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Defective TiO_2 with Intrinsic Point Defects for Photocatalytic Hydrogen Production: A Review

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Abstract

Titanium dioxide (TiO_2) has been intensively investigated for solar hydrogen conversion via photocatalytic and photoelectrochemical water splitting. However, the performance of TiO_2 photocatalyst for hydrogen generation is low due to the rapid electron-hole recombination and its wide band gap (3.0-3.2 eV) which is only feasible for UV light absorption of solar spectrum. There are various strategies have been used for TiO_2 modification to harvest the sunlight and improve the surface chemical reaction between TiO_2 and H_2O for water splitting. Among the TiO_2 modification strategies, intrinsic point defects such as vacancies and interstitials on TiO_2 surface have been proven to improve the TiO_2 properties for photo-catalytic activity. In this article, the recent progress achieved in defective TiO_2 with intrinsic point defects for photocatalytic hydrogen evolution and photoelectrochemical water splitting has been reviewed. The fabrication methods of defective TiO_2 along with their structural, optical, and charge carrier properties have been introduced. It has appeared that the intrinsic point defects are a promising strategy to improve the performance of TiO_2 for photocatalytic hydrogen production, and more efforts are still needed to improve the TiO_2 performance for photocatalytic hydrogen production in this area of research.

Keywords TiO_2 Surface; vacancies; interstitials; photoelectrochemical water splitting; Photocatalytic hydrogen evolution; intrinsic point defects.

Contents

1. Introduction

Photocatalytic hydrogen production is being considered as a promising solution for supplying environmentally friendly and sustainable energy. There are two methods to produce hydrogen directly from the sunlight: photocatalytic (PC) and photoelectrochemical (PEC) water splitting [1, 2]. Semiconductor photocatalysts has been considered to be used for the conversion of solar energy to chemical energy. When the photocatalyst absorbs photons of sunlight with energy greater than or equal to its band gap, the electrons are excited from the valance band (VB) to the conduction band (CB) and then the photoinduced electron-hole pairs are formed. The holes oxidize the water to oxygen and the electrons reduce protons (H^+) to hydrogen, respectively[3]. However, most of semiconductors have ability to absorb UV light which constitute only 4% of solar spectrum. Therefore, in order to improve the solar hydrogen conversion, a modification of photocatalyst properties should be conducted to improve the visible light absorption, which constitute 43% of solar energy. Besides, low-cost and stable semiconductors are required [4, 5].

Titanium dioxide (TiO_2) is one of the most attractive materials which is used as a photocatalyst for hydrogen production because it is a non-toxic, cheap, abundant and stable in aqueous solutions. Besides, it has the right conduction and valence band edge position for water reduction and oxidation. However, TiO_2 still has some limitations as a photocatalyst in terms of wide band gap 3.0 eV (415 nm) for rutile and 3.2 eV (380 nm) for anatase. Therefore, it only absorbs light in the ultraviolet (UV). Moreover, the photogenerated charge carrier recombination of TiO_2 is high[4, 6]. Thus, due to the low harvesting of sunlight and rapid recombination of charge carrier, TiO_2 is not efficient enough for hydrogen production. In order to overcome these limitations, various strategies have been used to improve the photocatalytic hydrogen production by water splitting. The metal or non-metal doping on TiO_2 is used to enhance the photocatalytic activity of TiO_2. However, the high concentration of dopants creates recombination center and the low concentration of dopants is not enough for the visible light absorption [7, 8, 9, 10]. In addition, metal loading such as Ag or Au nanoparticles is used to enhance the absorption of visible light due to the surface plasmon resonance[11, 12]. The metal co-catalyst like Pt and Pd prevent the charge carrier recombination. However, all these metals are expensive to be used for enhancing the absorption of TiO_2 [13, 14]. Furthermore, semiconductor heterojunction is a common method to modify the photocatalytic properties of TiO_2. In this process, p-type and n-type semiconductors are contacted, the electrons and holes are diffuse and form a built-in electrical potential. The formation of the electrical field might enhance the charge separation and improve the photocatalytic activity of TiO_2 [15]. Nonetheless, the accumulation of electrons might create a photo-corrosion for one of semiconductors or both of them [16].

Apart of the above-mentioned strategies, intrinsic point defects have attractive attention to promote the photocatalytic properties of TiO_2 for hydrogen production. Thesedefects have essential impact for improving TiO_2 performance for H_2 generation. For instance, oxygen vacancies/Ti^{3+} extend the light absorption to visible light and enhance the charge carrier separation [17, 18], while titanium vacancies increase the charge mobility[19]. Furthermore, oxygen vacancy-defected/ titanium vacancy-defected TiO_2 on anatase phase increase the photocatalytic activity of TiO_2 for hydrogen production[20].

This review focuses on the recent developments in intrinsic point defects in TiO_2 for photocatalytic and photo-electrochemical hydrogen production. In addition, the basic principles and preparation methods of intrinsic point defects in TiO_2 are discussed. The structural, optical and charge transfer properties are reviewed.

2. Principles of intrinsic point defects in TiO_2

Intrinsic point defect of TiO_2 has been considered in terms of ionic and electronic defects. The ionic defects in TiO_2 include oxygen vacancies (V_o), titanium interstitials ($\mathrm{Ti_{int}}$), titanium vacancies ($\mathrm{V_{Ti}}$), and oxygen interstitials ($\mathrm{O_{int}}$), while the electronic defects involve electrons and electron holes as shown in Figure 1(a). The electrons are located on Ti^{3+} ions in their lattice sites, whereas, the electron holes are located on lattice sites of O^- ions. These defects occur due to the introduction of disorder in the crystal pattern of TiO_2 [21, 22, 23, 24]. Thus, nonstoichiometric titanium dioxide is considered to be either TiO_{2-x} with oxygen deficient, or TiO_{2+x} with titanium deficient. Oxygen vacancies and titanium interstitials are donors of electrons and form donor level in the electronic structure of TiO_2. The existence of the donors shifts the Fermi level towards the lower part of the band gap. In contrast, the titanium vacancies and oxygen interstitials are acceptors and form acceptor level in TiO_2. As a result, the presence of the acceptors moves the Fermi level towards the upper part of the band gap. For instance, the oxygen vacancies and titanium vacancies form energy levels in TiO_2 at 1.18 and 1.15 eV, respectively [25, 23, 24, 26, 27, 28].

Additionally, defects enhance the photocatalytic activity of TiO_2. For instance, titanium vacancies act as surface active sites for adsorption of water on TiO_2 surface. Titanium vacancies are needed to transfer electrons from water molecules to TiO_2 surface in order to enhance the oxidation reaction [29]. As depicted in Figure 1(b), when the water molecules are adsorbed on the specific surface-active site (titanium vacancies), the titanium vacancies have a strong electron affinity and the ability to donate electron holes. Active complexes of titanium vacancies are formed when electrons holes transfer to adsorbed water species. These active complexes are metastable and decomposed into gaseous oxygen and hydrogen ions[26].

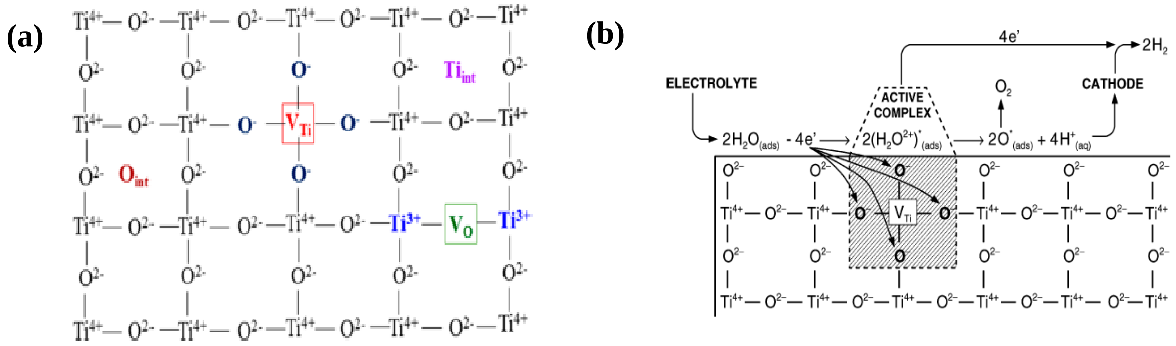

Figure 1: (a) Intrinsic point defects in TiO_2 [19]. (b) titanium vacancies(V_{Ti}) in TiO_2 for charge transfer and water splitting [26].

3. Preparation methods for intrinsic point defects on TiO_2

Several strategies were employed to form the intrinsic point defects on TiO_2 as summarized in table 1. Ti^{3+}/oxygen vacancies defects can be fabricated using various metheds such as hydrogenation, and reduction.The thermal treatment with hydrogen gas (hydrogenation) is used to Ti^{3+}/oxygen vacancies formation. Amano et al. [30] calcined TiO_2 (anatase phase/rutile phase = 3.4/ 96.6 wt %) under hydrogen gas. TiO_2 was treated in calcination temperature range of 300−1100 °C under hydrogen gas flow rate of 50 mL/ min at atmospheric pressure, and then the samples were cooled down to room temperature. Hydrogen treatment at calcination temperature 500 °C formed Ti^{3+}, whereas the density of electrons was enhanced at 700 °C. Liu et al. [31] fabricated the T^{3+}/ oxygen vacancies in TiO_2 using a high pressure gas with temperature treatment. The formation of Ti^{3+} and oxygen vacancies on TiO_2 nanotubes were fabricated by heat treatment with Ar or Ar/H_2 under atmospheric pressure, and high H_2 pressure. The Ti^{3+} formation was recorded at 500 °C under hydrogen pressure 20 bar. in another study, the oxidation of TiH_2 in H_2O_2 to form Ti^{3+} on TiO_2 was conducted by Liu et al. [32]. Ti^{3+} self-doped TiO_2 in anatase phase was synthesized by oxidation of TiH_2 in H_2O_2 which followed by the calcination temperature (300-600°C), calcination time (2-4 h) and flow rate of argon was at 20 mL min^{-1}. Grabstanowicz et al. [33] also used the oxidation of TiH_2 in H_2O_2 to form Ti^{3+}/TiO_2 in rutile phase as directed in Figure 2(a), the gray TiH_2 reacted with H_2O_2 and formed yellow gel which calcined at 630 °C for 3 h. under argon flow to form black $Ti^{3+/}TiO_2$ powder. Wei et al. [34] synthesized Ti^{3+} self-doped anatase TiO_2 by using H_2O_2 with hydrothermal method. It was observed that when the hydrothermal reaction time was 12 h and the amount of H_2O_2 was 100 µL, oxygen vacancies was formed after calcination with N_2.

The reduction method has also been utilized for intrinsic point defects formation on TiO_2. The utilization of $NaBH_4$ to form Vo/Ti^{3+} on TiO_2 have been reported by many authors in the literature[35, 36, 37, 38,39, 40, 41, 41,]. Xing et al. [38] used Solvo-thermal method with $NaBH_4$ for Ti^{3+}/oxygen vacancies formation on TiO_2. After adding 0.13g of $NaBH_4$ as reduction agent, Ti^{3+}/oxygen vacancies were formed. TiO_2 powder with different amount of $NaBH_4$ was used to form Vo/Ti^{3+} by hydrothermal method. Addition of 12 g of $NaBH_4$ to TiO_2 exhibited the highest photocatalytic degradation efficiency of methylene blue [39]. Tian et al. [40] synthesized TiO_2 nanobelts with Vo/Ti^{3+} by using $NaBH_4$ with heat treatment and argon gas. The defects were formed by adding of 5 mL of $NaBH_4$, and heat treatment at 380

°C for 24 h. It was claimed that $NaBH_4$ reduced Ti^{4+} to Ti^{3+} as is shown in the following reaction (1) and (2).

$$NaBH_4 + 8OH^- \rightarrow NaBO_2 + 8e^- + 6H_2O \qquad (1)$$

$$Ti^{4+} + e^- \rightarrow Ti^{3+} \qquad (2)$$

Kang et al. [41] used $NaBH_4$ as a reduction agent to form oxygen vacancies on the surface and interior of the TiO_2 nanotube arrays (NTAs). NTAs were fabricated by anodizing a Ti foil in ethylene glycol solution including NH_4F (0.3 wt%) and H_2O (2 vol%) at 80V for 30 min with a graphite cathode. The nanotube arrays were annealed at 450 C for 3 h. To form the oxygen vacancies, NTAs were dipped in $NaBH_4$ at room temperature for different times. Ariyanti et al. [42] synthesized defective TiO_2 with oxygen vacancies. TiO_2 nanoparticles were mixed with $NaBH_4$ and then heated at temperature in the range 300-450 °C with Ar. The color of TiO_2 has changed when the treatment temperature was changed as shown in Figure 2(b).

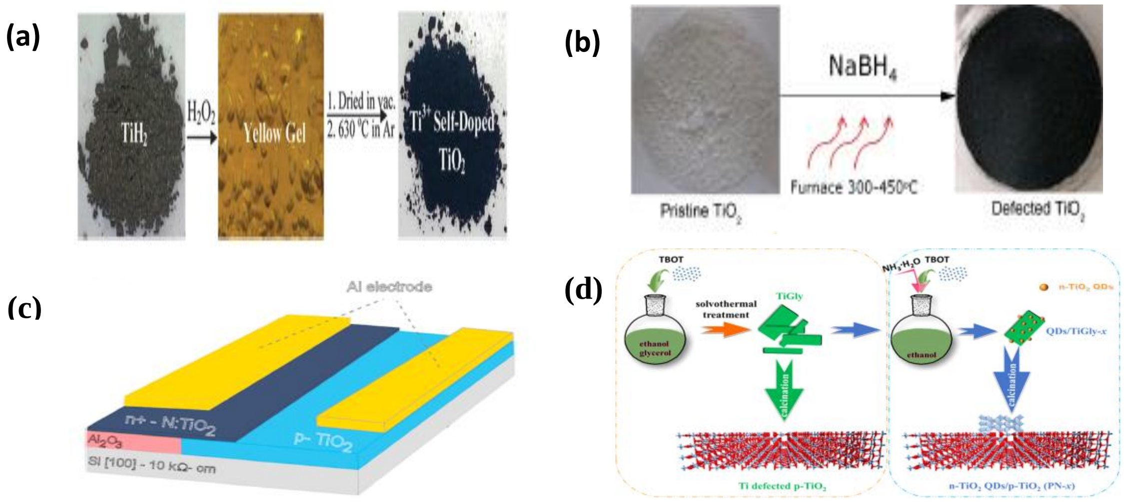

Figure 2: (a) Ti^{3+} self-doped rutile TiO_2 by oxidation of TiH_2 in H_2O_2[33]]. (b) Ti^{3+} self-doped TiO_2 by $NaBH_4$ [42]. (c) Synthesis of p-type TiO_2 by atomic layer deposition[43] [51]. (d) Formation of TiO_2 p-n homo-junction by in-situ decorating n-type TiO_2 QDs on p-type TiO_2 sheets [20].

In addition, there are other methods which have been used to form the intrinsic defects. Blue Ti^{3+} self-doped TiO_2 nanoparticles with anatase and rutile phases was fabricated by solvothermal method [44]. Sasikala et al.[45] synthesized Ti^{3+} nanoparticles by various methods which were solvothermal, sonochemical and polyol methods. Saputera et al. [46] used three different methods to synthesize TiO_2 with Ti^{3+} and oxygen vacancies defects. Reduction, calcination, and hydrogenation methods were used to fabricate the nanoparticles with the defects. Ice-water Quenching and Imidazole(as reducing agent) also were utilized for preparation of intrinsic defects [46, 47].

In comparison with Ti^{3+}self-doped TiO_2 and introducing oxygen vacancies which exhibits n-type properties, few studies have been conducted for the formation of un-doped p-type TiO_2 with titanium vacancies or oxygen interstitials. Wang et al. [19] formed TiO_2 with titanium vacancies by solvothermal method. The reaction of tetrabutyle titanate in ethanol-glycerol mixture formed V_{Ti} after calcination treatment. V_{Ti} was formed when 20 mL glycerol and 60 mL ethanol were used and then the product was calcined at 470 °C for one hour. In another study, V_{Ti} was formed in rutile TiO_2 by thermal oxidation at annealing temperature 1323 K for~ 3450-3500 h and under oxygen pressure = 75 kPa [49, 50]. Bhowmik et al. [51] synthesized undoped anatase p-type TiO_2 by sol–gel method, and then was deposited on thermally oxidized p-type Si substrate by drop coating and then annealed in air at 450 °C for 3 hrs. However, it was not explained if the p-type properties of TiO_2 either due to titanium vacancies or oxygen interstitials existence. Iancu et al. [43] synthesized undoped p-type TiO_2 films with oxygen interstitial defects films by atomic layer deposition (ALD). Three types of TiO_2 films were deposited: two un- doped TiO_2 were deposited at 200 and 250 °C, and N-doped TiO_2 was deposited at 250 °C. One sample of each type was left without post-deposition treatment. The rest samples of each type were annealed at temperature ranged from 400 to 900 °C. Some samples were annealed with nitrogen gas, while others were annealed with oxygen gas. The post-deposited samples exhibited p-type conductivity, which contributed to the presence of oxygen interstitials. Then TiO_2 p-n homojunction diodes were fabricated by a lithography method on silicon wafer as shown in Figure 2(c).

Besides, there are few studies which have been focused on synthesis of intrinsic donor and acceptor defects on TiO_2 simultaneously. Pan et al. [20] fabricated TiO_2 p-n homojunction by decorated n-type oxygen-defected TiO_2 on p-type titanium-defected TiO_2. The source of n-type TiO_2 was added to Titanium glycerolate (TiGly) as presented in Figure 2(d). Then the resulting powder of oxygen-defected TiO_2/titanium-defected TiO_2 was calcined in air at 470 °C. Moreover, the titanium vacancies with titanium interstitials can cause defects on TiO_2. Wu et al. [24] synthesized titanium vacancies-titanium interstitials/TiO_2 by sol gel method with UV light pre-treatment. The titanium vacancies and titanium interstitials were formed when TiO_2 nanoparticles were treated with UV light and its color changed from pale blue to yellow.

Table 1. Synthesis, properties and applications of defective TiO_2 with intrinsic point defects

Fabrication method	Phase	Morphology	Defects	Application	Reference
Hydrogenation of TiO_2	Pure rutile or mixed rutile and anatase phase	TiO_2 particles and films.	Ti^{3+} ions/ oxygen vacancies	Water oxidation	[30]
Hydrogenation of TiO_2 with high pressure	Anatase	TiO_2 nanotubes	Ti^{3+} ions/ oxygen vacancies	Photocatalytic hydrogen production	[31]
Oxidation of TiH_2 in H_2O_2	Anatase	Nanoparticles	Ti^{3+} ions/ oxygen vacancies	Photodegradation of Methylene blue (MB)	[32]
Oxidation of TiH_2 in H_2O_2	Rutile	Nanoparticles	Ti^{3+} ions	Photodegradation of organic species in water	[33]
Hydrothermal method	Anatase	Nanorod-type microstructure	Ti^{3+} ions/ oxygen vacancies	photocatalytic hydrogen production	[34]
Reduction with $NaBH_4$	Anatase	Nanoparticles	Ti^{3+} ions/ oxygen vacancies	Photodegradation of methyl orange and phenol	[38]
Reduction with $NaBH_4$	Mixed anatase and rutile phase	Nanoparticles and hierarchical structures	Ti^{3+} ions/ oxygen vacancies	Photodegradation rate of methylene blue	[39]
Reduction with $NaBH_4$	anatase	Nanobelts	Ti^{3+} ions/ oxygen vacancies	Photodegradation of methyl orange and water splitting for hydrogen production	[40]
Reduction with $NaBH_4$	Anatase	Nanotube arrays	Ti^{3+} ions/ oxygen vacancies	photoelectrochemical water splitting	[41]
Reduction with $NaBH_4$	Anatase	Nanoparticles	Ti^{3+} ions/ oxygen vacancies	Rhodamine B photodegradation	[42]
Solvothermal method	Anatase	NM	Titanium vacancies	Photodegradation of organic pollutants and photocatalytic hydrogen production	[19]
Thermal oxidation	Rutile	NM	Titanium vacancies	NM	[49, 50]
Sol–gel method	Anatase	Thin film	P-type TiO_2	Acetone detection	[51]
Atomic layer deposition	Rutile	Thin film	Oxygen interstitials	As homojunction diode	[43]
Decorating n-type TiO_2 QDs on p-type TiO_2 sheets	Anatase	Particles	P-n homojunction(oxygen and titanium vacancies)	Photoelectrochemical and photocatalytic hydrogen generation	[20]
Sol gel method with UV light pre-treatment	Anatase	Nanoparticles	Titanium vacancies and titanium interstitials	Photocatalytic hydrogen production	[24]

NM: Not Mentioned.

4.Properties of defective TiO_2 with intrinsic point defects

4.1 Structural properties

The intrinsic defects are characterized by different techniques such as X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR), and Raman spectrometry. Xing et al. [38] used solvothermal method with $NaBH_4$ for Ti^{3+}/oxygen vacancies formation on TiO_2. After adding 0.13 g $NaBH_4$ as reduction agent, the samples were washed with HCl. XPS was used to detect the existence of Ti^{3+} and oxygen vacancies. As shown in figure 3, after washing the samples with HCl, the peak 458 eV of Ti 2p XPS spectra showed the presence of Ti^{3+}. Moreover, peak 531.8 eV on O 1s XPS spectra was related to oxygen vacancies formation, respectively.

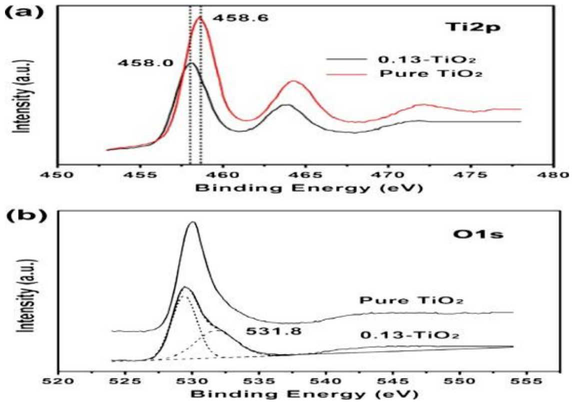

Figure 3. XPS spectra of Ti^{3+} self-doped TiO_2: (a) Ti2p and (b) O1s XPS spectra, the red line of XPS spectra for pure TiO_2 and the black for reduced TiO_2 with 0.13 g $NaBH_4$[38].

Ti^{3+} defects which formed in mesoporous black TiO_2/graphene assemblies were investigated in the literature. The XPS spectrum of Ti 2p1/2 and 2p3/2 showed peaks at 463.6 and 457.8 eV which can be assigned to Ti^{4+}. Meanwhile, there were two peaks at 462.7 and 457.0 eV which corresponded to the Ti 2p1/2 and Ti 2p3/2 peaks of Ti^{3+} species. According to O 1s XPs spectrum, two peaks at 529.8 and 532.1 eV were used as indication for Ti-O and the -OH group. The XPS spectrum of Ti 2p and O 1s were indicated that the surface hydrogenation successfully formed Ti^{3+} ions which enhanced the visible light absorption [18]. Yin et al. [52] studied the chemical composition of self-doped TiO_2 hierarchical hollow spheres by XPS spectrum. The study observed that after the TiO_2 was reduced by $NaBH_4$, the Ti 2p peak shifted to lower binding energy which can be due to the formation of Ti^{3+} species . The O 1s peak shifted from 529.8 to 529.2 eV, which indicated the electrons transfer from conduction band to oxygen vacancy level. Furthermore, electron paramagnetic resonance (EPR) showed strong signal at 2.002 which can be assigned to oxygen vacancies. Moreover, the super-paramagnetic behavior was observed because of the presence of Ti^{3+} species. As a result, the EPR signal and super-paramagnetic behavior confirmed the existence of oxygen vacancies and Ti^{3+} species in self-doped TiO_2 hierarchical hollow spheres, respectively.

Yang et al. [53] analyzed the chemical states of core/shell TiO_2/C nanostructure with Pt loading to form Ti^{3+} species (Ti^{3+}/TCP) by XPS spectrum. Two peaks at 458.7 (Ti 2p3/2) and 464.5 eV (Ti 2p1/2) were related to Ti^{4+}, while two peaks were centered at 457.6 and 463.2 eV, corresponding to the Ti 2p1/2 and Ti 2p3/2 peaks of Ti^{3+} ions. For O 1s XPS spectra, the peak at 529.2 eV was assigned to Ti^{4+}-O, and 530.2 eV were assigned to Ti^{3+}-O or -OH. Amano et al. [30] calcined TiO_2 with hydrogen gas. Ti^{3+} and oxygen vacancies were characterized by electron spin resonance (ESR) spectra. It was demonstrated that at 500 °C under H_2 treatment signal at g = 2.002 has indicated that there were electrons trapped in oxygen vacancies, and at signal g = 1.974 was related to Ti^{3+} species as shown in Figure 4(a). Liu et al. [31] synthesized the Ti^{3+} self-doped TiO_2 by temperature treatment with different type of gases including H_2/Ar or Ar under atmospheric pressure, and high H_2 pressure. The signals (g_{xx} = 1.991, g $_{yy}$= 1.974 g_{zz}=1.939) of ESR at 4 K, indicated the formation of Ti^{3+} under high hydrogen pressure.

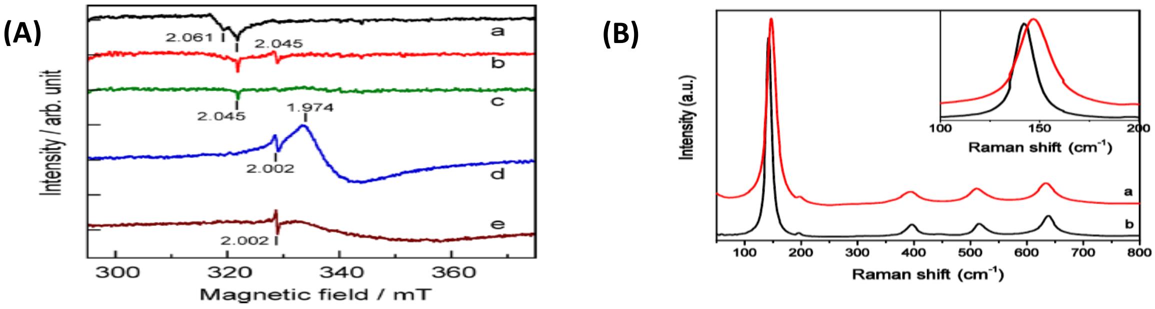

Figure 4: (A) ESR spectra of TiO_2 samples treated: (a) without H_2 treatment, (b) H_2 treatment at 300 °C, (c) H_2 treatment at 400 °C, (d) H_2 treatment at 500 °C, (e) H_2 treatment at 700 °C [30]. (B): Raman spectra of (a) Ti^{3+} self-doped blue TiO_2 with anatase-rutile mixture, (b) P25-TiO_2 [44].

Xin et al. [54] fabricated anatase self-doped TiO_2 nanocrystals by solvothermal method and followed by post-annealing at various temperatures. Raman spectroscopy was employed to investigate the defects in TiO_2. The peak of anatase 144.4 cm^{-1} shifted to 152.6 cm^{-1} and became more broader compared to P25-TiO_2, which indicated the existence of Ti^{3+} with oxygen vacancies or the disorder in the crystal. The mixture of anatase and rutile for Ti^{3+} and oxygen vacancies defects formation on TiO_2 reported by [44]. The authors formed Ti^{3+} self-doped blue TiO_2 with anatase-rutile mixture by solvothermal method. Raman spectrometry was used to characterize the forming of Ti^{3+} and oxygen vacancies. In comparison with P25-TiO_2, the Raman band at 142 cm^{-1} shifted to 147 cm^{-1} of Ti^{3+} self-doped blue TiO_2 with anatase-rutile mixture as is shown in Figure 4(b). The peak shifting of 5 cm^{-1} and broadening ascribed to disorder in TiO_2 which occurred due to the localized Ti^{3+} associated with oxygen vacancies. Qiu et al. [55] used Raman spectrum to detect the presence of Ti^{3+} species in TiO_2 nanocrystal, where there were peaks at 146.2 cm^{-1}, 409.1 cm^{-1}, 516.6 cm^{-1}, and 640.1 cm^{-1} due to anatase phase nature. The Eg mode at 144 cm^{-1} and 639 cm^{-1} were shifted to 146.2 cm^{-1} and 640.1 cm^{-1}, respectively, which indicated the formation of Ti^{3+} ions in TiO_2. Wu et al [24] investigated the formation of titanium interstitials and titanium vacancies on the ultra-small yellow TiO_2 nanoparticles. The XPS peak at 456.9 eV which related to Ti^{3+} ions have not found. Moreover, it was observed that the Fermi energy was 1.0 eV which is lower than Fermi level of oxygen vacancies, thus indicating that the defect was titanium interstitials. The XPS data and Fermi level confirmed the donor intrinsic defects was titanium interstitials and was not oxygen vacancies with Ti^{3+} defects. Besides, titanium vacancies were also found. From ESR spectra, the signal $g = 1.998$ was found due to the formation of titanium vacancies. Wang et al. [19] claimed that synthesized TiO_2 by solvothermal method formed titanium vacancies. There was no XPS peaks related to Ti^{3+} or Vo. Furthermore, from ESR analysis there was a new signal at $g = 1.998$ which is not related to Ti^{3+}, Vo, or O^{2-} and was presumably related to titanium vacancies.

4.2 Optical properties

The intrinsic defects affect the optical properties of TiO_2. The absorption of sunlight is shifted to the visible or near red-infrared light region duo to the formation of intrinsic point defects energy level between the valence bands and conduction bands of TiO_2 as shown in Figure 5. The calculated energy level are 1.17 eV, 1.23 eV, and 1.15 eV for V_O, Ti_{int} and V_{Ti}, respectively [56].

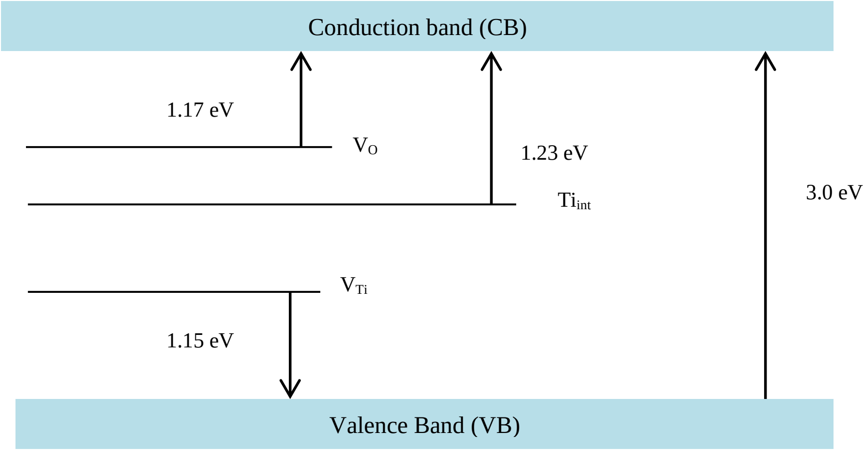

Figure 5. Energy level of V_O, Ti_{int}, and V_{Ti} between VB and VB of TiO_2, calculated energy level from Ref[56].

Moreover, due to the formation of energy level of the intrinsic defects, the band gap of TiO_2 is narrowed. Table 2 shows a summary of the narrowed band gap that reported from previous literature. Qui et al. [55] synthesized Ti^{3+} self-doped TiO_2 nanocrystals by hydrothermal method based on Le Chatelier's principle. The study investigated the effect of Ti^{3+} and oxygen vacancies on band gap and visible light absorption of TiO_2. The formation method of oxygen vacancies and Ti^{3+} was performed by controlling the ratio between $TiCl_3$ and $(NH_4)_2TiF_6$. It was indicated that the defect of Ti^{3+} and oxygen vacancies prompted the absorption in visible light range 400-800 nm(Figure 6(a)) and the band gap was reduced to 2.68 eV as shown in Figure 6(b). The enhancement of absorption in visible region was due to the reduced band gap of TiO_2. Reducing the band gap was because of the new mid gap level below conduction band which produced by Ti^{3+} and oxygen vacancies defects.

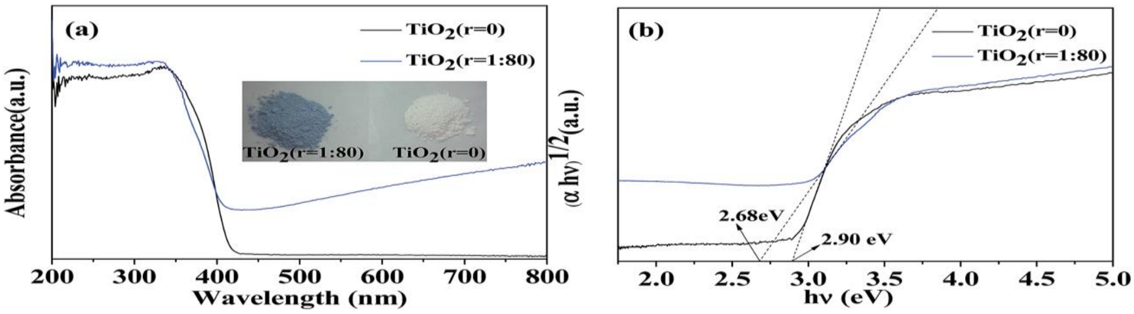

Figure 6. (a) UV-visible diffuse reflectance spectra and (b) reduced band gap of TiO_2 nanocrystals prepared with (r = 1: 80) and without(r = 0) $(NH_4)_2TiF_6$. The inset in (a) shows color-change of the two TiO_2 sample[55].

Xin et al. [54] fabricated anatase TiO_2 nanocrystals with different concentration of Ti^{3+} species by solvothermal method and followed by post-annealing. All samples which were treated by post-annealing at different temperatures (300-700°C) showed higher absorption in the longer wavelengths comparison to TiO_{2-x} without post-annealing. TiO_{2-x} which was annealed at 500 °C has the narrowest band gap (2.63 eV) in comparison with the other samples. The narrowest band gap was ascribed to the abundance of Ti^{3+}in the bulk of TiO_2. Xing et al. [38] used $NaBH_4$ as reduction agent for Ti^{3+}-doped TiO_2, and consequently the absorption intensity increased. The Ti^{3+}/TiO_2 with the 0.13 g of $NaBH_4$ showed the highest absorption intensity and the band gap was 2.71 eV. Zhou et al. [18] investigated the optical properties of Ti^{3+} self-doped mesoporous black TiO_2/graphene assemblies and mesoporous black TiO_2/graphene assemblies. The existence of Ti^{3+} ions increased the visible light absorption in comparison with mesoporous black TiO_2/graphene assemblies which exhibited a slight absorption in visible light. Furthermore, the band gap of Ti^{3+} self-doped mesoporous black TiO_2/graphene assemblies was 2.7 eV, while the band gap of mesoporous black TiO_2/graphene assemblies was 3.2 eV. The wide absorption in visible light and narrowed band gap has improved the photocatalytic properties due to the synergistic effect of Ti^{3+}, mesoporous TiO_2, and graphene.

Table 2. The band gap of defective TiO_2 with Ti^{3+} and V_O

Started TiO_2	Defect	Band gap (eV)	Reference
TiO_2 nanocrystals	Ti^{3+}, V_O	2.68	[55]
TiO_2 nanocrystals	Ti^{3+}	2.63	[54]
TiO_2 nanoparticles	Ti^{3+}, V_O	2.71	[38]
mesoporous black TiO_2/graphene assemblies	Ti^{3+}, V_O	2.7	[18]
ultra-small yellow TiO_2 nanoparticles	Ti_{int}	2.76	[24]

Liu et al. [32]fabricated Ti^{3+} self-doped TiO_{2-x} nanoparticles in anatase phase by oxidation of TiH_2 in H_2O_2, then the defective nanoparticles were calcined at different temperatures (300-600 °C) with various times (2-4 h). It was observed that all samples treated at different temperatures and times had absorbed the visible light in range between 400 and 800 nm decreased the band gap. It has been demonstrated that although the two samples of TiO_{2-x} which were treated at 500 °C for 3 h. and at 400 °C for 4 h showed strong visible light absorption, these samples has also shown weak UV absorption. The strong absorption in visible region ascribed to the untreated TiH_2. Among all samples, TiO_{2-x} at 500 °C for 4 h which had a better crystallinity and higher content of Ti^{3+} exhibited the strongest visible light absorption. Zhou et al. [44] prepared Ti^{3+} self-doped anatase-rutile TiO_2 nanoparticles by solvothermal method. During the sample's preparation, the volume ratios of $TiCl_3$ to titanium isopropoxide was controlled (0:4, 5:4, 10:4, 15:4, and 30:4). When the volume of $TiCl_3$ during synthetic reaction increased, the absorption in visible light increased and optical absorption band edge shifted to longer wavelengths. Furthermore, when the amount of $TiCl_3$ was increased, the band gaps of all samples were decreased. It was noted that the formation of Ti^{3+} defects and increased percentage of rutile phase were associated with decreases in the band gaps of the samples. Similar to Ti^{3+} and oxygen vacancies, titanium interstitials also reduce the band gap and enhance the visible light absorption. The ultra-small yellow TiO_2 nanoparticles with the titanium interstitials and titanium vacancies reduced the band gap to 2.76 eV which attributed to the titanium interstitials formation. The sample absorbed the light at 450 nm which was related to visible light absorption [24]. However, compared to the intrinsic donor defects, titanium vacancies which as intrinsic acceptor defect do not reduce the band gap of TiO_2. Bak et al. [50] synthesized the defective TiO_2 with titanium vacancies by prolong oxidation. The authors evaluated the effect of prolong oxidation on the band gap of TiO_2. It was observed that the wide band gap of TiO_2 was not reduced by prolonged oxidation which formed the titanium vacancies. That means there was no change in band gap before and after forming the titanium vacancies.

4.3 Transfer charge properties

In order to achieve an efficient photo-catalyst, the high separation efficiency of photoinduced electron-hole pairs and rapid charge transfer are required to enhance the chemical reaction and accordingly improve the photo-catalytic activity. Therefore, numerous studies have focus on the effect of intrinsic defects in TiO_2 on charge separation and transfer. Zhang et al. [57] synthesized different types of TiO_2 by hydrothermal; anatase TiO_2 sheet, Ti^{3+} self-doped rutile TiO_2, Ti^{3+} self-doped anatase-rutile TiO_2 sheet (fabricated with anatase TiO_2 sheet), and Ti^{3+} self-doped anatase-rutile TiO_2 (fabricated with Degussa P25TiO_2). The authors investigated the separation efficiency of the photogenerated electron-hole pairs by photoluminescence (PL) spectra. PL intensity of Ti^{3+} self-doped anatase-rutile TiO_2 was lower than Ti^{3+} self-doped rutile TiO_2. The lower PL intensity indicated much higher charge separation than self-doped rutile due to the transfer of photo-excited charge carriers between anatase and rutile TiO_2 under visible light irradiation. Furthermore, as compared with anatase TiO_2 and Ti^{3+} rutile TiO_2, self-doped anatase-rutile TiO_2 showed larger photocurrent. As a result, the PL intensity and photocurrent indicated self-doped anatase-rutile enhanced significantly the photogeneration charge carrier. Amano et al. [30] claimed that reduced TiO_2 with hydrogenation at various temperatures forming Ti^{3+} defects showed high donor density and low resistance, which attributed to the increase of n-type conductivity due to increasing the amount of conduction electrons. As the electrical conductivity enhanced, the charge carrier recombination reduced and accordingly improve the photocatalytic activity. Deng et al. [58] prepared Ti^{3+} self-doped TiO_2 nanorods/nanosheets by hydrothermal method and then treated with $NaBH_4$. The charge carrier transfer and photogenerated electron-hole pairs separation were tested by electrochemical impedance spectroscopy (EIS). The radius on the EIS Nyquist plot of Ti^{3+} self-doped TiO_2 nanorods/nanosheets was smaller than the radius of TiO_2 nanorods/nanosheets with or without light illumination, which attributed to enhancement of charge separation and transfer. Thus, the interface resistance became lower and the electrochemical reaction became more facilitated. Xin et al. [54] studied the electrochemical properties of Ti^{3+} self-doped TiO_2 nanocrystals (Ti^{3+}/ TiO_2 NCs) in anatase phase by EIS. It was observed that the radius of arc in EIS Nyquist plot of Ti^{3+}/ TiO_2 NCs was smaller than that samples without Ti^{3+} ions in dark and under light irradiation.

Moreover, various studies have investigated the effect of p-type TiO_2 on charge mobility. Table 3 shows the charge mobility of p-type TiO_2 which fabricated and investigated by various studies. Wang e al. [19] conducted a study on the effect of p-typeTiO_2 with titanium vacancies on charge mobility and resistivity. The existence of titanium vacancies increased the charge mobility and decreased the resistivity. Hall Effect measurement was used to determine the type of electrical conductivity and the charge mobility. The Hall coefficient was positive (+134 cm^3/C) for defective TiO_2 with titanium vacancy defects, which indicated the product was p-type and conducted via holes, while the non-defective TiO_2 with titanium vacancy defects exhibited negative Hall coefficient (−33.3 cm^3/C). In addition, the charge mobility of p-type TiO_2 was 1.39×10^{-4} $cm^2/V\cdot S$), which was higher than the charge mobility of n-type TiO_2 (0.223×10^{-4} $cm^2/V\cdot s$). It was reported that the mobility of Mn-doped p-TiO_2 is lower than that of pure TiO_2. Thus, unlike foreign p-type dopants, V_{Ti} has no deteriorating effect on the charge transfer. Furthermore, the Mott−Schottky plots showed negative slope which gave another evidence of p-type TiO_2 formation. From electrochemical impedance spectra (EIS), the radius in the Nyquist plot of p-type TiO_2 was smaller than the radius of n-type TiO_2, which indicated the titanium vacancies on TiO_2 enhanced the charge transfer between the TiO_2 and electrolyte interface. As a result, the charge carrier separation increased. Bak ea al. [50] formed titanium vacancies in TiO_2 by prolong oxidation with mixture of argon and oxygen gas. The effect of prolonged oxidation of TiO_2 on charge mobility was evaluated. The mobility of electrons increased to 0.8×10^{-5} $m^2 V^{-1} s^{-1}$ after 2470 h. Bhowmik et al. (2014) claimed that the charge carrier (hole) concentration and mobility of undoped p-type TiO_2 were 7.893×10^{15} cm^{-3} and 2.198×10^3 $cm^2 V^{-1} S^{-1}$, respectively. The authers observed that the carrier (hole) mobilities of undoped p-type (with oxygen interstitials) were larger than 400 $cm^2 V^{-1} S^{-1}$.

Table 3 Charge mobility of p-type TiO_2

Photocatalyst	Defect	Charge mobility	Reference
p-type TiO_2	V_{Ti}	1.39×10^{-4} $cm^2/V\cdot S$	[19]
p-type TiO_2	V_{Ti}	0.8×10^{-5} $m^2 V^{-1} s^{-1}$	[50]
p-type TiO_2 thin film	O_{int}	2.198 10^3 $cm^2 V^{-1} S^{-1}$	[51]
p-type TiO_2 thin film	V_{Ti}	400 $cm^2 V^{-1} S^{-1}$	[43]

5. Photocatalytic hydrogen production

Hydrogen production by photocatalytic water splitting is measured by two methods: photo-chemical reaction and photo-electrochemical reaction. In photochemical reaction(Figure 6(a)), the powder or thin film photo-catalyst is put in solution to perform the water splitting reaction. Mostly sacrificial agent is used for photochemical reaction to prevent the charge carrier recombination [57, 58, 59, 60]. Gas chromatograph with thermal conductive detector is used to estimate photocatalytic H_2 evolution rate. On the other hand, in the photoelectrochemical reaction as shown in Figure 6(b), the thin film photocatalyst acts as a working electrode. An external circuit is used to transfer the electrons from the anode to the cathode where hydrogen is generated. The photoelectrochemical water splitting is evaluated by measuring the photocurrent [57, 61].

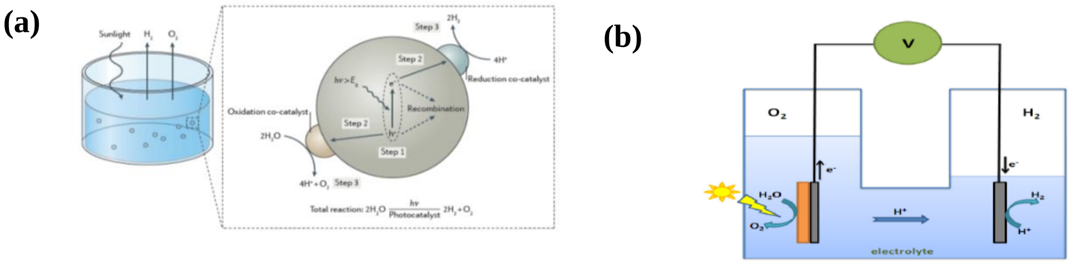

Figure 7. Photocatalytic water-splitting reactions: (a) photo-chemical reaction [60]. (b) photo-electrochemical reaction [57]

In this section, the recent advances of defective TiO_2 with intrinsic point defects for photocatalytic hydrogen evolution and photoelectrochemical water splitting were discussed. Table 4 and Table 5 summarize the photocatalytic hydrogen evolution and photoelectrochemical water splitting of defective TiO_2 with intrinsic point defects, respectively.

5.1 Photocatalytic hydrogen evolution

It is essential to measure the photocatalytic activity of TiO_2 for hydrogen evolution in order to know if the modified TiO_2 by different strategies improved the photocatalytic hydrogen generation. Yang et al. [53] synthesized Ti^{3+}/TCP nanorods by preparation of core/shell TiO_2/C nanostructure and then loaded of platinum (Pt) on the TiO_2/C surface. The hydrogen evolution was high (8117 µmol h^{-1} g^{-1}), which ascribed to the absorption of visible light. Furthermore, the carbon layers helped to promote the electrical conductivity which improve the separation and the transfer of photogenerated charge carrier. Most importantly, Ti^{3+}/TCP obtained a good catalytic stability after a 40h cycle reaction. Ti^{3+}/TiO_2 nanobelts was investigated for photocatalytic hydrogen generation. Ti^{3+}/oxygen vacancies formed on TiO_2 nanobelts by using $NaBH_4$ as reduction agent. The defects hindered the charge carrier recombination. Furthermore, the defects enhanced the charge carrier trapping and the visible light absorption. Thus, the H_2 evolution of reduced TiO_2 nanobelts (7.02 mmol $h^{-1}g^{-1}$) was higher than TiO_2 nanobelts (0.67 mmol $h^{-1}g^{-1}$)[40]. Yu et al. [64] synthesized Ti^{3+}/TiO_2 mesocrystals which exhibited mesoporous structure. H_2 generation of Ti^{3+}/TiO_2 mesocrystals (301.1 µmol $h^{-1}g^{-1}$) was higher than P25 TiO_2 (2.3 µmol g^{-1} h^{-1}). The enhanced photocatalytic activity attributed to the formation of Ti^{3+} and mesocrystal structure, resulting in enhancing the visible light absorption and electron-hole pair separation. Wang et al. [19] synthesized p-type-TiO_2 with titanium vacancies by solvothermal method. P-type TiO_2 exhibited H_2 evolution of 29.8 mmol $h^{-1}g^{-1}$, while the normal TiO_2 generated only 6.8 mmol $h^{-1}g^{-1}$. The existence of titanium vacancies increased the charge mobility and subsequently the photocatalytic activity increased. Pan et al. [20] investigated the effect of TiO_2 p-n homojunction on photocatalytic hydrogen generation. It exhibited the higher photoactivity for hydrogen evolution than p-type TiO_2 or n-type TiO_2. Hydrogen evolution rate of p-n TiO_2 was 50.3 mmol $h^{-1}g^{-1}$. Whereas the hydrogen evolution rate was recorded tobe 29.8 mmol $h^{-1}g^{-1}$ and 6.75 mmol $h^{-1}g^{-1}$ for p-type TiO_2 and n-type TiO_2, respectively. Wu et al. [24] synthesized TiO_2 with titanium vacancies and titanium interstitials by UV light pretreatment. Titanium vacancies (V_{Ti}) is as acceptor and titanium interstitials (Ti_{int}) is as donor. The acceptor-donor on TiO_2 enhanced the photocatalytic activity for H_2 generation. Hydrogen evolution was 48.4 µmol $h^{-1}g^{-1}$ under solar simulator illumination. The photocatalysis was enhanced due to V_{Ti}-Ti_{int} defects act as active sites. Li et al. [65] created a black Ti^{3+}/ TiO_2 by treated Ti foil in 1-methyl-imidazolium tetrafluoroborate ionic liquid containing acetic acid (HAc), and lithium acetate (LiAc) under ionothermal conditions. The photocatalytic activity for hydrogen production was 0.26 mmol $h^{-1}m^{-2}$, which was higher than TiO_2 P25 (0.13 mmol $h^{-1}m^{-2}$). The abundance of Ti^{3+} ions in TiO_2 lattice and oxygen vacancies had promoted the absorption of visible light and photoelectron-hole separation. Zhao et al. [36] produced four types of TiO_2 nanorods: stoichiometric nanorods (TiO_2 NRs), nanorods with surface oxygen vacancies (S-TiO_{2-x} NRs), nanorods with bulk oxygen vacancies (B-TiO_{2-x} NRs), and nanorods with bulk and surface oxygen vacancies (S-B-TiO_{2-x} NRs). S-TiO_{2-x} was treated by $NaBH_4$ reduction, while B-TiO_{2-x} was treated by hydrothermal method. Then B-TiO_{2-x} was treated by surface reduction treatment with $NaBH_4$ to form S-B-TiO_{2-x} NRs. Under solar-light irradiation, the H_2 evolution rate of S-B-TiO_{2-x} NRs (106.98 µmol/h) was higher than B-TiO_{2-x} NRs (56.58 µmol/h), S-TiO_{2-x} NRs (48.94 µmol/h), and TiO_2 NPs (8.49 µmol/h). All samples of TiO_2 NRs which contain oxygen vacancies showed higher photocatalytic activity in comparison with TiO_2 NRs without oxygen vacancies. The existence of oxygen vacancies improved the donor density, photogenerated charge carrier, and electronic conductivity.

Hydrothermal method was used to synthesize rice-shaped Ti^{3+} self-doped TiO_{2-x} nanoparticles by oxidation of TiH_2 in H_2O_2. The obtained photocatalyst exhibited higher H_2 evolution rate in comparison to P25 TiO_2 due to the formation of oxygen vacancies and Ti^{3+} ions [66]. Zhou et al. [18] formed Ti^{3+} self-doped mesoporous black TiO_2/graphene assemblies by solvothermal method and then the product was treated by surface hydrogenation. The structural properties of the photocatalyst effect the photocatalytic activity. The two-dimensional graphene structure and TiO_2 mesoporous architecture improved the charge carrier separation and the visible light absorption. Thus, hydrogen evolution rate of Ti^{3+} self-doped mesoporous black TiO_2/graphene assemblies (186 μmol h^{-1} $0.01g^{-1}$) was higher than mesoporous black TiO_2/graphene assemblies (~ 50 μmol h^{-1} 0.01 g^{-1}) and mesoporous black TiO_2 (~ 96 μmol h^{-1} 0.01 g^{-1}).

Table 4. Photocatalytic hydrogen evolution of defective TiO_2 with intrinsic point defects

Started TiO_2	Defect	Reactant solution	Light source	H_2 evolution	Reference
TiO_2 nanobelts	Ti^{3+}, V_O	1 wt% Pt & 100 mL 20 vol% methanol aqueous solution	350 W Xe arc lamp (350–750 nm)	7.02 mmol h^{-1}	[40]
Anatase TiO_2	V_{Ti}	1.0 wt. % Pt &120 mL 30 vol% methanol aqueous solution	300 W high-pressure Xenon lamp	29.86 mmol h^{-1}	[19]
Anatase TiO_2	V_{Ti} , $V_{O,}$ Ti^{3}	1.0 wt. % Pt &120 mL 30 vol% methanol aqueous solution	300 W high-pressure Xenon lamp	50.3 mmol h^{-1}	[20]
TiO_2 nanoparticles	$V_{Ti,}$ Ti_{int}	100 ml 3.7 vol% formaldehyde aqueous solution	solar simulator illumination	0.0484 mmol h^{-1}	[24]
black single-crystal TiO_2	Ti^{3+}, V_O	1 wt% Pt & 100 mL aqueous solution with 20 mL methanol	300 W Xenon lamp	0.26 mmol h^{-1} m^{-2}	[65]
TiO_2 nanorods	Ti^{3+}, V_O	1 wt.% Pt & 120 mL 30 vol.% methanol aqueous solution	300 W Xe lamp	106.98 μmol/h	[36]
TiO_2 nanotube arrays	Ti^{3+}, V_O	methanol/water (50/50 vol %)	AM1.5 (100mW/cm^2)	7 μmol h^{-1} cm^{-2}	[31]
TiO_{2-x} anatase nanoparticles	Ti^{3+}, V_O	0.4 wt% Pt & 150 mL 10%, V/V methanol and hexachloroplatinic acid	300 W Xe lamp	19.9 μmol/h/0.1 g	[32]
Black TiO_2	Ti^{3+}, V_O	1 wt% Pt & 20 vol% methanol aqueous solution	visible light	440 μmol h^{-1} g^{-1}	[67]
TiO_2 nanocrystals	Ti^{3+}	1 wt% & 2 mL 50 vol% formic acid aqueous solution	visible light (> 420 nm, 200 mW cm^{-2})	52 μmol h^{-1} g^{-1}	[68]
mesoporous black TiO_2	Ti^{3+}	1 wt.% Pt & 80 mL of water and 20 mL of methanol	solar simulator (equipped with AM 1.5G filter), power density of 100 mW/cm^2	136.2 μmol h^{-1}	[69]
mesoporous black TiO_2/graphene assemblies	Ti^{3+}, V_O	0.5 wt% & 80 mL of water and 20 mL of methanol	300 W xenon lamp (equipped with optical cut-off filters)	186 μmol h^{-1} $0.01g^{-1}$	[18]
TiO_2	Ti^{3+}, V_O	1% Pt & 120 mL 25% methanol aqueous solution	300WXe lamp (equipped with 400nm cut-on filter)	14.8 mmol/h/0.3 g	[48]

5.2 Photoelectrochemical water splitting

As the optical and charge transfer properties of modified TiO_2 improved, the photoelectrochemical properties was accordingly improved comparison to unmodified TiO_2. There are several studies evaluated the photoelectrochemical properties of modified TiO_2 by different strategies [68, 69, [70, 71, 56, 72, 73, 74, 75, 76, 24, 77, 17, 78]. Deng et al. [58] fabricated Ti^{3+} self-doped TiO_2 nanorods/nanosheets photoelectrode by hydrothermal reaction with sodium borohydride reduction. The photocurrent density of Ti^{3+} self-doped TiO_2 nanorods/nanosheets photoelectrode (0.022 mA cm^{-2}) was higher than TiO_2 nanorods/nanosheets (0.006 mA cm^{-2}). Ti^{3+} and oxygen vacancies enhanced the charge carrier separation and the photocatalytic activity. Huo et al. [74] synthesized Ti^{3+} self-doped TiO_2 particles by in situ surface hydrogenation synthetic strategy. The photocurrent density of Ti^{3+}/TiO_2 (1090 nA cm^{-2}) was higher than TiO_2 (428 nA cm^{-2}). The photoelectrochemical properties of Ti^{3+}/TiO_2 improved due to the absorption of visible light. Furthermore, it has found that after switching off the light, the Ti^{3+}/TiO_2 continued to generate current which means Ti^{3+} extended the lifetimes of charge carrier. Furthermore, Ti^{3+} self-doped TiO_2 nanotubes which were fabricated by electrochemical reduction evaluated for photoelectrochemical activity. The photocurrent of Ti^{3+} self-doped TiO_2 nanotubes was 0.525 mA cm^{-2}, whereas the photocurrent of pristine TiO_2 nanotubes was 0.170 mA cm^{-2}. The PEC performance of Ti^{3+} self-doped TiO_2 nanotubes were improved because the absorbed light was in the visible light region and the charge transfer was accelerated at the TiO_2 and electrolyte interface. Moreover, Ti^{3+} and oxygen vacancies defects increased the charge density and improved the electrical conductivity [75]. fabricated Ti^{3+} self-doped TiO_2 by sol-gel method and using aluminum acetylacetonate as catalyst to form Ti^{3+}ions. The enhancement of photo-electrochemical activity correlated to Ti^{3+} existence. Li et al. created Ti^{3+} self-doped TiO_2 nanotube arrays by microwave-assisted chemical reduction method with sodium borohydride. The photocurrent density and photoconversion efficiency under AM1.5 of Ti^{3+} self-doped TiO_2 nanotube arrays was 3.05 mA cm^{-2} and 1.66% respectively, which was 8 times higher than pristine TiO_2 nanotube arrays. The abundance of Ti^{3+} ion into the bulk of TiO_2 nanotube arrays exhibited stable and enhanced PEC performance as well as efficient absorption of visible light and fast charge carrier separation. One-dimensional Ti^{3+}/ TiO_2 crystals were synthesized by hydrothermal reaction and Ti foil was used as a substrate [78]. The concentration of Ti^{3+} was controlled by N_2H_4 reduction. It was observed that the high level of Ti^{3+} species improved the photoelectrochemical activity, leading to high photocurrent density of 0.64 $mAcm^{-2}$.

Ti^{3+} self-doped TiO_2 nanoparticles were created by hydrothermal method. Under visible-light irradiation, the obtained photocurrent density of Ti^{3+} self-doped TiO_2 was higher than the photocurrent of pure TiO_2. The existence of Ti^{3+} and oxygen vacancies improved the electrons and holes separation and transportation [24]. Yang et al. [79] synthesized Ti^{3+} self-TiO_2 nanotube arrays by the electrochemical reduction method. The transient photocurrent density of Ti^{3+} self-dope TiO_2 nanotube arrays was 3.3 μA cm^{-2}, while the photocurrent of TiO_2 nanotube arrays was 1 μA cm^{-2}. The doping of Ti^{3+} formed shallow donor level separated the photogenerated electron-hole pairs and increased the charge carrier density. As a result, the electrical conductivity has improved the charge transfer at semiconductor-electrolyte interface. Furthermore, the light absorption was enhanced by the hierarchical nanotube arrays. Ti^{3+} self-doped blue TiO_2 single-crystalline nanorods are fabricated by sol-gelation with hydrothermal methods and then reduced by $NaBH_4$. The rod-shape single-crystalline structure and Ti^{3+} with oxygen vacancy formation has promoted the charge generation, separation and transfer, leading to higher photocurrent density of 56 μA cm^{-2}, which was 28-fold higher than that of TiO_2 nanoparticles (2 μA cm^{-2})[17]. Zhang et al. [80] prepared Ti^{3+} self-doped black TiO_2 nanotubes with mesoporous nanosheet architecture by solvothermal method, and then the product was treated by ethylenediamine encircling strategy. The photocurrent of defected TiO_2 was 92.4, while the photocurrent of non-defected TiO_2 was 51.7 μA cm^{-2}. The enhancement of photoelectrochemical properties attributed to utilization of wide range of sunlight due to the reduced bandgap. Furthermore, the Ti^{3+} formation improved the photogenerated charge carrier, and exhibited more surface-active sites.

Table 5. photoelectrochemical water splitting of defective TiO_2 with intrinsic point defects

Started TiO_2	Defect	Electrolyte	Light source	Photo-current	Reference
TiO_2 nanorods/nanosheets	Ti^{3+}, Vo	0.1 mol L^{-1} Na_2SO_4	35 W Xenon lamp irradiation	0.022 mA cm^{-2}	[80]
TiO_2 nanoparticles	Ti^{3+}	0.5 mol L^{-1} Na_2SO_4	300 W Xe lamp	1090 nA cm^{-2}	[74]
TiO_2 nanotubes	Ti^{3+}, Vo	1 M KOH	300 W xenon arc lamp (equipped with AM 1.5 G filter)	0.525 mA cm^{-2}	[75]
TiO_2 nanoparticles	Ti^{3+}, Vo	0.5 M Na_2SO_4	simulated solar irradiation, 84.0 mW/cm2	-	[76]
TiO_2 nanotube arrays	Ti^{3+}, V_O	1 M KOH	simulated solar light (AM1.5, 100 mW cm_2)	3.05 mA cm^{-2}	[77]
One-dimensional TiO_2 crystals	Ti^{3+}	1M KOH	150 W xenon lamp (equipped with AM 1.5G filter)	0.64 mA cm^{-2}	[78]
TiO_2 nanotube arrays	Ti^{3+}, V_O	1 M KOH	stimulated sunlight (AM 1.5, 100 mW cm−2)	3.3 μA cm^{-2}	[79]

blue TiO_2(B) single-crystalline nanorods	Ti^{3+}, V_O	1M KOH	simulated sunlight AM 1.5	56 µA cm^{-2}	[17]
Black TiO_2 Nanotubes with mesoporous nanosheet architecture	Ti^{3+}, V_O	1 M KOH	AM 1.5 light from a 300 W Xe lamp	92.4 µA cm^{-2}	[80]
TiO_2 nanotube arrays	Ti^{3+}	1 M KOH	300 W Xe lamp	2.8 mA cm^{-2}	[70]
TiO_2 nanotubes	Ti^{3+}, V_O	1M KOH	He–Ne laser (632nm)	16.85 mA cm^{-2}	[71]
TiO_2 Nanowire Arrays	V_O	1 M NaOH	150Wxenon lamp (coupled with an AM 1.5G filter)	1.97 mA cm^{-2}	[72]
Black TiO_2 nanotube arrays	Ti^{3+}, V_O	1 M NaOH	100 mW cm2 illumination	3.65 mA cm^{-2}	[73]
TiO_2 p-n homojunction	Ti^{3+}, V_O, V_{Ti}	0.2 M Na_2SO_4	xenon lamp (equipped with an AM 1.5G filter)	-1.8 mA cm^{-2}	[20]

6. Summary and perspective

The intrinsic point defects in TiO_2 have been developed for solar hydrogen production via solar water splitting. Oxygen vacancy (V_O) and titanium interstitial (Ti_{int}) defects act as intrinsic donor defects, whereas titanium vacancy (V_{Ti}) and oxygen interstitial (O_{int}) defects act as intrinsic acceptor defects. Various preparation methods such as hydrogenation, reduction, oxidation, solvothermal, and atomic layer deposition (ALD) are utilized to form either intrinsic donor defects or intrinsic acceptor defects. Furthermore, in-situ decoration and UV light assisted sol–gel methods could be used to form the intrinsic donor and acceptor defects simultaneously. Depending on the type of synthetic methods and its preparation parameters for formation of intrinsic defects in TiO_2, the structural, optical, charge transfer properties of TiO_2 are modified. The defects such as Ti^{3+} and V_O could enhance the visible light absorption of solar spectrum due to the narrowing of band gap or formation of midgap states. In addition, the defects improve the photoinduced electron-hole pair separation and significantly promote the charge carrier transfer. Thus, the modified properties enhance the photocatalytic activity for hydrogen production. However, the effect of intrinsic defects on photocatalytic properties for hydrogen production is still far from the satisfactory level. The formation of titanium interstitial (Ti_{int}), titanium vacancy (V_{Ti}) or oxygen interstitial (O_{int}), or oxygen vacancies defects in TiO_2 is rarely studied. For future work, the effect of parameters of preparation methods on formation of intrinsic point defects on TiO_2 are needed to be evaluated. The shifting of light absorption from UV to visible region, by narrowing the band gap of TiO_2, should be improved by formation of intrinsic donor defects on TiO_2. The adsorption of water molecules on TiO_2 surface for better water splitting to produce more hydrogen should be improved by intrinsic acceptor defects. Moreover, the effect of intrinsic donor and acceptors defects simultaneously on TiO_2 performance for photocatalytic hydrogen generation should be considered. Since TiO_2 is a promising photocatalyst, intrinsic defects would attract more attention for the improvement of TiO_2 performance for photocatalytic hydrogen production.

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