Review Article

Ti$^{3+}$ in the Surface of Titanium Dioxide: Generation, Properties and Photocatalytic Application

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Titanium dioxide (TiO$_2$) is the most investigated crystalline oxide in the surface science of metal oxides. Its physical and chemical properties are dominantly determined by its surface condition. Ti$^{3+}$ surface defect (TSD) is one of the most important surface defects in TiO$_2$. According to publications by other groups and the studies carried out in our laboratory, the formation mechanism of TSD is proposed. The generation, properties, and photocatalytic application of TSD are overviewed; the recent exploration of TSD is summarized, analyzed, and evaluated as well in this paper.

1. Introduction

Titanium dioxide (TiO$_2$) has been studied extensively in the field of surface science due to the wide range of its applications and the expectation for insights into surface properties on the fundamental level [1]. These studies have been motivated in part by the discovery that TiO$_2$ is a photocatalyst with relatively high efficiency for the decomposition of water [2–8] and the degradation of organic species [9–19]. The photocatalytic activity of TiO$_2$ is often dependent on the nature and density of surface defect sites. Liu et al. [20] have shown that the dominant defects in TiO$_2$ surfaces are Ti$^{3+}$ defects and oxygen vacancies. Much work has been focused on the TSD and the possible effect of the TSD in TiO$_2$. It has been shown that the chemistry of stoichiometric TiO$_2$ surfaces differs markedly from surfaces containing Ti$^{3+}$. Ti$^{3+}$ is considered to be an important reactive agent for many adsorbates; hence many surface reactions are influenced by these point defects [21]. Sirisuk et al. [22] reported that Ti$^{3+}$ sites play an essential role in photocatalytic process over TiO$_2$ photocatalyst. Sakai and coworkers [23–25] reported that TSD in anatase is an important parameter controlling the hydrophilic property. Also, as a support with high-surface area of anatase, TSD plays a significant role in enhancing the dispersion and stability of supported metal such as gold cluster and cobalt via the strong interaction between defect site and metal cluster [26]. Furthermore, for practical applications, pristine TiO$_2$ is not a good candidate, because it is only active under ultraviolet (UV) irradiation in order to overcome the band gap of above 3.0 eV. Reduced TiO$_2$ (TiO$_2$−$\chi$), which contains the Ti$^{3+}$, however, has been demonstrated to exhibit visible light absorption [27–31]. It is therefore highly important to have a comprehensive understanding of the methods and the techniques of Ti$^{3+}$ generation and monitoring as well as Ti$^{3+}$ property exploration.

TSD is not hard to be produced because its generation does not need harsh preparation conditions. The reported methods to produce TiO$_2$ containing TSD include UV irradiation [29, 32, 33], heating TiO$_2$ under vacuum [34, 35], thermal annealing to high temperatures (above 500 K) [36], reducing conditions (C [37], H$_2$ [20]), plasma-treating [38], laser [39], and high-energy particle (neutron [40–42], Ar$^+$ [43], electron [44], or $\gamma$-ray [45],) bombardment. Averaging spectroscopic techniques like X-ray photoelectron spectroscopy (XPS) [46–48], electron spin (or paramagnetic) resonance (ESR or EPR) [49–59], and temperature-programmed desorption (TPD) [22, 60] have given valuable
information for monitoring Ti$^{3+}$ defects in TiO$_2$ surfaces. In addition, TiO$_2$ with TPD shows not only the properties of acidic oxide but also reducing characteristics. Besides photocatalysis, it can also be applied to gas absorption [61, 62], photochromism [30, 31], biology [63], and energy storage [28, 64].

Since Ti$^{3+}$ strongly influences the surface chemistry of TiO$_2$, a detailed picture of TSD may help to understand reactivity and overall material performance in photocatalytic applications. Up to now, the knowledge of TiO$_2$ has been reviewed extensively, but that of TiO$_2$ containing TSD has not yet been mentioned until now. According to the publications by other groups and studies carried out in our laboratory, we will present a general overview of the subject on the generation, properties, and photocatalytic application of Ti$^{3+}$ in the surface of TiO$_2$.

2. Generation of Ti$^{3+}$ Surface Defects

2.1. Formation Mechanism of Ti$^{3+}$ Surface Defects. TSD can be generated by reduction of Ti$^{4+}$ ions. There are two typical processes for Ti$^{4+}$ reduction to Ti$^{3+}$.

One is that a Ti$^{4+}$ ion receives a photoelectron, which is usually generated due to UV irradiation on TiO$_2$. As shown in Figure 1 [33], photogenerated electrons and holes are produced in TiO$_2$ under UV irradiation. The electrons can be trapped and tend to reduce Ti$^{4+}$ cations to Ti$^{3+}$ state, and the holes oxidize O$^{2-}$ anions for the formation of O$^{-}$ trapped hole or even oxygen gas [65]. The charge transfer steps are as follows:

$$\text{TiO}_2 + h \nu \rightarrow e^{-}_{\text{CB}} + h^{+}_{\text{VB}} \quad (1)$$
$$e^{-}_{\text{CB}} + \text{Ti}^{4+} \rightarrow \text{Ti}^{3+} \text{trapped electron} \quad (2)$$
$$h^{+}_{\text{VB}} + \text{O}^{2-} \rightarrow \text{O}^{-} \text{trapped hole} \quad (3)$$
$$4h^{+}_{\text{VB}} + 2\text{O}^{2-} \rightarrow \text{O}_2. \quad (4)$$

Another process for Ti$^{4+}$ reduction to Ti$^{3+}$ is usually accompanied by a loss of oxygen from the surface of TiO$_2$. TSD can be introduced deliberately by annealing in vacuum condition, thermal treatment under reducing atmosphere (H$_2$, CO), or by bombardment using electron beam, neutron, or y-ray. In these processes, Ti$^{4+}$ ions receive electrons from these reducing gases or lattice oxygens which are usually removed from stoichiometric TiO$_2$. Figure 2 [20] shows the EPR intensity of Ti$^{3+}$ and oxygen vacancies versus H$_2$ treatment temperature during the H$_2$ treatment. Liu et al. [20] proposed that the interaction between H$_2$ and TiO$_2$ proceeded more drastically, in which the electrons transferred from oxygen vacancies to Ti$^{4+}$ ions, and then Ti$^{3+}$ ions were formed. In this case, the higher the temperature is, the more Ti$^{3+}$ ions were produced. Furthermore, when the temperature increased to 560°C, more energy was supplied, and the electrons already in the oxygen vacancies were driven away and transferred to Ti$^{4+}$. This result is in accordance with the EPR data which indicated the intensity of oxygen vacancies decreased and that of Ti$^{3+}$ increased.

Chen et al. [66] reported that some Ti$^{4+}$ ions in the surface of TiO$_2$ were reduced into Ti$^{3+}$ state by carbon formed from pyrolysis of titanyl organic compounds. The mechanism for this reduction reaction is that the carbon from organic component carbonizing could reduce Ti$^{4+}$ to Ti$^{3+}$ at high temperature, which is similar to Liu’s report. However, Chen et al. may hold a wrong idea that TSD is the same as oxygen vacancies. According to the publications by Berger et al. [33] and Liu et al. [20], the TSD is quite different from the oxygen vacancies because both TSD and oxygen vacancies can be generated, respectively. Here, we can see that the principal character of the second reduction process different from the first one is that Ti$^{4+}$ ions are not reduced
by photoelectrons generated by UV irradiation, but reduced by electron donators such as H$_2$, C, or lattice oxygen in TiO$_2$.

2.2. Generation Methods for Ti$^{3+}$ Surface Defects

2.2.1. UV Irradiation. Figure 1 is a scheme for the generation of TSD in anatase TiO$_2$ powder at 140 K and below by UV irradiation. As discussed in Section 2.1, photogenerated electrons and holes are produced by UV radiation in TiO$_2$, and the electrons can be trapped and tend to reduce Ti$^{4+}$ cations to Ti$^{3+}$ state. However, it has been shown that only a limited fraction of electrons are actually localized as in Ti$^{3+}$ state, while the major fraction remains in the conduction band after UV excitation [36]. After discontinuation of UV exposure, the electrons trapped in Ti$^{3+}$ can be stored for hours when TiO$_2$ particles are electronically isolated and kept at low temperatures. A high quantum yield and much longer life of the Ti$^{3+}$ ions can be achieved in wet TiO$_2$ gels. Kuznetsov et al. [67] reported that the quantum yield of Ti$^{3+}$ as high as 22–25% has been independently obtained from the absorption delay and extinction measurements. These Ti$^{3+}$ centers can be produced by the wet TiO$_2$ gels under the UV irradiation in the spectral range between 3.25 and 4.4 eV. All photo-induced Ti$^{3+}$ centers are chemically active and long lived. Under a prolonged UV-laser irradiation, their lifetime can be extremely long and exceeds months at room temperature in the absence of oxygen [28]. The electrons are stored in the gel network as small polarons, Ti$^{3+}$ centers, whereas the holes are stored in the liquid phase as H$^+$ ions or radicals. Some other research groups also reported the generation of Ti$^{3+}$ defects by UV irradiation [68, 69].

2.2.2. Annealing or Calcination. Vacuum annealing and calcination are widely used to generate TSD [34–36, 63, 70–72]. Guillemot et al. [63] reported that low-temperature vacuum annealing could create a controlled number of TSD ranging from low concentration (<3% Ti$^{3+}$/Ti$^{4+}$) to high concentration (around 21% Ti$^{3+}$/Ti$^{4+}$) at 323 and 573 K, respectively. Figure 3 shows the variation of the Ti$^{3+}$ to Ti$^{4+}$ ratio with vacuum annealing temperature. Nevertheless, TSD stability has been ascertained by first UHV annealing at 523 K and stored under di
erent conditions. Figure 3 shows the variation of the Ti$^{3+}$ to Ti$^{4+}$ ratio with vacuum annealing temperature. Nevertheless, TSD stability has been ascertained by first UHV annealing at 523 K and stored under different conditions. In fact, in relation to storage conditions, one night under UHV or one week under a laboratory atmosphere, the initial Ti$^{3+}$/Ti$^{4+}$ only decreased from 9.1% to 8.7 or 3.4%, respectively.

Xu and coworker [70] prepared TiO$_2$ ultrafine particles by the colloid chemical method. They found that as the calcining temperature decreased, the size of TiO$_2$ ultrafine particles decreased, and the contents of TSD and the number of hydroxyl active species increased, which were considered to be essential to the photocatalytic activity of the samples. Huizinga and Prins [71] reported that the reduction of Pt/TiO$_2$ at 573 K led to the formation of a Ti$^{3+}$ ESR signal. After reduction at 573 K, 0.3% of the total number of Ti$^{4+}$ ions in TiO$_2$ was reduced to Ti$^{3+}$. They found that the reduction of the TiO$_2$ by hydrogen was catalyzed by the platinum. The reduction mechanism has been proposed as follows:

\[
\frac{1}{2} \text{H}_2 \xrightarrow{\text{Pt}} \text{H}
\]

\[
\text{Ti}^{4+} + \text{O}^{2-} + \text{H} \rightarrow \text{Ti}^{3+} + \text{OH}^-
\]

2.2.3. Particles (Electron, Neutron, and $\gamma$-Ray) Bombardment. Zhang et al. [47] prepared TiO$_2$/Si films on silicon substrates by the DC reactive sputtering method. The TiO$_2$/Si structures with different TiO$_2$ film thickness were irradiated by electron beams. It is found that the number of Ti$^{3+}$ ions increased and Ti$^{4+}$ ions decreased after the irradiation. The relative abundance can be calculated. The number of Ti$^{3+}$ increased to 10% and that of Ti$^{4+}$ decreased from 98% to 90%. This implies that in the transition layer, a fraction of Ti$^{4+}$ ions turned to Ti$^{3+}$ ions and the chemical composition changed as follows:

\[
e + \text{Ti}^{4+} \rightarrow \text{Ti}^{3+}
\]

\[
2\text{TiO}_2 \rightarrow \text{Ti}_2\text{O}_3 + \text{O}_2
\]

Jun et al. [44] reported the improvement of the photoactivity of TiO$_2$ which underwent electron beam (EB) treatment (1 MeV) as a function of the absorbed radiation dose (MGy). The radiation-induced effects on the TiO$_2$ crystal structure, for example, change of the Ti$^{3+}$/Ti$^{4+}$ ratio, were investigated. As shown in Figure 4, the quantitative analyses of Ti$^{4+}$ and Ti$^{3+}$ surface states in EB-treated TiO$_2$ at different radiation doses are presented by XPS data. It shows that a maximum decrease of Ti$^{4+}$ amount treated at higher EB doses and approximately the same amount of Ti$^{3+}$ on the surface state in Ti2p up to about 3 MGy is observed. Both Ti2p$_{1/2}$ and Ti2p$_{3/2}$ states showed a change in Ti$^{3+}$ and Ti$^{4+}$, and the Ti$^{3+}$ states increased by about 15% as a consequence of EB treatment. The Ti$^{3+}$ state on TiO$_2$ surface is important because it can play a similar role as observed...
in TiO\textsubscript{2} doped with metal atoms, which can trap the photogenerated electrons and thereafter leave behind unpaired charges to promote photoactivity.

Figure 5(a) [45] shows the ESR signals of O\textsuperscript{−} anion radicals and Ti\textsuperscript{3+} cations on TiO\textsubscript{2} powder after \gamma-ray irradiation of 150 MR under N\textsubscript{2} atmosphere. Before \gamma-ray irradiation, no signal could be observed in the ESR signals, while after \gamma-ray irradiation, the ESR signals attributed to the O\textsuperscript{−} anion radicals and associated Ti\textsuperscript{3+} were observed. It increased with the increase of the \gamma-ray irradiation dosage shown in Figure 5(b) [45].

Huang et al. [30] reported that upon exposure to \gamma-radiation, a concentrated TiO\textsubscript{2} sol changed from colorless to deep blue with an absorption maximum at 540 nm. The absorption has been assigned to trapped electrons or \textsuperscript{•}\textsubscript{O}\textsuperscript{2−}. This model is in accordance with those proposed by Weyl and Forland [73] and Breckenridge and Hosler [74]. In their models, Ti\textsuperscript{3+} ions are also on sites adjacent to the oxygen vacancy. In addition, Weyl and coworkers have drawn a schematic picture of the structure of Ti\textsuperscript{3+} ions (Figure 7). Figure 7 [73] shows schematically what happens when a crystal of Ti\textsuperscript{4+}O\textsubscript{2}\textsuperscript{2−} loses one oxygen atom, and the two electrons of the O\textsuperscript{2−} ion change two Ti\textsuperscript{4+} to Ti\textsuperscript{3+} ions. These Ti\textsuperscript{3+} ions are strongly polarized and a state is assumed, in which its extreme can be described as two Ti\textsuperscript{4+} ions and two additional electrons. The latter may assume the position of the missing O\textsuperscript{2−} ion. The intensive light absorption in such partly reduced crystals is the result of the strong distortion of the outer orbitals of the Ti\textsuperscript{3+} ions. Ti\textsuperscript{3+} ions in this state absorb light more intensively than undeformed Ti\textsuperscript{3+} ions.

3. Properties of Ti\textsuperscript{3+} Surface Defects

3.1. Structural Properties of Ti\textsuperscript{3+} Surface Defects. Lu et al. [72] described the structure of ideal rutile single crystal and rutile with insufficient oxygen. In the ideal rutile single crystal, each titanium ion is located in the center of oxygen octahedron. The symmetry of the oxygen octahedron is rhombic symmetry (D\textsubscript{3h}). The parallel (R\textsubscript{∥}) and vertical (R\textsubscript{⊥}) Ti\textsuperscript{4+}-O\textsuperscript{2−} bonding lengths are 1.988 and 1.944 Å (see Figure 6), and the bonding angle in the vertical plane is about 80.83°. When a host Ti\textsuperscript{4+} ion is changed to Ti\textsuperscript{3+} ion, the local electrostatic balance is broken, and an O\textsubscript{V} (oxygen vacancy) should be introduced because of charge compensation. In order to determine the position of the O\textsubscript{V} as well as the local structure of the [Ti\textsuperscript{3+}-O\textsubscript{V}] center in the reduced rutile crystal, the structure model is established, and the optical spectra is calculated by using the crystal field theory. In this structure model, the axial O\textsubscript{V} is located on the nearest position of central Ti\textsuperscript{3+} ion. When an O\textsubscript{V} appears on the nearest position of central Ti\textsuperscript{3+} ion along the R\textsubscript{∥} direction of the oxygen octahedron, the local symmetry would change from D\textsubscript{3h} to C\textsubscript{2v}. Since the effective charge of the O\textsubscript{V} is positive, the central Ti\textsuperscript{3+} is expected to shift away from the O\textsubscript{V} along the R\textsubscript{∥} direction by an amount \Delta R, due to the electrostatic repulsion. Similarly, the four O\textsuperscript{2−} ions on the vertical plane would also move towards the O\textsubscript{V} by an amount \Delta R\textsubscript{p} due to the electrostatic attraction (see Figure 6). Considering the much larger distance between the O\textsubscript{V} and the remaining O\textsuperscript{2−} ion of the R\textsubscript{⊥} direction, the displacement of the only axial O\textsuperscript{2−} ion may be much smaller than \Delta R\textsubscript{∥} or \Delta R\textsubscript{p} and can be omitted for simplicity.

This model is in accordance with those proposed by Weyl and Forland [73] and Breckenridge and Hosler [74]. In their models, Ti\textsuperscript{3+} ions are also on sites adjacent to the oxygen vacancy. In addition, Weyl and coworkers have drawn a schematic picture of the structure of Ti\textsuperscript{3+} ions (Figure 7). Figure 7 [73] shows schematically what happens when a crystal of Ti\textsuperscript{4+}O\textsuperscript{2−} loses one oxygen atom, and the two electrons of the O\textsuperscript{2−} ion change two Ti\textsuperscript{4+} to Ti\textsuperscript{3+} ions. These Ti\textsuperscript{3+} ions are strongly polarized and a state is assumed, in which its extreme can be described as two Ti\textsuperscript{4+} ions and two additional electrons. The latter may assume the position of the missing O\textsuperscript{2−} ion. The intensive light absorption in such partly reduced crystals is the result of the strong distortion of the outer orbitals of the Ti\textsuperscript{3+} ions. Ti\textsuperscript{3+} ions in this state absorb light more intensively than undeformed Ti\textsuperscript{3+} ions.

3.2. Optical Properties of Ti\textsuperscript{3+} Surface Defects. Optical properties of TSD lie in two aspects. One is that Ti\textsuperscript{3+} ions are the origin of the blue coloration or coloration center [27, 58, 64, 74] and the other is that Ti\textsuperscript{3+} species has a characteristic visible absorption spectrum [27–31, 75–78]. Ookubo et al. [58] developed a method that examined the quantitative relation between degree of blue coloration and the concentration of the Ti\textsuperscript{3+} ions. The method has been proposed based on the phenomenon that a Ti\textsuperscript{3+} salt was hydrolyzed slowly with the presence of urea in an aqueous solution. With this method, a blue TiO\textsubscript{2} was obtained,

![Figure 4](image-url)
and the degree of the coloration has been controlled by changing the period of refluxing the solution in the synthetic procedure. In addition, numerous studies have verified that the Ti$^{3+}$ species induced oxygen vacancy states between the valence and the conduction bands, which would contribute to the visible response. Xiong et al. [64] identified the conversion of Ti$^{4+}$ to Ti$^{3+}$ in the TiO$_2$/Cu$_2$O bilayer film after the visible-light irradiation by the UV-vis diffuse reflectance measurement. Because Ti$^{4+}$ has no response to visible light while Ti$^{3+}$ does, the presence of Ti$^{3+}$ ions leads to a weaker absorbance of the bilayer film in the short wavelength range while stronger in the long wavelength range. It was also found that the transparent TiO$_2$ film turned blue under the irradiation (Figure 8(a)).

Bityurin et al. [29] proposed several models fitting the experimental data on the kinetics of UV laser-induced darkening in TiO$_2$ gels. Samples were exposed to various average laser intensities in the range of $0.05 \sim 0.5 \text{ W/cm}^2$ by using beam attenuators. After irradiation of a sample by a laser beam, the modified area looked like a dark spot on the transparent material surface (Figure 8(b)). The dark color spot was believed to be caused by the transformation of Ti$^{4+}$ to Ti$^{3+}$. TiO$_2$ sol was also shown to change from

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Figure 5: (a) ESR signals of O$^-$ anion radicals and Ti$^{3+}$ cations on the TiO$_2$ powder after y-ray irradiation of 150 MR under N$_2$ atmosphere. (b) Variation of the intensity of the signals due to y-ray induced O$^-$ anion radicals and Ti$^{3+}$ cations with y-ray irradiation time under N$_2$ atmosphere [45].

Figure 6: The schematic diagram model, that is, the central Ti$^{3+}$ ion associated with an oxygen vacancy on its nearest position along the parallel direction [72].

Figure 7: Schematic picture of a flaw on partly reduced TiO$_2$ [73].
colorless to deep blue with an absorption maximum at 540 nm upon exposure to γ-radiation [29]. The absorption has been assigned to trapped electrons or Ti3+ ions in the solid matrix based on its spectroscopic similarity to the samples irradiated with UV light.

3.3. XPS Properties of Ti3+ Surface Defects. According to the standard binding energy of Ti2p3/2 in TiO2, that for Ti3+ is usually located at 457.7 eV and that for Ti4+ is at 459.5 eV. The O (1 s) binding energy for TiO2 is 529.3 eV [79]. Generally speaking, the binding energy peak of Ti2p in stoichiometry TiO2 is not broad and no shoulder peak. However, that for TiO2 containing Ti3+ in the surface is usually tortured and turns into much broader. In this case, a fitting skill such as Gaussian of the Gauss-Lorentzian fitting can be taken to obtain the information of Ti3+ and Ti4+ in the surface of reduced TiO2. The relative contents of Ti3+ in the surface of reduced TiO2 can also be obtained according to the XPS peak areas.

Greenlief et al. [46] reported the Ti2p binding energy data of TiO2 thin films with different monolayers on polycrystalline Pt after vacuum annealing by XPS technique. The measured binding energy 458.9 eV was the Ti2p3/2 peak for the TiO2 thin films with coverages more than 3 monolayers (1 monolayer is assumed to be an evenly dispersed film 2.6 Å thick). The O (1 s) binding energy for these TiO2 thin films were 530.3 eV. The O/Ti ratio (as determined by XPS peak areas) was stoichiometric (2.0) for these TiO2 thin films. After vacuum annealing, the ratio dropped to between 1.0 and 1.5, and a mixture of Ti3+ and Ti4+ was obtained. The binding energy 458.9 eV was observed and attributed to Ti3+ state.

Recently, our group [64] found that the TSD can be generated in TiO2/Cu2O bilayer film under visible-light irradiation. By means of XPS (Figure 9), it can be seen that the binding energy of Ti2p3/2 in bilayer film without the irradiation was 458.7 eV (Figure 9(a)). It is difficult to simulate this peak since the peak was not so broad, and there was no shoulder peak. The binding energy of Ti2p3/2 in the bilayer film after the irradiation was 458.1 eV. Compared with the peak for Ti2p3/2 in the same bilayer film without the irradiation, the one after the irradiation was much broader and there was 0.6 eV shift. This Ti2p3/2 spectrum can be simulated with Gaussian simulation. The peaks at 457.8 eV and at 459.2 eV were attributed to Ti3+ and Ti4+, respectively (Figure 9(b)). The result is in accordance with the reported data [79]. The content of Ti3+ ions was as high as 74% in TiO2/Cu2O bilayer film after visible-light irradiation according to the comparison of the peaks area.

3.4. EPR Properties of Ti3+ Surface Defects. EPR is a highly sensitive technique which allows investigation of paramagnetic species having one or more unpaired electrons either in the bulk or at the surface of various solids. EPR technique is already widely used by many researchers to characterize TSD. The data of EPR signals assigned to Ti3+ in some published paper are shown in Table 1.

Tijana et al. also presented some published data of EPR signals of Ti3+ in the book edited by Kokorin and Bahnemann [90]. They proposed that Ti3+ in the surface and that in the bulk of TiO2 can be distinguished by the differences of their EPR parameters. The values of the g-factors for surface Ti3+ particles are significantly lower than those usually found in bulk TiO2. Similar result was also reported by Nakaoka and Nosaka [91]. There is a small change in the g-values of the axially symmetrical g-tensor (previously identified as interstitial interior Ti3+ ions) upon the sample heating ($g_\parallel = 1.957, g_\perp = 1.990$ for untreated sample and $g_\parallel = 1.961, g_\perp = 1.992$ for sample heated at 700°C for 5 h). They attributed the first signal to the photo-generated electron trapped on the surface Ti3+ ions, and the second one to the inner Ti3+ ions.
In addition, Tijana et al. found the difference of EPR signal shapes for surface and inner Ti$^{3+}$ ions. According to the characters of EPR signals, they proposed two general types of traps (Ti$^{3+}$ ions): internal, having a narrow axially symmetric EPR signal, and surface, with broad EPR lines. Magnetic resonance parameters of the internal, interstitial (inner) Ti$^{3+}$ ions slightly vary due to the different delocalization of the unpaired electron density and symmetry of the local surroundings (presence of vacancies and impurities in the nearest coordination sphere). It also happens for the surface electron trap. In this case, $g$-values and the linewidth of the surface Ti$^{3+}$ ions mainly depend upon surface modification.

3.5. Temperature Program Reduction (TPD). Temperature-programmed desorption using carbon dioxide (CO$_2$-TPD) as a probe can be employed to monitor surface defects in TiO$_2$ [22, 60, 84, 92]. CO$_2$-TPD analysis indicates a signal of CO$_2$, which desorbs from the TiO$_2$ surface between the ranges of 123 and 253 K and results in two peaks: one peak at about 170 K attributed to CO$_2$ molecules bound to a regular five-coordinate Ti$^{4+}$ site which was a perfect TiO$_2$ structure, and another peak at about 200 K corresponding to CO$_2$ molecules bound to Ti$^{3+}$ which was a defected TiO$_2$ structure [60, 84] (Figure 10). The positions of the peaks are shifted slightly from those reported by Sirisuk and coworkers [22]. Thompson et al. [60] have observed the characteristic two-step desorption process which is indicative of the presence of both Ti$^{3+}$ defects and nondefective TiO$_2$ sites. Moreover, they have measured the activation energy for both of the desorption peaks of CO$_2$. For CO$_2$ desorption from the fully oxidized (or perfected) surface, where the CO$_2$ is bound to Ti$^{4+}$ sites, a zero-coverage activation energy for CO$_2$ desorption of 48.5 kJ/mol is measured. It is in approximate agreement with theoretical calculations value of 65 kJ/mol [93]. For CO$_2$ desorption from the Ti$^{3+}$ sites produced by annealing TiO$_2$ (110) in vacuum, a zero-coverage activation energy of $\sim$54 kJ/mol was measured. This indicates that Ti$^{3+}$ sites bind CO$_2$ slightly more strongly (TPD peak at 200 K) than the fivefold coordinated Ti$^{4+}$ sites (TPD peak at 170 K) do.

4. Photocatalytic Application

4.1. Photocatalytic Reaction Mechanism of Ti$^{3+}$ Surface Defects. The photocatalytic reaction mechanisms are widely studied. The principle of TiO$_2$ photocatalytic reaction is straightforward. Upon absorption of photons with energy larger than the band gap of semiconductor materials, electrons are excited from the valence band to the conduction band, producing electron-hole pairs. These charge carriers migrate to the surface and react with the chemicals adsorbed on the surface to decompose these chemicals. This photodecomposition process usually involves one or more of radicals or intermediate species such as $\cdot$OH, O$_2^-$, H$_2$O$_2$, or O$_2$, which play important roles in the photocatalytic reaction. The photocatalytic activity of a semiconductor is largely
Table 1: The data of EPR signals assigned to Ti\(^{3+}\) in some published paper.

<table>
<thead>
<tr>
<th>ESR parameters (g-value)</th>
<th>Condition</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9495, 1.9640</td>
<td>Anatase nanoparticles exposure to UV light</td>
<td>[33]</td>
</tr>
<tr>
<td>1.9600</td>
<td>Anatase nanoparticles exposure to UV light</td>
<td>[33]</td>
</tr>
<tr>
<td>1.902, 1.953</td>
<td>Laser-irradiated TiO(_2)</td>
<td>[39]</td>
</tr>
<tr>
<td>1.962, 1.960</td>
<td>Titanium silicalite</td>
<td>[49]</td>
</tr>
<tr>
<td>1.905, 1.912</td>
<td>Ti-SiO(_2) by a sol-gel method</td>
<td>[49]</td>
</tr>
<tr>
<td>1.88, 1.925</td>
<td>Fe(^{3+})-doped colloids: 6 g dm(^{-3}) TiO(_2), 0.5 wt% Fe, irradiated 6 h</td>
<td>[54]</td>
</tr>
<tr>
<td>1.988, 1.897</td>
<td>Fe(^{3+})-doped colloids: 5 g dm(^{-3}) TiO(_2), 0.1 wt% Fe, irradiated 3 h</td>
<td>[54]</td>
</tr>
<tr>
<td>1.975, 1.944</td>
<td>Self-doped TiO(_2)</td>
<td>[78]</td>
</tr>
<tr>
<td>1.996, 1.901</td>
<td>KTa(_0.9 Nb_0.1)O(_3)</td>
<td>[80]</td>
</tr>
<tr>
<td>1.994, 1.896</td>
<td>Hydrated TiO(_2)</td>
<td>[81]</td>
</tr>
<tr>
<td>1.9482, 1.9707</td>
<td>Carbon-doped TiO(_2)</td>
<td>[82]</td>
</tr>
<tr>
<td>1.975, 1.963</td>
<td>Ultratine-powdered TiO(_2)</td>
<td>[83]</td>
</tr>
</tbody>
</table>

controlled by (i) the light absorption properties, for example, light absorption spectrum and coefficient, (ii) reduction and oxidation rates on the surface by the electron and hole, (iii) and the electron-hole recombination rate [92].

As for TiO\(_2\) containing TSD, its photocatalytic activity is definitely dominated by TSD. TSD improves the photocatalytic activity of pure TiO\(_2\) from the following two aspects: (i) it extends the photosresponse of TiO\(_2\) from UV to visible light region, which leads to visible-light photocatalytic activity; (ii) it provides important reactive agents for many adsorbates and results in the reduction of an electron-hole pair recombination rate [44].

Park et al. [83] proposed the mechanism of TSD participating in photocatalytic reaction. When the TiO\(_2\) photocatalysts were irradiated, e\(^-\)/h\(^+\) pairs were formed. In the absence of the electron and hole scavengers, most of them recombined with each other within a few nanoseconds. If the scavengers or surface defects were present to trap the electron or hole, e\(^-\)/h\(^+\) recombinations could be prevented, and the subsequent reactions caused by the electrons and holes were dramatically enhanced. In this case, electrons donors reacted with holes. The electron can be trapped by Ti\(^{4+}\) to generate an isolated Ti\(^{3+}\) ion. In the presence of O\(_2\), the Ti\(^{3+}\) sites easily react with O\(_2\), leading to the formation of radicals such as O\(_2^-\), H\(_2\)O\(_2^-\), and •OH. The charge transfer processes may be as follows:

\[
e_{cb}^- + \text{Ti}^{4+}\text{OH} \rightarrow \text{Ti}^{3+}\text{OH} \quad (9)
\]

\[
\text{Ti}^{3+}\text{OH} + \text{O}_2 \rightarrow \text{Ti}^{4+}\text{OH} + \cdot \text{O}_2^- \quad (10)
\]
4.2. Photocatalytic Application of Ti$^{3+}$ Surface Defects

4.2.1. Ion-Doped TiO$_2$ Photocatalyst. A great deal of research has been focused on ion-doped TiO$_2$ with both transition metal and nonmetal impurities in order to lower the threshold energy and improve photocatalytic activity. Doping with transition metals has shown both positive and negative effects. Indeed, these metal-doped photocatalysts have been demonstrated to suffer from thermal instability, and metal centers acting as electron traps have reduced the photocatalytic efficiency [94].

Stimulated by the report of Asahi et al. in 2001 [95], there has been an explosion of interest in TiO$_2$ doping with nonmetal ions, N, C, S, B, especially with nitrogen. Livraghi et al. [96] reported the origin of photocatalytic activity of N-doped TiO$_2$ under visible light. As shown in Figure 11, the material contains single-atom nitrogen impurities that form either diamagnetic (N$_b^-$) or paramagnetic (N$_s^+$) centers. Both types of N$_b$ centers give rise to localized states in the band gap of the oxide. The relative abundance of these species depends on the oxidation state of the solid since upon reduction, electron transfer from Ti$^{3+}$ ions to N$_b$ results in the formation of Ti$^{4+}$ and N$_b^-$.

The presence of Ti$^{3+}$ ions is helpful to form the N paramagnetic centers at the expense of the Ti$^{3+}$ ions oxidized to Ti$^{4+}$. The photocatalytic activity of the N-doped TiO$_2$ catalyst was thought to be the synergistic effect of nitrogen and Ti$^{3+}$ species [76, 97].

Sun et al. [76] reported that the N-doped TiO$_2$ catalyst showed higher photocatalytic activity for degradation of 4-CP than pure TiO$_2$ under not only visible but also UV irradiation due to the presence of Ti$^{3+}$. Qin et al. [98] demonstrated that the enhancement of methyl orange and 2-mercaptobenzothiazole photodegradation using the N-doped TiO$_2$ catalysts is mainly involved in the efficient separation of electron-hole pairs owing to the presence of Ti$^{3+}$ and the improvement of the organic substrate adsorption in catalysts suspension and optical response in visible-light region. However, it is found that excessive Ti$^{3+}$ acted as a recombination center for holes and electrons, which is the reason for an optimal content of Ti$^{3+}$ in the nitrogen-doped TiO$_2$. The N-doped TiO$_2$ with N/Ti proportioning of 20 mol% calcined at 400$^\circ$C exhibited the highest visible-light activity. Therefore, the presence and optimal content of Ti$^{3+}$ might be the critical factors for the improvement of the photoactivity.

Carban-doped TiO$_2$ has also shown much better photocatalytic activity due to the presence of TSD [37, 66, 82, 88, 92]. Chen et al. [66] reported that the C from pyrolyzing process of titanyl organic compounds could reduce the part of Ti$^{4+}$ in the surface of TiO$_2$ into Ti$^{3+}$, and some OH groups were formed on crystal surface with the presence of water from pyrolysis. This allowed TiO$_2$ to possess abundant TSD, which acted as the active center for both photocatalytic reaction and matching OH at its surface. When Ti$^{3+}$/OH ratio in the surface of nanometer crystalline TiO$_2$ approaches 1, there is more effective photocatalytic activity. Li et al. [82] reported that the carbon-doped TiO$_2$ with high surface area and good crystallinity showed an obvious enlarged range of absorption up to 700 nm and had much better photocatalytic activity for gas phase photo-oxidation of benzene under artificial solar light than pure TiO$_2$. The visible-light photocatalytic activity is ascribed to the presence of oxygen vacancy state because of the formation of Ti$^{3+}$ species between the valence and the conduction bands in the TiO$_2$ band structure, which results in the as-synthesized carbon-doped TiO$_2$ responsive to the visible light.

4.2.2. Self-Doped TiO$_2$ Photocatalyst. Here, self-doped TiO$_2$ photocatalyst can be interpreted as Ti$^{3+}$-doped TiO$_2$, in which nothing but Ti and O ions exists. As discussed in Section 2.2, self-doped TiO$_2$ photocatalyst can be produced by UV irradiation, heating under vacuum, thermal annealing to high temperatures (above 500 K), reducing conditions (C, H$_2$), plasma treating, laser, and high-energy particle (neutron, Ar$^+$, electron, or γ-ray) bombardment. Abundant presented data and numerous valuable conclusions indicate that TSD in self-doped TiO$_2$ photocatalysts is responsible for the enhancement of photocatalytic activity [20, 34–36, 38–40, 42–44, 70, 83, 89, 99–102].

In addition, our group reported the high photocatalytic degradation of methylene blue by TiO$_2$/Cu$_2$O composite film [79] and photocatalytic water splitting by TiO$_2$/Cu$_2$O bilayer film owing to the presence of Ti$^{3+}$ [64]. For photocatalytic degradation reaction, electrons excited from TiO$_2$/Cu$_2$O composite film under visible light were transferred from the conduction band of Cu$_2$O to that of TiO$_2$. The formed intermediate state of Ti$^{3+}$ ion was observed by X-ray photoelectron spectroscopy (XPS) on the TiO$_2$/Cu$_2$O composite film. Additionally, the accumulated electrons in the conduction band of TiO$_2$ were transferred to oxygen on the TiO$_2$ surface for the formation of O$_2^-$ or O$_2^{2-}$, which combines with H$^+$ to form H$_2$O$_2$. The evolved H$_2$O$_2$ with FeSO$_4$ and EDTA forms Fenton reagent to degrade methylene blue. With regard to photocatalytic water splitting process, the photogenerated electrons from the conduction band of Cu$_2$O were captured by Ti$^{3+}$ ions in TiO$_2$, and Ti$^{4+}$ ions were further reduced to Ti$^{3+}$ ions. The Ti$^{3+}$ ions have a long lifetime and bear the photogenerated electrons as a form of reducing force.
of energy. The electrons trapped in Ti3+ ions as stored energy lead to evolve H2 from H2O. The electron transfer processes may be as follows:

\[
\text{Cu}_2\text{O} + h\nu (\lambda > 420 \text{ nm}) \rightarrow h\nu_{\text{VB}}^+ + e_{\text{CB}}^- 
\]

(14)

\[
e_{\text{CB}}^- + \text{Ti}^{4+} \rightarrow \text{Ti}^{3+} \text{OH} 
\]

(15)

\[
2\text{Ti}^{3+} + 2\text{H}^+ \rightarrow \text{H}_2. 
\]

(16)

5. Concluding Remarks

An overview on current literature on the subject of TSD in TiO2 has been provided here, but the works that have been done and the progresses that have been achieved on this subject are far from being completely resolved. While some of these results reviewed here might be turned out to be of mere fundamental interest and irrelevant for the particular environment and applications, some might help to understand the behavior of this material. Since TiO2 is used in so many different fields, TSD would attract more attention. It is expected that this paper will help to link the more fundamental and more applied lines of research on this subject.

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