

Defective TiO₂ with oxygen vacancies: synthesis, properties and photocatalytic applications†

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Xiaoyang Pan, Min-Quan Yang, Xianzhi Fu, Nan Zhang and Yi-Jun Xu*

Titanium dioxide (TiO₂), as an important semiconductor metal oxide, has been widely investigated in the field of photocatalysis. The properties of TiO₂, including its light absorption, charge transport and surface adsorption, are closely related to its defect disorder, which in turn plays a significant role in the photocatalytic performance of TiO₂. Among all the defects identified in TiO₂, oxygen vacancy is one of the most important and is supposed to be the prevalent defect in many metal oxides, which has been widely investigated both by theoretical calculations and experimental characterizations. Here, we give a short review on the existing strategies for the synthesis of defective TiO₂ with oxygen vacancies, and the defect related properties of TiO₂ including structural, electronic, optical, dissociative adsorption and reductive properties, which are intimately related to the photocatalytic performance of TiO₂. In particular, photocatalytic applications with regard to defective TiO₂ are outlined. In addition, we offer some perspectives on the challenge and new direction for future research in this field. We hope that this tutorial minireview would provide some useful contribution to the future design and fabrication of defective semiconductor-based nanomaterials for diverse photocatalytic applications.

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1 Introduction

Titanium dioxide (TiO₂), as an industrially important wide-band gap semiconductor, has been widely used in sunscreens, paints, ointments, toothpastes and catalysis.^{1–5} Since the discovery of the phenomenon of photocatalytic water splitting on a TiO₂ electrode by Fujishima and Honda,⁷ enormous efforts have been devoted to the research of TiO₂ materials, which enables its use as an active material in photovoltaics, photo-electrochemical cells, and photocatalysts.^{8–56} As compared to other semiconductor materials, TiO₂ has several advantages for photocatalytic reactions, including earth abundance, low toxicity, chemical and thermal stability, and resistance to photocorrosion.^{11,57} However, the applications of TiO₂ are greatly hindered by its low quantum efficiency in photocatalytic reactions and ineffective utilization of visible light, which result from its high recombination of photo-generated electron–hole pairs, and wide band gap (3.2 eV), respectively. Therefore, various strategies have been utilized to modify the properties of TiO₂, aiming to increase the lifetime of photogenerated electron–hole pairs and narrow the band gap, such as coupling TiO₂ with a narrow band gap semiconductor,^{25,29,35,58,59} metal ion/nonmetal ion doping,^{60–64} co-doping with two or more foreign ions,^{11,65} hybridization with carbon materials,^{66–72} surface

sensitization by organic dyes and noble metal deposition or encapsulating noble metal cores to form metal core@TiO₂ shell composite photocatalysts.^{8,73–76} In particular, recent studies have revealed that some physical and chemical properties of TiO₂, such as light absorption, photocatalytic reactivity and selectivity *etc.*, can be modulated by its defect disorder.^{77–79}

Among all the defects identified in TiO₂, oxygen vacancy is one of the most important and is supposed to be the prevalent defect in many metal oxides.⁸⁰ Oxygen vacancies in metal oxides have been extensively investigated both by theoretical calculations and experimental characterizations.^{81–84} It has been revealed that oxygen vacancies can behave as important adsorption and active sites for heterogeneous catalysis, which are able to strongly influence the reactivity of metal oxides.⁸² Moreover, it has been shown that the photocatalytic properties including the electronic structure,^{81,85,86} charge transport,⁸⁷ and surface properties of TiO₂-based metal oxides are closely related to oxygen vacancies.⁸⁸ In principle, the formation of oxygen vacancies on TiO₂ leads to the creation of unpaired electrons or Ti³⁺ centers, which could form donor levels in the electronic structure of TiO₂.⁷⁹ In addition, oxygen vacancies are believed to affect the electron–hole recombination process in photocatalysts, causing a change in chemical rates that depends on charge transfer from either electrons or holes.⁸⁹ Theoretical and experimental results indicate that the excess electrons located on the oxygen vacancy states affect surface adsorption and reactivity of key adsorbates such as O₂ or H₂O on TiO₂.^{83,90} For these reasons, there is a great interest in the development of controllable synthesis of TiO₂ with oxygen

State Key Laboratory Breeding Base of Photocatalysis, College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou 350002, P.R. China. E-mail: yjxu@fzu.edu.cn

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vacancies and exploiting their unique properties for photocatalytic applications.

In this tutorial minireview, we summarize the available routes for the synthesis of TiO₂ with oxygen vacancies and discuss their properties and photocatalytic applications. The syntheses of TiO₂ nanomaterials with oxygen vacancies are primarily categorized with the preparation method. For detailed instructions on each synthesis, the readers can refer to the corresponding literature. The structural, optical, adsorption and reductive properties of TiO₂ nanomaterials with oxygen vacancies are reviewed in Section 3. Photocatalytic applications using these materials are concerned with visible light driven photocatalysts, charge separation, photocatalytic selectivity, and oxygen vacancies and N co-doped TiO₂. It is hoped that this minireview can provide a useful source for engineering the defect of semiconductors to achieve highly efficient photocatalysts and expand their functional applications related to photocatalysis.

2 Synthesis

2.1 Hydrogen thermal treatment

The hydrogen treatment is a usual method to modulate the surface and photoelectrochemical properties of TiO₂.^{1,91–95} Under thermal conditions,⁹³ hydrogen atoms interact with lattice oxygen of TiO₂ on the surface, which results in the formation of oxygen vacancies and changes the surface properties of TiO₂. During this process, the interaction between H₂ and TiO₂ can be divided into three steps:⁹³ firstly, hydrogen interacts physically with the adsorbed oxygen at a temperature below 300 °C, which can be proved by the disappearance of the ESR signals of adsorbed oxygen as shown in Fig. 1. Secondly, when the temperature is higher than 300 °C, electrons are transferred from hydrogen (H) atoms to the oxygen (O) atoms in the lattice of TiO₂. Then, the lattice oxygen is abstracted from the surface of TiO₂, by which the O atom leaves with the H atom to form H₂O. Thus, the oxygen vacancies are formed on the surface of TiO₂, as displayed in Fig. 1. Thirdly, the interaction between H₂ and TiO₂ proceeds more dramatically, when the temperature is up to 450 °C. The electrons of the H atoms are transferred to the Ti⁴⁺ of TiO₂, and Ti³⁺ defects are formed. When the temperature is further increased to 560 °C, more energy is supplied and the electrons located on the oxygen vacancy states are driven away and transferred to Ti⁴⁺, resulting in the decrease in ESR signal intensity of oxygen vacancies and increase in that of Ti³⁺ until the temperature reaches 600 °C.

Notably, the reduction of TiO₂ by hydrogen treatment not only results in oxygen vacancies formation but also creates Ti interstitials in the TiO₂ matrix.⁹⁴ In both cases, (i) Ti is in excess with respect to O, and (ii) they both decrease the optical band gap of TiO₂. In comparison to Ti interstitials, oxygen vacancy formation is slightly more favorable in anatase than rutile, while Ti interstitials form more easily in rutile than anatase, as revealed by Morgan and Watson.⁹⁶ Under oxygen-rich conditions, oxygen vacancies are the favored defect type, but both defect types have high formation energies. Under O-poor conditions, both defect types are stabilized, with Ti interstitials predicted to become the favored defect in rutile samples,

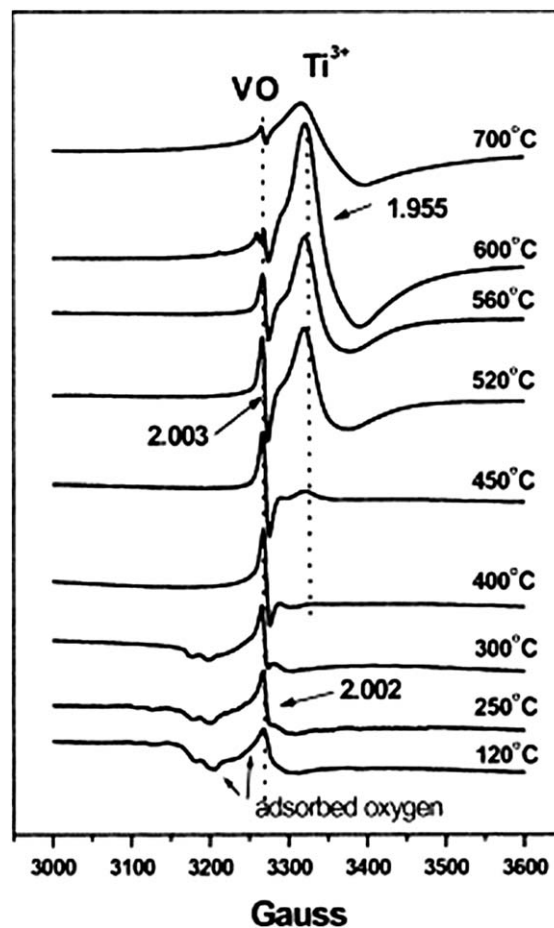


Fig. 1 The ESR spectra of oxygen vacancies (Vo) and trivalent titanium (Ti³⁺) in TiO₂ during the H₂ treatment. (Reprinted with permission from Elsevier.)⁹³

particularly at elevated temperatures. In addition, it is suggested that the interstitial Ti ions most probably formed under more severe conditions (*i.e.*, high temperature, vacuum annealing) than oxygen vacancies.⁹⁴ Moreover, oxygen vacancies are not only the important defects in TiO₂ but also the prevalent defects in many oxides, which largely affect the chemical and physical properties of these oxides.⁸⁰ Therefore, oxygen vacancies are potentially more interesting than Ti interstitials and have been widely investigated.

2.2 High energy particle bombardment

A number of studies have shown that high-energy electrons and ions can preferentially desorb oxygen ions and neutral atoms from TiO₂ surfaces, thereby generating vacancies.^{97–100} Knotek and Feibelman found that electrons with energy greater than 34 eV desorb surface oxygen through an interatomic Auger recombination process.^{99,100} A possible formation mechanism of oxygen vacancies under electron irradiation was also proposed in their research work. They postulated that the O⁺ ejection from the TiO₂ surface as a result of electron stimulated desorption is responsible for the oxygen vacancies formation. The advantage of using this method for the purpose of defect creation is that electron bombardment at moderate energy

causes little damage to the surface and produces oxygen vacancies exclusively. The electron irradiated surfaces, which contain only surface bridging oxygen vacancies, can be easily healed by exposure to molecular oxygen even at low temperature.¹⁰¹

Similar to electron bombardment, ion sputtering such as argon ion (Ar^+) sputtering also creates oxygen vacancies on the surface of TiO_2 .^{83,101} However, the surface defects on the Ar^+ sputtered surface do not disappear when exposed to oxygen under low temperature. This indicates that Ar^+ sputtered surfaces contain surface bridging oxygen vacancies as well as other defects, which are proposed to be subsurface defects or more “highly reduced surface species”. These sorts of defects cannot be healed by the addition of oxygen at low temperature.^{83,101}

In addition, plasma treatment at low temperature under reducing gas atmosphere is often utilized to create oxygen vacancies on the surface of a metal oxide.^{81,102,103} In low temperature plasma, high-energy species such as electrons, atoms and radicals are available for reactions in a non-equilibrium condition. Because of the mild reaction conditions, only the skin layer of the metal oxides is modified with no deterioration of the bulk materials.

2.3 Doping of metal or nonmetal ions

The doping of metal or nonmetal ions is often accompanied by formation of oxygen vacancies in the lattice of TiO_2 . For example, Krol and Wu have revealed that the substitution of Fe^{3+} for Ti^{4+} ions in the lattice can result in formation of oxygen vacancies in the lattice of TiO_2 .¹⁰⁴ In addition, Domen *et al.* have reported that the doping of aliovalent metal cations can be utilized as an effective method for defect engineering of a photocatalyst.¹⁰⁵ They have disclosed that the doping of a cation with valence lower than that of the parent cation (Ti) extrinsically introduces oxygen vacancies, inhibiting the formation of Ti^{3+} , as shown in Fig. 2a. The doping of the trivalent cation (M^{3+}) can occupy the Ti^{4+} sites as a lower valence cation. As a result, the formation of oxygen vacancies is facilitated without forming Ti^{3+} species, as denoted in the equation of Fig. 2a. In contrast,

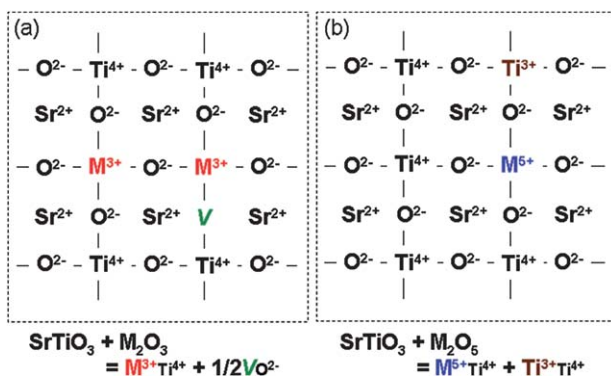


Fig. 2 Schematic illustration of aliovalent-doped SrTiO_3 : doping of the trivalent cation (a) and pentavalent cation (b). (Reprinted with permission from the American Chemical Society.)¹⁰⁵

the higher valence cation stabilizes the Ti^{3+} without producing oxygen vacancies, as displayed in Fig. 2b. The pentavalent cation (M^{5+}) dopants occupy Ti^{4+} sites as a higher valence cation would result in the formation of Ti^{3+} , inhibiting the formation of oxygen vacancies, as expressed by the equation in Fig. 2b.

Similar to the doping of metal ions, doping of nonmetal ions, such as fluorine (F) or nitrogen (N), can also create oxygen vacancies in the lattice of TiO_2 .^{106–111} As for N doping, the density functional theory (DFT) calculation has drawn a conclusion that N doping induces a substantial reduction of the formation energy of oxygen vacancies in bulk TiO_2 .¹¹⁰ This indicates that N doping facilitates the formation of oxygen vacancies.¹¹² In addition, N doping is often carried out under reducing condition. This reducing atmosphere can cause partial reduction of TiO_2 , resulting in formation of oxygen vacancies.¹¹⁰

2.4 Oxygen vacancies generation under reaction conditions

The involvement of lattice oxygen in the thermally driven catalytic reaction of organic compounds can also result in oxygen depletion on the surface of TiO_2 .^{113–115} During this process, the oxidation of an organic substrate on an oxide surface occurs at the expense of a surface lattice oxygen atom, and results in the formation of a surface vacancy. For example, Panayotov and Morris have revealed that the thermally activated bridging lattice oxygen can burn a methoxy group, creating a shallow donor state (oxygen vacancies and Ti^{3+} color centers) below the conduction band of TiO_2 , as illustrated in Fig. 3.¹¹³

The mechanism of reaction driven oxygen vacancies formation is also operative in photochemically initiated oxidation reactions on the surfaces of many semiconductors.^{116–120} For instance, our group has recently observed the photo-induced formation of oxygen vacancies on TiO_2 under photocatalytic reaction conditions.¹²¹ The detailed formation mechanism is described as follows: under the irradiation of UV light, the photo-generated electrons are captured by molecular oxygen, while the holes diffuse to the TiO_2 surface, being trapped at lattice oxygen. Subsequently, the trapped holes weaken the

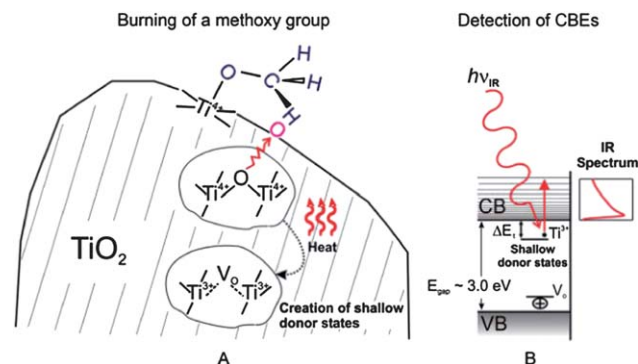
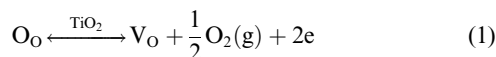


Fig. 3 Schematic diagram illustrating thermally activated bridging lattice oxygen leaving behind $\text{Ti}^{3+}\text{-V}_{\text{O}}\text{-Ti}^{3+}$ donors. The oxygen atom diffuses to the particle surface where it burns a methoxy group that is bound to a CUS Ti^{4+} Lewis acid site (A). Electrons trapped at shallow donor states are detected when they are excited into the conduction band via absorption of IR radiation (B). (Reprinted with permission from the American Chemical Society.)¹¹³

binding bond between Ti atom and the lattice oxygen, and adsorbed molecular benzyl alcohol breaks this bonds. Thus, the lattice oxygen is extracted from the TiO₂ surface, forming oxygen vacancy sites on the surface of the catalyst.

2.5 Thermal treatment under oxygen depleted condition

Oxygen vacancies can also be created by annealing pure TiO₂ at elevated temperatures (generally >400 °C) in an oxygen-poor environment, such as a pure He, N₂, Ar gas atmosphere or vacuum condition.^{83,122} Using the standard Kröger-Vink notation,⁷⁹ the formation of oxygen vacancies at elevated temperatures can be described by the following equilibrium:



The equilibrium constant of this reaction can be expressed as follows:

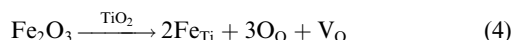
$$K = [\text{V}_\text{O}]n^2p(\text{O}_2)^{(1/2)} \quad (2)$$

Transforming eqn (2), the concentration of oxygen vacancies can be expressed as a function of $p(\text{O}_2)$:

$$[\text{V}_\text{O}] = Kn^{-2}p(\text{O}_2)^{-(1/2)} \quad (3)$$

where O_O denotes the lattice oxygen; V_O denotes the oxygen vacancies; [V_O] denotes the concentration of oxygen vacancies; $p(\text{O}_2)$ denotes the oxygen pressure. From eqn (3), we can deduce that the concentration of oxygen vacancies increases with the decrease of O₂ pressure, *i.e.*, the oxygen depleted condition under thermal annealing would facilitate the formation of oxygen vacancies.

However, the as-formed oxygen vacancies will slowly disappear while the TiO₂ is exposed to air, even at room temperature, since reaction (1) is reversible.¹⁰⁴ To stabilize the oxygen vacancies, one can consider doping the TiO₂ nanoparticles with the acceptor-type foreign ions, such as Fe dopants:



This dissolution reaction is irreversible. The incorporation of Fe³⁺ in the lattice of TiO₂ would compensate the positively charged oxygen vacancy.⁶ As a result, the concentration of free electrons in TiO₂ is decreased. Therefore, oxygen vacancies are stabilized by the doping of Fe³⁺ ions in TiO₂.

3 Properties

3.1 Structural properties

3.1.1 Electronic structure. In TiO₂, a missing oxygen atom from the bulk or surface results in one or two electrons localized in an oxygen vacancy state. The driving force for the localization of the electrons in the oxygen vacancy state is the Madelung potential of the highly ionic crystal.⁸⁰ In this way, the place occupied by the O²⁻ anion in the regular lattice is taken by one or two “free” electrons in the defective crystal, and the energetic cost of the vacancy formation is minimized.⁸⁰ These electrons located on the oxygen vacancy states have a

direct effect on the electronic structure of TiO₂ by forming a donor level below the conduction band, as shown in Fig. 4.⁸¹ The energy level of localized donor states originating from oxygen vacancies is located at 0.75–1.18 eV below the conduction band of titania. Moreover, the removal of neutral oxygen atoms to form oxygen vacancies can also cause the redistribution of the excess electrons among the nearest neighboring Ti atoms around the oxygen vacancy site, and form shallow donor states below the conduction band originating from Ti 3d orbitals.¹²³ It is demonstrated that these donor states in both anatase and rutile titania increase with increasing oxygen vacancies, and can even overlap the conduction band in the case of highly deficient anatase titania.¹²⁴ These results indicate the great shift of the Fermi level of TiO₂ toward high energy by oxygen vacancies formation.

3.1.2 Geometric structure. The introduction of oxygen vacancies in TiO₂ not only modifies the electronic structure but also the geometric structure of TiO₂.^{94,123,125–128} As demonstrated by Park and Siegel, the formation of oxygen vacancies in titania crystals causes up-shift of the E_g mode of the Ti–O bond in the Raman spectrum, indicating that the surface structure of TiO₂ has been changed by oxygen vacancies formation.¹²⁸ This may be attributed to the atomic rearrangement due to the presence of oxygen vacancies. Upon removal of an O atom, the three nearest Ti atoms tend to relax away from the vacancy in order to strengthen their bonding with the rest of the lattice.¹²⁹ This outward relaxation decreases the overlap between the three Ti dangling bonds and causes reduction of the Ti–O bond length, as shown in Fig. S1 and S2.[†]⁹⁶ This result is confirmed by experimental electron diffraction results, as revealed by Dal Santo *et al.* They have observed a lattice contraction of TiO₂ induced by the presence of oxygen vacancies.⁹⁴

Recently, Cheng *et al.* have observed that oxygen vacancies in TiO₂ sheets with surface-terminated fluorine result in the remarkable surface reconstruction, which is evidenced by two new Raman modes at 155 and 171 cm⁻¹ and the weakened B1g mode at 397 cm⁻¹, as shown in Fig. 5.¹²⁷ Interestingly, the two modes at 155 and 171 cm⁻¹ completely disappeared after the

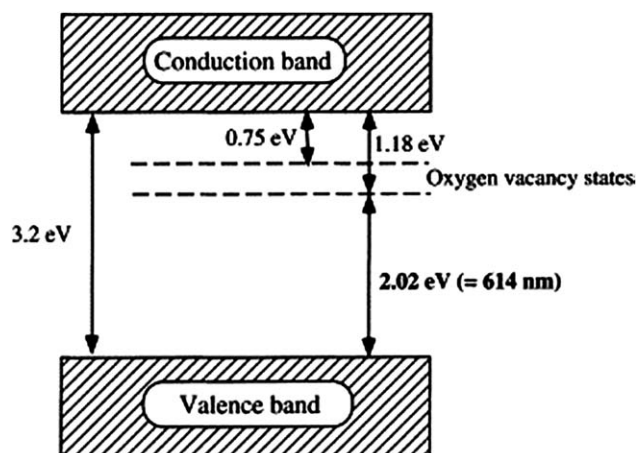


Fig. 4 A proposed band structure model for anatase TiO₂ with oxygen vacancies. (Reprinted with permission from Elsevier.)⁸¹

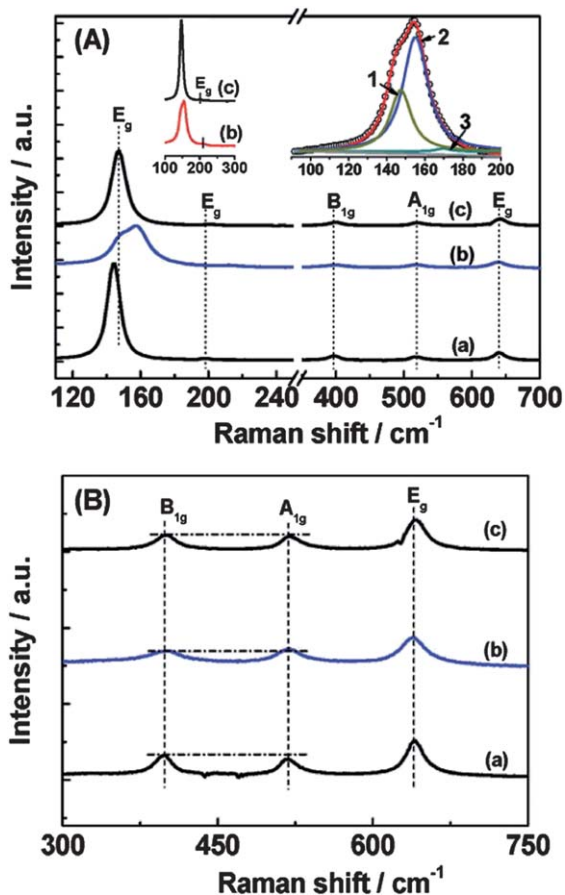


Fig. 5 Raman spectra in the ranges of (A) 110–700 cm^{-1} and (B) 300–750 cm^{-1} of the reference anatase TiO_2 (Aldrich, product no. 232033) (a), oxygen deficiency anatase sheets (b), and anatase sheets free of oxygen deficiency (c). The left inset in panel A is the partial Raman spectra of curves b and c between 100 and 300 cm^{-1} , and the right inset is the fitted E_g mode at 100–200 cm^{-1} in curve b. (Reprinted with permission from the American Chemical Society.)¹²⁷

removal of both oxygen vacancy and surface fluorine from TiO_2 sheets by simply calcining the sample.¹²⁷ In addition, no new active mode is generated in only fluorine-terminated anatase TiO_2 sheets, as shown in Fig. S3.† This result indicates that the two new Raman modes are independent of the sole surface fluorine. Moreover, it was found that the sole oxygen vacancy can only cause some new weak modes at wavenumbers higher than 300 cm^{-1} .¹²⁷ Therefore, the two new modes are the synergistic effects of the oxygen vacancy and surface fluorine probably by changing both atomic coordination numbers and bonding length of the Ti–O–Ti network in oxygen-deficient anatase TiO_2 sheets with surface adsorbed fluorine. The reconstructed surface is proposed to consist of exposed Ti atoms with lower coordination numbers, *i.e.*, four-coordinated Ti, which may be more favorable sites for reactants in catalytic reactions.¹²⁷ Importantly, such a reconstruction surface can strengthen the interaction between the Pt-loaded and TiO_2 matrix *via* a special electron-transfer process involving oxygen vacancies, which enhances photoactivity in hydrogen evolution of TiO_2 sheets with oxygen vacancies in contrast to TiO_2 sheets free of oxygen vacancies.¹²⁷

3.2 Optical properties

The concept of heterogeneous photocatalysis is based on the ability of photocatalysts to absorb light energy that is required to generate electron–hole pairs for a surface reaction. However, due to the wide band gap of TiO_2 , it can only absorb UV light. Fortunately, the optical property of TiO_2 can be manipulated by defect engineering. By introducing oxygen vacancies, one can extend the light absorption of TiO_2 from the UV to the visible ranges, because the oxygen vacancies give rise to the local states below the conduction band edge. The as-formed oxygen vacancy states can take part in a new photoexcitation process. That is, the electron is excited to the oxygen vacancy states from the valence band with the energy of visible light, which gives rise to typical excitations in the visible region of the spectrum. For this reason, oxygen vacancies are called F centers, from *Farbe*, the German word for color. In addition, the electrons left in the oxygen vacancies can also interact with adjacent Ti^{4+} to give the Ti^{3+} species.¹³⁰ The Ti^{3+} defects can form a shallow donor level just below the conduction band, which could also contribute to the visible light response.

3.3 Dissociative adsorption properties

The study of defects by adsorbing probe molecules has contributed to the understanding of the active sites on TiO_2 . Small molecular probes such as CO, N_2O , H_2O , HCOOH , O_2 , and H_2 have been used on TiO_2 single-crystal surfaces in an attempt to understand the reactivity of these defect sites.^{131–134} Defects associated with oxygen vacancies are found to alter the characteristics of the adsorption of some of these molecules, promoting dissociative over molecular adsorption.¹³⁵ In photocatalysis, electrons and holes generated in the TiO_2 crystal by absorption of UV photons can diffuse to the surface, where they can be transferred to adsorbed species causing their reduction and oxidation, respectively.¹³⁶ Although the microscopic details of these electron-transfer processes are not yet well understood, the transfer is expected to be more efficient if the adsorbate and the surface are strongly coupled, as and when adsorbed species are dissociated.¹³⁶

3.3.1 O_2 adsorption on defective TiO_2 with oxygen vacancies. The interaction of oxygen with TiO_2 is crucial in fields such as heterogeneous catalysis, photocatalysis, and gas sensing.^{83,137,138} Molecular oxygen is the oxidizing reagent for many photo-oxidation processes which are catalyzed by TiO_2 .¹³⁷ During these processes, the adsorption of molecular oxygen on the surface of TiO_2 is a key step of the photocatalytic reaction.^{137,139} However, as revealed previously, O_2 does not adsorb on a perfect neutral TiO_2 surface.¹³⁹ O_2 only adsorbs onto the TiO_2 surface when excess negative charge is available to form O–Ti bonds, which can be provided by a photo-excited electron or subsurface oxygen vacancy, in which the adsorption energies are -0.94 and -2.52 eV, respectively, as illustrated in Fig. 6.¹⁴⁰ The O_2 adsorbed on the surface of TiO_2 can capture photo-induced electrons as well as the free electrons located on oxygen vacancy states, simultaneously producing superoxide radical groups. The formation of these radical groups is active to promote the charge separation process as well as the oxidation of organic substances.

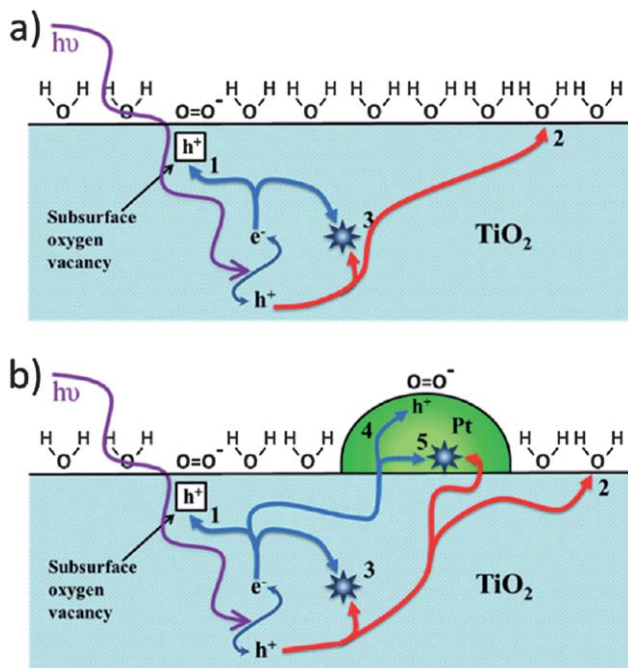


Fig. 6 Schematic representation of the photoexcited electron and hole paths in (a) TiO_2 and (b) Pt/TiO_2 . Process 1 represents an excited electron annihilating the hole created by O_2 scavenging electrons from the TiO_2 subsurface O vacancy; process 2 represents water acting as a hole acceptor; process 3 represents electron-hole recombination in TiO_2 ; process 4 represents the excited electron annihilating the hole created in the Pt cluster by O_2 adsorption; process 5 represents the electron-hole recombination in the supported Pt cluster. (Reprinted with permission from the American Chemical Society.)¹⁴⁰

3.3.2 H_2O adsorption on defective TiO_2 with oxygen vacancies. Water dissociation on TiO_2 is of fundamental interest as an example of a simple surface chemical process with significant applications.^{90,141} The surface interaction between water and titanium dioxide, affecting to a great extent the photocatalytic processes, has been systematically studied.^{51,142–144} In particular, it is well documented that the chemically dissociated water molecules are energetically favored on the defective TiO_2 surface; contrarily, water molecules are only physically adsorbed on the perfect TiO_2 surface.^{143,145,146} Besenbacher *et al.* used a combined experimental and theoretical approach to show that, at low coverage, water dissociation takes place exclusively on defect sites associated with oxygen vacancies.⁹⁰ By the use of scanning tunneling microscopy (STM) they demonstrated that a direct correlation between oxygen vacancies before water exposure and surface hydroxyl groups after exposure exists, and using density functional theory (DFT) they showed water dissociation to be energetically feasible only on the defect sites. Oxygen vacancies in the surface layer are shown to dissociate H_2O through the transfer of one proton to a nearby oxygen atom, forming two hydroxyl groups for every vacancy.

3.3.3 Adsorption of alcohols on defective TiO_2 with oxygen vacancies. Alcohols have been used extensively as probes of reactive sites on metal oxides both in the single crystal and powder form. The adsorption of alcohols on TiO_2 has been widely investigated both by theoretical calculations and

experimental characterizations.^{135,147,148} Oviedo *et al.* have revealed that dissociation of methanol is thermodynamically favorable on the oxygen vacancy states using theoretical calculations.¹⁴⁹ The role of oxygen vacancies in the adsorption of aliphatic alcohols on TiO_2 is studied by means of temperature programmed reaction spectroscopy (TPRS) and X-ray photoelectron spectroscopy (XPS), as shown by Farfan-Arribas and Madix. They have found that the presence of oxygen vacancies on the surface results in increased adsorption of the alcohol on the surface.¹³⁵ The adsorbed aliphatic alcohols are spontaneously dissociated on the TiO_2 - (110) surfaces with oxygen vacancies at room temperature, forming alkoxide and hydroxide groups. Notably, the alkoxide species is found to be more photocatalytically reactive than the physisorbed species.^{150,151} Moreover, chemically dissociated alcohols can quickly scavenge the photogenerated holes, which could effectively prolong the lifetime of photogenerated electrons.¹⁵²

3.3.4 CO_2 adsorption on defective TiO_2 with oxygen vacancies. Photochemical conversion of CO_2 into solar fuels by photocatalysts such as TiO_2 is one of the promising alternatives in reducing CO_2 emissions and using CO_2 as a building block to generate useful products. CO_2 adsorption on TiO_2 is the preceding step of its photo-reduction.^{153,154} Theoretical studies have revealed that the adsorption energies for physisorption and the most stable chemisorption of CO_2 on the neutral charge of perfect anatase TiO_2 (001) are -9.03 and -24.66 kcal mol⁻¹ on the spin-unpolarized TiO_2 with oxygen vacancies.¹⁵⁵ This indicates that CO_2 is strongly bound by oxygen vacancies on a defective surface of TiO_2 . In addition, it is disclosed that the activation barrier of CO_2 on the TiO_2 with oxygen vacancies is smaller than that on the perfect anatase TiO_2 (001).¹⁵⁵ Moreover, the energetically preferred conversion of CO_2 to CO is found to take place on the surface of defective TiO_2 with oxygen vacancies as the photocatalyst.¹⁵⁵ Surprisingly, Li *et al.* have observed that CO_2 is spontaneously dissociated into CO even in the dark on a partially oxygen depleted $\text{Cu}(1)/\text{TiO}_{2-x}$ surface prepared by thermal annealing in an inert environment.¹²² The spontaneous dissociation of CO_2 in the dark is to a large extent associated with the surface oxygen vacancies that provide not only the electronic charge but also the sites for the adsorption of oxygen atoms from CO_2 , as shown in Fig. 7. Moreover, the CO_2 activation and dissociation can be remarkably improved under photo-irradiation, as compared to those in the dark.

In summary, oxygen vacancies on the TiO_2 surface would facilitate the dissociative adsorption of the reactant molecule. It appears that the dissociative adsorption of the reactant molecule on the TiO_2 surface reduces their activation energy and affects the reaction mechanism at the molecular level in the photocatalytic processes. In addition, chemically dissociated molecules are more photocatalytically reactive than the physisorbed species. However, it should be noted that the dissociative adsorption of the adsorbates is often accompanied by the re-oxidation of the TiO_2 surface. Therefore, we first need to stabilize the oxygen vacancies in reduced TiO_2 , before exploring its dissociative adsorption properties for photocatalytic application. This can be achieved by doping the TiO_2 nanoparticles with Fe, a process we have discussed in Section 2.5.

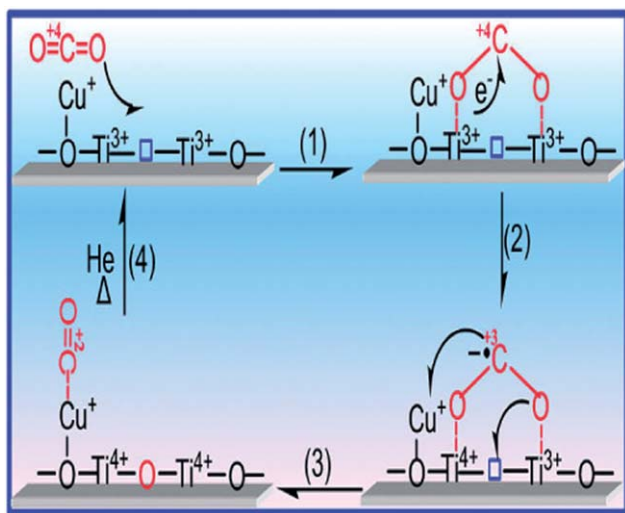


Fig. 7 Possible mechanism for spontaneous dissociation of CO_2 on the defective Cu/TiO_2 catalyst in the dark at room temperature. (Reprinted with permission from the American Chemical Society.)¹²²

3.4 Reductive properties

Oxygen vacancies on catalyst surfaces not only alter the characteristics of adsorbates but also are active for the reduction of several of these adsorbates. Lu *et al.* have clearly shown that, by adsorbing a test molecule on the defective surface as well as a fully stoichiometric surface and comparing the results of temperature programming desorption (TPD), one can observe the reactivity of thermally created oxygen vacancy sites for the reduction of D_2O , $^{13}\text{CH}_2\text{O}$, or ^{15}NO .¹⁵⁶ After adsorbing these adsorbates on the defective surface, the reductive products (D_2 , $^{13}\text{C}_2\text{H}_4$, and $^{15}\text{N}_2\text{O}$) are found by TPD measurement. The deoxygenation of adsorbates is accompanied by the oxidation of surface defect sites. The yield of reduction products is therefore proportional to the coverage of surface oxygen vacancies. No deoxygenation reactions are observed on the defect-free surface.

Surface oxygen vacancy sites are also shown to be active for the reduction of metal ions. In our recent research work, we have revealed that oxygen vacancies participate in significant charge transfer from the defective surface to gold ions.¹⁵⁷ Therefore, a very fast, direct growth of metallic gold nanoparticles on the semiconductor TiO_2 surface with oxygen vacancies has been achieved spontaneously. The spontaneous reduction of metal ions on defective surfaces was also observed by Ye and coworkers. They have revealed that noble metal ions are involved in redox reactions with the defective surface of WO_{3-x} , in which the reduced oxygen vacancy states are partially oxidized by the metal ions.¹⁵⁸ Thus, the metal ions are immediately reduced and nucleated rapidly on its surface, growing into a cluster and further into nanoparticles. This synthetic method takes place in one step and requires no foreign reducing agents, stabilizing molecule, or pretreatment of the precursors, making it a practical strategy for the controlled synthesis of metal/semiconductor hybrid nanomaterials. Interestingly, Li *et al.* have observed that the sub-stoichiometric WO_{3-x} formed by creating oxygen vacancies in WO_3 using

hydrogen treatment, is thermodynamically stable at room temperature, and is highly resistive to re-oxidation.¹⁵⁹

Therefore, hydrogen treated WO_3 is stabilized for water oxidation in neutral medium without the need for oxygen evolution catalysts. These pioneering results suggest that the property of oxygen vacancy states can be finely modulated by carefully choosing the preparation methods.

4 Photocatalytic application

4.1 Visible-light-driven photocatalyst

The presence of oxygen vacancies in TiO_2 can effectively expand the visible light absorption range of titania, because the localized oxygen vacancy states are located at 0.75 to 1.18 eV below the conduction band minimum of TiO_2 . However, it was believed that the low mobility of the electrons in these states due to the localization, and their location below the $\text{H}_2/\text{H}_2\text{O}$ redox potential, make the photocatalytic activity of the reduced TiO_2 with oxygen vacancies negligible.^{160,161} Fortunately, theoretical calculations show that a high vacancy concentration could induce a vacancy band of electronic states just below the conduction band.¹⁶² The relevant experiments also prove the improved activity of reduced TiO_2 under visible light. Therefore, these results demonstrate that it is possible to fabricate visible-light responsive TiO_2 by introducing oxygen vacancies.

As discussed in Section 2, reduced TiO_2 with oxygen vacancies can be produced by hydrogen thermal treatment, high energy particle bombardment or thermal annealing under oxygen depleted condition *etc.*, by which oxygen vacancies can be effectively created on the surface of titania. However, surface oxygen vacancies are not stable and are even susceptible to oxidation by dissolved oxygen in water. For this reason, one may consider creating oxygen vacancies in the bulk of TiO_2 to achieve a stable reduced TiO_2 photocatalyst, which can avoid the interaction of the oxygen vacancies with the O_2 . However, oxygen vacancies in the lattice may serve as recombination centers for the photoinduced electrons and holes, which reduce the photocatalytic activity.¹⁶¹

Another approach for achieving stable reduced TiO_2 is to introduce disorder in the surface layers of TiO_2 through hydrogenation.^{1,91,92,94,95} This novel strategy was devised by Mao and his co-workers, as shown in Fig. 8.¹ The optical absorption of such hydrogenated TiO_2 nanocrystals shifts from the ultraviolet (UV) to near infrared, accompanied by a dramatic color change of the TiO_2 sample from white to black. The band gap of the hydrogenated black TiO_2 is about 1.0 eV, indicating that this material can harvest the visible and even infrared photons for photocatalysis. Furthermore, the hydrogenated black TiO_2 exhibits excellent solar-driven photocatalytic activities and stabilities. About 0.2 mmol of hydrogen gas can be generated by the black TiO_2 loaded with 0.6 wt% Pt in a 1 : 1 water-methanol solution, which is about two orders of magnitude greater than the yields of most semiconductor photocatalysts reported previously. Throughout 15 testing cycles in 15 days, the high H_2 yield remains unchanged without catalyst regeneration, indicating an excellent stability for the black TiO_2 photocatalyst.

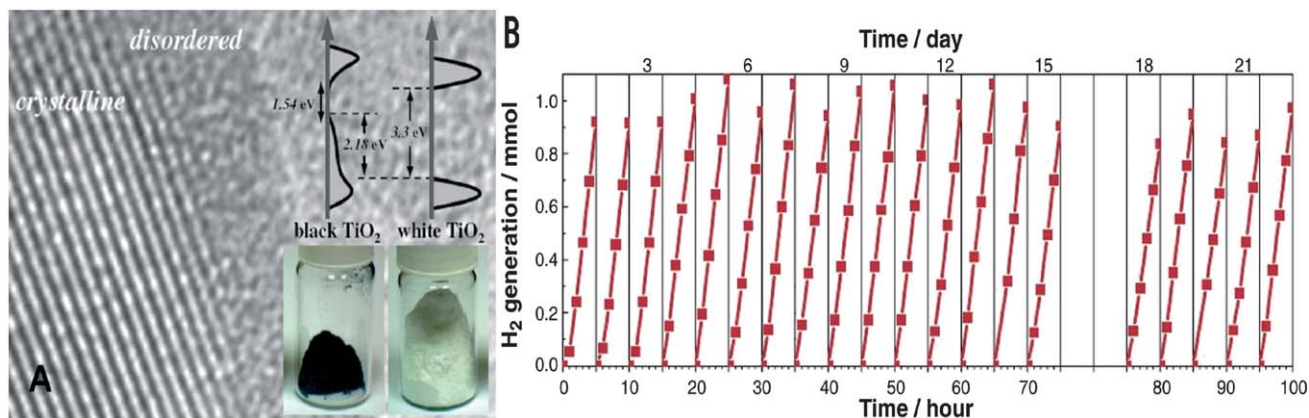


Fig. 8 (A) Schematic illustration of the density of states of disorder-engineered TiO_2 nanocrystals as compared to that of unmodified TiO_2 nanocrystals. The background is part of a disorder-engineered TiO_2 nanocrystal. Photos of disorder-engineered (black) and unmodified (white) TiO_2 nanocrystals are also shown. (B) Cycling measurements of hydrogen gas generation through direct photocatalytic water splitting with disorder-engineered black TiO_2 nanocrystals under simulated solar light. (Reprinted with permission from the American Association for the Advancement of Science.)¹

4.2 Charge separation

Besides the contribution from the enhanced visible light response mediated by oxygen vacancies, separation of photo-excited hole–electrons is also affected by these oxygen vacancies. It is generally accepted that the oxygen vacancies play an important role in mediating the interfacial electron transfer and thus photocatalytic activity.^{87,89,95,163–165} But how the oxygen vacancies affect the charge separation process is still under debate. Some of the research workers hold the opinion that oxygen vacancies act as the recombination centers for the photo-induced electrons and holes.^{110,166} For example, our group has revealed that the oxygen vacancies induced by photocatalytic reactions (Fig. 9a) serve as recombination centers, hampering the photoinduced charge carriers' separation process.¹²¹ This is evidenced by the decrease of photocurrent of used TiO_2 -001 with oxygen vacancies under UV light irradiation, compared to the original TiO_2 -001, as shown in Fig. 9b. This is also reflected by the photoluminescence (PL) spectra analysis.¹²¹ As shown in Fig. 10, the used TiO_2 -001 with oxygen vacancies under UV light irradiation shows much stronger PL intensity than the original sample of TiO_2 -001, indicating the increase of recombination of charge carriers on used TiO_2 -001. This decreased fate of charge carriers can be attributed to the easy recombination of charge carriers on the oxygen vacancy sites of the used TiO_2 -001. However, some others have just the opposite opinion that the presence of oxygen vacancies would facilitate the charge separation process.^{87,89,95} For instance, Li *et al.* have observed that the photo-current densities of the hydrogenated TiO_2 with oxygen vacancies are at least two times higher than that of pristine TiO_2 nanowires (Fig. 11a).⁹⁵ Furthermore, electrochemical impedance measurements revealed that hydrogen treatment of TiO_2 nanowires increases their donor densities. The oxygen vacancies are demonstrated to be electron donors in TiO_2 and are considered to contribute to the enhanced donor density in hydrogenated TiO_2 . Therefore, the charge transport in TiO_2 is improved, and the Fermi level of TiO_2 is shifted toward the

conduction band, which facilitates the charge separation process. Thus, the enhanced charge separation and transportation are believed to be major reasons for the observed

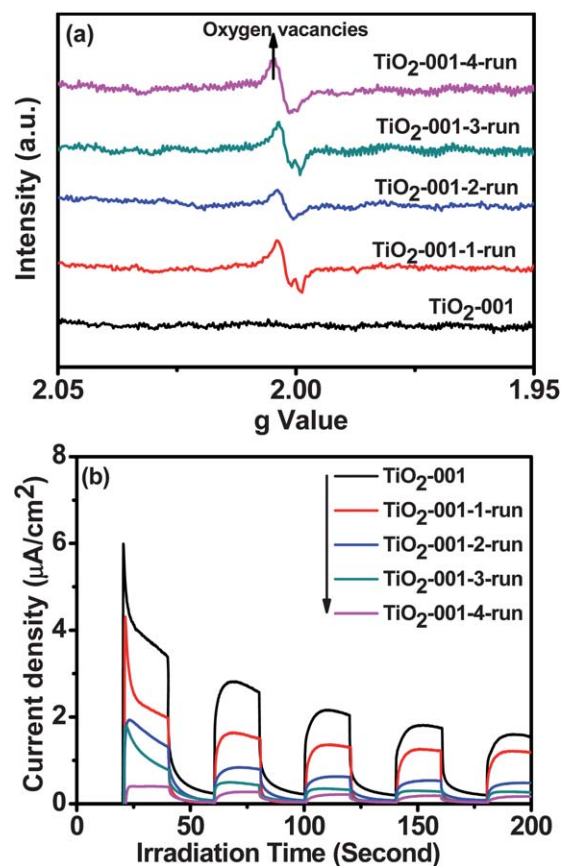


Fig. 9 (a) ESR spectra of the original and used TiO_2 -001 catalysts after photocatalytic aerobic reaction under UV light irradiation; (b) photocurrent responses of the original and used TiO_2 -001 catalysts after photocatalytic aerobic reaction under UV light irradiation. (Reprinted with permission from Elsevier.)¹²¹

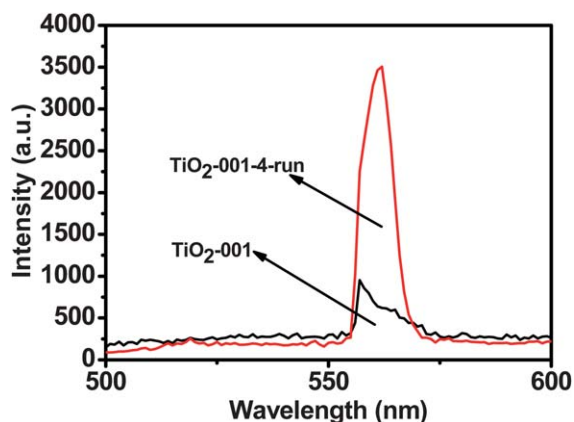


Fig. 10 Photoluminescence (PL) spectra of the original and used TiO₂-001 catalysts after photocatalytic aerobic reaction under UV light irradiation. (Reprinted with permission from Elsevier.)¹²¹

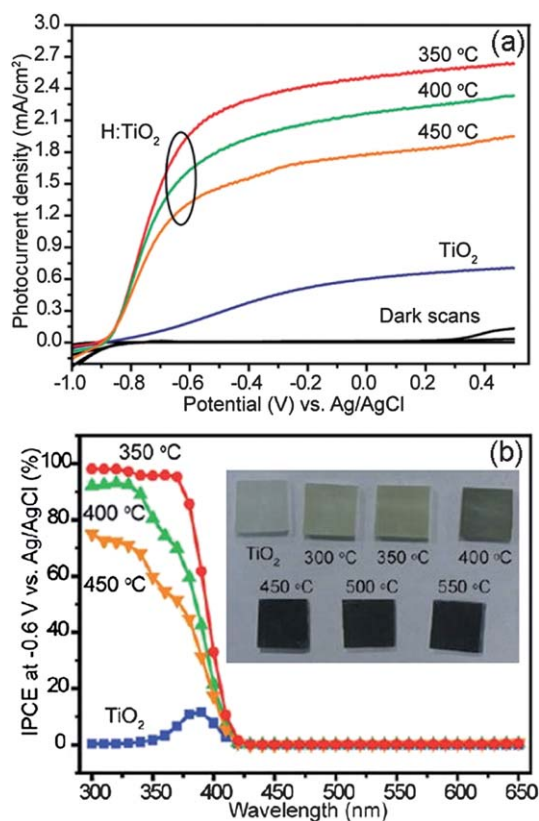


Fig. 11 (a) Measured photocurrent density for the pristine TiO₂ and H:TiO₂ nanowire samples, as a function of applied potential vs. Ag/AgCl; (b) IPCE spectra of pristine TiO₂ and H:TiO₂ nanowires prepared at 350, 400, and 450 °C. Inset: digital pictures of pristine TiO₂ and H:TiO₂ nanowires annealed in hydrogen at various temperatures. (Reprinted with permission from the American Chemical Society.)⁹⁵

incident-photon-to-current-conversion efficiency (IPCE) enhancement in the UV region (Fig. 11b).

To resolve these conflicts, one should make clear the microscopic structure of the defective TiO₂ with oxygen vacancies created by different methods, because the influence of

defects on the specific photocatalytic process is sensitive to their location and surface chemistry.^{94,167,168} It is believed that defects located on the surface can serve as charge carrier traps as well as adsorption sites where the charge transfer to adsorbed species can prevent the e-h recombination, whereas bulk defects only act as charge carrier traps where e-h recombine.^{167,168} In addition, the creation of oxygen vacancies often couples with the introduction of other components (such as Ti³⁺, highly reduced species or hydrogen, *etc.*). These species are also found to largely affect the charge separation process. For example, hydrogen treated black TiO₂ not only creates oxygen vacancies but also Ti-H bonds on its surface, which has a direct effect on the electronic structure of TiO₂.¹⁶⁹ Thereby, the charge separation process on hydrogenated TiO₂ is influenced both by oxygen vacancies and surface Ti-H bonds.

4.3 Photocatalytic selectivity

The development of TiO₂ photocatalysts with the desirable selectivity toward targeted transformation and degradation of organic pollutants is crucial for organic synthesis and environmental applications. A well-known method in catalysis to change the selectivity of a reaction is to change the coordination number of the metal ions of catalysts.¹⁷⁰ Significantly, the coordination geometry of Ti ions in TiO₂ can be tuned by creating a large and stable concentration of oxygen vacancies, as revealed by Krol and coworkers (Fig. 12).¹⁰⁴ In the case of TiO₂, changing the Ti coordination number from its usual value of 6 (octahedral TiO₆) to 4 (tetrahedral, TiO₄) is indeed found to change the reaction mechanism of NO degradation from photo-oxidation (forming nitrates) to photo-reduction (forming N₂ and O₂).⁶ Namely, the selectivity toward NO photo-reduction can be greatly improved, and the photo-oxidation reaction can be largely suppressed by the creation of oxygen vacancies (Fig. 13). In addition, the activity of the photo-reduction reaction is largely enhanced by doping the TiO₂ with Fe³⁺, an accept-type dopant that stabilizes the oxygen vacancies.⁶ Moreover, the photoinduced reduction of Fe³⁺ to Fe²⁺ provides a recombination pathway that almost completely suppresses the formation of NO₂ and thus enhances the selectivity of the reaction for N₂

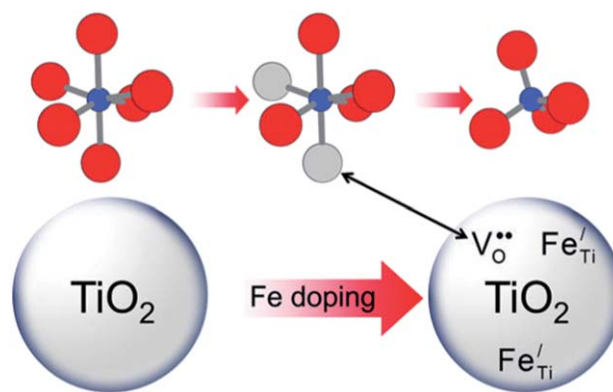


Fig. 12 Transformation from octahedrally coordinated to tetrahedrally coordinated Ti⁴⁺ in TiO₂ when high concentrations of oxygen vacancies are present. (Reprinted with permission from the American Chemical Society.)¹⁰⁴

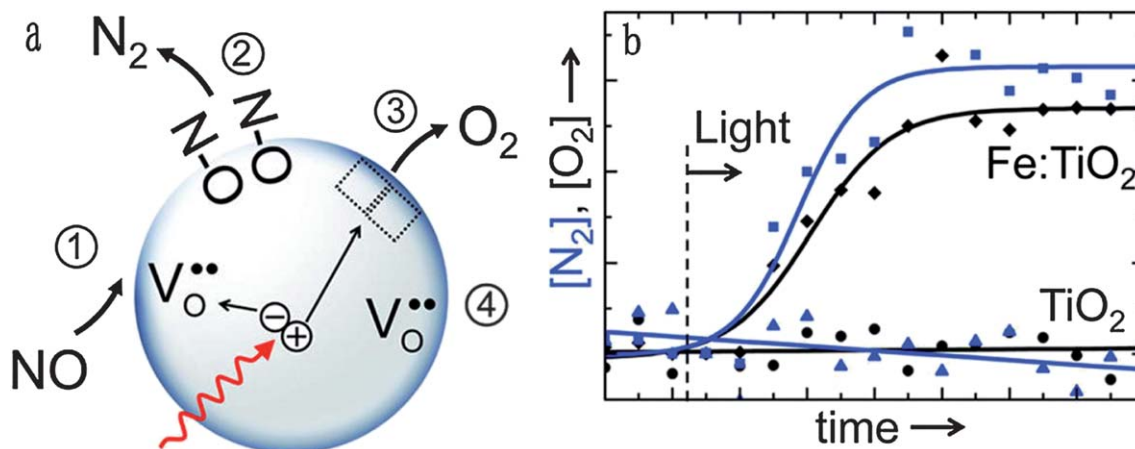


Fig. 13 (a) Possible mechanism for NO selective reduction over Fe-doped TiO₂ with oxygen vacancies: process 1: oxygen vacancies act as catalytic centers that capture the oxygen end of the NO molecules; process 2: the O–N species react with each other to form N₂; process 3: the trapped oxygen atoms are released from the lattice sites, resulting in the formation of O₂; process 4: the photogenerated holes re-oxidize the neutral oxygen vacancies to their normal 2⁺ state; (b) photocatalytic conversion of NO to N₂ and O₂ over 1% Fe-doped TiO₂. The sample is irradiated with UV light and the target pollutant is 100 ppm NO in He. (Reprinted with permission from the American Chemical Society.)⁶

formation.⁶ The deliberate use of oxygen vacancies to modify the coordination geometry of metal ions represents a new strategy that offers exciting possibilities to tune the selectivity of photocatalytically active metal oxide nanoparticles.

4.4 Oxygen vacancies and N co-doped TiO₂

TiO₂ co-doping with oxygen vacancies and nitrogen is reported to achieve significant synergistic effects compared to their single component doped or undoped TiO₂.^{171–176} The strong interaction between oxygen vacancies and N within the TiO₂ matrix alters the charge carrier transfer–recombination dynamics and also shifts the band gap absorption to the visible region.^{173,174} The coupling of N doping with oxygen vacancy formation has been proposed to inhibit the photogenerated charge carrier recombination as well as enhance the visible light absorbance.^{173,174} In the case of NH₃ treated TiO₂, it is suggested that the visible light photocatalytic activity of N-doped TiO₂ is co-determined by the formation of oxygen vacancies in the TiO₂ matrix and existence of doped-N on the surface.¹⁷³ The oxygen vacancy formation enhances the visible light absorption in a wavelength range of 400–520 nm.¹⁷³ Meanwhile, the doped N is able to prevent photogenerated electron–hole from recombination, making it feasible for photogenerated electrons to transfer to the catalyst surface and facilitating the visible light photo-oxidation of the reactants.¹⁷⁴ In another study, the N-doped TiO₂ is treated by hydrogen (H₂) reduction. It is found that N doping would facilitate the formation of the oxygen vacancies under H₂ treatment.¹⁰⁹ It is also demonstrated that oxygen vacancies are stabilized by doped N and together act as a source for the photogenerated electron transfer to reducible adsorbates like oxygen.^{109,176} The synergistic effect of oxygen vacancies and doped N species contributes to the enhancement of photocatalytic activity of N-doped TiO₂ samples.

5 Summary and outlook

This tutorial minireview presents the available approaches to the formation of defective TiO₂ with oxygen vacancies. The oxygen vacancies can be introduced deliberately by thermal treatment under a reducing or oxygen depleted atmosphere, bombardment using high energy particles, doping with metal or non-metal ions or even by *in situ* catalytic reactions. In these processes, lattice oxygen is removed from the surface or bulk of the TiO₂ under the reactive condition, resulting in a vacancy state in TiO₂. The characteristic electronic and geometrical structures associated with oxygen vacancies endow the defective TiO₂ with unique physical and chemical properties, being a consequence of favored visible light absorption, dissociative adsorption and reductive properties. Although a deep understanding of the role of oxygen vacancies in photocatalytic processes is still in an infant stage and there are some contradictory statements on the role of oxygen vacancies related to the photocatalytic performance of semiconductors, it has been demonstrated that the defective TiO₂ is advantageous for a wide range of applications, including visible light response, charge separation, and photocatalytic selectivity.

In spite of the significant development of theoretical calculations and experimental results for the defective TiO₂ with oxygen vacancies, further efforts are still required in this area to rationally engineer the defects in TiO₂, aiming to tune its properties in a desired manner for advancing environmental and energy-related applications. For example, considering that defects on metal oxide surfaces play a key role in the nucleation and growth of metal particles,¹⁷⁷ defect engineering on metal oxide surfaces may be utilized to guide the growth of metal particles, aiming to manipulate the size and shape of metal particles as well as to modulate their chemical properties. In addition, a better understanding of the influence of oxygen vacancies on the charge separation process, especially the

microscopic details of interfacial electron transfer mediated by oxygen vacancies, is challenging but crucial for optimization of photocatalytic reactions. Importantly, defects in metal oxide surfaces are believed to be the active sites in thermal catalysis.⁸² Thereby, one can consider coupling solar energy with thermal energy to drive the catalytic reactions on defective catalysts, which may achieve a more energy efficient and robust catalytic process. Notably, the re-oxidation of the oxygen vacancies over the time is still a challenge for utilizing defective TiO₂ as a stable photocatalyst for target application. In particular, oxygen vacancies are inevitably consumed during photochemical reduction of CO₂. Namely, the oxygen vacancy states in TiO₂ just act as stoichiometric sites for CO₂ reduction. Therefore, it remains an urgent need to convert these stoichiometric sites into catalytic sites for photocatalytic application. Besides creation of surface disorder and ion doping (Fe, N), one can also consider regenerating oxygen vacancies *in situ* under the reaction condition. Hopefully, this minireview would stimulate further ongoing interest in the development and thorough characterizations of semiconductor TiO₂ and other semiconductor materials with defect sites, and advance their applications for solving the current and future environment- and energy-related challenges.

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