

Review Article

Ti³⁺ in the Surface of Titanium Dioxide: Generation, Properties and Photocatalytic Application

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Titanium dioxide (TiO₂) 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. Ti³⁺ surface defect (TSD) is one of the most important surface defects in TiO₂. 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 (TiO₂) 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 TiO₂ 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 TiO₂ is often dependent on the nature and density of surface defect sites. Liu et al. [20] have shown that the dominant defects in TiO₂ surfaces are Ti³⁺ defects and oxygen vacancies. Much work has been focused on the TSD and the possible effect of the TSD in TiO₂. It has been shown that the chemistry of stoichiometric TiO₂ surfaces differs markedly from surfaces containing Ti³⁺. Ti³⁺ 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 Ti³⁺ sites play an essential role in photocatalytic process over TiO₂ 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 TiO₂ 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 TiO₂ (TiO_{2-x}), which contains the Ti³⁺, 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 Ti³⁺ generation and monitoring as well as Ti³⁺ property exploration.

TSD is not hard to be produced because its generation does not need harsh preparation conditions. The reported methods to produce TiO₂ containing TSD include UV irradiation [29, 32, 33], heating TiO₂ under vacuum [34, 35], thermal annealing to high temperatures (above 500 K) [36], reducing conditions (C [37], H₂ [20]), plasma-treating [38], laser [39], and high-energy particle (neutron [40–42], Ar⁺ [43], electron [44], or γ -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

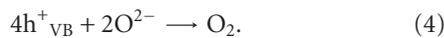
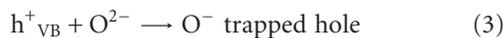
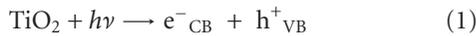
information for monitoring Ti^{3+} defects in TiO_2 surfaces. In addition, TiO_2 with TPD shows not only the properties of acidic oxide but also reducing characteristics. Besides photocatalysis, it can also be applied to gas absorption [61, 62], photochromism [30, 31], biology [63], and energy storage [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:



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 γ -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 fell into three types. Firstly, hydrogen interacted physically with the adsorbed oxygen on the surface of TiO_2 at a temperature below $300^\circ C$. Secondly, when the temperature was higher than $300^\circ C$, electrons were transferred from the H atoms to the O atoms in the lattice of TiO_2 . Then, the oxygen vacancies were formed when the O atom left with the H atom in the form of H_2O . Thirdly, when the temperature was up to

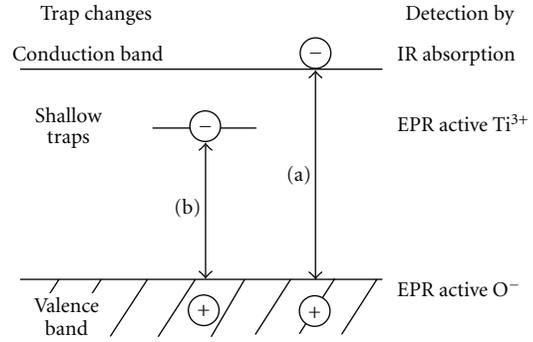


FIGURE 1: Scheme of UV induced charge separation in TiO_2 [33].

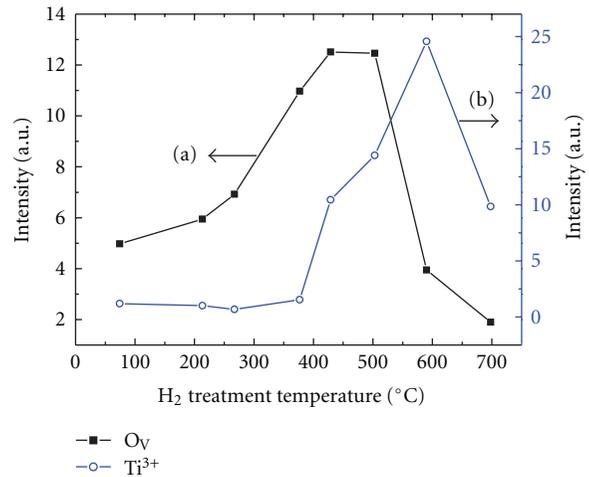


FIGURE 2: EPR intensity of Ti^{3+} and oxygen vacancies versus H_2 treatment temperature during the H_2 treatment [20].

$450^\circ C$, 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 $560^\circ C$, 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 donors such as H₂, C, or lattice oxygen in TiO₂.

2.2. Generation Methods for Ti³⁺ Surface Defects

2.2.1. UV Irradiation. Figure 1 is a scheme for the generation of TSD in anatase TiO₂ 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 TiO₂, and the electrons can be trapped and tend to reduce Ti⁴⁺ cations to Ti³⁺ state. However, it has been shown that only a limited fraction of electrons are actually localized as in Ti³⁺ state, while the major fraction remains in the conduction band after UV excitation [36]. After discontinuation of UV exposure, the electrons trapped in Ti³⁺ can be stored for hours when TiO₂ particles are electronically isolated and kept at low temperatures. A high quantum yield and much longer life of the Ti³⁺ ions can be achieved in wet TiO₂ gels. Kuznetsov et al. [67] reported that the quantum yield of Ti³⁺ as high as 22–25% has been independently obtained from the absorption delay and extinction measurements. These Ti³⁺ centers can be produced by the wet TiO₂ gels under the UV irradiation in the spectral range between 3.25 and 4.4 eV. All photo-induced Ti³⁺ 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, Ti³⁺ centers, whereas the holes are stored in the liquid phase as H⁺ ions or radicals. Some other research groups also reported the generation of Ti³⁺ 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% Ti³⁺/Ti⁴⁺) to high concentration (around 21% Ti³⁺/Ti⁴⁺) at 323 and 573 K, respectively. Figure 3 shows the variation of the Ti³⁺ to Ti⁴⁺ ratio with vacuum annealing temperature. Nevertheless, TSD stability has been ascertained by first UHV annealed 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 Ti³⁺/Ti⁴⁺ only decreased from 9.1% to 8.7 or 3.4%, respectively.

Xu and coworkers [70] prepared TiO₂ ultrafine particles by the colloid chemical method. They found that as the calcining temperature decreased, the size of TiO₂ 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/TiO₂ at 573 K led to the formation of a Ti³⁺ ESR signal. After reduction at 573 K, 0.3% of the total number of Ti⁴⁺ ions in TiO₂ was reduced to Ti³⁺. They found that the reduction of the TiO₂ by hydrogen was catalyzed by the

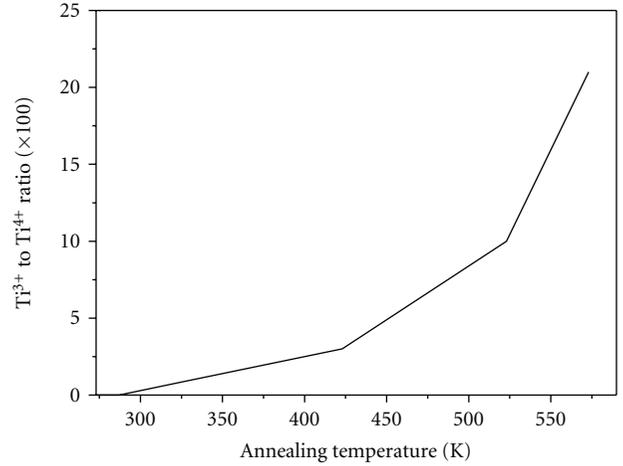
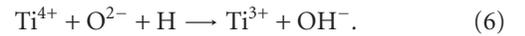
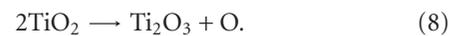


FIGURE 3: Variation of the Ti³⁺ to Ti⁴⁺ ratio with vacuum annealing temperature [63].

platinum. The reduction mechanism has been proposed as follows:



2.2.3. Particles (Electron, Neutron, and γ -Ray) Bombardment. Zhang et al. [47] prepared TiO₂/Si films on silicon substrates by the DC reactive sputtering method. The TiO₂/Si structures with different TiO₂ film thickness were irradiated by electron beams. It is found that the number of Ti³⁺ ions increased and Ti⁴⁺ ions decreased after the irradiation. The relative abundance can be calculated. The number of Ti³⁺ increased to 10% and that of Ti⁴⁺ decreased from 98% to 90%. This implies that in the transition layer, a fraction of Ti⁴⁺ ions turned to Ti³⁺ ions and the chemical composition changed as follows:



Jun et al. [44] reported the improvement of the photoactivity of TiO₂ which underwent electron beam (EB) treatment (1 MeV) as a function of the absorbed radiation dose (MGy). The radiation-induced effects on the TiO₂ crystal structure, for example, change of the Ti³⁺/Ti⁴⁺ ratio, were investigated. As shown in Figure 4, the quantitative analyses of Ti⁴⁺ and Ti³⁺ surface states in EB-treated TiO₂ at different radiation doses are presented by XPS data. It shows that a maximum decrease of Ti⁴⁺ amount treated at higher EB doses and approximately the same amount of Ti³⁺ 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 Ti³⁺ and Ti⁴⁺, and the Ti³⁺ states increased by about 15% as a consequence of EB treatment. The Ti³⁺ state on TiO₂ surface is important because it can play a similar role as observed

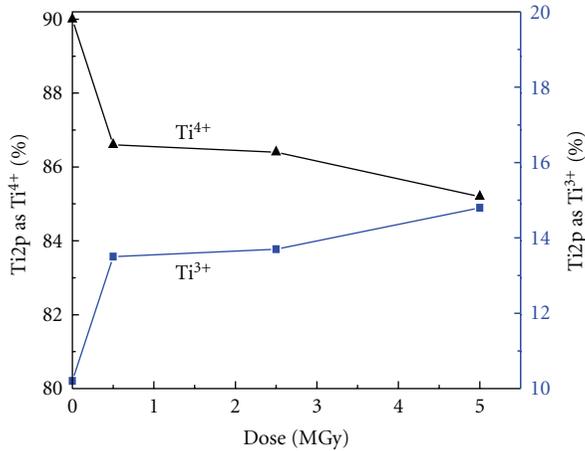


FIGURE 4: Surface of Ti as Ti^{3+} and Ti^{4+} of unirradiated and EB-treated TiO_2 samples as a function of absorbed radiation doses [44].

in TiO_2 doped with metal atoms, which can trap the photo-generated electrons and thereafter leave behind unpaired charges to promote photoactivity.

Figure 5(a) [45] shows the ESR signals of O^- anion radicals and Ti^{3+} cations on TiO_2 powder after γ -ray irradiation of 150 MR under N_2 atmosphere. Before γ -ray irradiation, no signal could be observed in the ESR signals, while after γ -ray irradiation, the ESR signals attributed to the O^- anion radicals and associated Ti^{3+} were observed. It increased with the increase of the γ -ray irradiation dosage shown in Figure 5(b) [45].

Huang et al. [30] reported that upon exposure to γ -radiation, a concentrated TiO_2 sol changed from colorless to deep blue with an absorption maximum at 540 nm. The absorption has been assigned to trapped electrons or Ti^{3+} ions in the solid matrix based on its spectroscopic similarity to the samples irradiated with UV light. The origin of the trapped electrons during γ -ray irradiation may be traced to a series of reducing species produced by the high-energy electrons, which in turn are the direct result of γ -ray irradiation. The absorption intensity is linearly related to the duration of exposure to γ -ray irradiation.

The reduction effect (from Ti^{4+} to Ti^{3+}) in rutile induced by neutron irradiation is also reported. Lu et al. [72] found that Ti^{4+} ions reduced to Ti^{3+} , Ti^{2+} , and even Ti^+ after the neutron irradiation by means of characteristic techniques of UV-VIS-IR, XPS, XRD, and AFM.

TiO_2 irradiated by UV light can create TSD with ease. However, a special gel structure, which has a poor chemical stability, is definitely needed for a high quantum yield of TSD. Thus, this method is subjected to the certain restriction in the practical photocatalytic application. Annealing and calcination can effectively control concentration of TSD and morphology of TiO_2 . Thus, both of them are extensively studied and used although they are still tedious, for example, high temperature, high vacuum, and atmosphere frequently needed. The bombardment method is atypical, but important.

3. Properties of Ti^{3+} Surface Defects

3.1. Structural Properties of Ti^{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_{2h}). The parallel ($R_{||}^o$) and vertical (R_{\perp}^o) $Ti^{4+}-O^{2-}$ 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^{4+} ion is changed to Ti^{3+} ion, the local electrostatic balance is broken, and an O_V (oxygen vacancy) should be introduced because of charge compensation. In order to determine the position of the O_V as well as the local structure of the $[Ti^{3+}-O_V]$ 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_V is located on the nearest position of central Ti^{3+} ion. When an O_V appears on the nearest position of central Ti^{3+} ion along the $R_{||}^o$ direction of the oxygen octahedron, the local symmetry would change from D_{2h} to C_{2v} . Since the effective charge of the O_V is positive, the central Ti^{3+} is expected to shift away from the O_V along the $R_{||}^o$ direction by an amount ΔR_c due to the electrostatic repulsion. Similarly, the four O^{2-} ions on the vertical plane would also move towards the O_V by an amount ΔR_p due to the electrostatic attraction (see Figure 6). Considering the much larger distance between the O_V and the remaining O^{2-} ion of the $R_{||}^o$ direction, the displacement of the only axial O^{2-} ion may be much smaller than ΔR_c or ΔR_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^{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^{3+} ions (Figure 7). Figure 7 [73] shows schematically what happens when a crystal of $Ti^{4+}O_2^{2-}$ loses one oxygen atom, and the two electrons of the O^{2-} ion change two Ti^{4+} to Ti^{3+} ions. These Ti^{3+} ions are strongly polarized and a state is assumed, in which its extreme can be described as two Ti^{4+} ions and two additional electrons. The latter may assume the position of the missing O^{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^{3+} ions. Ti^{3+} ions in this state absorb light more intensively than undeformed Ti^{3+} ions.

3.2. Optical Properties of Ti^{3+} Surface Defects. Optical properties of TSD lie in two aspects. One is that Ti^{3+} ions are the origin of the blue coloration or coloration center [27, 58, 64, 74] and the other is that Ti^{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^{3+} ions. The method has been proposed based on the phenomenon that a Ti^{3+} salt was hydrolyzed slowly with the presence of urea in an aqueous solution. With this method, a blue TiO_2 was obtained,

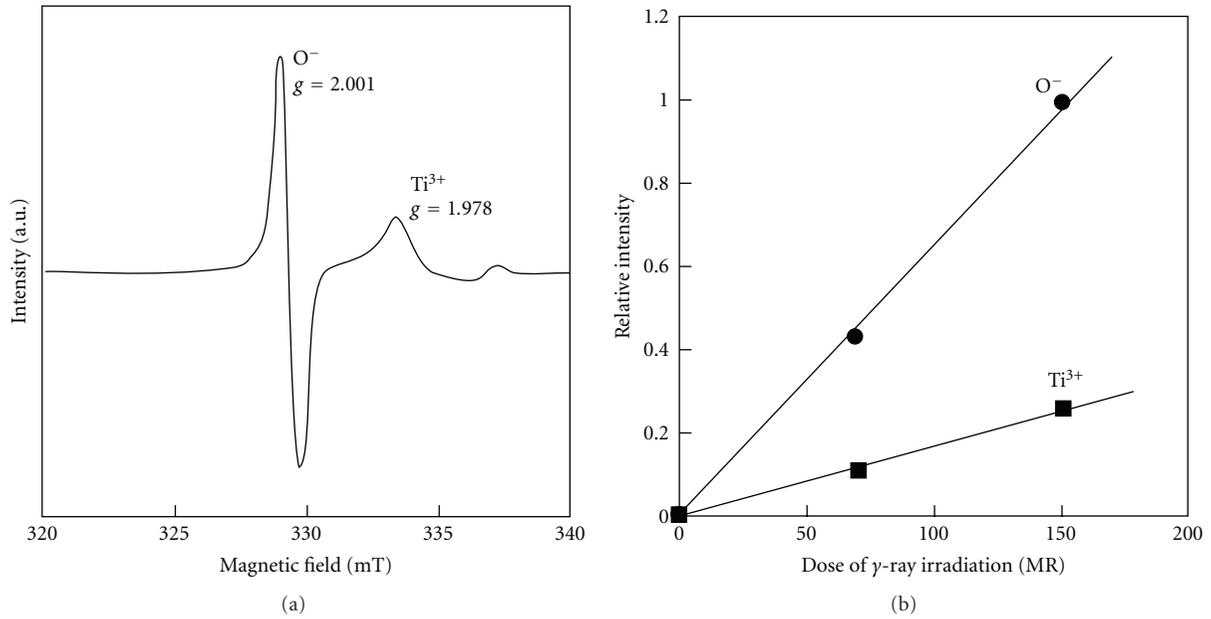


FIGURE 5: (a) ESR signals of O^- anion radicals and Ti^{3+} cations on the TiO_2 powder after γ -ray irradiation of 150 MR under N_2 atmosphere. (b) Variation of the intensity of the signals due to γ -ray induced O^- anion radicals and Ti^{3+} cations with γ -ray irradiation time under N_2 atmosphere [45].

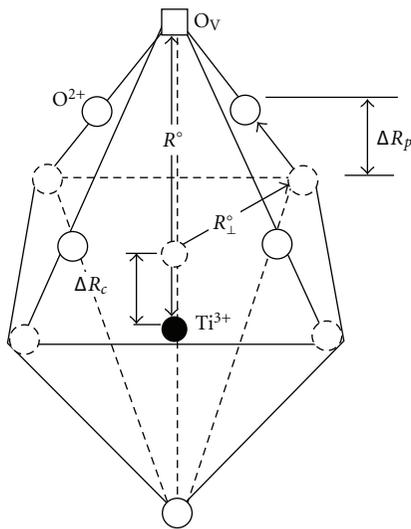


FIGURE 6: The schematic diagram model, that is, the central Ti^{3+} ion associated with an oxygen vacancy on its nearest position along the parallel direction [72].

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_2O 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

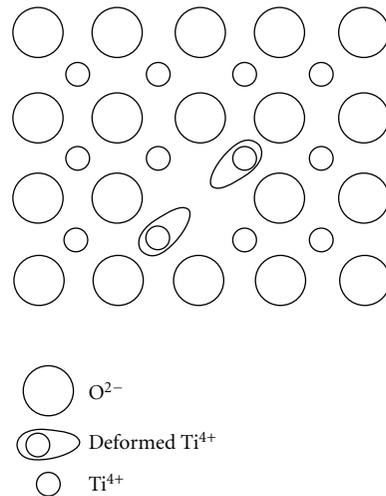


FIGURE 7: Schematic picture of a flaw on partly reduced TiO_2 [73].

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

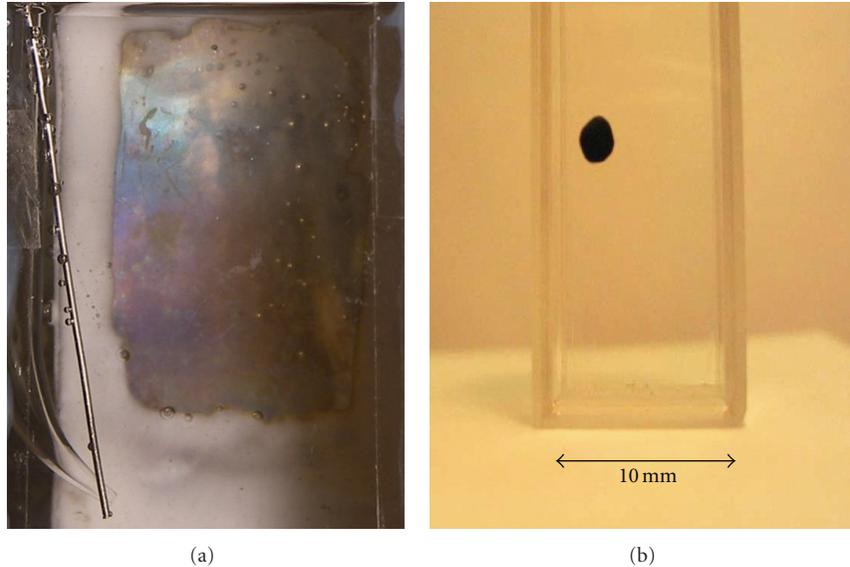


FIGURE 8: Light-induced color change in (a) $\text{TiO}_2/\text{Cu}_2\text{O}$ bilayer film [64] and (b) titanium-oxide gel [29].

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 Ti^{3+} ions in the solid matrix based on its spectroscopic similarity to the samples irradiated with UV light.

3.3. XPS Properties of Ti^{3+} Surface Defects. According to the standard binding energy of $\text{Ti}2p_{3/2}$ in TiO_2 , that for Ti^{3+} is usually located at 457.7 eV and that for Ti^{4+} is at 459.5 eV. The O (1s) binding energy for TiO_2 is 529.3 eV [79]. Generally speaking, the binding energy peak of $\text{Ti}2p$ in stoichiometry TiO_2 is not broad and no shoulder peak. However, that for TiO_2 containing Ti^{3+} 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 Ti^{3+} and Ti^{4+} in the surface of reduced TiO_2 . The relative contents of Ti^{3+} in the surface of reduced TiO_2 can also be obtained according to the XPS peak areas.

Greenlief et al. [46] reported the $\text{Ti}2p$ binding energy data of TiO_2 thin films with different monolayers on polycrystalline Pt after vacuum annealing by XPS technique. The measured binding energy 458.9 eV was the $\text{Ti}2p_{3/2}$ peak for the TiO_2 thin films with coverages more than 3 monolayers (1 monolayer is assumed to be an evenly dispersed film 2.6 Å thick). The O (1s) binding energy for these TiO_2 thin films were 530.3 eV. The O/Ti ratio (as determined by XPS peak areas) was stoichiometric (2.0) for these TiO_2 thin films. After vacuum annealing, the ratio dropped to between 1.0 and 1.5, and a mixture of Ti^{3+} and Ti^{4+} was obtained. The binding energy 458.9 eV was observed and attributed to Ti^{3+} state.

Recently, our group [64] found that the TSD can be generated in $\text{TiO}_2/\text{Cu}_2\text{O}$ bilayer film under visible-light irradiation. By means of XPS (Figure 9), it can be seen that the binding energy of $\text{Ti}2p_{3/2}$ 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 $\text{Ti}2p_{3/2}$ in the bilayer film after the irradiation was 458.1 eV. Compared with the peak for $\text{Ti}2p_{3/2}$ in the same bilayer film without the irradiation, the one after the irradiation was much broader and there was 0.6 eV shift. This $\text{Ti}2p_{3/2}$ spectrum can be simulated with Gaussian simulation. The peaks at 457.8 eV and at 459.2 eV were attributed to Ti^{3+} and Ti^{4+} , respectively (Figure 9(b)). The result is in accordance with the reported data [79]. The content of Ti^{3+} ions was as high as 74% in $\text{TiO}_2/\text{Cu}_2\text{O}$ bilayer film after visible-light irradiation according to the comparison of the peaks area.

3.4. EPR Properties of Ti^{3+} 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 Ti^{3+} in some published paper are shown in Table 1.

Tijana et al. also presented some published data of EPR signals of Ti^{3+} in the book edited by Kokorin and Bahnmann [90]. They proposed that Ti^{3+} in the surface and that in the bulk of TiO_2 can be distinguished by the differences of their EPR parameters. The values of the g -factors for surface Ti^{3+} particles are significantly lower than those usually found in bulk TiO_2 . 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 Ti^{3+} 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 Ti^{3+} ions, and the second one to the inner Ti^{3+} ions.

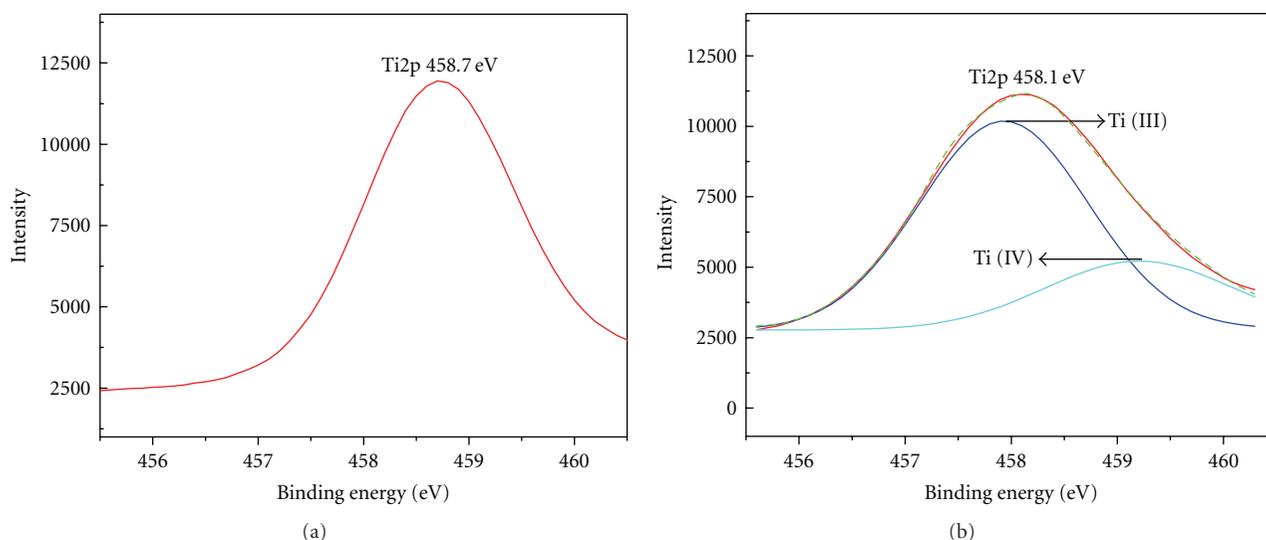


FIGURE 9: XPS of Ti2p of TiO₂/Cu₂O bilayer film before (a) and after irradiation (b). XPS of Ti2p is simulated by Gaussian equation [64].

In addition, Tijana et al. found the difference of EPR signal shapes for surface and inner Ti³⁺ ions. According to the characters of EPR signals, they proposed two general types of traps (Ti³⁺ ions): internal, having a narrow axially symmetric EPR signal, and surface, with broad EPR lines. Magnetic resonance parameters of the internal, interstitial (inner) Ti³⁺ 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 Ti³⁺ ions mainly depend upon surface modification.

3.5. Temperature Program Reduction (TPD). Temperature-programmed desorption using carbon dioxide (CO₂-TPD) as a probe can be employed to monitor surface defects in TiO₂ [22, 60, 84, 92]. CO₂-TPD analysis indicates a signal of CO₂, which desorbs from the TiO₂ surface between the ranges of 123 and 253 K and results in two peaks: one peak at about 170 K attributed to CO₂ molecules bound to a regular five-coordinate Ti⁴⁺ site which was a perfect TiO₂ structure, and another peak at about 200 K corresponding to CO₂ molecules bound to Ti³⁺ which was a defected TiO₂ 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 Ti³⁺ defects and nondefective TiO₂ sites. Moreover, they have measured the activation energy for both of the desorption peaks of CO₂. For CO₂ desorption from the fully oxidized (or perfected) surface, where the CO₂ is bound to Ti⁴⁺ sites, a zero-coverage activation energy for CO₂ desorption of 48.5 kJ/mol is measured. It is in approximate agreement with theoretical calculations value of 65 kJ/mol [93]. For CO₂ desorption from the Ti³⁺ sites produced by annealing TiO₂ (110) in vacuum, a zero-coverage activation energy of ~54 kJ/mol was measured. This indicates that Ti³⁺

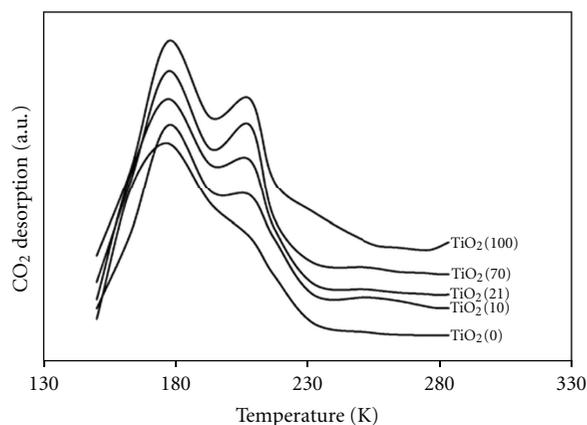


FIGURE 10: Thermal desorption spectra for CO₂ adsorbed on TiO₂ calcinations [84].

sites bind CO₂ slightly more strongly (TPD peak at 200 K) than the fivefold coordinated Ti⁴⁺ sites (TPD peak at 170 K) do.

4. Photocatalytic Application

4.1. Photocatalytic Reaction Mechanism of Ti³⁺ Surface Defects. The photocatalytic reaction mechanisms are widely studied. The principle of TiO₂ 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 •OH, O²⁻, H₂O₂, or O₂, 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.

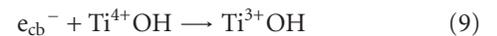
ESR parameters (g-value)		Condition	Ref.
$g_{ }$	g_{\perp}		
1.9495	1.9640	Anatase nanoparticles exposure to UV light	[33]
1.9600	1.990	Anatase nanoparticles exposure to UV light	[33]
1.902	1.953	Laser-irradiated TiO_2	[39]
1.962	1.960	Titanium silicalite	[49]
1.905	1.912	Ti- SiO_2 by a sol-gel method	[49]
1.88	1.925	Fe^{3+} -doped colloids: 6 g dm^{-3} TiO_2 , 0.5 wt% Fe, irradiated 6 h	[54]
1.988	1.897	Fe^{3+} -doped colloids: 5 g dm^{-3} TiO_2 , 0.1 wt% Fe, irradiated 3 h	[54]
1.975	1.944	Self-doped TiO_2	[78]
1.996	1.901	$KTa_{0.9}Nb_{0.1}O_3$	[80]
1.994	1.896	Hydrated TiO_2	[81]
1.9482	1.9707	Carbon-doped TiO_2	[82]
1.975	1.963	Ultrafine-powdered TiO_2	[83]
	1.996	TiO_2 powder was heated in hydrogen (H_2) gas	[20]
	1.990, 1.990, 1.960	Hydrated anatase	[32]
	1.970, 1.965	The untreated fresh and used TiO_2 catalysts	[51]
	1.93	TiO_2 exposure to flowing H_2 at 573 K for 4 h	[53]
	1.908, 1.981	Pt/ TiO_2 reduced at 623 K	[56]
	1.975	sol-gel processing of $Ti(i-OPr)_4$ (i-OPr isopropoxy group)	[69]
	1.92	Anatase reduction at 573 K	[75]
	1.9605, 2.0059	Nitrogen-doped TiO_2	[76]
	1.996	TiO_2 calcined at 21% O_2	[84]
	1.98	TiO_2 nanotubes	[85]
	1.996	TiO_2 obtained under vacuum	[86]
	1.964	Silver/ TiO_2 (1.026 wt.% loading)	[87]
	1.9880 ± 0.0005	Carbon-Doped TiO_2	[88]
	1.996	Nanocrystalline TiO_2 via solvothermal synthesis	[89]

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 photoresponse 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 electrohole 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 $\bullet O_2^-$, $HO_2\bullet$, and $\bullet OH$. The charge transfer processes may be as follows:



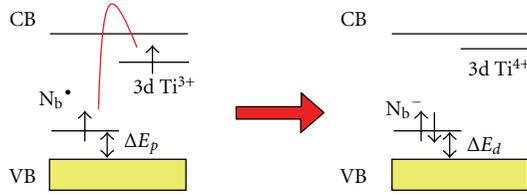
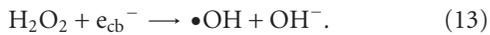
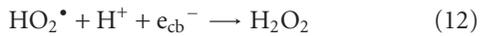
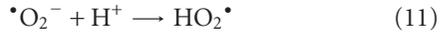


FIGURE 11: Electronic band structure modifications resulting from the interactions between N_b^\bullet (N_s^\bullet or N_i^\bullet) and Ti^{3+} defects [96].



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_b^\bullet) 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

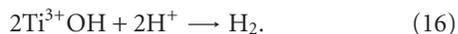
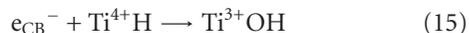
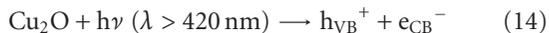
the nitrogen-doped TiO_2 . The N-doped TiO_2 with N/Ti proportioning of 20 mol% calcined at $400^\circ C$ exhibited the highest visible-light activity. Therefore, the presence and optimal content of Ti^{3+} might be the critical factors for the improvement of the photoactivity.

Carbon-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_2O composite film [79] and photocatalytic water splitting by TiO_2/Cu_2O bilayer film owing to the presence of Ti^{3+} [64]. For photocatalytic degradation reaction, electrons excited from TiO_2/Cu_2O composite film under visible light were transferred from the conduction band of Cu_2O 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_2O 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_2O_2 . The evolved H_2O_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_2O were captured by Ti^{4+} 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 energy. The electrons trapped in Ti^{3+} ions as stored energy lead to evolve H_2 from H_2O . The electron transfer processes may be as follows:



5. Concluding Remarks

An overview on current literature on the subject of TSD in TiO_2 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 TiO_2 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.

Acknowledgments

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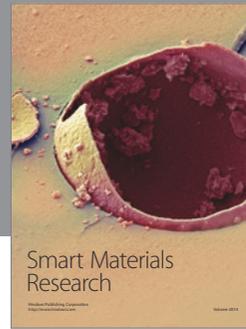
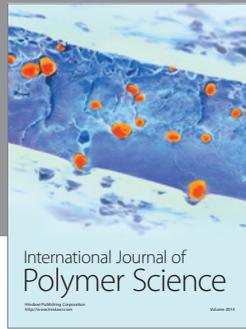
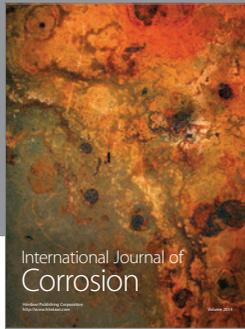
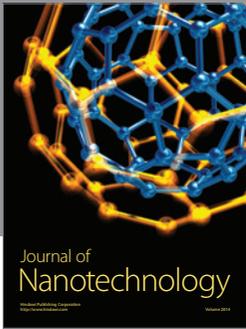
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