

## Review Article

# Function of TiO<sub>2</sub> Lattice Defects toward Photocatalytic Processes: View of Electronic Driven Force

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Oxygen vacancies and Ti-related defects (OTDs) are the main lattice defects of TiO<sub>2</sub>, which have great influence on its photocatalytic activity. To understand the relationship between the defects and photocatalytic activities, detailed discussions based on the electronic driven force provided by these defects are carried out during the three commonly accepted processes in photocatalytic reactions. It is found that these defects inevitably (i) influence the energy structure of the pristine TiO<sub>2</sub> as the isolate acceptor/donor level or hybrid with the original orbital, (ii) provide a disordered short-range force that confuses the charge carriers transferring to surface active sites, (iii) act not only as the surface active sites for trapping the charge carriers but also as the main chemisorption sites for O<sub>2</sub>, H<sub>2</sub>O, and organic species. These effects of the defects make them one of the key factors that determine the efficiency of heterogeneous photocatalysis. Clarifying the role of the defects will further facilitate the exploration and the construction of high-performance photocatalysts for practical applications.

## 1. Introduction

The construction of photocatalysis system provides a promising strategy to solve energy and environmental issues by converting solar energy to hydrogen/electric energy and oxidizing the organic compounds to reduce the chemical oxygen demand (COD) in the environment. Titanium dioxide (TiO<sub>2</sub>) has been studied extensively due to its fundamental properties and wide range applications [1–4]. As light can go as deep as about 1 μm down to the surface [5], photocatalytic reaction automatically occurs on the surface/subsurface. Attentions were paid intensively to surface science of TiO<sub>2</sub> and other oxide photocatalysts, and an expectation for the surface properties insights into the molecular level is in urgent need. The surface properties are largely influenced by the defects, and the dominant defects in TiO<sub>2</sub> surfaces are oxygen vacancies and Ti-related defects (OTDs) [6–11].

OTDs can be created during the diverse workable synthesis strategies (e.g., doping [12–14], loading [15, 16], and constructing Z-scheme photocatalytic system [17]) and can also be found in many kinds of efficient photocatalysts (e.g.,

solid solution [18], heterostructure composites [17, 19], and multilayer films [20]). During these systems, the enhanced photocatalytic activities are always attributed to the structure [21], composition, particle size [22], or surface area [23], which do not seem to have direct relationship with defects. However, during the deep discussion of the intrinsic factor for photocatalysis, the importance of the defects in reactions is gradually recognized and commonly accepted as the dominant limitation of photocatalytic efficiency nowadays.

It is the energy structure that makes TiO<sub>2</sub> a semiconductor photocatalyst. And OTDs have been widely concerned to the so-called “self-doping” effect [24]. Pristine TiO<sub>2</sub> is traditionally thought to be inert under visible light for its broad band gap ( $E_g \approx 3.2$  eV). To narrow the band gap, foreign anion elements (e.g., N [12, 25], C [13], F [26], S [27]) and cation elements (e.g., Fe<sup>3+</sup> [28], Cr<sup>3+</sup> [29], and Ce<sup>4+</sup> [16]) are frequently introduced into TiO<sub>2</sub> lattice, forming new energy state in solids. Defect state caused by OTDs was also found to influence the electronic structure of pristine TiO<sub>2</sub>, and visible light response was clearly observed in reduced TiO<sub>2-x</sub> specimens [11, 30]. OTDs were found to

be the active response sites from the scanning tunneling microscopy (STM), which came out to be one of the powerful techniques in detecting surface configuration in materials [31–33]. The formation of OTDs is called “self-doping.” The effect of narrowing the band gap is proved to exist not only in  $\text{TiO}_2$  but also in other metal oxides [34]. Avoiding introducing excess foreign elements, OTDs self-doping is recognized as a green and promising strategy for exploring environmentally friendly photocatalysts.

When an electron in the ground state absorbs a photon which possesses sufficient energy larger than  $E_g$  of the semiconductor, it can be excited from the valence band to the conduction band, leaving a hole behind. Once the electron-hole (e-h) pair is generated, the charge carriers may immediately start the journey to the surface active sites, mainly to the OTDs. Reduced  $\text{TiO}_2$  OTDs surface is found to have enhanced photocatalytic efficiency than defect-free surface. The efficiency may rise when increasing the concentration of OTDs in a moderate range on surface [35, 36]. Density functional theory (DFT) calculation, photoemission spectroscopy (PL), atomic force microscopy (AFM) [37, 38], and STM reveal that lattice distortion induced electronic density variation at OTDs accumulates the spontaneous charge migration to the surface, where the OTDs act as the trap center. They serve to promote the separation of e-h pair and prolong the life time of charge carriers in  $\text{TiO}_2$  [39]. OTDs at subsurface are recognized more as the e-h recombination center, also caused by the trapping effect. Kong et al. [40] found from STM and positron annihilation lifetime spectroscopy (PALS) [41, 42] that the larger the proportion of surface defects was in the whole defects of  $\text{TiO}_2$ , the higher the photocatalytic activity was. This competitive relationship between surface OTDs and subsurface OTDs on trapping charge carriers should be attributed to their electronic properties.

Owing to the feature electronic density, OTDs can not only gather charge carriers but also function as the absorbing sites for external species (e.g.,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and plenty of organic substances) [43, 44]. The adsorption of these species toward OTDs may occur in the form of dissociative adsorption (chemical adsorption). This is of vital importance for mediating the transfer of charges, undergoing from the surface  $\rightarrow$  OTDs  $\rightarrow$  dissociated species  $\rightarrow$  further redox reaction [45]. For instance,  $\text{H}_2\text{O}$  can dissociate at bridging oxygen vacancy, forming two neighbouring hydroxyls ( $-\text{OH}$ ). This hydroxyl facilitates the photocatalytic reactions by lowering the charge transfer barrier, assisting the adsorption of organic substances, and further catalyzing the decomposition of them. Besides, the  $-\text{OH}$  was deduced to have an effect on the redistribution of subsurface OTDs. The dissociating mechanisms of species at OTDs active sites remain very rough, and the function of these dissociated species in photocatalysis still needs further investigation.

This review focuses on the understanding of the function of OTDs in photocatalytic reactions, from the view of the electronic driven force toward neutralizing. The generation of OTDs is always followed by the redistribution of electronic density. This variation has compact relationship with the photocatalytic efficiency. Upon the three basic photocatalytic processes, further discussion was carried out and the effects

of OTDs were provided. The findings of this work would facilitate the design and exploration of high-performance green photocatalysts in the molecule level.

## 2. General Issues of Photocatalysis

The general mechanism of heterogenous photocatalysis is always described as Figure 1. When the photon energy is sufficient to promote the electrons in the valence band to jump to the conduction band, three main steps can happen successively: (i) photon absorption and electron-hole pair generation, (ii) charge separation and migration to surface reaction sites or to recombination sites, and (iii) surface chemical reaction at active sites containing donor oxidation at valence-band hole and acceptor reduction at electron center. Upon these three photocatalytic processes, several defects-related photocatalytic issues should be clarified.

*2.1. Photoexcited Location.* The process of heterogenous photocatalysis starts by irradiation. That is, photoexcitation of electron at ground state is the prerequisite. It should be noticed that the excitation step of electron under irradiation may not only occur in the semiconductor but also occasionally happen in the substance adsorbed on its surface, like the reaction happening in dye-sensitized solar cell [22]. The charge carriers may experience different pathways in these two situations. Hence in this review, we focus on the cases that initial excitation happens in the semiconductor itself.

*2.2. Point Defects and Standard Specimen.* The concept of defects initially lies in the solid state physics description of lattice distortion. Such distortion can be in the form of point defect, liner defect, two-dimensional flaw or interface and three-dimensional valley or heteroimpurity. Among these, point defect is the most investigated case and provides the primary realization of properties of lattice defects, including energetic, thermal, electrical, optical, and magnetic features in solids [46–49]. OTDs are generally recognized as point defects. The analysis of OTDs and OTDs-related clusters in photocatalytic reactions is usually carried out by performing the point trap model.

Lattice defects are inevitably generated during synthesis procedure and are thermal- and preparation-dependent products [50]. Intrinsic point defects exist automatically in lattice as vacancies, interstitials, and atomic impurities which are frequently observed in doping materials. It was observed by STM images that these defects distributed scatteredly on the flat surface or centralized violently at the terrace boundaries which are proved to be responsible for the increased photocatalytic efficiency. However, the existence of the incoordinate and disordered defects in different samples makes it hardly possible to compare the photocatalytic properties precisely even in the same photocatalytic system. The well-defined particles hardly exist at room temperature under ambient conditions. As a result, to simplify the analysis in molecule scale, a hypothesis about well-defined samples is made in the vast majority of researches, and point defects are well-distributed ignoring the boundary defects.

Thus, preparation of comparable standard specimen is in urgent need for better understanding the nature of photocatalytic reaction.

**2.3. Energy Structure.** As is known, ground state energy structure of a pure semiconductor is composed by valence band (VB), conduction band (CB), and the band gap between them. Light absorption for photocatalytic reaction is determined by the range of band gap ( $E_g$ ). When the photon energy is sufficient to excite an electron in valence band to overcome  $E_g$  to the conduction band, photocatalytic reactions may occur.

The point defects as impurities are recognized to have a “self-energy” in short range, creating a variation in the host electronic structure. There are two general identified manners on the influence of defect energy level to the host energy structure: (i) to introduce an isolated mid gap as the acceptor/donor level, leaving the primary structures unchanged, and (ii) to hybrid with the host VB or CB, narrowing or broadening the band gap. These two phenomena were proposed in N-doped TiO<sub>2</sub> samples by Irie et al. [51] and Asahi et al. [52]. OTDs also have been found to undergo these two manners favorably in oxide semiconductors. It is crucial to study the energy structure of defects, for the long-range force of charge transfer is provided by the position of valence band/conduction band versus the redox potential of the adsorbed substance on the external surface of photocatalyst, which determines whether the photocatalytic reaction with special substances would happen or not (see Figure 1).

**2.4. *n/p*-Type.** TiO<sub>2</sub> is one of the most extensively studied photocatalysts. Pure TiO<sub>2</sub> samples synthesized from conventional preparation methods are mostly oxygen-deficient nonstoichiometric compound or a solid solution of oxygen into TiO<sub>2-x</sub> lattice [5]. In consequence, oxygen vacancies as well as Ti interstitials in TiO<sub>2</sub> make it an *n*-type property of dominant materials, precisely written as TiO<sub>2-x</sub> [13]. However, the formation of metal-deficient TiO<sub>2</sub> can be obtained under strong oxidation at elevated temperatures [9, 53, 54] and relatively a *p*-type behavior is found.

It should be clear that, in the nonstoichiometric *n*-type TiO<sub>2</sub>, the charge carriers not only are the electrons but also may be the holes during the photocatalytic procedure. As the transfer rate of the holes is several orders of magnitudes slower than electrons, the dominating charge carriers are electrons and thus the TiO<sub>2</sub> is called an *n*-type semiconductor. When the proportion of O atom in TiO<sub>2</sub> rises, the TiO<sub>2</sub> may be identified as the *p*-type semiconductor taking holes as the main charge carriers. The coexistence of *n*- and *p*-type in TiO<sub>2</sub> is shown in Figure 2 [8], as a result of distribution of OTDs.

To simplify the model of photocatalytic reactions in particles, it is hypothesized that *n/p*-type can counteract with each other during the long routes to the surface; thus a conception of “surplus *n*-type” or “surplus *p*-type” is usually introduced as there are only photoelectrons in *n*-type TiO<sub>2</sub> and vice versa. When TiO<sub>2</sub> is used as an electrode, the electrons and holes move efficiently toward the opposite

direction and the relationship between them seems more to be the coworker than to be the competitor.

The ability of intrinsic defects to influence the transfer of charge carriers can be judged by electrical conductivity [55], considering the cooperation of both the *n*-type and the *p*-type aspects. The resistance of TiO<sub>2</sub> can be influenced by the trapping of the charge carriers in ionic defects and overcome the barriers in the distorted bond. An increase of the electrical conductivity with the increase of oxygen vacancies was observed by Nowotny et al. when changing the oxygen partial pressure [48]. Accordingly, it is revealed by the enhanced electrical conductivity that the surface investigated is an *n*-type dominant surface and oxygen vacancies facilitate the charge transfer.

**2.5. Main Characterization Methods of Defects.** Based on the first principles computation, the modified local density approximation (LDA) and the related generalized method as well as some other computational modelings are used to calculate the ground state energy structure of the host semiconductor, despite of the error [56, 57]. As to the energy level of the defects and the excited states, however, it becomes more complicated to choose the most suitable calculation method/model and confirm the initial settings of the parameters. Estimations are always handled by empirical adjustment without precise specifications. Among these modeling principles, density functional theory (DFT) provides the relatively acceptable data and is widely used in the calculation of electronic structure of TiO<sub>2</sub> [58–62].

Several experimental methods for OTDs are listed in Table 1 and they are always used together to get the defects information.

**2.6. Transient Local Heat.** As has been reported, the kinetic rate of photocatalytic reactions can be varied from different temperature and light intensity [63], and heat is one problem. For the sake of practical application of photocatalysts in ambient environment, a set of coolers (mostly condensate water) is usually equipped to provide moderate temperature for laboratory-scale tests. However, ambient temperature could not prevent the transient local heat that comes from (i) the released nonradiative thermal energy form recombination and (ii) the slow diffusion of the adsorbed radiative infrared light of the light source (solar or specially the Xe lamp with the power of 300 W or 500 W) in some lattice distortions. Here a hypothesis is made that such heat do not or has little influence on the separation and migration of charge carriers.

### 3. Generation of OTDs in TiO<sub>2</sub>

**3.1. Removal of Oxygen in TiO<sub>2</sub>.** Ideal structure model of bridging oxygen vacancy in TiO<sub>2</sub> (110) surface lattice is shown in Figure 3(a). Figure 3(b) gives a direct picture for the position of oxygen vacancies by STM, and it can be found that the bridging oxygen vacancies (O<sub>b</sub>-vac) are the main surface defects. Figure 3(c) represents the electronic density scattering around a single oxygen vacancy [64] and it could be seen that the potential field of the neighbouring Ti is

TABLE 1: Common characterization techniques for defects.

Technique	Characterization	Evidence	References
Colour of the materials	Different from pristine TiO <sub>2</sub>	The defects maybe exist	[123]
High-resolution transmission electron microscopy (HR-TEM)	The atomic lattice is blurred	Maybe exists	[72, 123]
Ultraviolet-visible spectroscopy (UV-vis)	An optical absorption band above 400 nm	Maybe exists	[30]
Photoemission spectroscopy (PL)	The emission position and intensity	Type, relative concentration of defects	[124]
Raman spectroscopy	Variation in vibration of O and Ti-related region	Type of defects	[30, 38, 72]
X-ray photoelectron spectroscopy (XPS)	Valence state variation	Type of defects mainly Ti <sup>3+</sup>	[30, 37, 72, 89]
Electron paramagnetic resonance (EPR)	<i>g</i> factor calculated from the position of the sharp signal	Type of paramagnetic defects	[35, 123, 125, 126]
Positron annihilation lifetime spectroscopy (PALS)	The lifetime of the positrons	Size, type, and relative concentration of defects	[68]
Scanning tunneling microscopy (STM)	Light dot in pictures	The type, position of defects	[31, 113, 120]
Atomic force microscopy (AFM)	Comparison of pictures	The type, position of defects	[38]
Temperature programmed deoxidation (TPD)	A narrow peak related to partial oxygen loss according to temperature.	Rough concentration of oxygen defects	[112, 123, 125]
Electron energy loss spectroscopy (EELS)	Energy loss	Electronic change in defects	[112]
Synchrotron radiation X-ray absorption fine structure spectroscopy (XAFS)	Peak position	Geometrical structure of active sites	[127]

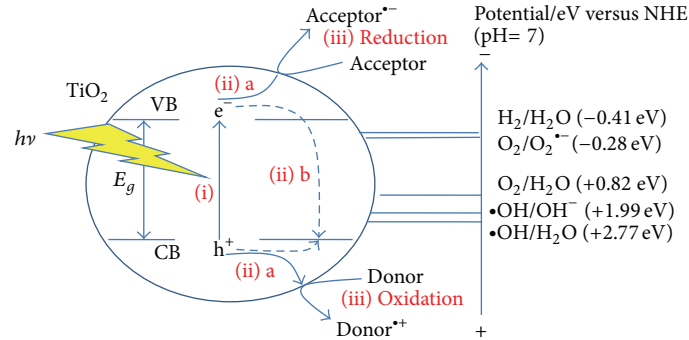
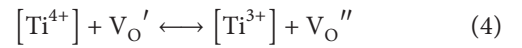
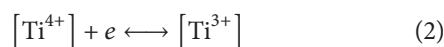
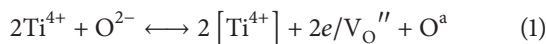


FIGURE 1: Main steps occurring in the photoelectrochemical mechanism. ((i) Photon absorption and electron-hole pair generation. (ii) Charge separation and migration (a) to surface reaction sites or (b) to recombination sites. (iii) Surface chemical reactions at surface active sites, donor oxidation at valence-band hole, or acceptor reduction at electron center.)

the most influenced site whereas the variations die largely in distance. It reveals that OTDs can work as short-range traps in capture charge carriers, which is crucial for charge migration in photocatalytic reactions. The formation processes of these defects assist in the understanding of Figure 3(c).

In an ideal defect-free lattice of TiO<sub>2</sub>, the removal of an oxygen atom in lattice is usually accompanied with the exposure of the neighbouring metal atoms and the material would tend to maintain electrostatic balance according to the following reactions:



where O<sup>a</sup> represents the oxygen atom that is taken away from the lattice, V<sub>O</sub>'' represents the corresponding empty position (1), and V<sub>O</sub>' also represents the empty position which originated from the removal of oxygen but with a localized single electron (3). [Ti<sup>4+</sup>] represents the exposed neighbouring Ti<sup>4+</sup> at oxygen vacancy (1) and [Ti<sup>3+</sup>] represents the exposed Ti reduced by the excess electron (2) from O removal.

It can be seen from (1) that the removal of oxygen from the lattice generates V<sub>O</sub>'' and further causes the formation of V<sub>O</sub>' (3) and the reduction of the neighbour metals (4) [6, 65]. Liu et al. [7] showed the relationship between the formation of V<sub>O</sub>' and the corresponding existence of Ti<sup>3+</sup> during

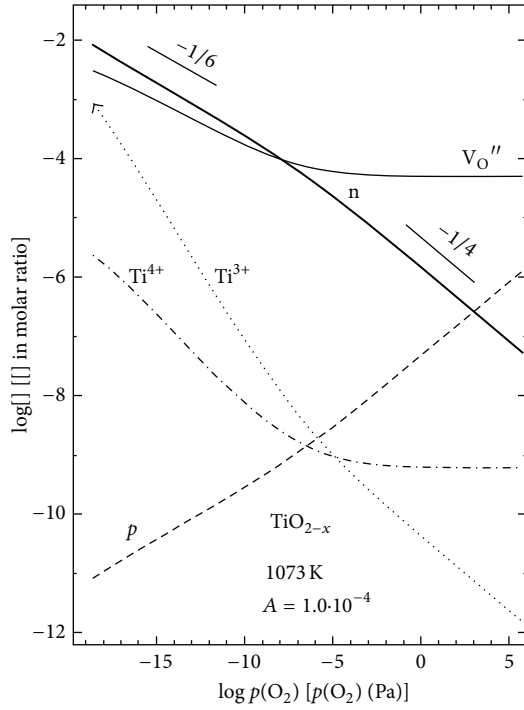


FIGURE 2: Oxygen vacancies and Ti-related defects (OTDs) related  $n/p$ -type  $\text{TiO}_2$  at 1073 K [8].

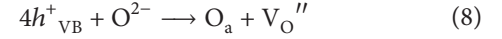
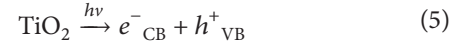
$\text{H}_2$  treatment up to  $700^\circ\text{C}$  (Figure 4). As the temperature increased, more  $\text{O}^{\text{a}}$  were removed by  $\text{H}_2$ . Magnetic  $\text{Ti}^{3+}$  defects generation followed the  $\text{V}_{\text{O}}'$  formation, indicating the reaction of the trapped localized single electron of  $\text{V}_{\text{O}}'$  with the near  $\text{Ti}^{4+}$  (4). This process was mainly controlled by temperature [66]. Besides, temperature has great influence on the transition of the crystalline structures of  $\text{TiO}_2$ , and the formation energy order of oxygen vacancies on surfaces is brookite (5.52 eV) > anatase (5.58 eV) > rutile (5.82 eV), which may result in the different concentration of OTDs [67].

The control of ambient  $\text{O}_2$  concentration/pressure can also adjust the concentration and the distribution of defects in a feasible range [8]. The occurrence of  $\text{V}_{\text{O}}''$  may suffer the reverse reaction under a wide range of oxygen activities and Ti vacancies can be obtained from the prolonged oxidation of  $\text{TiO}_2$  at elevated temperatures [9]. Under ambient condition at room temperature, the  $\text{V}_{\text{O}}''$  in  $\text{TiO}_2$  dies out gradually, and this usually causes weakened photocatalytic efficiency in  $\text{TiO}_2$ .

Considering the oxygen activity and temperature, surface treatment methods (e.g., annealing in vacuum condition [68], thermal treatment under reducing atmosphere ( $\text{H}_2$ , CO, NO), and bombardment using electron beam [69, 70], neutron, or  $\gamma$ -ray) are introduced to obtain defective surfaces. The bulk OTDs can be directly obtained from sputtering method without further modifications on the  $\text{TiO}_2$  samples.

**3.2. Light-Induced Defects in  $\text{TiO}_2$ .** Another way generating OTDs came out of the application of  $\text{TiO}_2$  in photocatalytic

reactions under light irradiation. Once photoinduced e-h pair is generated, the subsequent reactions could happen:



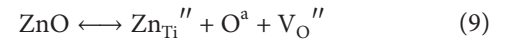
The photoinduced electrons and holes should also be identified as defects [71]. Accordingly, the recombination of electrons and holes may be also called the reaction of “electron defects” with “hole defects” in photocatalysts.

The excited electrons could react with lattice  $\text{Ti}^{4+}$  and then  $\text{Ti}^{3+}$  is generated with a trapped electron (6). At the same time, a hole could oxidize a nearby lattice  $\text{O}^{2-}$ , leaving an  $\text{O}^-$  in lattice (7). Further, oxygen vacancy would be created under strong oxidizing conditions, generating atom O ( $\text{O}_a$ ) in lattice (8). Thus, the photoinduced defective surface/subsurface is performed under irradiation, and light energy can be stored as the form of electronic energy during this process.

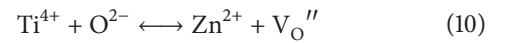
**3.3. Doping-Induced Defects in  $\text{TiO}_2$ .** Foreign elements are usually introduced to pristine  $\text{TiO}_2$  to make full use of solar light. The formation of dopant defects is frequently accompanied by the generation of OTDs [72].

**Anion Doping.** Di Valentin et al. [73] found from DFT calculation that N doping was likely to be accompanied by the formation of oxygen vacancy, because the energy consumed by oxygen vacancy was substantially reduced by N doping. Chen et al. [74] obtained an N-doped  $\text{TiO}_2$  samples in  $\text{NH}_3$ , and OTDs were found to be coexisted on the surface with N impurities. Recent work of Di Valentin and the coworkers [75] revealed that oxygen vacancies generated when doping F in  $\text{TiO}_2$ . The formation of  $\text{Ti}^{3+}$  occurred when doping B due to the charge compensation, while C and N did not donate excess electrons to lattice oxygen.

**Cation Doping.** It is found by Jing et al. [76] that doping of Zn increased the concentrations of oxygen vacancies and oxygen vacancies also served to assist the formation of Zn-doped  $\text{TiO}_2$  samples. Following the static equilibrium, the Zn atoms would



where  $\text{Zn}_{\text{Ti}}''$  represents Ti substituted by Zn in lattice,  $\text{O}^{\text{a}}$  is also the O atom removed, and  $\text{V}_{\text{O}}''$  represents the Zn-doping-induced generation of oxygen vacancy, or according to the charge neutrality,



The introduction of Cr [77] and Fe [78] as the acceptor-type defects in  $\text{TiO}_2$  practically undergoes the similar way in generating oxygen vacancy:



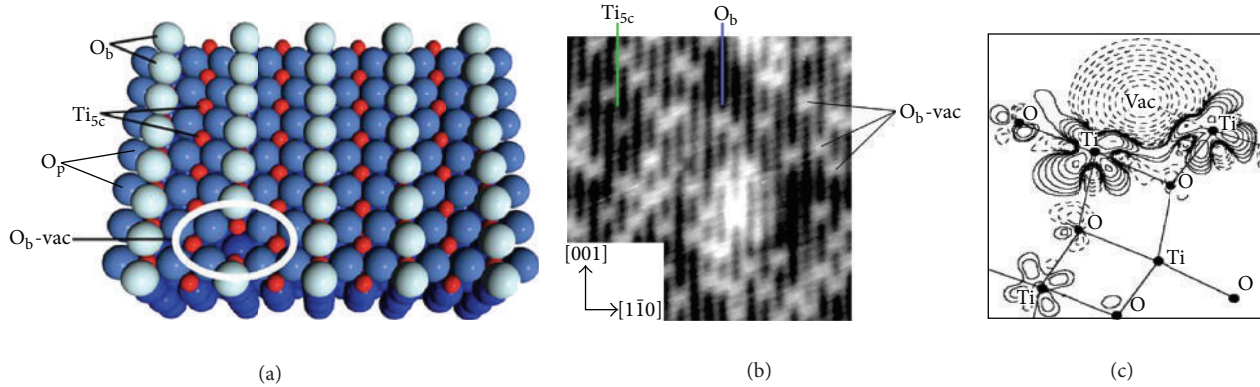


FIGURE 3: (a) Pseudospace-filling model of ideal bulk-terminated  $\text{TiO}_2$  (110) with a bridging oxygen vacancy. Blue (red) spheres are oxygen (titanium) atoms. (b) STM image of  $(1 \times 1)$   $\text{TiO}_2$  (110) surface. The bright rows correspond to surface  $\text{Ti}_{5c}$  sites (red ball in (a)). Black row is bridging oxygen ( $\text{O}_b$ ) and  $\text{O}_b$ -vacs are marked as the bright protrusions in the black row [43]. (c) Redistribution of the surface electronic density caused by single oxygen vacancy [64].

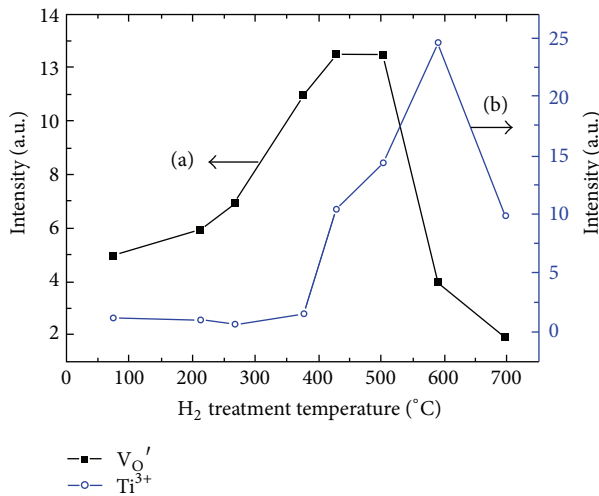
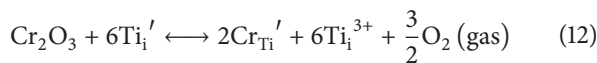


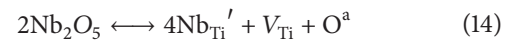
FIGURE 4: EPR intensity of oxygen vacancies and  $\text{Ti}^{3+}$  generation under thermal treatment with  $\text{H}_2$  [7].

or



The  $\text{Ti}_i'$  in (12) presents the interstitial Ti. It could be seen from (11) and (12) that Cr atoms would undergo different reaction pathways. Besides the oxygen activity, the chromium concentration was found to be another factor to influence these two reactions [77]. When the chromium concentration was lower than 3 atom %, it mainly underwent (12), producing interstitial  $\text{Ti}^{3+}$  in lattice. When the chromium concentration was in the range of 4-5 atom%, oxygen vacancies were mainly created by (11), balancing the charge variation during Cr-doping as the acceptor defect center.

When it comes to the donor-type Nb-doped  $\text{TiO}_2$ , the reactions are [79–81]



$V_{\text{Ti}}$  is Ti vacancy in (14). The occurrence of (13) and (14) is also controlled by the doping condition, commonly the oxygen activity. It can be seen in (13) that electron can be released by Nb doping under the reduced conditions [81]. The excess electrons result in the remarkably enhanced conductivity, and this metallic-type property may be helpful to promote the migration of the charge carriers in photocatalytic reactions.

It could be found that chemical valence states of the dopants play an important role on the formation of defects under preparation conditions. Besides, it was also reported that the doping of anions and cations in pristine  $\text{TiO}_2$  was all accompanied by the formation of oxygen vacancies [82]. At the same time, the formation of the corresponding color centers (e.g., F,  $\text{F}^+$ ,  $\text{F}^{++}$  [83], and  $\text{Ti}^{3+}$ ) revealed the probable effects of defects in photocatalytic reactions [84].

#### 4. The Function of Defects in Photocatalysis

The function of OTDs in photocatalysis can mainly be

- (1) to modify the band energy structure of the pristine  $\text{TiO}_2$  as the defect states,
- (2) to trap charge carriers in the migration pathways as the electron pool or recombination center,
- (3) to influence the adsorption of reactants (e.g.,  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{CO}_2$ , and organic pollutants) as the active sites.

**4.1. Function of OTDs on Energy Structure.** The host energy structure of pristine  $\text{TiO}_2$  is constructed by valence band (O  $2p$  orbitals) and conduction band ( $\text{Ti}^{4+}$   $3d$  orbitals). The energy level of  $\text{TiO}_2$  as well as other outstanding photocatalysts is shown in Figure 5 [85].

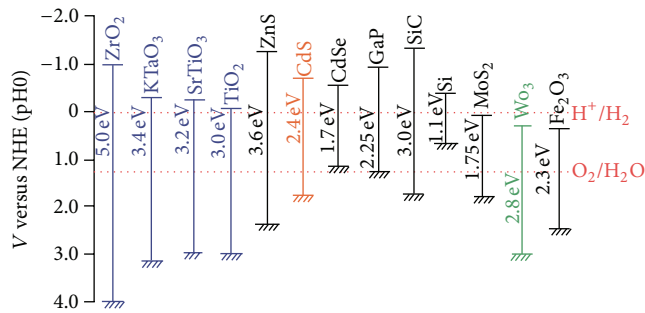


FIGURE 5: Band structures of  $\text{TiO}_2$  and other popular semiconductors [85].

The energy level of OTDs is recognized to aid band gap narrowing and the formation of the main active sites in favor of visible light adsorption [34, 46, 66, 86]. Figure 6 gives the STM images of defective  $\text{TiO}_2$  surface before and after visible light irradiation. These images provide a clear evidence of oxygen vacancies function as the visible light response sites [87], which can be attributed to the electronic structure of OTDs. Accurate calculation of the defect state of OTDs in  $\text{TiO}_2$  energy structure is in urgent need, because energy structure of photocatalyst will influence light absorption and charge carriers migration.

According to (1)–(4), once oxygen atom is removed, and  $\text{V}_\text{O}''$ ,  $\text{V}_\text{O}'$ , and  $\text{Ti}^{3+}$  are left behind. The defect states of these defects are different in the band gap, as has been reported by Janotti et al. [88] and Zou et al. [89]. Janotti and the coworkers [88] found that oxygen vacancies were shallow donor and  $\text{V}_\text{O}''$  defect state presented lower energy than  $\text{V}_\text{O}'$  for all Fermi-level positions in the band gap. Zou et al. [89] introduced  $\text{V}_\text{O}'$  in  $\text{TiO}_2$  by calcining  $\text{TiO}_2$  precursor with imidazole and hydrochloric acid at the elevated temperature. The paramagnetic oxygen vacancies  $\text{V}_\text{O}'$  were proven to form mid gap electronic state within the band gap of  $\text{TiO}_2$ , and thus visible light photocatalytic activity was performed by the electron transition from the  $\text{V}_\text{O}'$  mid gap to the conductor band of  $\text{TiO}_2$ . Here the  $\text{V}_\text{O}'$  acts as the donor. This conclusion is the same with the results that were previously reported by Serpone [90] and Chen et al. [83]. As to oxygen vacancies  $\text{V}_\text{O}''$ , Zou and the coworkers [89] believed that they could serve as an acceptor as well as  $\text{Ti}^{3+}$ , forming an unoccupied state below the bottom of the conduction band. The energy levels of OTDs in  $\text{TiO}_2$  were summarized by Nowotny and his group as in Figure 7 [5].

However, the isolate electronic band fails to explain the contradiction of the strongly localized small polarons versus the delocalized free polarons in experiments. Hence, hybrid function is introduced appropriately and serves as a workable theory. Janotti et al. [91] proposed that there exist two kinds of hybrid functions in the electronic band: (i) between the electrons and the conduction band in the presence of delocalized free electrons and (ii) between the electrons and the oxygen vacancies as the form of oxygen vacancies complexes and the ionized shallow-donor impurities. This reveals the influence of the defect states on shifting the position of the lowest unoccupied molecular orbital (LUMO)

and the highest occupied molecular orbital (HOMO), from the crystal field theory point of view.

More discussion of the relationship between OTDs states and the crystal field arguments was carried out by Morgan and Watson [65]. They used an on-site correction DFT calculation to study the oxygen vacancies in rutile (110), (100), (101), and (001) reduced surfaces, and it was found that the oxygen vacancy of the reduced (110) surface introduced an occupied defect state of 0.7 eV below the bottom of the conduction band. The defect states were also shown in the other three reduced surfaces and varied from each other. However, the defect states seem more important than the exposed surface or crystal form in photocatalytic reactions. Liu et al. [92] compared the oxygen vacancies in anatase, rutile, and brookite obtained from helium pretreatment in moderate temperature. The characterization results revealed that the oxygen vacancies were created in anatase and brookite, which led to a remarkable increase in photocatalytic  $\text{CO}_2$  reduction ability. On the contrary, the treated defect-free rutile and the untreated  $\text{TiO}_2$  samples did not have photocatalytic activity in this reaction. Liu et al. [92] also examined the intermediates/radical and the corresponding final products and found that the reduction of  $\text{CO}_2$  may undergo different pathways. It is deduced that OTDs are crucial to such difference, for the reactants ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2^-$ , and  $\text{CO}$ ) are all tend to adsorb on these surface active sites, which are about to discuss later in this review.

**4.2. Function of OTDs on Charge Transfer.** When irradiated with light, an excited single electron moves rapidly in response to an applied electric field (i.e., voltage supplied by power source or difference of potential between energy structure of  $\text{TiO}_2$  and the redox potential of the adsorbed species) by HOMO-LUMO promotion. Franck-Condon factors of this process are usually very small as a result of little lattice distortion when creating an electron.

The transfer of charge carriers follows the band model and the hopping model [93] and is limited by the vanishing reorganization of energy according to Marcus-Hush electron transfer theory. The energy initially provided by a photon to an electron can be consumed by the lattice distortion, and if the remaining energy is sufficient to overcome the surface barrier, the charge could be utilized by the adsorbed species. The annihilation at the recombination center is another quick vanishing approach for the charge carriers. Yu et al. [94] proposed three recombination mechanisms in semiconductors: (i) band-to-band recombination, which happens between the excited electron and the hole lying in the empty VB, and this reaction is limited by the production of available electrons and holes and is a second order to the concentration of charge carrier (ii) trap-assisted recombination, which directly happens between the excited electrons and holes in the VB under the aid of “trap” state, and this reaction is also limited by the concentration of charge carriers described as Shockley-Read-Hall Model (SRH model); (iii) Auger recombination, which happens when the excited electron and hole recombine, releasing the energy to enhance the energy of another electron or hole. It is discovered by Zhang et al.

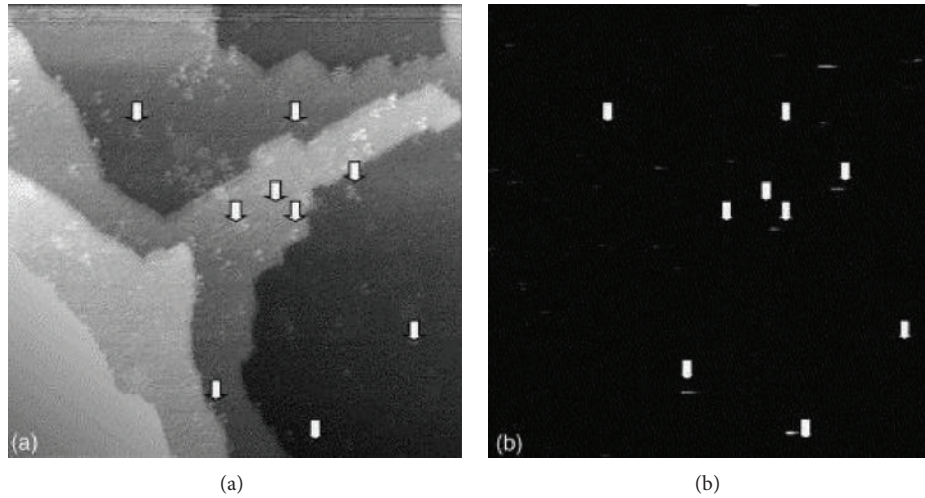


FIGURE 6: STM images of oxygen deficient  $\text{TiO}_2$  surface before (a) and after (b) visible light irradiation [87].

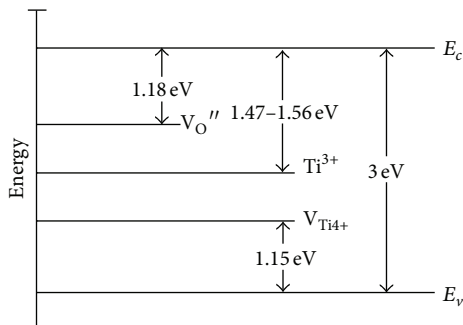


FIGURE 7: The energy levels of OTDs in  $\text{TiO}_2$  [5].

[95] that charge transfer follows the first order kinetic model on surface under UV irradiation, because of the abundant OTDs serving as trap-assisted recombination centers. In the subsurface, charge transfer mainly follows the second order kinetic model for the OTDs.

The exciting sites are widely distributed among the solid. Under light irradiation, the excitation mainly occurs around the OTDs as shown in Figure 6, and the recombination would be in the form of SRH model. However, exact dynamic behavior of a single charge carrier remains unclear. The scope into the molecular level and the study on defect-related characterization techniques are urgently needed.

From the molecular point of view, short-range electronic driven forces provided by bulk OTDs can work efficiently only in the distance of several angstroms in bulk. This force is weaker than that provided by surface OTDs as a result of the broken symmetry in lattice. Despite working in short range, the effect of OTDs cannot be ignored but taken into account seriously.

As calculated by Janotti et al. [91],  $V_{\text{O}}''$  primly acts as the acceptor but when it receives one electron, then  $V_{\text{O}}'$  was formed and it acts more as a donor than an acceptor, in the photocatalytic reaction. If the prime  $V_{\text{O}}''$  is located in

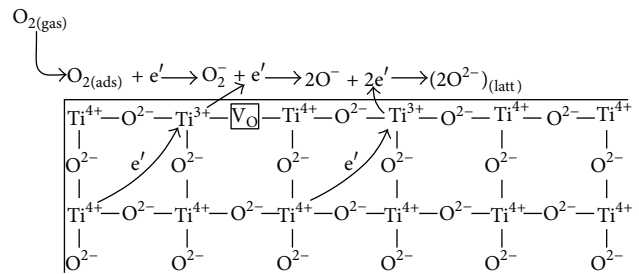


FIGURE 8: The Ti vacancy functions as the active site [96].

the subsurface of an  $n$ -type  $\text{TiO}_2$ , it can be deduced that this one excess electron in  $V_{\text{O}}'$  would subsequently

- (i) meet the  $h^+$  and recombine,
- (ii) reduce one  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$  hindering the entrance of other electrons into this Ti-site,
- (iii) transfer along the surrounding  $\text{Ti}^{4+}$  to the surface active sites, maybe as the form of neutralized state,
- (iv) enter into another  $V_{\text{O}}''$ .

By this mean, the original  $V_{\text{O}}''$  is regenerated and this process repeats until photocatalytic reaction ends. This reiteration behavior not only prolongs the migration routes for the electron to the surface but also highly increases the recombination opportunity of  $e^-$  with  $h^+$ . If the prime  $V_{\text{O}}''$  is located on the surface, the entered electrons can be given to the dissociative adsorbed species here. Besides, if the arrival of electrons on the surface occurs along Ti atoms, the finally formed  $\text{Ti}^{3+}$  can also serve as the active sites toward adsorbing  $\text{O}_2$  scavenger. The transfer of the charge carriers to the active sites are shown in Figure 8.

Except for these defects, Ti vacancy reported by Nowotny et al. [96] also assisted the transfer of electrons to the adsorbed species, as shown in Figure 9. OTDs on the surface can enhance the separation of photogenerated electrons



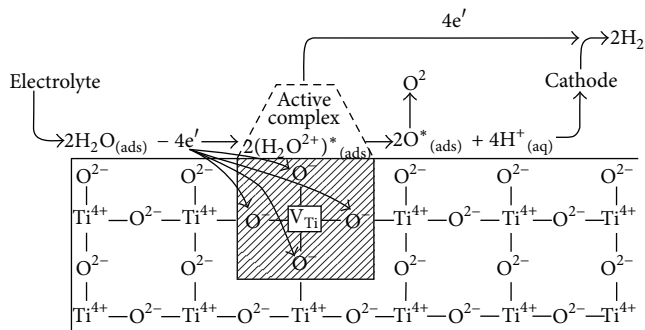


FIGURE 9: The Ti vacancy functions as the active site [96].

and holes by acting as the electron pools on surface and thus prolong the lifetime of both the electrons and holes.

In a typical reaction procedure, the photogenerated charge carriers experience different procedures between the photocatalytic reactions and the photogeneration of electricity when TiO<sub>2</sub> is used as the electrode. Photocatalytic excitation mainly happens in surface and subsurface, and the charge carriers must conquer these blockings as

- (i) localization or trapping in the recombination centers,
- (ii) consuming of migration energy in the distorted Ti–O bond caused by lattice defects in the subsurface,
- (iii) localization or trapping in the surface ionic defects,
- (iv) consuming of migration energy in the distorted Ti–O bond caused by lattice defects on the surface,
- (v) surface barriers caused by the binding of the dissociative adsorbed molecules with surface active sites such as oxygen vacancies and Ti-related defects.

Photocatalytic reaction (i.e., degradation of organic compounds and water splitting) processes mainly suffer the surface/subsurface OTDs, whereas the photovoltaic reaction must bear the OTDs in bulk. Here the movement of charge carriers can be delayed [97] by trapping or localizing in the lattice of bulk OTDs and the migration energy can be reduced by the bulk lattice distortion. Furthermore, in the interface with large amount of lattice defects (e.g., the connected interface of the layered electrode/film be constructed by multilayered materials), the bond distortion may cause a large problem [98, 99] because of the chemical tension. However, the defects, which function as donor or acceptor in the interfaces, could promote the charge transfer by chemical adsorption, which is of vital importance in the photovoltaic cells.

**4.3. Function of OTDs on Adsorption.** Oxygen, water, or organic compounds with electron-rich functional groups can adsorb at OTDs by the electronic driven force toward electrostatic equilibrium. The adsorption behavior of OTDs promotes the charge transfer efficiency from solids to external reactants, and thus makes OTDs flexible active sites on the surface.

**4.3.1. Adsorption of Oxygen.** The introduction of O<sub>2</sub> is of significant importance in photocatalytic reactions, such as photoinduced refractory organics degradation systems and water splitting. Experimental results have proven that the existence of O<sub>2</sub> can significantly enhance the degradation efficiency, and the addition of O<sub>2</sub> with different dosages is widely investigated in water treatment processes. During these processes, the adsorbed O<sub>2</sub> at the active sites can serve as the electron scavenger [100]. These scavengers can facilitate the charge separation, prevent the electron-hole recombination, and generate the  $\cdot\text{O}_2^-$  for deep oxidation of the organic species. Figure 10 shows the subsequent reactions of  $\cdot\text{O}_2^-$ .

It can be seen that the intermediate products are hydroxyl radical ( $\cdot\text{OH}$ ) and other oxidation species, which further promote the mineralization of organic pollutants. The half reaction led by photogenerated electrons is equally important to the reaction led by photogenerated holes, for these two pathways have a synergistic effect. However, during water splitting, the existence of O<sub>2</sub> in water tends to assist the generation of O<sub>2</sub> gas but not the H<sub>2</sub>. By consequence, the experimental tests or comparisons of the H<sub>2</sub> evolution activity of photocatalysts are always performed in vacuum or inert gases (i.e., N<sub>2</sub>, Ar). Besides, the adsorption of oxygen by the active sites can also be capable of causing upward band bending, which is of great importance in many of the applications of TiO<sub>2</sub> (i.e., as the film electrodes). Thus it is necessary to study the oxygen adsorption behavior and its distribution feature on the TiO<sub>2</sub> surfaces.

It is mostly accepted that adsorbed O<sub>2</sub> species occur at oxygen vacancies in an idealized model, and the bridge-bonded oxygen vacancies are believed to be the most preferred sites for oxygen chemisorption on the surface [101]. Xu et al. [102] investigated the interaction between O<sub>2</sub> and reduced TiO<sub>2</sub> (110) surface by DFT calculations, and the results showed oxygen interaction with oxygen vacancies as the dissociative configuration form of O–O complex between in-plane oxygen and Ti atoms in room temperature. Other reports proposed that surface Ti-related defects (mainly interstitial Ti and Ti<sup>3+</sup>) were also the active adsorption sites for oxygen [34].

The OTDs on the surface can act as the charge donor for the transfer of charge carriers from TiO<sub>2</sub> to oxygen atoms. Except for the surface OTDs, bulk OTDs like Ti<sup>3+</sup> ion can also provide excess electrons to the adsorbed O<sub>2</sub> at ~410 K and the desorption of O<sub>2</sub> occurs when the surface interstitial Ti and Ti<sup>3+</sup> act as the electron acceptor in the same condition. These two models are shown in Figure 11. Aschauer and the coworkers [103] further proposed that O<sub>2</sub> was more favorable to adsorb at shallow subsurface interstitial Ti. The bulk defects were also estimated to have more pronounced effect than lower-lying interstitials at providing excess electrons and contributing to O<sub>2</sub> adsorption. Zhang and Yates [95] proposed that desorption of oxygen could happen when photoinduced holes reacted with adsorbed O<sub>2</sub><sup>-</sup>. However, the molecular-scale mechanism of desorption of the oxygen and its subsequent reaction with other adsorbed substances is still unclear.

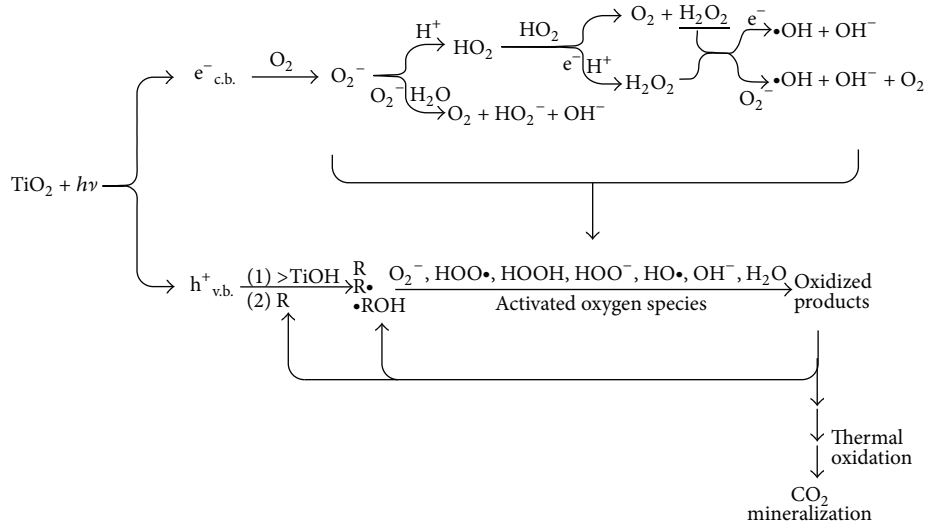


FIGURE 10: The photocatalytic reactions with electrons and holes [121].

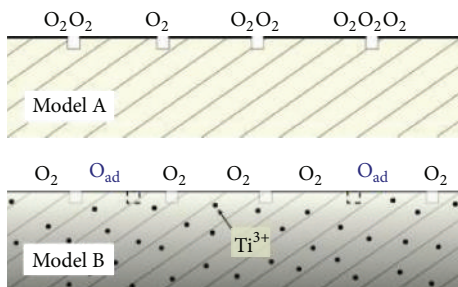


FIGURE 11: The schematic diagram for the influences of OTDs on  $\text{O}_2$  adsorption. Model A:  $\text{O}_2$  adsorption on surface OTDs and Model B: surface oxygen distribution influenced by surface and bulk OTDs [103].

4.3.2. *Adsorption of Water.* The efficiency of photocatalytic degradation of gas phase organic compounds can be improved by moderating the dosage of water [104]. In aqueous solution, the hydrophilic surfaces tend to possess higher photocatalytic activity than hydrophobic surfaces. It is proposed that water serves as a vital media to promote the fast diffusion of OH radicals from  $\text{TiO}_2$  surface to the near-surface region and thus remarkably improve the photocatalytic efficiency. Another reason for this improvement is attributed to the tendency of organic contaminant adsorption toward the OTDs (the adsorption of organic compounds by surface defects is illustrated in the next section). The importance of the application of water in water splitting as the reactant and in photovoltaic cell as the electrolyte solution is very clear and needs no further illustration.

The occurrence of  $\text{H}_2\text{O}$  adsorption on  $\text{TiO}_2$  surface can be in the forms of molecular adsorption, dissociative adsorption, and the transition state between them (Figure 12). Molecular adsorption as physical absorption occurs mostly at surface radical groups as  $-\text{OH}$  and surface defects, and this kind of  $\text{H}_2\text{O}$  serves more as solution or media than as reactant. The vast majority of dissociative adsorption

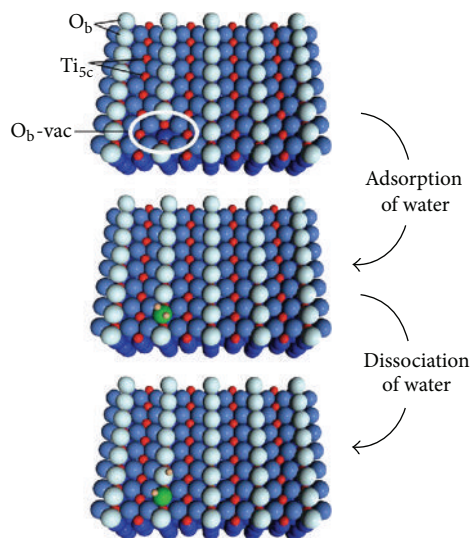


FIGURE 12: The dissociation of water in bridging oxygen vacancy. Green spheres denote O atoms with two H pink spheres [122].

happens at OTDs [105–108], mainly at the bridge-bonded oxygen vacancies, where  $\text{H}_2\text{O}$  dissociates leaving one pair of neighbouring  $-\text{OH}$  groups (Figure 12). The newly formed  $-\text{OH}$  can assist the redistribution of the defect electrons which are originally trapped at subsurface sites to its neighboring surface  $\text{Ti}^{4+}$  sites [109, 110], and thus the excess electrons (e.g., the photogenerated electrons) can be forced onto exposed surface and undergo further reactions. Further, Aschauer et al. [111] proposed that subsurface defects could promote the binding between water and surface defects by lowering the desorption energy of adsorbed water at OTDs. The water adsorption energy to the defect-free stoichiometric surface is higher than defective surfaces [111] (shown in Figure 13), implying a less effective photocatalytic activity on the stoichiometric  $\text{TiO}_2$ .

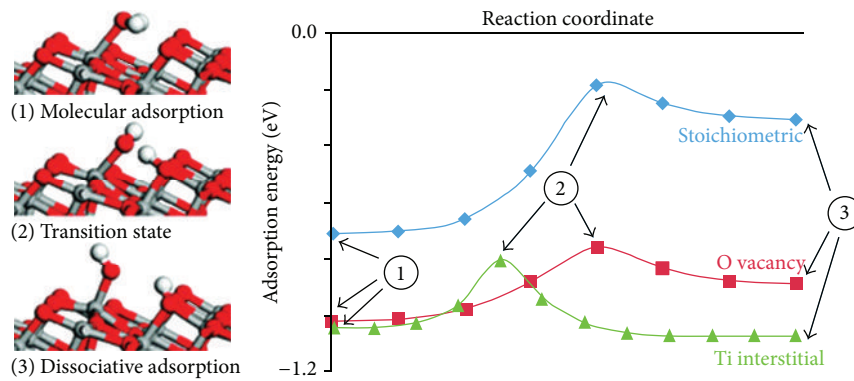


FIGURE 13: The water adsorption state on O vacancy, Ti interstitial and stoichiometric surface [111].

TABLE 2: Possible reaction pathways for defective TiO<sub>2</sub>.

Phase	CO <sub>2</sub> photoreduction with H <sub>2</sub> O vapor	
Defective TiO <sub>2</sub> anatase and brookite	$\text{H}_2\text{O} + \text{h}^+ \rightarrow \text{H}^+ + \text{OH}\cdot$ (1)	$\text{CO}_2 + \text{Ti}^{3+} \rightarrow \text{Ti}^{4+} + \text{CO}_2^-$ (2)
	$\text{OH}\cdot + \text{CO}_2^+ \rightarrow \text{HCO}_3^-$ (3)	$\text{CO}_2^- + \text{H}^+ + \text{e}^- \rightarrow \text{CO} + \text{OH}^-$ (4)
	$\text{CO}_2^- + \text{CO}_2^- \rightarrow \text{CO} + \text{CO}_3^{2-}$ (5)	$\text{CO}_2^- + [\text{Ti}^{3+} - \text{V}_o - \text{Ti}^{4+}] \leftrightarrow \text{CO} + [\text{Ti}^{4+} - \text{O}^{2-} - \text{Ti}^{4+}]$ (6)
	$\text{CO}, \text{HCO}_3^-, \text{HCOOH} \xrightarrow{\text{e}^-} \text{C(ads)} \xrightarrow{\text{H}^+} \text{CH}_3\cdot \xrightarrow{\text{H}^+} \text{CH}_4$ (7)	
Defective TiO <sub>2</sub> brookite	$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$ (8)	$\text{CO}_2^- + 2\text{H}^+ + \text{e}^- \rightarrow \text{HCOOH}$ (9)
	$\text{HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O}$ (10)	$\text{CO}, \text{HCOOH} \xrightarrow{\text{e}^-, \text{H}^+} \text{CH}_4$ (11)

It is interesting that the electronic structure of surface oxygen vacancies can hardly be affected via water dissociation at these sites [112], not influencing the subsequent physical adsorption of O<sub>2</sub> toward these oxygen vacancies [113] and the bridging hydroxyls [114]. Henderson and the coworkers [112] also explained the negative effect of excess water in gas-phase photocatalysis. It is proposed that the second-layer H<sub>2</sub>O is sufficient to inhibit O<sub>2</sub> adsorption towards the active sites. As the effect of O<sub>2</sub> scavenger was weakened, the photocatalytic efficiency would be lowered.

**4.3.3. Adsorption of Organic Species.** Degradation of organic compounds by heterogeneous photocatalysts starts by adsorbing organic species, the rate of which is commonly recognized to determine the overall photocatalytic efficiency. The adsorption behavior of the organic compounds follows the single molecule adsorption to the surface active sites and can be described by Langmuir adsorption isotherm. The adsorption mass of the substrate by TiO<sub>2</sub> particles is usually very small due to the limitation of surface active sites. TiO<sub>2</sub> nanostructures with high surface area have been widely studied in the adsorption of organic species. However, the surface area can hardly essentially change the adsorption behavior of the organic substrates, moving from the near-surface region to the surface active sites. It can be supposed by the deduction from O<sub>2</sub> and H<sub>2</sub>O adsorption that surface defects as OTDs are the main sites for the dissociative adsorption/chemical adsorption whereas the subsurface disordering defects tend to assist the physical adsorption on the surface. On the other hand, the chemical adsorption of organic compounds and their by-products in

different defects may cause different degradation pathways [45, 115, 116]. This variation would result in the change of the reaction kinetic, adsorption-desorption completion toward surface active sites with O<sub>2</sub> and H<sub>2</sub>O [117], mineralization degree, photocatalytic quantum yield, and catalyst poisoning degree as well [118]. Therefore, it is still necessary to discuss this problem in the view of microscopic view. Zhang et al. [119] studied the adsorption behavior of methanol on TiO<sub>2</sub> and found that the methanol molecules are mainly distributed on bridging oxygen vacancies (Figure 14).

The adsorption of organic species to TiO<sub>2</sub> surface defects is widely studied by modeling of the process and theoretical calculation. However, it is hard to build the adsorption model because of the complexity of the various organic compounds. There exist no generally acceptable results even for a single alcohol molecule. Zhang et al. [120] introduced an in situ STM to study the methanol adsorption on TiO<sub>2</sub> surface. O–H bond scission on oxygen vacancies was found to be the dominant manner for methanol dissociation, prior to C–O bond scission. This result is of great importance for the exploration of the mechanisms in the methanol reforming and organic species degradation. Farfan-Arribas et al. [69] compared the adsorption behavior of ethanol, n-propanol, and 2-propanol. It is found that the coverage of these compounds increased and they tended to undergo decomposition with the increased concentration of oxygen vacancies. Table 2 also provides an evidence for altering the reaction pathways by surface defects as OTDs in photocatalytic reactions. This reveals a surface defects-related change in reaction pathways which is occurring, and it is important to understand the mechanism of photocatalytic reactions.

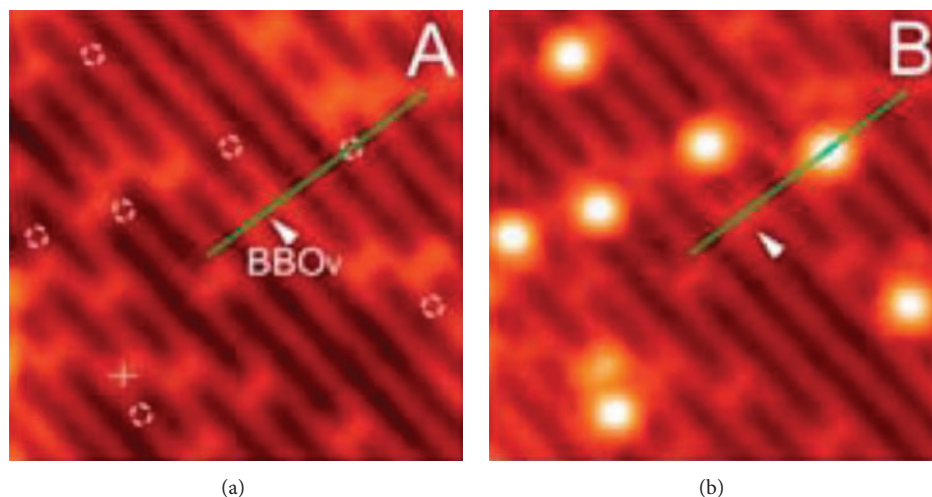


FIGURE 14: STM images of the methanol molecules and oxygen vacancies distribution on TiO<sub>2</sub> surface. (a) Before methanol exposure, BBOV represents the bonding bridging oxygen in the shallow bright color. (b) After methanol exposure, the strong bright dots reveal the methanol adsorption sites [119].

## 5. Conclusion Remarks

Oxygen vacancies and Ti-related defects are the main lattice defects in TiO<sub>2</sub>. The formation of oxygen vacancies,  $V_O''$  and  $V_O'$ , and the related  $Ti^{3+}$  defects are described. It provides an internal relationship between the defects, which is vital for understanding the behavior of the charge carriers in photocatalysis. Once the defects are introduced, HOMO-LUMO orbital can be reconstructed and the electronic cloud density of pristine TiO<sub>2</sub> can be redistributed. Such electric properties directly result in the narrowing of band gap and the trapping of photoinduced charge carriers in surface/subsurface. OTDs in the subsurface mainly serve as the recombination center, and the concentrated lattice distortion would largely consume the motion energy of excited charge carriers. Both of them would greatly lower the life time of the photogenerated charge carriers. OTDs in surface tend to function as the electron pool favoring the e-h separation and serve to adsorb active species as a result of the electronic force toward electrostatic neutralization. Surface OTDs would also mediate the charge transfer between the solid and the external reactants. Moreover, the selective dissociated adsorption of substance onto different kinds of OTDs is probably decisive to the exploration of the reaction mechanism. To study the behavior of defects caused by electronic driven forces is vitally necessary for photocatalysis, and it will promote the construction of environmentally friendly high-performance photocatalysts for diverse specific applications.

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2013J4100110), the Key Laboratory of Fuel Cell Technology of Guangdong Province, and the Key Laboratory of Environmental Pollution Control and Remediation Technology of Guangdong Province (no. 2011K0011).

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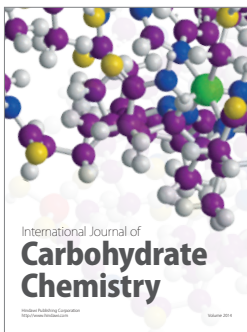
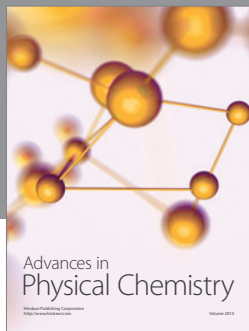
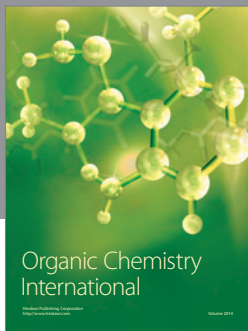
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