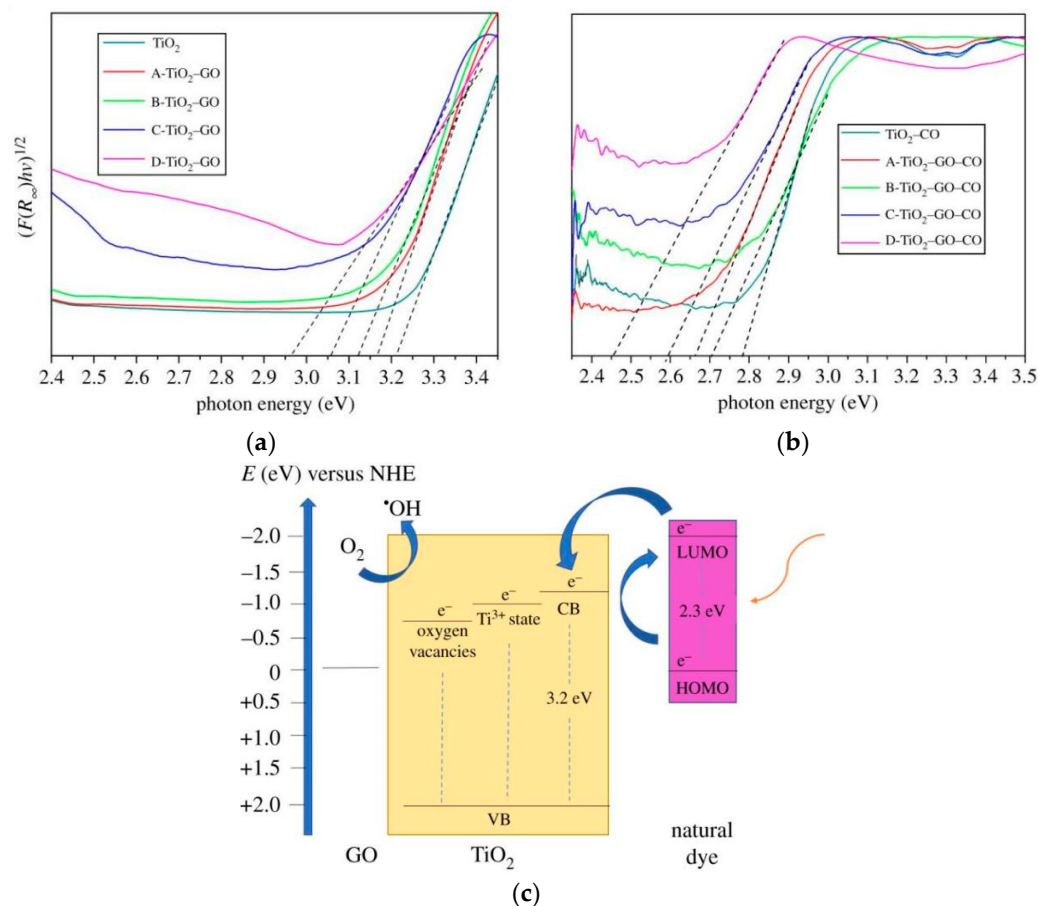


Figure 12. Band gaps estimated on the basis of the Kubelka–Munk plots for (a) TiO_2 -GO thin films and (b) TiO_2 -GO thin films sensitized with anthocyanin that was extracted from the fruit of *Bactris guineensis* (TiO_2 -GO-CO). The samples A, B, C, and D were prepared by adding 0.15%, 0.26%, 0.51%, and 1.1% GO in mass into TiO_2 . (c) Schematic illustration of the energy levels for the TiO_2 -GO thin films sensitized with natural dye [170].

4.5. Loading on Supports

Loading on supports is an effective way to solve the problems of agglomeration and tough recycling of TiO_2 nanoparticles. In addition, the supporting materials of high electrical conductivity could provide channels for quick transfer of electrons, thereby decreasing the recombination rate of photogenerated e_{CB}^- and h_{VB}^+ . For example, Li et al. [176] reported a catalyst of nitrogen-doped carbon nanofiber supporting $\text{MoS}_2/\text{TiO}_2$, in which the photogenerated electrons could quickly transfer to the carbon fiber along the basal plane of MoS_2 . Many natural materials are preminent supports, so it is not essential for scientists to design and construct supports with special structures. In literature, zeolite, SiO_2 , and carbon materials are frequently used as the supporting materials for TiO_2 [177–182]. Najafabadi et al. [180] reported four kinds of zeolites (Na-Y, Na-mordenite, H-Y, and H-beta) supporting TiO_2 , which all exhibited high hydrogen evolution rates. For the Na-Y zeolite supporting TiO_2 , the rate reached $250.8 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, which was almost three times that of Degussa P25 ($84.2 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) under the same conditions. Kim et al. [182] prepared TiO_2 supported by SiO_2 , showing much higher photocatalytic activity than pure TiO_2 which could be attributed to the large specific surface area. Ti-O-Si

bonds modified the narrow band gap and the local structure. Loading on supports is frequently associated with other reactions such as ion doping and forming heterojunctions. Thus, it can combine the advantages of varied strategies. Yin et al. [183] synthesized Bi plasmon-enhanced mesoporous $\text{Bi}_2\text{MoO}_6/\text{Ti}^{3+}$ self-doped TiO_2 microsphere heterojunctions. The formation of heterojunctions, Ti^{3+} , and surface plasmon resonance (SPR) of Bi jointly achieved high catalytic activity of TiO_2 under visible light. Xing et al. [184] combined ion doping with supports and synthesized a F-doped- $\text{TiO}_{2-x}/\text{MCF}$ composite, which exhibited high photocatalytic activity for hydrogen evolution.

4.6. Crystal Facet Engineering

The exposed facets of traditional TiO_2 photocatalysts are the thermodynamically stable (101) facets. However, the specific surface energy of (001) facets is higher than that of (101) facets, implying that the (001) facets have higher reaction activity. In addition, the uncoordinated Ti_{5c} atoms in the (001) facets can narrow the band gap of TiO_2 . Therefore, exposing more (001) facets will help to improve the photocatalytic performance of TiO_2 , which is generally realized by controlling the synthesis conditions [185,186]. For instance, Wang et al. [187] synthesized a series of (001) facet-dominated TiO_2 nanosheets with high visible-light photoactivity by a simple hydrothermal method at different temperatures. Shang et al. [188] synthesized graphene- TiO_2 nanocomposites with dominantly exposed (001) facets through various dosages of graphite oxide (GO) and hydrofluoric acid (HF) during a facile solvothermal process. The well-conductive and highly reactive (001) facets enhanced the photocatalytic properties and facilitated the separation of photogenerated carriers.

As a summary, Table 3 lists the hydrogen evolution efficiency from photocatalytic water splitting over typical titanium oxide-based photocatalysts. Obviously, noble-metal-modified TiO_2 photocatalysts have incomparable advantages on hydrogen evolution over the other titanium oxide-based counterparts. However, the searches for alternative non-noble metals are still one of the focuses in this field because of the high cost and scarcity of noble metals. Additionally, combining multiple modification methods can achieve better results than using a single method. Table 3 lists also lists some typical non- TiO_2 -based photocatalysts for comparison. As can be seen, noble-metal-modified TiO_2 photocatalysts obviously perform much better than metal sulfides and phosphides in hydrogen evolution reactions. The composites clearly perform better than single materials for TiO_2 , metal sulfides, and phosphides.

Table 3. Hydrogen evolution efficiency of photocatalytic water splitting over various TiO_2 -based photocatalysts in comparison with those of typical photocatalysts reported in the literature.

Catalyst	Light Source	Reaction Condition	H_2 Production (mmol h^{-1})	Ref.
N-doped TiO_2	>400 nm	Water	0.315	[139]
N-doped TiO_2	>420 nm	EDTA-2Na solution	2.21	[134]
(B,N)-co-doped TiO_2	>420 nm	EDTA-2Na solution	10.45	[134]
(Sb,N)-co-doped TiO_2	Xe lamp	10% aqueous TEOA solution	2.33	[189]
B-doped TiO_2	365 nm	0.2 M HCl and absolute ethanol aqueous solution (1:1)	0.099	[141]
N-doped TiO_2	visible light	$\text{H}_2\text{S}/0.25$ M KOH solution	8.8	[137]
N-doped TiO_2	Xe lamp	20% aqueous methanol solution	2.98	[136]
S-doped TiO_2	Xe lamp	1 M NaOH aqueous solution	0.17	[140]
Fe-doped TiO_2	solar light radiation	tri ammonium phosphate aqueous solution	4.01	[135]
Co-doped TiO_2	solar light radiation	tri ammonium phosphate aqueous solution	9.82	[135]
(Fe,Co)-co-doped TiO_2	solar light radiation	tri ammonium phosphate aqueous solution	17.41	[135]

Table 3. Cont.

Catalyst	Light Source	Reaction Condition	H ₂ Production (mmol h ^{−1})	Ref.
La-doped TiO ₂	Hg UVA lamp	12 M aqueous methanol solution	80	[190]
Ce-doped TiO ₂	visible light	sulphide wastewater from refinery	6.789	[191]
H-doped TiO ₂	365 nm	25% aqueous methanol solution	0.286	[145]
F-doped TiO ₂	365 nm	25% aqueous methanol solution	0.0928	[145]
Cl-doped TiO ₂	365 nm	25% aqueous methanol solution	0.336	[145]
V-doped TiO ₂ /rGO	Xe lamp	20% aqueous methanol solution	0.12	[192]
N-doped Ni/C/TiO ₂	Hg lamp	30% aqueous methanol solution	0.383	[193]
Sr-doped TiO ₂ − δ	>400 nm	water	1.092	[194]
TiO ₂ − δ	>420 nm	30% aqueous methanol solution	0.00058	[195]
Pt/TiO ₂ − δ	visible light	50% aqueous methanol solution	4.9	[47]
Ag-decorated TiO ₂	Hg lamp	water	120	[196]
Au-decorated TiO ₂	254 nm	aqueous methanol solution	106	[168]
Au,Pd-decorated TiO ₂	254 nm	aqueous methanol solution	266	[168]
Au,Ni-decorated TiO ₂	254 nm	aqueous methanol solution	256	[168]
Au,Co-decorated TiO ₂	254 nm	aqueous methanol solution	171	[168]
Pd-decorated TiO ₂	254 nm	aqueous methanol solution	59	[168]
Ni-decorated TiO ₂	254 nm	aqueous methanol solution	20	[168]
Co-decorated TiO ₂	254 nm	aqueous methanol solution	10	[168]
Cu(OH) ₂ /TiO ₂	ultraviolet light	10% aqueous methanol solution	14.94	[197]
Cu/TiO ₂	UV lamp	25% aqueous methanol solution	5	[198]
Cu/TiO ₂	visible light	25% aqueous methanol solution	0.22	[198]
Co ₃ O ₄ @C/TiO ₂	365 nm	25% aqueous methanol solution	11.4	[199]
NiO/TiO ₂	Hg lamp	glycerol and distilled water	1.2	[200]
g-C ₃ N ₄ /N-TiO ₂	Xe lamp	20% aqueous methanol solution	8.931	[201]
EosinY-sensitized TiO ₂ /ZrO ₂	Xe arc lamp	15% DEA aqueous solution	1.87	[202]
β -Ga ₂ O ₃ /TiO ₂	254 nm	50% aqueous methanol solution	0.244	[150]
N-doped TiO ₂ /N-doped graphene	Xe lamp	10% aqueous TEOA solution	0.039	[203]
FeO-TiO ₂ /ACF	visible light	20% aqueous methanol solution	6.178	[204]
TiO ₂ /ACF	visible light	20% aqueous methanol solution	1.672	[204]
Cu-doped TiO ₂ with preferred (001) orientation	Xe lamp	10% aqueous methanol solution	0.81	[205]
g-C ₃ N ₄ /TiO ₂ with preferred (001) orientation	>420 nm	10% aqueous TEOA solution	0.033	[206]
TiO ₂ /graphene with exposed (001) facets	Xe lamp	25% aqueous methanol solution	0.736	[207]
CdS	>420 nm	0.5 M Na ₂ S-0.5 M Na ₂ SO ₃ aqueous solution	0.063	[208]
CdS-CoSx	>420 nm	0.5 M Na ₂ S-0.5 M Na ₂ SO ₃ aqueous solution	0.1686	[208]
Pt/CdS	>420 nm	1.0 M aqueous (NH ₄) ₂ SO ₃ solution	1.158	[209]
ZnS	Xe lamp	0.1 M Na ₂ S-0.1 M Na ₂ SO ₃ aqueous solution	0.04	[210]
Cu-ZnS/Zeolite	Xe lamp	0.1 M Na ₂ S-0.1 M Na ₂ SO ₃ aqueous solution	0.48	[210]
ZnO/ZnS	Xe lamp	0.064 M Na ₂ S aqueous solution	0.228	[211]
ZnO	Xe lamp	0.064 M Na ₂ S aqueous solution	0.138	[211]
Ni ₂ P	>420 nm	0.35 M Na ₂ S-0.25 M Na ₂ SO ₃ aqueous solution	0.28	[212]
Ni ₂ P/CdS	>420 nm	0.35 M Na ₂ S-0.25 M Na ₂ SO ₃ aqueous solution	16.02	[212]
CoP	visible light	Na ₂ S-Na ₂ SO ₃ aqueous solution	1.75	[213]
CdS/CoP	visible light	Na ₂ S-Na ₂ SO ₃ aqueous solution	15.74	[213]

5. Conclusions and Outlooks

(1) Oxygen-deficient titanium oxide ($\text{TiO}_{2-\delta}$) shows higher photocatalytic activity than stoichiometric TiO_2 , which can be mainly attributed to the presence of Ti^{3+} species and oxygen deficiencies. The Ti^{3+} species would lead to new intermediate defect states (shallow donor) forming below the bottom of the conduction band of TiO_2 , which narrows the band gap of TiO_2 . The presence of oxygen deficiencies can decrease the transfer resistance of electrons. Resultantly, the photogenerated electrons can quickly transfer, thereby avoiding recombining with holes.

(2) Reductive treatment is the most direct and effective method to introduce oxygen defects in titanium oxides, for which H_2 is the most common reductant, while other reductants such as carbon, NaBH_4 , and NH_3 can also be selected. Moreover, ion doping, pulsed laser irradiation, calcination under anoxic conditions, plasma assistance, and so forth, have also been proven efficient strategies for introducing oxygen defects into titanium oxides. Other modification methods for TiO_2 , including ion doping, composite, surface noble metal deposition, dye sensitization, and loading on supports are also exploited to broaden the light-absorption region and suppress the recombination of photogenerated e_{CB}^- and h_{VB}^+ for $\text{TiO}_{2-\delta}$. The photocatalytic activity of titanium oxides is hopefully improved further by the combination of introducing oxygen defects with these modification methods, which have reached some remarkable results.

(3) Hydrogen production by photocatalytic water splitting over $\text{TiO}_{2-\delta}$ -based photocatalysts shows a strong development momentum. However, there exists at least three major challenges at present. The first is how to control the concentration of oxygen defects in $\text{TiO}_{2-\delta}$. Although the density of oxygen deficiencies can be controlled by adjusting the conditions of the reduction treatment, the spontaneously introduced oxygen defects during other modification processes, such as ion doping and surface treatment, are difficult to control and predict accurately. Secondly, current studies on regulating energy band structures mainly concentrate on enhancing light harvesting. Actually, the positions of CB and VB are also critical for photocatalytic water splitting, especially the position of CB. The CB position of TiO_2 is very close to the reduction potential of H^+/H_2 (0 V vs. NHE at pH = 0). The decrease in the CB minimum can lead to a wider light-absorption region but the reducing ability of photogenerated electrons is also impaired at the same time. If the CB minimum is more positive than the reduction potential of H^+/H_2 , the photocatalytic hydrogen evolution activity will take a mighty blow. Thus, regulating the band gap of TiO_2 is a challenging task because there are numerous factors that can affect the band position of $\text{TiO}_{2-\delta}$ during the modifying process. Combining theoretical calculation prediction with precise control of synthesis conditions may be a solution to solve this issue. In addition, the current studies pay little attention to the adsorption of reactants (H_2O) and the desorption of products (H_2 and O_2). The dissolved O_2 and H_2 can react with each other at the cocatalyst surface. O_2 dissolved in water will also compete photogenerated electrons with the hydrogen evolution reaction. These factors weaken the efficiency of photocatalytic hydrogen evolution. Therefore, this might be the next hot topic in studies of this nature. Although photocatalytic hydrogen evolution remains in the laboratory stage, further study may bring promising results.

Author Contributions: Y.C.: literature surveying, drawing of figures and tables, sorting data, writing of original manuscript; X.F.: literature surveying, revision and finalizing of the manuscript; Z.P.: revision and finalizing of the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: Many thanks for the financial support for this work by the National Natural Science Foundation of China (grant nos. 12174035 and 61274015).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data sharing not applicable. No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflict of interest.

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