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Review (Special Issue on Photocatalysis)

Photocatalysis fundamentals and surface modification of TiO₂ nanomaterials

Jiuqing Wen, Xin Li *, Wei Liu, Yueping Fang, Jun Xie, Yuehua Xu

College of Materials and Energy, South China Agricultural University, Guangzhou 510642, Guangdong, China

ARTICLE INFO

Article history:

Received 1 September 2015

Accepted 21 October 2015

Published 20 December 2015

Keywords:

Titanium oxide

Surface chemistry

Surface modification

Surface fluorine-effects

Co-catalyst

ABSTRACT

As a green and sustainable technology, heterogeneous photocatalysis using semiconductors has received much attention during the past decades because of its potential to address energy and environmental problems. Among various semiconductors, TiO₂ has been regarded as the best and most widely investigated photocatalyst in the past 10 years. Based on the fundamentals of photocatalysis and surface chemistry of TiO₂ nanomaterials, we herein summarize and discuss the achievements in the different surface modification strategies employed to date such as surface doping and sensitization, construction of surface heterojunctions, loading of nano-sized co-catalysts, increase in the accessible surface areas, and usage of surface F effects and exposure of highly reactive facets. Especially, the interesting synergistic effects of these different surface modification strategies deserve more attention in the near future. Studying these important advances in photocatalysis fundamentals, and surface chemistry and modification may offer new opportunities for designing highly efficient TiO₂-based and non-TiO₂-based photocatalysts for solar fuel production, environmental remediation, organic photosynthesis, and other related fields such as solar cell device fabrication, thermal catalysis, and separation and purification.

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1. Introduction

TiO₂, a white solid substance, has been widely used as a commercial pigment additive since the early 20th century [1]. Especially, since Fujishima et al. [2] reported for the first time the photoelectrochemical water splitting on a n-type TiO₂ electrode under ultraviolet (UV) light illumination in 1972, TiO₂ nanomaterials have been extensively applied in various areas including photovoltaics (dye-sensitized solar cells) [3–8], sensors [9], photo(electro)catalytic hydrogen production from water splitting [1,10–17], degradation of pollutants [18–25], selective organic transformations [26,27], and CO₂ reduction

for fuel generation [11,28–34]. The global environment and energy issues, as two main challenges in the 21st century, are becoming increasingly severe with each passing day [35]. Importantly, TiO₂ is versatile, economical, stable, abundant, non-toxic, and environmentally friendly. And it has been regarded as one of the most ideal photocatalysts for energy and environment applications [13,16,23,36,37]. Thus, among these research fields, heterogeneous photocatalysis using solar energy and TiO₂ has drawn much attention in the past decade because it is a promising means to address both global energy crises and environmental pollution [13,38,39].

To date, there has been a growing number of publications

* Corresponding author. Tel: +86-20-85280325; Fax: +86-20-85282366; E-mail: Xinliscau@yahoo.com

This work was supported by the Industry and Research Collaborative Innovation Major Projects Of Guangzhou (201508020098), the National Natural Science Foundation of China (20906034, 21173088, and 21207041), and the State Key Laboratory of Advanced Technology for Material Synthesis and Processing, Wuhan University of Technology (2015-KF-7).

DOI: 10.1016/S1872-2067(15)60999-8 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 12, December 2015

on the use of heterogeneous photocatalytic redox reactions over TiO_2 in energy and environmental applications [40], as contributed by scholars from various academic and industrial research communities. Clearly, the photocatalytic performance of TiO_2 is largely dependent on its optical and electronic structures, morphological properties, crystallinity, (nano) size, and surface chemistry [41]. However, its low quantum efficiency and wide band gap greatly limit its applications in the visible light region. Therefore, extensive research efforts have been devoted to improve its photocatalytic efficiency and absorption ability of visible light via diverse modification technologies [12,17,25,27].

The recent breakthroughs made in developing TiO_2 -based photocatalysts have been presented in many excellent reviews [11,41–45]. However, most of these reviews focus on the achievements made in the synthesis and modification of nanoscale titania and its diverse applications in specific areas of photocatalysis [1,11,43,45,46]. In contrast, some issues on the deeper understanding of the relationship between surface chemistry and photocatalysis enhancement of TiO_2 photocatalysts at the molecular level are often neglected despite the increasing interest in this exciting field of research and numerous review articles on TiO_2 photocatalysis. As much progress has been made in the development of TiO_2 -based photocatalysts through suitable surface modification strategies, it is believed that a comprehensive review on the deeper understanding of the molecular mechanisms for various surface modification strategies of TiO_2 is timely to better design photocatalytic systems and promote state-of-the-art developments in this area. Such developments are also expected to offer additional unexplored opportunities regarding the design and improvement of other non- TiO_2 -based photocatalysts. In this review, we highlight the fundamentals of photocatalysis, and surface chemistry and corresponding surface modification strategies of TiO_2 nanomaterials for various applications. Particularly, we focus on the relationship between surface chemistry and emerging surface modification strategies for the activity improvement of TiO_2 -based photocatalysts. It is expected that this review will offer some new opportunities for designing and developing both TiO_2 -based and non- TiO_2 -based photocatalysts.

2. Photocatalysis fundamentals of TiO_2 nanomaterials

2.1. Thermodynamic fundamentals of TiO_2 nano-photocatalysts

In general, there are many typical photocatalytic processes such as water splitting, degradation of pollutants, selective organic transformations, and CO_2 reduction for fuel generation. The unique photocatalytic property of TiO_2 originates from the thermodynamic properties of its band structure including the band gap and positions of the valence band (VB) and conduction band (CB). The band structural properties determine the light absorption capability and redox ability of TiO_2 nano-photocatalysts [11]. The thermodynamic fundamentals for photocatalytic water splitting, degradation of pollutants, and CO_2 reduction over TiO_2 nano-photocatalysts are presented in Fig. 1. As observed in Fig. 1, these processes share some typical features. First, the TiO_2 nano-photocatalyst absorbs light of wavelengths shorter than ~ 387.5 nm ($\lambda \leq hc/E_g \approx 1240/3.2$ nm = 387.5 nm; h = Planck's constant, c = speed of light, E_g = band gap) upon exposure to incident light with sufficient energy. Then, electrons in the CB are photo-generated and holes in the VB are created, which promptly reach the surface of the TiO_2 nano-photocatalyst to initiate the corresponding reduction and oxidation reactions, respectively [47]. Therefore, the oxidation and reduction capabilities of trapped holes and electrons on the surface active sites of TiO_2 nano-photocatalysts are directly dependent on the positions of the VB and CB, respectively. The holes on the surface of TiO_2 can directly oxidize adsorbed water/ OH^- to O_2 (Fig. 1(a) and (c)) or to reactive oxidants such as hydroxyl radicals toward the degradation of contaminants (Fig. 1(b)). Furthermore, it should be noted that the photo-generated electrons in anatase TiO_2 can initiate most reduction processes (including O_2 reduction to superoxides, H_2 generation, and CO_2 reduction to methane, methanol, or formaldehyde) except for CO_2 reduction to HCO_2H and CO . Accordingly, it is not surprising that anatase TiO_2 has been widely used in various photocatalytic fields.

The free energy, ΔG , and standard redox potential, ΔE^0 , of the multi-electron water splitting (Eq. 1) and CO_2 reduction (Eqs. 2–6) processes are given below [30]. From the viewpoint of the Gibbs free energy change, the ΔG values of these reactions are highly positive, indicating that they cannot proceed spontaneously at ambient temperature because they are all thermodynamically unfavorable uphill processes with a multi-

Fig. 1. Similarities in diverse photocatalysis-related processes. (a) Water splitting; (b) Degradation of pollutants; (c) CO_2 reduction over anatase TiO_2 . (HER, hydrogen evolution reaction; OER, oxygen evolution reaction; ORR, oxygen reduction reaction; WOR, water oxidation reaction; CRR, CO_2 reduction reaction).

step procedure. Especially, the more negative ΔG values of CO_2 reduction reactions indicate that such reactions are more difficult to proceed when compared with water splitting reactions. The ΔG values additionally indicate that the CO_2 reduction reactions can store more energy than the water splitting reactions [48,49]. As observed from Fig. 1, for the water splitting and CO_2 reduction reactions, raising the position of the CB can enhance the driving forces for these reduction reactions to proceed.

In contrast, photocatalytic environmental treatment processes, such as photo-oxidation of organic pollutants by O_2 molecules, are generally thermodynamically favorable as they are regarded as typical downhill-type processes [16]. Such processes have been extensively investigated using TiO_2 photocatalysts. The formation of highly oxidative species (e.g., hydroxyl radicals and O_2^-) on the surface of TiO_2 semiconductors during catalytic processes is needed to overcome the activation barrier. However, these photo-generated OH radicals and superoxide anions are crucial for the oxidation of organic compounds in water or air. The CB energy level ($E_{\text{CB}} = -0.51 \text{ V}$ at pH 7) is slightly more negative than the one-electron reduction potential of oxygen ($E^0(\text{O}_2/\text{O}_2^-) = -0.33 \text{ V}$), thus achieving facile reduction of O_2 , which has been considered as the rate-determining step in photocatalysis for environmental purification (Fig. 1(b)) [25]. In contrast, the VB energy level of TiO_2 ($E_{\text{VB}} = 2.69 \text{ V}$ at pH 7) is more positive than the oxidation potential of surface-adsorbed H_2O or OH^- to produce $\cdot\text{OH}$ radicals ($E^0(\text{H}_2\text{O}/\cdot\text{OH}) = 2.29 \text{ V}$), thereby confirming that the photo-generated holes in VB of TiO_2 can directly oxidize organic substances or water to their radicals [24]. It has also been demonstrated that free $\cdot\text{OH}$ is more reactive than the surface-bound analogue owing to the reorganization of energy [25]. All these favorable thermodynamic factors make TiO_2 the most suitable semiconductor photocatalyst for various photocatalytic applications.

2.2. Charge carrier dynamics of TiO_2 nano-photocatalysts

Besides the favorable thermodynamic aspects, the charge carrier dynamics properties in photocatalysis employing TiO_2 nanoparticles are important factors in determining the photocatalytic activity. It is commonly agreed that the four-step tandem process (Fig. 2) must take place for achieving the final interfacial redox reactions of electrons and holes over TiO_2 : light harvesting (step (1)), charge generation (step (2)), charge separation and transport (steps (3), (4), and (7)), and surface catalytic reactions (steps (5) and (6)). Therefore, only the pho-

Fig. 2. Processes involved in photocatalytic redox reactions over TiO_2 photocatalyst. (1) Light harvesting; (2) Charge generation; (3) Charge transport in bulk; (4) Charge recombination in bulk; (5) Surface reduction reactions; (6) Surface oxidation reactions; (7) Charge recombination on the surface (RC, reduction co-catalyst; OC, oxidation co-catalyst; BR, bulk recombination; SR, surface recombination).

to-generated charge carriers that reach the surface of TiO_2 can be used for photocatalytic redox reactions. The overall efficiency of the various photocatalytic processes can be described as follows:

$$\eta_c = \eta_{\text{abs}} \times \eta_{\text{cs}} \times \eta_{\text{cmt}} \times \eta_{\text{cu}} \quad (7)$$

where η_c is the solar energy conversion efficiency, η_{abs} is the light absorption efficiency, η_{cs} is the charge excitation/separation efficiency, η_{cmt} is the charge migration and transport efficiency, and η_{cu} is the charge usage efficiency for photocatalysis reactions. Among the different parameters efficiencies, high charge separation efficiencies (η_{cs} and η_{cmt}) and surface catalytic reaction efficiency (relating to η_{cu}) are the key factors determining the overall efficiency of the photocatalytic processes.

The fast charge recombinations of steps (4) and (7), as deactivation processes, take place in the time scale of femtoseconds to microseconds, and are unfavorable to improving the photocatalytic activity. Thus, investigations of charge carrier dynamics inside and on the surface of TiO_2 photocatalysts are essential for thoroughly understanding photocatalytic reaction mechanisms. Generally, the charge carrier dynamics in semiconductor nanoparticles can be directly measured by means of ultrafast time-resolved absorption spectroscopy [50]. The transient absorption spectra can efficiently identify the reactive species, trapped holes, trapped electrons, and quasi-free electrons, whereas the decay profiles can be used to determine the rate of recombination of electrons and holes [51]. In fact, time-resolved spectroscopic studies have revealed that the relatively low photocatalytic efficiency over TiO_2 is mainly due to the rapid recombination rate of photo-generated electron (e^-)-hole (h^+) pairs ($\sim 90\%$) after excitation [21]. The time-resolved microwave conductivity technique can be employed to study charge carrier dynamics in TiO_2 nanoparticles; this technique is very sensitive to the particle size and morphology of the photocatalyst [52,53]. For example, the mean lifetime of a single electron-hole pair in a TiO_2 particle (12 nm in diameter) was determined as 30 ns [54]. Furthermore, hole trapping processes are much slower ($\tau \sim 250 \text{ ns}$) than electron

Fig. 3. Schematic illustration of the spatial and energetic distribution of electron traps in a TiO₂ film. Reprinted with permission from Ref. [56].

trapping processes ($\tau \sim 30$ ps) [54]. As reported by Bahnemann et al. [55], flash radiolysis can provide strong evidence of the existence of trapped charge carriers. Studies on the complex relaxation dynamics of electrons revealed that photo-generated electrons (after reaching the surface within 170 fs) can migrate between the surface and shallow bulk trap sites that are in equilibrium (Fig. 3) [56]. These shallow-trapped electrons are capable of relaxing into deeper sites with a time constant of 500 ps through a hopping process involving energetically distributed trapping sites. More interestingly, TiO₂ colloids doped with Fe³⁺, V⁴⁺, Mo⁵⁺, or Ru³⁺ were found to exhibit much slower charge carrier recombination rates, of which the decay times could be extended to 50 ms [57]. The reaction dynamics of photo-generated charge carriers in TiO₂ are summarized in Fig. 4. As observed from Fig. 4, the trapping, recombination, and interfacial transfer of charge carriers are very fast processes. Therefore, employing strategies that can inhibit bulk and surface charge recombination and improve charge transport to the surface sites of TiO₂ can boost the charge carrier dynamics and the photocatalytic activities of TiO₂ photocatalysts. These strategies include decreasing the defect sites in the bulk and on the surface, increasing the accessible surface areas, coupling with nanocarbon materials, and constructing heterojunctions

Fig. 4. Photo-induced reactions in TiO₂ photocatalysis and the corresponding time scales. Reprinted with permission from Ref. [42].

and nano-structured photocatalysts, all of which will be discussed in detail in Section 3.

As the optical penetration depth, δ_p , in TiO₂ ($\delta_p \approx 250$ nm at $\lambda = 308$ nm) is very short, the photo-generated electron-hole pairs are generally created in the outer surface region of TiO₂ [58]. Thus, the photocatalytic reactions over TiO₂ are strongly dependent on its surface and interfacial properties. However, it is also seen from Fig. 4 that the interfacial charge transfer rates (steps (5) and (6), Fig. 2) are much slower than those of charge trapping and recombination in the bulk and on the surface of TiO₂ nano-photocatalyst. Hence, interfacial charge recombination will proceed rapidly if the interfacial charge transfer rates are not greatly enhanced. Therefore, improving the surface reaction kinetics is essential for suppressing the fast surface recombination of charge carriers and boosting the overall photocatalytic efficiency. Accordingly, to achieve this aim, many different strategies, such as loading co-catalysts, increasing the accessible surface active sites, and exposing highly reactive facets, have been widely studied during the past decades, and will be thoroughly discussed.

2.3. Surface chemistry of TiO₂ nano-photocatalysts

The surface properties of TiO₂ nano-photocatalysts have significant effects on their photochemical applications. The complex surface physicochemical properties of TiO₂ nano-photocatalysts are shown in Fig. 5. Typically, the surface charge of TiO₂ plays an important role in determining the photocatalytic efficiency, especially for the kinetics of photo-oxidation of organic dyes. The surface charge properties of TiO₂ in water at different pH levels are typically influenced by its zero-point charge (zpc) as the acid-base equilibrium reaction can be observed for the surface titanol groups of TiO₂ as follows [25]:

The pH of the zero point of charge is calculated as:

$$\text{pH}_{\text{zpc}} = 1/2(\text{p}K_{\text{a}1} + \text{p}K_{\text{a}2}) \quad (10)$$

The point of zero charge (pH_{zpc}), corresponding to the pH at the point of zero net proton charge (isoelectric point or zero zeta potential), is typically obtained by measuring the electrokinetic potentials (zeta potential, ZP) of suspended particles at different pH levels. For example, the pH_{zpc} of Degussa P25 TiO₂ is ~ 6.2 ($\text{p}K_{\text{a}1} = 4.5$ and $\text{p}K_{\text{a}2} = 8$) [59,60]. Hence, at pH levels < 6.2 , the particle surface is positively charged, whereas at pH levels > 6.2 , it is negatively charged. In general, more efficient

Fig. 5. Surface physicochemical reactions on TiO₂ photocatalyst.

generation of hydroxyl radicals by TiO_2 is achieved in weak alkaline medium owing to the presence of an optimal concentration of OH^- , which is beneficial for the photocatalytic degradation of organic compounds in aqueous solution. Furthermore, it was found that the relative dielectric constant, ϵ , of the solvent in which TiO_2 was suspended has a strong effect on the ZP of TiO_2 owing to the electrostatic interactions between the TiO_2 powder and solvent [61]. The ZP of TiO_2 powder suspended in different alcohol solvents can be calculated by an empirical formula (Eq. (11)). Studies showed that TiO_2 powder suspended in methanol exhibited the highest ZP when compared with that suspended in other alcohols (e.g., ethanol, 1-propanol, isopropanol, and 1-butanol) owing to the high ϵ of methanol [61]. These results indicate that TiO_2 is the most stable in methanol. Consequently, the effect of process parameters, such as pH and solvent, on the photocatalytic performance should be carefully investigated for practical applications.

$$\text{ZP} = 13.43 - 213.63/\epsilon \quad (11)$$

Suitable control of surface hydroxyl groups can lead to the formation of other interesting photo-induced phenomena such as superhydrophilicity. These phenomena are intrinsically different from the well-known photocatalytic processes. In 1997, the UV light-induced superhydrophilicity behavior of TiO_2 film surfaces in both water and oil was first discovered by Fujishima and coworkers [62]. This unique photo-induced wetting behavior of TiO_2 under UV illumination can be elucidated by the following mechanism. The Ti^{3+} state and oxygen vacancies can be produced by the photo-generated electrons and holes, respectively (the right section of Fig. 5). Then, these oxygen vacancies can be occupied by water molecules, thus leading to the formation of adsorbed OH groups on the surface defect sites. Consequently, the increased density in surface hydroxyl groups gives rise to the surface hydrophilic properties [23,63–65]. Furthermore, as reported, ultrasonic treatment of amphiphilic TiO_2 surfaces in pure water can reduce the degree of surface hydrophilicity owing to partial re-oxidation of the photo-reduced surface upon generation of OH radicals, further demonstrating the hydrophilic–hydrophobic conversion mechanism [66]. It was also found that the contact angle of water on porous TiO_2 coating films decreased with increasing adsorbed hydroxyl content, capillary force, and roughness of the resultant coating films [67]. The addition of 10–20 mol% SiO_2 in the TiO_2 films generated the lowest water contact angle [68]. Further investigations confirmed that suitable mesopores, and surface microstructures and roughness could enhance the photo-induced superhydrophilic properties of porous TiO_2 thin films [69,70]. Moreover, TiO_2 nanofilms coated on suitable substrates exhibit superior photo-induced hydrophilicity, probably due to their higher surface roughness and hydroxyl content [71–73]. It is expected that TiO_2 -based thin films, exhibiting superhydrophilicity under visible light irradiation, will be further developed in the future [74].

The surface Ti^{3+} states and oxygen vacancies on TiO_2 photocatalysts can be created by many other strategies such as by thermal treatment under vacuum conditions or a reducing or oxygen-depleted atmosphere, bombardment using high energy particles, or doping with metal or non-metal ions [75]. The

as-obtained defective or self-doped TiO_2 generally exhibits excellent activities toward various photocatalytic applications [76–82], which will be not discussed in this review. For more information, recently published reviews are available [41,75,83].

The density of surface hydroxyl groups can be altered by employing high-temperature calcination treatments [84–87] and by exchange of surface $-\text{OH}$ groups [88,89]. For example, using a simple sulfuric acid treatment can significantly enhance the photocatalytic activity of TiO_2 films toward the oxidation of acetone in air owing to the reduction of sodium ions and increase in the surface-adsorbed hydroxyl content [90]. Further research studies showed that SO_4^{2-} species could replace the surface $-\text{OH}$ groups at high temperatures and introduce strong acidic sites onto the surface of mesoporous TiO_2 molecular sieve films (Fig. 6(a)) [89]. The highly polarized state of surface strong acid sites would allow more effective hole trapping, thus suppressing the photo-carrier recombination, which can be further evidenced by time-resolved photoluminescence studies (Fig. 6(b)). The resulting mesoporous sulfated TiO_2 films, as solid superacid photocatalysts, exhibited a 2-fold enhancement in the photocatalytic oxidation of CH_3Br in air when compared with mesoporous TiO_2 films [89]. Moreover, the crystallization of TiO_2 or the number of OH groups per TiO_2 particle can be significantly increased by increasing the calcination temperature, thus leading to enhanced photocatalytic performances [87,91,92]. However, if the calcination temperature is excessively high, the photocatalytic activity typically decreases because of the formation of rutile and sintering and growth of TiO_2 crystallites that result in a reduction in the surface area

Fig. 6. (a) Schematic representation of mesoporous nanocrystalline $\text{SO}_4^{2-}/\text{TiO}_2$ superacid molecular sieve film formation. (b) Time-resolved photoluminescence profiles of mesoporous TiO_2 and mesoporous sulfated TiO_2 films. Reprinted with permission from Ref. [89].

[84–86,93]. Therefore, the calcination temperature should be optimized to obtain optimal photocatalytic performances. Furthermore, using suitable inhibitors for suppressing grain growth and rutile phase formation of TiO_2 (such as carbon layer, ZrO_2 , phosphoric acid, and Na_2SO_4) is favorable for obtaining anatase TiO_2 with high crystallinity and surface area, thus achieving higher photoactivities [94–97]. The use of surface fluorination modification for enhancing the photocatalytic activity will be thoroughly discussed in Section 3.5.

2.4. General principles for designing TiO_2 nano-photocatalysts

Based on the above analysis, it is clear that pristine TiO_2 typically has unfavorable charge carrier dynamics and a wide band gap. Therefore, surface modification is often necessary to enhance charge carrier separation and visible light absorption to improve the photocatalytic activity. Based on the photocatalytic mechanism, some typical surface modification strategies can be proposed to design high activity TiO_2 nano-photocatalysts, as shown in Fig. 7. First, the wide band gap of pristine TiO_2 (3.0–3.2 eV) greatly limits its visible light absorption capabilities. Thus, narrowing the band gap of TiO_2 by doping or loading suitable visible light photosensitizers onto TiO_2 has been widely employed to enable usage of a wider range of the solar spectrum. Second, constructing surface heterojunctions has been used to improve the charge carrier dynamics and prolong the charge lifetime, thus resulting in enhanced photocatalytic performances. Third, loading nano-sized co-catalysts can also greatly accelerate the surface reaction kinetics, thus suppressing rapid surface charge recombination processes. Fourth, increasing accessible surface areas can efficiently promote light harvesting, and the adsorption and diffusion of reactants, thereby achieving improved photocatalytic activities. Fifth, introducing surface F effects on TiO_2 can increase the concentration of free OH radicals with larger oxidation potential and alter the photodegradation selectivity, thereby facilitating enhancements in the photodegradation performance. Finally, exposing highly reactive facets is beneficial for increasing the surface active sites and redox ability for target reactions and for improving photocatalytic reactivity. All these strategies are efficient for improving several unfavorable factors during photocatalysis, and have been widely studied by different groups. Herein, we select some typical examples to discuss

these strategies. Special attention is devoted to highlight potential research hotspots and directions for each strategy, thus providing new insights into the surface modification of TiO_2 nano-photocatalysts for further development in these fields.

3. Surface modification of TiO_2 nano-photocatalysts

3.1. Surface doping and sensitization

Conceptually, the low visible light absorption of TiO_2 nano-materials is a key factor restricting their photocatalytic efficiency. Owing to their wide band gap, TiO_2 nanomaterials can only use 3%–4% of UV light, and cannot fully exploit the visible light spectrum (~48% of the total sunlight energy). Thus, to address this issue, research has focused on increasing the visible light activity of TiO_2 nanomaterials by shifting the onset of their light response from the UV to visible region. During the past decades, second-generation (metal-doped) and third-generation (non-metal-doped) TiO_2 nanomaterials have been successively developed and widely applied in various photocatalytic fields [1]. Five strategies have been used to enhance the visible light activity of TiO_2 nanomaterials: impurity doping, structural defects insertion, surface sensitization, surface plasmon resonance effect generation, and solid solution [30]. Herein, two promising strategies i.e., impurity doping and surface sensitization, are highlighted.

Impurity doping can introduce localized electronic states into the band gap of wide band gap semiconductors, thus achieving an obvious red shift in the optical response and a significant enhancement in the visible light activity of the semiconductor material through a two-step photo-excitation by low energy visible light photons [12,30]. For example, mesoporous Cr-doped TiO_2 exhibits a marked red shift with respect to pure TiO_2 (Fig. 8(a)). This shift can be attributed to the charge-transfer band $\text{Cr}^{3+} \rightarrow \text{Ti}^{4+}$ or $4\text{A}_{2g} \rightarrow 4\text{T}_{1g}$ of Cr^{3+} in an octahedral environment [98]. The resulting homogeneous mesoporous Cr- TiO_2 shows a significant enhancement in the photocatalytic decomposition rate of methylene blue (MB) in the visible light region (Fig. 8(b)) owing to enhanced visible light absorption, crystallinity, and three-dimensional-interconnected mesochannels [98]. Although some doped TiO_2 solid solutions feature wide band gaps, improved photocatalytic activities can be achieved owing to the increased concentration

Fig. 7. Surface modification strategies for TiO_2 nano-photocatalysts.

Fig. 8. (a) UV-visible absorption spectra of pure TiO₂ (1) and Cr-TiO₂ (2). (b) Comparison of the photoactivities of pure TiO₂ (1) and Cr-TiO₂ (2) toward the decomposition of MB under visible light irradiation. Reprinted with permission from Ref. [98].

of hydroxyl radicals [99], oxidation–reduction potential [100], or improved lattice parameters [101]. Generally, suitable dopants can efficiently narrow the band gap of TiO₂-based photocatalysts by forming new localized electronic states or mid-gap states, thus leading to enhanced photoactivities [12,102]. To date, among various doped TiO₂ nanomaterials, non-metal nitrogen element has proved to be the best dopant for TiO₂ with respect to photocatalytic activity for environmental applications [45]. It was theoretically and experimentally demonstrated that the substitutional doping of N for O in anatase TiO₂ could efficiently narrow its band gap through the formation of mixed N 2*p* and O 2*p* states, thus achieving improved visible light photocatalytic activities [103]. Although there are debates on the origins of the red shift of the absorption onset of N-doped TiO₂ to the visible region [12], thousands of research papers on N-doped TiO₂ nanomaterials as visible light sensitive photocatalysts have been reported in the past 15 years [45,96,104–109]. For example, N-doped TiO₂ nanomaterials with mesoporous structures and exposed (001) facets have been reported to exhibit excellent visible light photocatalytic activities owing to improved visible light absorption and increased surface active sites content [104,105,110]. More interestingly, it was also reported that ZrO₂-modified TiO₂-xN_x displayed higher porosity, higher specific surface area, and an improved thermal stability over the corresponding unmodified TiO₂-xN_x samples [96]. Recently, the doping of other non-metal species, such as F, S [111,112], P [113,114], B, and C [115–119], and co-doping of these non-metal species [120–127] and metal species [128–130] have also been widely investigated to further increase the activity and stability of TiO₂ nanomaterials. However, to date, the photocatalytic reaction rates of N-doped TiO₂ nanomaterials remain low owing to their poor visible light absorption. In the future, based on the deeper understanding of mechanisms in photo-excited states, it is expected that the visible light photocatalytic rates and stabilities of N-doped TiO₂ nanomaterials can be further improved through different engineering modification strategies such as co-doping, surface co-catalyst and passive layer loading, surface heterojunction construction, and usage of their favorable synergistic effects, thus extending the practical applications of non-metal-doped TiO₂ materials [12,45].

Also, sensitizing TiO₂ using semiconductors with narrower

band gaps has proven to be a promising and practical strategy to enhance the visible light activity of TiO₂. Composites of TiO₂ and visible light semiconductors can not only enhance the visible light response of TiO₂, but also improve the stability of sensitizers with narrower band gaps owing to the efficient charge separation in the semiconductor–sensitizer interface electrical fields [30]. For example, CdS-sensitized TiO₂ crystallites generally exhibit significantly enhanced visible light activities toward the photodegradation of organic pollutants [131–133], photocatalytic CO₂ reduction [32], and hydrogen evolution in water splitting [134] owing to the improved charge separation and visible light absorption capabilities. In another example, the quantum size effects of MoS₂ and WS₂ nanoclusters were examined to alter the energy levels of the CB and VB edges to favor interparticle charge carrier separation and enhance the visible light photocatalytic activities of TiO₂ toward the degradation of MB and 4-chlorophenol in aqueous suspension (Fig. 9) [135]. Other sensitizers, such as CdSe nanoparticles [136], metal phthalocyanine [137], graphene quantum dots [138], and plasmonic metals [139–145], have also been successfully used to enhance the visible light photocatalytic activity of TiO₂. In the future, further modifications should be investigated to enhance the stability and activity of the above systems. More importantly, green sensitizers, such as graphene, carbon, and C₃N₄ quantum dots, deserve more attention in developing sensitized TiO₂-based photocatalysts [146–150].

3.2. Construction of surface heterojunctions

Constructing surface heterojunctions has been demonstrated to be another promising strategy to promote the photocatalytic activities of TiO₂-based nanomaterials. It is generally believed that well-defined junctions effectively facilitate charge transfer and suppress recombination of photo-generated electrons and holes, leading to extremely high activity and stability [12,151–156]. Herein, special emphasis will be placed on the heterojunctions between TiO₂ and other semiconductors or nano carbon materials.

To date, TiO₂ semiconductor heterojunctions including n–n and p–n junctions have been widely constructed to improve charge separation and prolong the lifetime of photo-excited charge carriers. For instance, TiO₂-based n–n heterojunctions,

Fig. 9. (a) Photodegradation of 4-chlorophenol over pure TiO_2 and MoS_2 and WS_2 nanocluster-sensitized TiO_2 under visible light irradiation ($\lambda > 400$ nm). (b) Energy levels of the CB and VB edges versus normal hydrogen electrode (NHE) for pure TiO_2 , WS_2 , and MoS_2 with various sizes at pH 7 (Q-size, quantum size). Reprinted with permission from Ref. [135].

including CdS/TiO_2 [32,157,158], $\text{CeO}_2/\text{TiO}_2$ [159], WO_3/TiO_2 [160–162], $\text{SrTiO}_3/\text{TiO}_2$ [163], ZnO/TiO_2 [164], $\text{BiVO}_4/\text{TiO}_2$ [165,166], $\text{TiO}_2/\text{In}_2\text{O}_3$ [167], $\text{Ag}_2\text{CO}_3/\text{TiO}_2$ [168], and $\text{C}_3\text{N}_4/\text{TiO}_2$ [169–174], have been available for various photocatalytic applications. Such semiconductor heterojunctions can suppress the recombination rate of e^-h^+ pairs owing to generation of interfacial electrical fields. In contrast, TiO_2 -based p–n heterojunctions, such as BiOI/TiO_2 [175], NiO/TiO_2 [176], $\text{Cu}_2\text{O}/\text{TiO}_2$ [177–179], $\text{CuCrO}_2/\text{TiO}_2$ [180], and $\text{MoS}_2/\text{TiO}_2$ [181], have been widely examined for extending the visible light absorption of TiO_2 semiconductors with wider band gap and enabling effective charge separation driven by the photo-induced generated p–n junction interface. For example, Dai et al. [175] constructed a p–n junction of BiOI/TiO_2 nanotube arrays (NTs) by coating the walls of TiO_2 NTs with BiOI using a novel impregnation–hydroxylation method. The results demonstrated a 3-fold enhancement in the photoelectrocatalytic degradation of methyl orange (MO) over the p–n junction of BiOI/TiO_2 under visible light irradiation. The schematic diagrams for the formation of the p–n junction between p- BiOI and n- TiO_2 are shown in Fig. 10. As displayed in Fig. 10, upon light irradiation, an equilibrium state is formed between BiOI and TiO_2 by raising the energy band of BiOI and reducing the Fermi level of TiO_2 . The resulting inner electric field can efficiently drive the photo-generated electrons and holes to TiO_2 and BiOI , respec-

tively, thus reducing the recombination of e^-h^+ pairs and accelerating the photocatalytic reactions with the reactants adsorbed on the surfaces of the heterojunction [175]. In the future, well-defined TiO_2 semiconductor heterojunctions, such as junctions with exposed facets [166,172,177] and core–shell structures [182–184], are believed to be very promising and generate much interest in constructing highly efficient TiO_2 -based heterojunction systems.

TiO_2 exists as four main crystalline polymorphs in nature: tetragonal rutile, tetragonal anatase, orthorhombic brookite, and monoclinic $\text{TiO}_2(\text{B})$ [11,41]. Distortion of the uniformly shaped TiO_6 octahedron units in the lattice structure of the four types of TiO_2 can cause different mass densities and band gaps in the different phase forms of TiO_2 [11]. Therefore, phase junctions would form between two phases upon contact, with suitable band alignments. Such phase junctions can greatly promote the photo-carrier separation and enhance the photocatalytic quantum yields [185–188]. Yu et al. [189] demonstrated that the high brookite content in mesoporous TiO_2 with a bicrystalline (anatase and brookite) framework played an important role in enhancing its photocatalytic activity toward the oxidation of *n*-pentane in air. In another study, Li and coworkers [190] demonstrated that the formation of exposed surface anatase–rutile phase junction is critical to achieve enhanced photocatalytic activity of TiO_2 nanoparticles owing to the efficient synergic effects of the two phases. Notably, the phase junctions between most frequently studied TiO_2 phases (rutile or anatase) and less common TiO_2 phases (brookite and B phase) and charge-separation mechanisms deserve more attention in future studies [191].

Apart from TiO_2 semiconductor heterojunction and phase junctions, the junctions between TiO_2 and nano carbon materials have attracted much attention owing to their superior photocatalytic performance. For instance, the junctions between TiO_2 and conductive carbon nanotubes [192–200], graphene [138,201–211], carbon black [212–215], graphitic carbon [95,216,217], or C60 [218,219] have been extensively fabricated to efficiently enhance the photocatalytic activity for various applications. The improved photoactivities can be primarily attributed to the enhanced charge separation by the Schottky junction between TiO_2 and the highly conductive nano carbon

Fig. 10. Schematic diagrams of the energy bands of p- BiOI and n- TiO_2 before light irradiation (a) and formation of a p–n junction under visible light irradiation (b). Reprinted with permission from Ref. [175].

materials and the improved adsorption performance through the introduction of the carbon materials. For example, Xiang et al. [220] fabricated graphene-modified TiO₂ nanosheets with exposed (001) facets using a two-step hydrothermal process. The H₂ production rate of the composite with an optimal graphene content of 1.0 wt% was 41 times higher than that achieved by pure TiO₂ nanosheets. The schematic illustration for the charge transfer/separation and the proposed mechanism are shown in Fig. 11. As displayed in Fig. 11, it is believed that the graphene sheets, as an electron acceptor, can efficiently extract the photo-generated electrons from the TiO₂ nanosheets and thus promote charge carrier separation owing to the outstanding electrical conductivity of the graphene sheets and suitable potential of graphene/graphene^{•-} (−0.08 V vs. standard hydrogen electrode (SHE), pH = 0). In the future, more attention should be paid to the in situ growth of TiO₂ on three-dimensional graphene [221,222] with high quality junctions and the hybridization of TiO₂ and composite carbon materials doped with bi- or multi-heteroatoms owing to the excellent synergistic effects exhibited by combining different carbon materials and heteroatom doping [218,223–225].

3.3. Loading of nano-sized co-catalysts

As shown in Fig. 4, slow surface reaction kinetics is an important factor negatively affecting the photocatalytic activity of TiO₂, especially for uphill H₂ evolution and CO₂ reduction reactions. To address this issue, an efficient strategy is to load suitable co-catalysts to accelerate surface reaction kinetics [12]. To date, various co-catalysts, including noble metal, earth-abundant metal, and metal-free and hybrid co-catalysts, have been developed to enhance photocatalytic H₂/O₂ evolution and CO₂/O₂ reduction reactions, as summarized in Table 1. For further information, the reader is invited to refer to some recently published reviews [12,226–228]. As shown in Table 1, noble metal, earth-abundant metal (such as Ni(OH)₂ [229], Cu(OH)₂ [230], MoS₂ [206], NiS_x [231], and NiO_x [232–234]), and metal-free and hybrid co-catalysts (Table 1) have been proven to greatly enhance the H₂ evolution activities of TiO₂ nano-photocatalysts. For example, Hu et al. [235] reported that Pt₃Co alloy co-catalyst loaded onto TiO₂ could achieve a 1.5-fold enhancement in the photocatalytic activity toward H₂ evolution when compared with Pt/TiO₂ photocatalyst. The high activity

Fig. 11. (a) Schematic illustration of the charge transfer and separation in a graphene-modified TiO₂ nanosheets system under UV light irradiation. (b) Proposed mechanism of photocatalytic H₂ production under UV light irradiation. Reprinted with permission from Ref. [220].

Table 1

Summary of various types of co-catalysts employed for photocatalysis.

Photocatalytic reaction	Noble metal co-catalysts	Earth-abundant metal co-catalysts	Metal-free and hybrid co-catalysts
H ₂ evolution	Pt, Au, Ag [242], Pt ₃ Co [235], AuPd [243,244]	Ni(OH) ₂ [229], WS ₂ [245–247], CuO [248,249], Cu(OH) ₂ [230], MoS ₂ [250,251], NiS _x [231,252–254], NiO _x [232–234,255], Co and Ni [256], Mo ₂ C and Mo ₂ N [257], Ni ₂ P [258]	g-C ₃ N ₄ /N-doped graphene [259–262], (N,P)-co-doped graphene [263], graphene [220,264], MoS ₂ /graphene [206,265], MoS ₂ (or WS ₂) clusters/N-doped graphene [266–268]
O ₂ evolution	RuO ₂ [269], IrO ₂ [269], Ru, Ir, and Pt [270]	NiCo ₂ O ₄ [271,272], CoMoO ₄ [273], Mn ₂ O ₃ [274], CoO _x [275], Co(OH) ₂ [276], cobalt phosphate (Co-Pi) [277], Ni _{1-x} Fe _x OOH [278]	g-C ₃ N ₄ /carbon nanotubes [279], Co ₃ O ₄ -carbon [280], graphene/ZnCo (or NiCo) layered double hydroxide [281,282], NiCo ₂ O ₄ /N-doped graphene [283], Ni@N-doped graphene [284], NiCo ₂ O ₄ /carbon nanotubes [285]
CO ₂ reduction	Pt [236,237], Au [286,287], Pd [288], Ag [289–294], RuO ₂ [307,308], CoO _x [309] [295–299], bimetallic Ag-Pt [300], Au-Cu [301], Cu-Pt [302,303]	Cu [304], CuO [305,306], Cu ₂ O [30,38], NiO _x	Graphene [239,310,311], carbon nanotubes [312,313], carbon dots [314,315], NiO _x /graphene [316], carbon nanotubes@Ni [317], Pt@Cu ₂ O [318]
O ₂ reduction	Pt [319,320], Ag [321,322], Au ₂₅ nanoclusters [323], bimetallic Au/Pt [324]	NiCo ₂ O ₄ [325–327], MnO ₂ [328], M _x Fe _{3-x} O ₄ (M = Fe, Cu, Co, Mn) [329], CaMnO ₃ [330,331]	g-C ₃ N ₄ @carbon [332,333], N/S or (B,N)-co-doped graphene [334,335], N-doped graphene/porous carbon [336], Co ₃ O ₄ /graphene [337], polyelectrolyte/carbon nanotubes [338], Mn ₃ O ₄ /N-doped graphene [339], graphene [340–344], N-doped graphene (carbon spheres, nanotubes, or nanocages) [345–349]

was attributed to the accumulation of photo-excited electrons onto Pt₃Co and improved H₂ evolution kinetics [235]. In another example, low-cost Cu(OH)₂ clusters, as an excellent co-catalyst, have been demonstrated to significantly enhance the H₂ evolution activity of TiO₂ (Fig. 12(a)) [230]. It is believed that the suitable potential of Cu(OH)₂/Cu lies between the CB of anatase TiO₂ (−0.26 V) and reduction potential of H⁺, thus favoring the efficient transfer of electrons and enhancements in the photocatalytic H₂ production activity (Fig. 12(b) and (c)). Typical O₂ evolution co-catalysts, which can be used in water oxidation or overall water splitting (combined with the H₂ evolution co-catalysts), are also listed in Table 1.

Interestingly, for the photocatalytic reduction of CO₂, co-catalyst loading can not only accelerate the kinetics of CO₂ reduction, but also achieve improved selectivity. A selective production of hydrocarbon (such as CH₄, other alkanes, and olefin) with a rate of 160 μL/(g·h) was reported over nitrogen-doped TiO₂ nanotube arrays loaded with both Cu and Pt co-catalysts under outdoor global AM1.5 sunlight (Fig. 13(a)) [236]. More recently, an optimum CH₄ yield of 1361 μmol/(g·h) was obtained over one-dimensional TiO₂ single crystal films

coated with ultrafine Pt nanoparticles (0.5–2 nm in diameter, Fig. 13(b)) [237]. Also, Cu₂O, as a co-catalyst, can enhance the photocatalytic selectivity toward the generation of methanol [30,238]. Other co-catalysts, such as nano carbon materials, and NiO_x and their hybrids (Table 1), have proven to be good co-catalysts for the selective production of CH₄ and CH₃OH, respectively [30,239–241].

Additionally, co-catalysts have been widely used to accelerate O₂ reduction reactions, which have been regarded as the rate-determining step in solar photocatalytic mineralization of organic pollutants [25,350]. For example, Yu et al. [351] fabricated Ag-TiO₂ multi-phase nanocomposite thin films using liquid-phase deposition method. The results demonstrated that the photocatalytic activity of the Ag-TiO₂ multiphase nanocomposite thin films toward the degradation of MO was about 6.3 times higher than that of pure TiO₂ thin films. The enhanced activity was attributed to the formation of multi-junctions and improved O₂ reduction kinetics over Ag co-catalyst (Fig. 14). Similarly, Ag@TiO₂ core-shell nanocomposite nanowires exhibited significantly enhanced photocatalytic decolorization of rhodamine B (RhB) in aqueous solution at ambient tempera-

Fig. 12. (a) Comparison of the photocatalytic activities of different samples CX (X, nominal molar ratios of Cu(OH)₂ to TiO₂+Cu(OH)₂, mol%) toward the photocatalytic H₂ production from ethylene glycol aqueous solution under UV-light-emitting diode irradiation. (b) Proposed mechanism of photocatalytic H₂ production under UV light irradiation. (c) Schematic illustration of charge transfer and separation. Reprinted with permission from Ref. [230].

Fig. 13. (a) Product generation rates obtained using a nitrogen-doped nanotube array film (annealed at 600 °C) surface-loaded with both Pt and Cu co-catalysts [236]. (b) CO and CH₄ yields obtained using P25, pristine TiO₂ columnar films (TiO₂ film), and Pt-TiO₂ films with different Pt deposition times [237].

Fig. 14. Interface charge carrier transfer dynamics of anatase-rutile, Ag-anatase, and Ag-rutile within Ag-TiO₂ composite thin films. Reprinted with permission from Ref. [351].

ture under UV light irradiation [352]. Furthermore, Au [323,353] and Pt [354] nanoparticles/clusters have been demonstrated to be excellent co-catalysts toward the photocatalytic oxidation decomposition of organic pollutants over TiO₂ nano-photocatalysts. The improved charge separation and O₂ reduction rate were responsible for the significantly enhanced activities. In the future, it is expected that further earth-abundant, metal-free, and hybrid co-catalysts (Table 1) will be developed and applied in the photocatalytic degradation of organic compounds.

3.4. Increase in the accessible surface areas

Fabricating hierarchical nanopores in TiO₂ nano-photocatalysts has also proved to be a feasible strategy to efficiently increase the accessible surface areas, prevent the aggregation of nano-photocatalysts, and enhance the photocatalytic activity and selectivity of nano-photocatalysts. Importantly, these hierarchically porous structures in TiO₂ photocatalysts feature readily accessible pore walls, high specific surface areas, and interconnected pore systems, which can not only enhance light harvesting and reactant adsorption efficiencies but also optimize the transport of guest species to framework binding sites (Fig. 15). Thus, the synergetic effects of different dimensional levels and multi-stage pore structures can result in superior photocatalytic performances in hierarchical photocatalysts. Unlike the application of TiO₂ nano-photocatalysts with hierarchical nanopores in photocatalytic H₂ evolution [355,356] and CO₂ reduction [357,358], their usage in photocatalytic pollutant degradation have been more extensively studied [205,359–374]. Thus, we focus on the application of hierarchical TiO₂ photocatalysts in the photocatalytic degradation of organic compounds.

Generally, such hierarchical TiO₂ photocatalysts are fabricated using (surfactant-)templated methods [365,368] or oriented assembly strategies of nano-sized building blocks such as nanorods, nanotubes, and nanoplates [375–381]. For example, Wang et al. [365] fabricated macro/mesoporous TiO₂ photocatalysts via a surfactant-templated method. The resulting photocatalysts featured an intact macro/mesoporous structure

Fig. 15. Three-dimensional mesoporous architecture in a TiO₂ nanocrystalline thin film with continuous and periodically porous networks that offer transport routes for gaseous reactants to move into and out of the framework. Reprinted with permission from Ref. [368].

(Fig. 16), which exhibited a 1.6-fold enhancement in photocatalytic activity toward ethylene photodegradation in gas-phase medium when compared with commercial P25 TiO₂. The enhanced activity can be attributed to the increased light absorption efficiency and improved diffusion of gaseous molecules owing to the existence of macrochannels. In contrast, a 30% drop in photocatalytic activity was observed in the absence of light-penetrating and molecular-diffusing macrochannels, further indicating the key roles of macrochannels in improving the photocatalytic activity. Enhanced photocatalytic activities toward the decomposition of formaldehyde and acetone in air were also demonstrated using hierarchical TiO₂ photocatalysts [205,359,362,382]. For example, hierarchically flower-like TiO₂ superstructures (HFTS) were fabricated through self-assembly of anatase TiO₂ nanosheets with exposed (001) facets (up to 87%, Fig. 17(a)–(d)) [360]. The resulting HFTS exhibited a higher photocatalytic activity than tabular-shaped TiO₂ particles (TSTP) and P25 owing to the syner-

Fig. 16. SEM images of TiO₂ monolithic particles calcined at 350 °C (a–c) and 500 °C (d). Reprinted with permission from Ref. [365].

Fig. 17. SEM (a, b), TEM (c) and high-resolution TEM images (d) of HFTS. Inset in (a) is a magnified image of an individual spherical superstructure. (e) Comparison of the photocatalytic activities of HFTS, TSTP, and P25 toward the photocatalytic decomposition of acetone in air. (f) Dependence of the concentration of produced CO_2 on irradiation time using HFTS, TSTP, and P25 as photocatalysts. Reprinted with permission from Ref. [360].

gistic effect of the intermeshed nanosheets, hierarchical porous structures, and exposed (001) facets (Fig. 17(e) and (f)). Similarly, hierarchically porous TiO_2 photocatalysts exhibited enhanced photocatalytic activities toward the degradation of organic dyes in aqueous solution under UV illumination [360,361,367]. Additionally, it was found that photocatalytic selectivity in decomposing MB and MO could be achieved by simple surface modification of hollow TiO_2 spherical photocatalysts [383]. Recently, Li et al. [384] reported that porous TiO_2 materials with a hierarchically interconnected structure could be fabricated by templating Pickering high-internal phase emulsions. It was demonstrated that the parent emulsion droplets and the interfacially adsorbed microgel stabilizers could promote the formation of macropores/interconnecting large pores with sizes of ~ 50 and ~ 10 μm and smaller pores (~ 100 nm). The photocatalytic degradation of RhB over porous materials with such bimodal porous structures was considerably more efficient than that over crystalline commercial P25 sample owing to the existence of the hierarchical pore structure. However, there are very few reports on the application of hierarchically structured semiconductors in CO_2 photoreduction and photocatalytic organic synthesis [358,385,386]. Therefore, it is highly expected that low-cost, hierarchically structured semiconductors with high activities will be subsequently exploited and applied in photocatalytic CO_2 reduction and organic synthesis in the future. Furthermore, different modification strategies for such hierarchical TiO_2 photocatalysts, such as doping, formation of hetero-junctions, and loading of suitable co-catalyst, would be worth investigating in future studies.

3.5. Usage of surface F effects

Recently, it was shown that using surface F effects could also

significantly improve the physicochemical and photocatalytic properties of TiO_2 photocatalysts toward the degradation of organic compounds [25,88]. Generally, surface F doping of TiO_2 cannot lead to an obvious red shift in the fundamental absorption edge of TiO_2 [387,388]. However, surface fluorination can significantly alter the hydrophobic–hydrophilic properties of TiO_2 , increase the photogeneration of $\cdot\text{OH}$ and surface acidity of TiO_2 particles (Fig. 18), and reduce the recombination rate of e^- – h^+ pairs, thus achieving a significant enhancement (by a factor of 1.4–6.3) in the photocatalytic oxidation rates of various (in)organic compounds (Table 2) [25]. It is believed that surface fluorination can not only trap the CB electrons owing to the high electronegativity of fluorine and thus accelerate the O_2 reduction, but also favor the transformation of VB holes into free OH radical species, thereby reducing the recombination of photo-generated electrons and holes and enhancing the photo-

Fig. 18. Hole transfer and transformation into hydroxyl radicals on bare TiO_2 and fluorinated TiO_2 (F-TiO_2) surfaces under UV irradiation. Reprinted with permission from Ref. [25].

Table 2Summary of surface-fluorinated TiO₂ for photocatalysis.

Photocatalyst	Preparation method	Application (Enhancement factor)	Enhancement mechanism	Ref. (Year)
TiO ₂ powders	Hydrolysis of titanium tetraisopropoxide in a solution of NH ₄ F	Oxidation of acetone in air (1.4×)	Improved crystallinity of anatase, suppressed formation of brookite, and enhanced visible light absorption	[389] (2002)
Mesoporous TiO ₂ thin films	Treatment with trifluoroacetic acid (TFA)	Oxidation of acetone in air (2×)	Reduced recombination rate of e ⁻ -h ⁺ pairs by the chemisorbed TFA complex	[390] (2003)
Mesoporous TiO ₂ microspheres	Sonochemical/hydrothermal treatment of titanium isopropoxide in the presence of NaF	Degradation of MB (7.6×)	Increased content of hydroxyl radicals and adsorption of MB, reduced recombination rate of e ⁻ -h ⁺ pairs	[391] (2009)
Mesoporous TiO ₂ powders	Hydrothermal method in a NH ₄ HF ₂ /H ₂ O/C ₂ H ₅ OH mixed solution	Oxidation of acetone in air (3×)	Increased content of hydroxyl radicals and crystallinity of anatase, reduced recombination rate of e ⁻ -h ⁺ pairs	[394] (2009)
TiO ₂ hollow microspheres	Hydrothermal treatment of Ti(SO ₄) ₂ in the presence of TFA	Oxidation of acetone in air (2×)	Enhanced transfer of light and acetone, reduced recombination rate of e ⁻ /h ⁺ pairs	[395] (2010)
TiO ₂ hollow microspheres	Hydrothermal strategy using NH ₄ HF ₂ as a controlling agent	Decolorization of RhB (2×)	Improved crystallinity, reduced recombination rate of e ⁻ -h ⁺ pairs	[393] (2010)
Square-shaped TiO ₂ nanocrystals	Sonochemical treatment of titanium isopropoxide in the presence of NH ₄ F	Degradation of phenol (6.3×)	Reduced recombination rate of e ⁻ -h ⁺ pairs, increased content of surface hydroxyl groups and crystallinity of anatase	[392] (2012)
Hemisphere-like TiO ₂	Hydrothermal treatment of TiF ₄ aqueous solution in the presence of starch	Degradation of acid orange II under visible light	Formation of oxygen vacancies and good crystallinity	[387] (2010)
Hierarchically nanoporous TiO ₂ spheres	Hydrothermal treatment of TiF ₄ powder in HCl solution	Degradation of 4-chlorophenol under visible light	Creation of oxygen vacancies, efficient transport of light and reactant molecules	[388] (2006)
TiO ₂ powders	Spray pyrolysis from an aqueous solution of H ₂ TiF ₆	Decomposition of acetaldehyde and trichloroethylene (16.4×)	Creation of oxygen vacancies	[402] (2005)
Porous (F,Ce)-co-doped TiO ₂	Ultrasound irradiation of titanium isopropoxide in the presence of NaF	Degradation of acid orange II (3×)	Increased content of surface hydroxyl groups, reduced recombination rate of e ⁻ -h ⁺ pairs	[403] (2012)
Hollow TiO ₂ microspheres	Hydrothermal treatment of Ti(SO ₄) ₂ in the presence of NH ₄ F and ethanol	Selective decomposition of MO and MB	Tunable adsorption selectivity, controlled hierarchical assembly, exposed (001) facets	[383] (2010)
Hierarchically porous TiO ₂ films	Hydrothermal treatment of Ti foil in a dilute aqueous HF solution	Selective degradation of MO and MV	Controlled surface charge and adsorption selectivity	[361] (2011)
(F,N)-co-doped TiO ₂ nanocrystals	Solvothermal treatment of Ti(OBu) ₄ in the presence of NH ₄ F and ethanol	Degradation of MB under visible light	Formation of Ti ³⁺ centers and oxygen vacancies	[404] (2013)
F-doped TiO ₂ nanoparticles	Hydrolysis of tetrabutyl titanate in the presence of NH ₄ F and ethanol	Degradation of MB under visible light	Reduced recombination rate of e ⁻ -h ⁺ pairs, increased content of hydroxyl groups and visible light absorption	[405] (2014)

catalytic activity. Importantly, the enhanced formation rate of free (unbound) hydroxyl radicals was evidenced on the surface of F-TiO₂ [25]. When compared with the surface-adsorbed OH radicals on TiO₂, free OH radicals are highly mobile and more oxidative owing to their higher redox potential and the existence of remote photocatalytic oxidation [25,88]. For example, Yu et al. [389] fabricated F-doped TiO₂ photocatalyst with anatase and brookite phases by hydrolysis of titanium tetraisopropoxide in a mixed NH₄F/H₂O solution. The prepared F-doped TiO₂ powders exhibited enhanced photocatalytic activity toward the oxidation of acetone in air. It was believed that F⁻ doping improved the crystallinity of anatase, suppressed the formation of brookite phase, prevented phase transition of anatase to rutile, and enhanced the visible light absorption, thus greatly promoting the photocatalytic activity. Further research demonstrated that all fluorinated, F-doped, and trifluoroacetic acid-modified TiO₂ photocatalysts exhibited remarkably enhanced activities and stabilities toward the degradation of organic pollutants in aqueous solution or oxidation decomposition of acetone in air (Table 2) [390–395]. The enhanced activity was ascribed to the reduced recombination rate

of photo-generated electrons and holes and enhanced formation of free OH radicals [392,394,395]. The combination of fluorination and other surface modification strategies, such as impregnation of co-catalysts [396], co-doping [397,398], construction of hierarchical mesoporous structures and heterojunctions, would be worth investigating in future studies.

Furthermore, it should be pointed out that the surface fluorination of TiO₂ in acidic environment could result in the generation of a positively charged surface, thus promoting preferential adsorption of negatively charged contaminants (such as MO) and favoring their degradation [361]. As shown in Fig. 19, fluorinated TiO₂ films exhibited higher selectivity toward the photodecomposition of MO. In contrast, selective degradation of MB could be achieved over TiO₂ films subjected to NaOH washing treatment [361]. Thus, the surface-bonded fluoride and hydroxyl groups of hollow TiO₂ microspheres could achieve selective adsorption and photocatalytic decomposition of negatively charged MO and positively charged MB, respectively [361,383]. More interestingly, the periodic density functional theory calculations revealed that F doping is not only thermodynamically stable for rutile, anatase, and brookite

Fig. 19. Comparison of the photocatalytic activity and selectivity of TiO₂ films calcined at 180 °C for 1 h (T1) toward the degradation of MO and methyl violet (MV) before (T1-F) and after NaOH washing (T1-OH). The photocatalytic activity and selectivity are defined by the apparent rate constant (k) and the ratio (r) of k , respectively. Reprinted with permission from Ref. [361].

polymorphs of TiO₂, but also can preferentially stabilize the (001) over the (101) facets of TiO₂, thus achieving stable and enhanced photocatalytic activity over TiO₂ anatase nanoparticles with a reactive (001) surface and adsorption of F atoms [399,400]. Time-resolved PL spectroscopy studies also demonstrated that the amount of surface traps originating from the long-lasting PL signal could be increased by fluorine doping, followed by calcination at high temperatures, which are beneficial for the improvement in photoactivity by ensuring long-living photo-produced charge couples [401]. In the future, more attention should be paid to more comprehensively understand the mechanisms of surface fluorides in enhancing photocatalysis.

3.6. Exposure of highly reactive facets

Since the breakthrough in synthesizing TiO₂ crystals constituting of 47% (001) and 53% (101) facets was first reported by Yang et al. [406] in 2008, exposing highly reactive facets has become a promising strategy to enhance the activity of TiO₂ for different photocatalytic applications [43,407–410]. Usually, different facets of TiO₂ crystals possess distinctive physicochemical properties, such as adsorption, and catalytic reactivity and selectivity, owing to the different optical/electronic structures [411]. Also, the crystal faces can facilitate the separation of electrons and holes [29]. Thus, exposing highly reactive facets of TiO₂ has gained much interest in the different photocatalytic applications [29,110,121,383,412–414]. For example, Zhang et al. [410] synthesized a micro-sheet anatase TiO₂ single crystal photocatalyst with a remarkable 80% level of reactive (001) facets using a microwave-assisted hydrothermal route involving titanium tetrafluoride and a tetrafluoroborate-based ionic liquid. The results showed that the anatase TiO₂ single crystals with exposed (001) facets exhibited considerably higher activities than those of the (001) unexposed TiO₂ single crystals (Fig. 20). The higher activities were due to the strong

Fig. 20. Photocatalytic efficiencies of photocatalyst samples with (★) and without (Δ) exposed reactive (001) facets toward the degradation of 4-chlorophenol under UV irradiation. For comparison, the photocatalytic result in the absence of photocatalyst is also shown. Reprinted with permission from Ref. [410].

ability of the exposed facets to dissociatively adsorb water to form hydrogen peroxide and peroxide radicals. Furthermore, it was demonstrated that N-doped and (N,S)-co-doped TiO₂ nanosheets with exposed (001) facets exhibited significantly enhanced visible light activities toward photocatalytic H₂ production and degradation of 4-chlorophenol, respectively [110,121]. The increased visible light absorption and highly reactive exposed (001) facets of TiO₂ nanosheets were thought to be the main reasons for the improved activities. In another example, Yu and coworkers [29] demonstrated that an optimal ratio of exposed (101) and (001) facets (45:55) of a TiO₂ nanosheet could achieve optimal activity toward the photoreduction of CO₂ to CH₄. It is believed that the synergistic effect of an overflow effect and surface heterojunction between the co-exposed (101) and (001) facets of anatase played an important role in enhancing the photocatalytic activity (Fig. 21). Importantly, the concept of surface heterojunction between two facets of TiO₂ nanocrystals may offer a new strategy for designing sufficiently efficient TiO₂-based photocatalysts [29].

4. Conclusions and prospect

To date, TiO₂ nano-photocatalysts have been widely applied in different photocatalytic fields owing to their superior properties. Based on the analysis of photocatalysis fundamentals and the surface chemistry of TiO₂, in the current review, we summarized and discussed some of the most recent state-of-the-art advancements in different surface modification strategies such as surface doping and sensitization, construction of surface heterojunctions, loading of nano-sized co-catalysts, increase in accessible surface areas, usage of surface F effects, and exposure of highly reactive facets. However, many challenges still remain in fabricating efficient and stable TiO₂-based visible light photocatalysts through suitable surface modification strategies and comprehensively understanding the associated photocatalytic enhancement mechanisms.

Special emphasis should be placed on the development of

Fig. 21. Overflow effect and hetero-facet junction between {101} and {001} facets in anatase. Reprinted with permission from Ref. [29].

visible light TiO_2 -based photocatalysts using simple and facile strategies such as co-doping, and loading of sensitizers and plasmonic metals. Especially, determining the mechanisms of visible light photocatalytic enhancements of N-doped TiO_2 nanomaterials deserves more attention. Importantly, their photocatalytic activity and stability should be improved further to meet requirements of practical applications. New, cheap, robust, efficient, and stable co-catalysts should be designed and developed in the near future. Furthermore, many non- TiO_2 -based visible light photocatalysts are unstable under light illumination. Thus, fabricating suitable protection layers using amorphous or crystalline TiO_2 [415–425] and other Ti-containing semiconductors with wide band gaps ($E_g > 3.0$ eV) and high stability (such as SrTiO_3) [426–428] should be a promising strategy to enhance the activity and stability of other unstable/visible light photocatalysts and should be thoroughly investigated. Additionally, hybrids of TiO_2 -based nanomaterials and earth-abundant semiconductors with narrow band gaps, such as Bi-based oxides [429–432], sulfides [433–435], (oxy)nitrides [436], metal-free $\text{g-C}_3\text{N}_4$ [6,437], elemental α -sulfur [438], and red phosphorus [439–442], are a promising type of visible light photocatalyst. TiO_2 /biomolecular composites are also very promising visible light photocatalysts for energy and environment applications [443]. In the future, it is expected that more efficient, cheap, and stable TiO_2 -based visible light photocatalysts would be constructed through combined strategies.

The surface chemistry of TiO_2 photocatalysts and the complex photocatalysis mechanism remain interesting topics worth investigating, which will favor the design and development of highly reactive TiO_2 -based photocatalysts. Although the quantum size effect can partially decrease the utilization efficiency of light, increasing the CB/VB potentials of TiO_2 nanomaterials is an excellent potential strategy to improve their photocatalytic activities as a result of enhanced redox abilities [28]. In contrast, TiO_2 nanocrystals doped with rare earth metals or up-conversion luminescence agents can exhibit much higher photocatalytic activity owing to improved utilization of visible or near infrared light [444,445]. Furthermore, the important roles of surface F effects, hetero(phase)junctions, reactive facets, and co-catalysts in enhancing the photocatalytic activity of TiO_2 photocatalysts should be further examined and elucidated. In this regard, first-principle periodic calculations based on density functional theory have shown great potential for elucidat-

ing the molecular-level mechanisms of TiO_2 photocatalysis and thus deserve more attention [29,123,124,408,446]. Accordingly, the synergistic effect of these different surface modification strategies is also very interesting in developing highly reactive TiO_2 -based photocatalysts [341,447].

Additionally, TiO_2 and their modified nanomaterials have been widely used in different fields related to photocatalysis including solar cells [5,6,448,449], light-induced superhydrophilicity [63], and photoelectrochemistry [450–452]. However, it should be noted that there has been no significant breakthrough in TiO_2 -based photocatalysts since the work reported by Fujishima et al. [11] in 1972, and a breakthrough is unlikely to occur even in the near future. Importantly, TiO_2 -based photocatalysts provide an excellent platform for thoroughly studying the mechanisms of photocatalytic reactions, which should be very helpful for the development of other highly efficient photocatalyst systems. We believe that the current review will contribute significantly toward further progress in the field of TiO_2 -based photocatalysts for emerging applications in the photocatalytic fields in the future.

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Graphical Abstract

Chin. J. Catal., 2015, 36: 2049–2070 doi: 10.1016/S1872-2067(15)60999-8

Photocatalysis fundamentals and surface modification of TiO₂ nanomaterials

Jiuqing Wen, Xin Li *, Wei Liu, Yueping Fang, Jun Xie, Yuehua Xu
South China Agricultural University

Thermodynamic fundamentals, charge carrier dynamics, and the surface chemistry of TiO₂ nanomaterials are summarized to offer a conceptual basis for designing and developing highly efficient TiO₂-based photocatalysts using different surface modification strategies.

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二氧化钛纳米材料的非均相光催化本质及表面改性

温九清, 李 鑫*, 刘 威, 方岳平, 谢 君, 徐悦华

华南农业大学材料与能源学院, 广东广州510642

摘要: 非均相光催化过程是指多相多尺度体系在光辐射作用下发生的一个复杂的催化过程, 被认为最有潜力解决环境污染和能源短缺问题的绿色及可再生的技术之一。在目前已经报道的各种非均相光催化剂中, TiO_2 纳米材料被证实是应用最广泛、光催化效果最好的催化剂, 是当前国际材料、环境和能源等领域的研究前沿和热点, 高性能 TiO_2 基光催化材料的设计及改性一直是该领域的难点, 其关键问题主要为: 如何增强 TiO_2 的表面光催化量子效率、促进光生载流子分离和拓展其可见光响应范围。尽管已经有很多关于 TiO_2 光催化的综述, 但大多综述集中在高性能 TiO_2 的制备及各种改性策略研究, 而对各种改性策略与光催化分子机理之间的关系阐述较少。为此, 本文深入分析了 TiO_2 纳米材料的非均相光催化本质并总结了各种表面改性策略。

首先从热力学角度阐明 TiO_2 的热力学能带能够确保其实现各种典型光催化反应(包括光催化降解、 CO_2 还原及光解水), 证实其广泛应用的可行性。然后, 对 TiO_2 光生载流子的动力学基础进行总结, 证实快速的广生载流子复合以及较慢的表面化学反应动力学是限制其光催化活性提高的关键制约性因素。于此同时, 对 TiO_2 纳米材料的表面 Zeta 点位、超亲水性、超强酸光催化剂制备(表面羟基取代)等重要的表面化学性质也进行了详细阐述。从而可以初步得出如下结论: 表面改性是设计高性能 TiO_2 光催化材料的重中之重, 并将各种改性策略浓缩在 6 个方面: 表面掺杂和敏化, 构建表面异质结, 负载纳米助催化剂, 增加可利用的比表面积, 利用表面氟效应以及暴露高活性晶面等。

显然, 表面掺杂和敏化可以减小 TiO_2 纳米材料的禁带宽度, 从而大幅拓宽其可见光吸收范围及光催化效率。而构建紧密的表面异质结可以创建界面电场, 不仅可以促进光生电荷分离效率, 而且可以有效提高界面电荷转移效率, 最终实现异质结的高光催化效率。负载纳米助催化剂则可以大幅加快表面化学反应速率, 降低光生载流子的表面复合并增加其利用率, 并有可能减少不期望的表面逆反应, 从而实现光催化活性提升。增加可利用的比表面积, 可以有效提升光催化剂与吸附质之间的有效接触面积, 缩短了载流子的传输距离以及通过多次反射与折射提升光能的利用率, 从而全方位地提升 TiO_2 纳米材料的光催化活性。对 TiO_2 纳米材料表面进行氟化, 可以增加光生羟基自由基的速率以及浓度, 并可以通过调节 TiO_2 表面酸碱性而控制其光催化选择性, 从而实现高效高选择性光催化。最后, 通过暴露 TiO_2 纳米材料的高活性晶面, 也可以促进光生载流子分离、增加吸附性能或羟基自由基生成速率, 从而获得高光催化效率。

另外, 这些表面改性策略的协同效应仍是较有前景的 TiO_2 纳米光催化剂改性技术, 值得深入研究。同时, 深入的光催化分子机理探索仍然是必须的, 其不仅有助于发现影响 TiO_2 纳米材料光催化活性提高的关键性制约因素, 而且也可以指导开发新型的 TiO_2 纳米光催化剂改性技术。总而言之, 通过总结 TiO_2 纳米材料在光催化、表面化学及表面改性等方面的重要进展, 可为设计高效的 TiO_2 基及非 TiO_2 基光催化剂并应用于太阳燃料生产、环境修复、有机合成及相关的领域(如太阳能电池、热催、分离和纯化)等提供新的思路。

关键词: 二氧化钛; 表面化学; 表面改性; 表面氟效应; 助催化剂

收稿日期: 2015-09-01. 接受日期: 2015-10-21. 出版日期: 2015-12-20.

*通讯联系人. 电话: (020)85280325; 传真: (020)85282366; 电子邮箱: Xinliscou@yahoo.com

基金来源: 广州市产学研协同创新重大专项(201508020098); 国家自然科学基金(20906034, 21173088, 21207041); 材料复合新技术国家重点实验室(武汉理工大学)开放基金(2015-KF-7).

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