available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Feature article

Charge separation promoted by phase junctions in photocatalysts

Yi Ma^{a,b}, Xiuli Wang^{a,b}, Can Li^{a,b,*}^a State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China^b Dalian National Laboratory for Clean Energy, Dalian 116023, Liaoning, China

ARTICLE INFO

Article history:

Received 9 April 2015

Accepted 22 April 2015

Published 20 xxxxx 2015

Keywords:

Photocatalysis

Phase-junction

Charge separation

Solar energy

Titanium oxide

ABSTRACT

Since the 1980s, photocatalysis research has expanded at an unexpected rate. Fabrication of phase junctions has proved to be an effective method to enhance photocatalytic performance. As a model photocatalyst, titanium dioxide (TiO₂) has been extensively studied. This feature article mainly reviews the study on TiO₂ surface phase junctions, including the characterization of the surface phases of TiO₂, the use of anatase: rutile TiO₂ phase junctions in photocatalytic hydrogen production, and the current understanding of how TiO₂ phase junctions work in photocatalysis. The surface structure of TiO₂ can be well characterized by ultraviolet (UV) Raman spectroscopy, unlike X-ray diffraction and visible Raman spectroscopy. Based on these results, the mechanism of phase transformation processes of TiO₂ was clearly identified. The infrared (IR) spectra of probe molecules CO and CO₂ on TiO₂ further characterized the surface structure of TiO₂, strongly supporting the UV Raman results. Furthermore, the typical visible emission of anatase and near-infrared emission of the rutile phase of TiO₂ make photoluminescence (PL) a suitable technique to characterize the surface phase structure of TiO₂. PL can also provide information about the carrier dynamics of TiO₂ in photocatalysis. Because of the surface phase junction formed between anatase and rutile, the mixed-phase structure of TiO₂ exhibits a superior H₂ production activity to those of pure anatase or rutile phase. The activity of Degussa P25 TiO₂ can be further increased by three to five times by tuning the phase structure through thermal treatment. Moreover, the phase transformation of TiO₂ from anatase to rutile can be controlled by surface modification with Na₂SO₄, resulting in catalysts with activity six times higher than that of P25. High-resolution transmission electron microscopy provided a clear phase-junction image of TiO₂, which showed atomic contact at the interface of the phase junction. The mechanism of phase junctions improving photocatalytic performance was investigated by time-resolved spectroscopic techniques. The charge transfer process across the anatase: rutile phase junction was confirmed by the results of time-resolved IR measurements, and electron transfer from anatase to rutile phases is proposed to occur in mixed-phase TiO₂. These studies on the phase junctions of TiO₂ improve our understanding of photocatalysis and may inspire new ideas for the design of promising photocatalytic systems.

© 2015, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

As a promising strategy to address environmental and en-

ergy issues, photocatalysis is attracting increasing attention [1–3]. Though extensive research on photocatalysis has been conducted, the crucial factors determining the efficiency of

* Corresponding author. Tel: +86-411-84379070; Fax: +86-411-84694447; E-mail: canli@dicp.ac.cn

This work was supported by the National Natural Science Foundation of China (21203185); the National Basic Research Program of China (973 program, 2014CB239403).

DOI: 10.1016/S1872-2067(15)60874-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 0, xxxxxx 2015

photocatalysis are still not well understood. Usually, photocatalytic reactions involve three major steps: (1) generation of electron-hole pairs on a semiconductor by absorption of photons with energy equal to or greater than its bandgap; (2) separation of electron-hole pairs and migration of these charge carriers to the surface of the semiconductor; (3) surface reduction and oxidation reactions involving electrons and holes, respectively, at the semiconductor surface. These three steps correspond to the three crucial factors of light absorption, charge separation and reaction kinetics. Among these, charge separation is the most complicated and important step.

Among semiconductor photocatalysts, TiO_2 is the earliest and most extensively investigated photocatalyst because it is cheap, stable, nontoxic, and environmentally friendly. Since the work by Fujishima and Honda published in 1972 [4], research on TiO_2 has dramatically increased and been extended to applications in environmental purification, self-cleaning, water splitting, CO_2 reduction, organic synthesis, and solar cells. An interesting phenomenon of TiO_2 is that the highest activity is usually not obtained for its two major crystalline forms, anatase and rutile, but from samples with a mixture of anatase and rutile phases. P25, a commercial TiO_2 material with mixed anatase and rutile phases, is the best example of this phenomenon. This produces questions about the intrinsic qualities that affect photocatalytic activity, and the step that the anatase: rutile mixed phase promotes, which need to be answered. Recently, the anatase: rutile mixed phase structures of TiO_2 have been systematically investigated [5–9]. The formation of anatase: rutile surface phase junctions has been confirmed, and is regarded as the main factor inducing the high photocatalytic activity of TiO_2 with mixed phase structure because of its excellent charge separation ability.

In this feature article, some sophisticated techniques and how they are used to characterize the surface phase structure of TiO_2 are first introduced. Then, research on the discovery of anatase: rutile TiO_2 phase junctions and how this concept has directed subsequent investigations is reviewed. Finally, the investigation of phase junctions by time-resolved mid-infrared (IR) spectroscopy to examine the mechanism behind its charge separation ability is discussed. This feature article also covers

some other important factors related to the performance of TiO_2 photocatalysts.

2. Characterization of TiO_2 with different phase structures

As mentioned above, the phase structure of TiO_2 strongly affects its photocatalytic activity. Numerous techniques have been used to characterize the structure of TiO_2 , such as X-ray diffraction (XRD), transmission electron microscopy (TEM), and Raman and Fourier transform infrared (FT-IR) spectroscopies. Herein, three typical spectroscopic techniques used to investigate the phase structure of TiO_2 are introduced. The unique features of these techniques can further our understanding of the structure and even the carrier dynamics of TiO_2 .

In heterogeneous catalysis, reactions take place on the surface of the catalysts. Therefore, the catalytic performance largely depends on the surface properties of the catalyst. Ultra-violet (UV) Raman spectroscopy has recently been proved a powerful tool in materials science [10], mainly because it can efficiently avoid the interference from fluorescence in visible Raman spectra and simultaneously enhance the Raman signal because of its short wavelength and the resonance Raman effect [11]. Here, UV Raman spectroscopy is used to monitor the phase transformation process of TiO_2 [6]. Because TiO_2 strongly absorbs UV light, UV Raman spectroscopy is more sensitive to the surface structure of TiO_2 than XRD and visible Raman spectroscopy. The results obtained from these techniques for the phase transformation process of TiO_2 disagree, which indicates that the surface region of anatase phase detected by UV Raman spectra is more stable at higher temperatures than that in bulk TiO_2 detected by XRD and visible Raman spectra. TEM images show that the phase transformation process of TiO_2 is accompanied by growth of anatase particles. If the surface of anatase particles is covered by dispersed lanthanum oxide (La_2O_3), the phase transformation can be efficiently restrained [6]. Based on these results, a clear phase transformation mechanism for TiO_2 is shown in Fig. 1. With increasing temperature, the phase transformation process of TiO_2 initiates from the surface of integrated anatase particles. The bulk of the new

Can Li (Dalian Institute of Chemical Physics, Chinese Academy of Science) received the **Catalysis Achievement Award (the Dayu Zhang Award) in 2014**, which was presented by The Catalysis Society of China. Professor Can Li received his Ph.D. degree in Physical Chemistry from Dalian Institute of Chemical Physics, Chinese Academy of Sciences, in 1989, and he joined the same institute and was promoted to full professor in 1993. He did postdoctoral research on catalysis and UV Raman spectroscopy at Northwestern University and was visiting professor at Lehigh University, the University of Liverpool, and The Queensland University, and he was awarded the JSPS Professor at Waseda University, Tokyo University of Technology, and Hokkaido University. He was an invited professor at Université Pierre et Marie Curie, Paris VI. He was the President of the International Association of Catalysis Societies (2008–2012). Currently, he is the director of the State Key Laboratory of Catalysis, and the director of the Dalian National Laboratory for Clean Energy (DNL). His research interests include (1) UV Raman spectroscopy and ultrafast spectroscopy; (2) environmental catalysis and green catalysis; (3) heterogeneous asymmetric catalysis; and (4) solar energy utilization based on photocatalysis, photoelectrocatalysis and photovoltaic cells. He has published more than 500 peer-reviewed papers with over 10 000 citations.

Fig. 1. The proposed mechanism for the phase transformation of TiO_2 at elevated temperatures Reprinted with the permission from Ref. [11]. Copyright 2009 Editorial Office of Chinese Journal of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

larger particle then gradually transforms to rutile phase. Finally, the transformation is completed within the entire particle.

Actually, the mechanism of phase transformation of TiO_2 is more complicated than one simple process. The following studies show that phase transformation of TiO_2 is a size-dependent process, where size determines not only the onset transition temperature but also the nucleation performance [7]. UV Raman spectroscopy is used to determine the variation of the surface phase structure of TiO_2 , while XRD is used to examine the variation of the bulk. As depicted in Fig. 2, the phase transformation temperature increases with the initial particle size. For small particles (< 60 nm), rutile nucleates at the interfaces between contacting anatase grains. Conversely, for large particles (> 60 nm), the free surface, interface and bulk of anatase TiO_2 can all function as rutile nucleation sites. UV Raman spectroscopy allows the difference between the surface and bulk transformation processes of TiO_2 to be distinguished.

Although UV Raman spectroscopy can in principle provide more information about surfaces than the bulk for materials that absorb UV light, direct evidence of surface behavior is still needed. Therefore, IR spectra of probe molecules adsorbed on TiO_2 were used to support the results obtained from UV Raman spectroscopy [12]. Such FT-IR spectroscopy is more complicated than UV Raman spectroscopy but undoubtedly a surface

Fig. 2. Proposed mechanisms for the phase transformation of TiO_2 with various particle size (a) smaller than 10 nm; (b) in the range of 10–60 nm; (c) larger than 60 nm. Reprinted with the permission from Ref. [11]. Copyright 2009 Editorial Office of Chinese Journal of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

technique. Because of the different surface properties of anatase and rutile TiO_2 , carbon monoxide (CO) and carbon dioxide (CO_2) can exhibit different adsorption behavior on these two phases. For example, CO is weakly adsorbed on Ti^{4+} ions of the anatase phase, but hardly adsorbed on the rutile phase at room temperature. Moreover, CO_2 mainly adsorbs as bidentate carbonate on the anatase phase, but adsorbs as a bicarbonate species on the rutile phase. Therefore, IR spectra of CO and CO_2 adsorbed on TiO_2 can reveal its surface structure. The IR spectra agreed well with the findings of UV Raman spectra, but differed from those of XRD [12], further confirming that UV Raman spectroscopy is a surface-sensitive technique for TiO_2 .

Photoluminescence (PL) spectroscopy is used to characterize the excited electronic states of materials. For semiconductor materials, PL spectroscopy can supply meaningful information about crystal structures, defect states and charge carrier dynamics. As an indirect wide-band-gap semiconductor, TiO_2 always displays trap-related luminescence bands, while the band-edge luminescence is difficult to observe. The position and intensity of PL from TiO_2 strongly depends on its crystal structure, particle size, dopants, impurities, annealing temperature and atmospheric environment during crystallization, and the ambient temperature and atmosphere during the PL measurements. The main luminescence features of TiO_2 are broad structureless emission bands. Anatase TiO_2 has a visible emission, which is attributed to self-trapped excitons [13], oxygen vacancies [14], defect sites [15], impurities or reduced metal ions [16], etc. Meanwhile, rutile TiO_2 exhibits a near-infrared (NIR) luminescence that is assigned to Cr^{3+} impurities [17], interstitial Ti^{3+} ions [16], intermediate species generated during the photooxidation reaction of water [18], or the intrinsic defects of rutile TiO_2 [19].

The PL characteristics of TiO_2 during phase transformation, in combination with UV Raman spectroscopy, reveal the progression of TiO_2 phase structure [20]. Anatase TiO_2 exhibits a visible emission band centered at about 505 nm, while rutile TiO_2 has a NIR emission band centered at about 835 nm. Comparison of the PL and UV Raman spectra of TiO_2 confirmed that the luminescence band position of TiO_2 is related to its crystalline structure. Namely, the visible emission band is related to anatase structure, while the NIR emission band is associated with rutile structure (Fig. 3). The visible emission of anatase and the NIR emission of the rutile phase both exhibit extremely long lifetimes of up to milliseconds under weak excitation conditions [21]. The power-law decay of the luminescence indicates that PL from both anatase and rutile TiO_2 has a close relation with trap states. The visible emission band of the anatase phase is assigned to donor–acceptor recombination, with mainly oxygen vacancies and hydroxyl groups as donor and acceptor sites, respectively. The NIR luminescence from rutile TiO_2 originates from the recombination of trapped electrons with free holes (Fig. 4).

Based on the relationship between PL bands and the crystalline structure of TiO_2 , PL measurements were used to study the role of trap states of TiO_2 in photocatalysis. The visible emission band of anatase TiO_2 is easily quenched by the deposition of Pt on its surface, while the NIR luminescence band of

Fig. 3. (a) Photoluminescence spectra of TiO₂ calcined at different temperatures. (b) Schematic illustration of the photoluminescence evolution with the phase transformation of TiO₂. Reprinted with the permission from Ref. [20]. Copyright 2007 American Chemical Society.

Fig. 4. Schematic illustration of relaxation processes of the photogenerated carriers in anatase (a) and rutile TiO₂ (b). (A) Electrons quenched to the bottom of the conduction band, (B) carriers captured by traps, (C) thermal excitation from traps, (D) electrons captured directly by deep traps, (E) carriers relax to luminescent sites, (F) nonradiative recombination process. Reprinted with the permission from Ref. [21]. Copyright 2010 Royal Society of Chemistry. Acknowledgements to be used by RSC authors.

rutile TiO₂ is not [20]. The lifetimes of anatase TiO₂ shortened considerably after it was treated under vacuum at 150 °C for 1 h, because of the desorption of H₂O molecules and change of surface hydroxyl groups [21]. In contrast, the luminescence decay profiles of NIR luminescence from rutile TiO₂ were not affected by the same thermal treatment. These results suggest that the trapped carriers in anatase TiO₂ may be involved in the photocatalytic reactions and the slow decay processes may be beneficial for photocatalysis performance, while the trapped carriers in rutile TiO₂ may be less likely to participate in photocatalytic reaction processes.

3. Photocatalytic H₂ generation on TiO₂ with phase junctions

The above characterization results provide us with an opportunity to better understand the phase transformation mechanism and structure of TiO₂, which may in turn allow us to optimize the performance of TiO₂ in photocatalysis by revealing what we can do to improve its activity. TiO₂ samples with different surface and bulk crystalline phases were prepared by thermal treatment of Ti(OH)₄ in air from 500 to 800 °C [5]. The rutile content of the bulk region and anatase content of the

surface region were estimated from visible and UV Raman spectra, respectively. Maximum activity was observed for TiO₂ samples calcined at 700–750 °C, where the bulk of TiO₂ was mostly rutile while the surface was a mixture of anatase and rutile phases. When the calcination temperature was further increased to 800 °C, the anatase phase at the surface region was completely transformed to rutile and correspondingly the photocatalytic activity decreased dramatically. These results show that the presence of anatase phase on the surface of rutile particles can maintain high photocatalytic activity. This led to the concept of surface phase junctions formed between anatase and rutile, which is proposed to facilitate charge separation at the surface of TiO₂. To further clarify this concept, anatase nanoparticles were deposited on rutile particles by a wet-impregnation method followed by thermal treatment. As shown in Fig. 5(a), the photocatalytic activity of the samples increased with the amount of anatase nanoparticles up to a certain threshold. However, when the amount of anatase was increased above the threshold, the activity decreased. This is because too many anatase nanoparticles will decrease the area of phase junctions exposed on the surface of TiO₂. The high-resolution transmission electron microscopy (HRTEM) image in Fig. 5(b) reveals that the loaded anatase nanoparticles

Fig. 5. (a) Photocatalytic activities for H₂ evolution of rutile TiO₂ loaded with increasing amount of anatase nanoparticles. (b) Surface phase-junction formed between anatase and rutile. Reprinted with permission from Ref. [5]. Copyright 2008 Wiley-VCH.

closely contacted with rutile particles to form phase junctions.

Degussa P25 is composed of approximately 80% anatase and 20% rutile phases and is a benchmark type of TiO₂ because of its high photocatalytic activity. The synergistic effect between anatase and rutile phases is considered the origin of its excellent performance. The activity of P25 can be further increased *via* elaborately controlled thermal treatment [8], which transforms P25 to a catalyst with optimized anatase-rutile structure. As shown in Fig. 6, in the photocatalytic reforming of methanol, propanetriol and glucose, the overall activity of P25 can be enhanced up to 3–5 times by thermal treatment. These results also show that the degree of crystallization is not the

major cause of the high photocatalytic activity of thermally treated P25, because further increasing the temperature during thermal treatment did not increase its photocatalytic activity. Therefore, the optimized phase structure obtained by carefully controlled thermal treatment of P25 is the main contributor to the enhancement of its photocatalytic activity.

As the importance of phase junctions has been realized, new methods to prepare TiO₂ that allow phase control have attracted increasing attention [22]. The phase transformation of TiO₂ from anatase to rutile can be restrained by surface modification with Na₂SO₄ [9]. When the content of SO₄²⁻ in TiO₂ was increased from 0 to 3 wt%, the percentage of anatase in the surface region increased from 2% to 75%. It should be mentioned that this method can be used to prepare TiO₂ with different phase structures at the same temperature, which facilitates comparison of these catalysts. Compared with P25, the as-prepared TiO₂-SO₄²⁻ samples showed activities for H₂ production *via* photocatalytic reforming of methanol that were up to six times higher. TEM images revealed that small anatase particles were dispersed on the edge of large rutile particles to form the junction structure. Because the junction formed during the phase transformation process, intimate contact formed between anatase and rutile phases. The example in Fig. 7 shows that the junction is formed at the atomic level, which consequently facilitates charge transfer. Besides Na₂SO₄, other additives such as NaNO₃, NaHCO₃, Na₃PO₄, Na₂SiO₃, and Na₂MoO₄ can also be used to control the phase of TiO₂ [23]. However, the photocatalytic activity of TiO₂ is not only influenced by its phase structure, but also by its surface chemical properties. Therefore, poorer performance might be obtained using certain control agents even when a perfect phase-junction structure is formed.

Since the anatase:rutile phase-junction concept was proposed, it has become a guideline for the preparation of TiO₂ nanoparticles [24,25], nanorod arrays [26], and nanobelts [27]. Similar junctions, such as anatase: TiO₂(B) phase junctions [28–33], and even other semiconductors such as the α:β phase

Fig. 6. (a) Average hydrogen production in photocatalytic reforming methanol, propanetriol and glucose and (b) surface-specific photocatalytic activity for hydrogen production in photocatalytic reforming methanol on Pt/P25-*w*%R photocatalysts (where *w* indicates the rutile content estimated by XRD. For P25-100%R-a, b, c, d photocatalysts, where a, b, c and d indicate different treatment conditions), the surface areas of P25-*w*%R photocatalysts are also displayed (dash dot). Reprinted with the permission from Ref. [8]. Copyright 2011 Elsevier.

Fig. 7. Atomic level contact of anatase: rutile phase-junction. Reprinted with the permission from Ref. [9]. Copyright 2012 Royal Society of Chemistry. Acknowledgements to be used by RSC authors.

junction of Ga_2O_3 , have since been successfully used in photocatalytic reactions [34].

4. Other aspects of TiO_2 -based photocatalysis

Besides phase junctions, some other aspects that affect the performance of TiO_2 photocatalysts, such as cocatalysts, by-products, and reaction environment, should also be considered. Recently, a synergetic effect of dual cocatalysts Pd- IrO_x loaded on TiO_2 in photocatalytic H_2 production reactions was found [35]. Pd and IrO_x particles located close together showed better performance than separated ones, which is quite different from the common situation. Undesired by-product CO obtained from the reactions of photocatalytic H_2 production *via* reforming of methanol or other biomass derivatives is always a problem, because there is a very strict CO limit that must be met for fuel cell applications [36]. CO-suppressing methods such as addition of a small amount of inorganic anions [37], using a smaller size of cocatalyst [38], and controlling the surface acidity of TiO_2 [8,9,23] have been developed.

Meanwhile, the overall water splitting reaction is seldom stoichiometric on TiO_2 . However, it has been found that the addition of Cl^- can facilitate the water splitting reaction [39]. Cl^- can not only trigger O_2 evolution, but also promote the H_2 evolution simultaneously. Besides overall water splitting, TiO_2 -based catalysts can also be used to convert biomass to value-added chemicals. For example, transformation of glycerol to hydroxyacetaldehyde [40] and glucose to sugar aldose [41] have been achieved recently, extending the scope of TiO_2 photocatalysts.

5. Mechanism of charge transfer across an anatase: rutile TiO_2 junction

Anatase: rutile mixed-phase TiO_2 is more active than anatase or rutile TiO_2 in photocatalytic reactions. It has been proposed that anatase: rutile phase junctions are responsible for the improved photoactivity. Such phase junctions are supposed to increase charge separation and then prolong charge lifetime to facilitate photocatalytic reactions. Many researchers are devoted to confirming the role of anatase: rutile phase junctions in photocatalysis both experimentally and theoretically.

Based on electron spin resonance experiments, Hurum et al.

[42] claimed that the electron transfer from rutile to anatase occurred at the transition points between anatase and rutile in Degussa P25, while Komaguchi et al. [43] proposed that photoinduced electron transfer proceeded from anatase to rutile in partially reduced P25. Kawahara et al. [44] suggested that the high photocatalytic activity of P25 was mainly caused by the increase in charge separation efficiency resulting from interfacial electron transfer from anatase to rutile phases based on TEM analysis of patterned $\text{TiO}_2(\text{anatase})/\text{TiO}_2(\text{rutile})$ bilayer-type photocatalysts.

Time-resolved spectroscopic techniques have also been used to study mixed-phase TiO_2 . Carneiro et al. [45] claimed that photogenerated holes were captured by rutile in mixed-phase TiO_2 according to the results of time-resolved microwave conductance spectroscopy of mixed-phase TiO_2 . The kinetics of photoinduced electrons in anatase, rutile, and mixed-phase TiO_2 have also been studied using time-resolved mid-IR spectroscopy [46], which has been proved to be a powerful tool to monitor the kinetics of photogenerated electrons in semiconductor photocatalysts [47]. It was found that the dynamics of the transient mid-IR absorption of anatase and rutile were different. Anatase showed a transient mid-IR absorption signal, whereas rutile did not display any detectable mid-IR absorption on the microsecond time scale. Based on the relationship between initial mid-IR absorption and phase composition, a charge transfer process across the anatase: rutile phase junction was confirmed, and electron transfer from anatase to rutile was proposed to occur in mixed-phase TiO_2 (Fig. 8).

To understand the charge transfer at the interfaces of anatase and rutile phases, the band alignment between anatase and rutile has been calculated theoretically. Kang et al. [48] claimed that the conduction band minimum of anatase was about 0.2 eV higher than that of rutile with similar valence band maxima for anatase and rutile, indicating that electron transfer from anatase to rutile is more likely than *vice versa*. Conversely, Scanlon et al. [49] reported that a type II staggered band alignment of 0.4 eV existed between anatase and rutile with rutile possessing the higher conduction band minimum, which is beneficial for electron transfer from rutile to anatase.

To date, the direction of charge transfer at anatase: rutile phase junctions and its role in photocatalysis are still debated, even though much work has been done using various techniques as discussed above. These points are still debated because charge-transfer behavior strongly depends on both the phase composition and preparation method of mixed-phase TiO_2 . Therefore, further work is still required to understand anatase: rutile junctions in greater detail and optimize the photocatalytic performance of TiO_2 .

6. Conclusions and perspectives

In this feature article, characterization techniques used to investigate the phase structure of TiO_2 were first introduced, including UV Raman, FT-IR and PL spectroscopies. UV Raman spectroscopy and FT-IR spectroscopy of adsorbed probe molecules provided unique evidence for the surface phase struc-

Fig. 8. (a) Transient mid-IR absorption decays of (1) anatase, (2) anatase-rutile mixed phase TiO₂-600, (3) anatase-rutile mixed phase TiO₂-700, and (4) rutile in a vacuum excited by 355 nm laser pulse of 6–8 ns duration. (b) Schematic band structure of anatase and rutile under UV light irradiation. Reprinted with the permission from Ref. [50]. Copyright 2014 American Chemical Society.

ture and phase transformation of TiO₂. PL spectra not only revealed the phase structure of TiO₂ and its emission-related trap states, but also the role of trap states in photocatalysis. The roles of surface phase junctions of TiO₂ in photocatalytic H₂ evolution reactions were then reviewed in detail. The presence of anatase:rutile surface phase junctions can increase the photocatalytic activity of TiO₂-based materials, which is ascribed to efficient charge separation between anatase and rutile phases. Some other factors that can affect the performance of photocatalysts in different ways, such as cocatalysts, by-products, and reaction environment, were then briefly introduced. Finally, the mechanism of charge transfer at anatase:rutile phase junctions was discussed. Electron transfer from anatase to rutile TiO₂ was confirmed by time-resolved mid-IR spectroscopy.

Conversion of solar energy into fuels *via* photocatalysis is considered a promising way to solve energy and environmental issues. As a benchmark photocatalyst, TiO₂ is the most widely investigated semiconductor photocatalyst. However, the majority of research in this field still focuses on environmental photocatalysis, mainly involving the degradation of pollutants such as organic wastes and dyes. Increasing attention is now being paid to fuel generation reactions such as overall water splitting and CO₂ reduction. However, the photocatalytic H₂ production in the presence of sacrificial reagent achieved to date cannot be considered true water splitting. Despite this, these reactions can provide meaningful insights into the mechanism of photocatalytic reactions to aid design of improved photocatalysts.

It should be mentioned that TiO₂ may not be a promising catalyst for photocatalytic water splitting reaction because of its intrinsic properties, such as only UV light absorption. It is also not expected that a great breakthrough on TiO₂ can be achieved in the near future. However, strategies such as extending the light absorption range of TiO₂ and combination with other materials to construct a photocatalyst system may overcome some disadvantages of TiO₂ itself. Furthermore, TiO₂

is still an ideal model for understanding the mechanisms of photocatalytic processes, which will help in the design and construction of more efficient photocatalyst systems. Therefore, research on TiO₂ will continue.

References

- [1] Ma Y, Wang X L, Jia Y S, Chen X B, Han H X, Li C. *Chem Rev*, 2014, 114: 9987
- [2] Kudo A, Miseki Y. *Chem Soc Rev*, 2009, 38: 253
- [3] Yang J H, Wang D G, Han H X, Li C. *Acc Chem Res*, 2013, 46: 1900
- [4] Fujishima A, Honda K. *Nature*, 1972, 238: 37
- [5] Zhang J, Xu Q, Feng Z C, Li M J, Li C. *Angew Chem Int Ed*, 2008, 47: 1766
- [6] Zhang J, Li M J, Feng Z C, Chen J, Li C. *J Phys Chem B*, 2006, 110: 927
- [7] Zhang J, Xu Q, Li M J, Feng Z C, Li C. *J Phys Chem C*, 2009, 113: 1698
- [8] Xu Q, Ma Y, Zhang J, Wang X L, Feng Z C, Li C. *J Catal*, 2011, 278: 329
- [9] Ma Y, Xu Q, Zong X, Wang D G, Wu G P, Wang X, Li C. *Energy Environ Sci*, 2012, 5: 6345
- [10] Fan F T, Feng Z C, Li C. *Chem Soc Rev*, 2010, 39: 4794
- [11] Fan F T, Xu Q, Xia H A, Sun K J, Feng Z C, Li C. *Chin J Catal* (范峰滔, 徐倩, 夏海岸, 孙科举, 冯兆池, 李灿, 催化学报), 2009, 30: 717
- [12] Su W G, Zhang J, Feng Z C, Chen T, Ying P L, Li C. *J Phys Chem C*, 2008, 112: 7710
- [13] Tang H, Berger H, Schmid P E, Levy F, Burri G. *Solid State Commun*, 1993, 87: 847
- [14] Mochizuki S, Shimizu T, Fujishiro F. *Physica B-Condensed Matter*, 2003, 340: 956
- [15] Zhang W F, Zhang M S, Yin Z, Chen Q. *Appl Phys B*, 2000, 70: 261
- [16] Fernandez I, Cremades A, Piqueras J. *Semicond Sci Technol*, 2005, 20: 239
- [17] Grabner L, Stokowski S E, Brower W S. *Phys Rev B*, 1970, 2: 590
- [18] Nakato Y, Akanuma H, Magari Y, Yae S, Shimizu J I, Mori H. *J Phys Chem B*, 1997, 101: 4934
- [19] Poznyak S K, Sviridov V V, Kulak A I, Samtsov M P. *J Electroanal Chem*, 1992, 340: 73
- [20] Shi J Y, Chen J, Feng Z C, Chen T, Lian Y X, Wang X L, Li C. *J Phys Chem C*, 2007, 111: 693

Graphical Abstract

Chin. J. Catal., 2015, 36: 0–0 doi: 10.1016/S1872-2067(15)60874-9

Charge separation promoted by phase junctions in photocatalysts

Yi Ma, Xiuli Wang, Can Li*

Dalian Institute of Chemical Physics, Chinese Academy of Sciences;
Dalian National Laboratory for Clean Energy

Charge separation is an important step in photocatalysis. Construction of phase junctions on semiconductors is a promising strategy to enhance the efficiency of charge separation, inspiring the design of future photocatalysts.

- [21] Wang X L, Feng Z C, Shi J Y, Jia G Q, Shen S A, Zhou J, Li C. *Phys Chem Chem Phys*, 2010, 12: 7083
- [22] Yu F, Wang J, Zhao K, Yin J, Jin C, Liu X. *Chin J Catal* (于福海, 王军虎, 赵昆峰, 尹杰, 金长子, 刘忻, 催化学报), 2013, 34: 1216
- [23] Ma Y, Xu Q, Chong R F, Li C. *J Mater Res*, 2013, 28: 394
- [24] Wang H M, Tan X, Yu T. *Appl Surf Sci*, 2014, 321: 531
- [25] Wang Y, Zhang J, Liu S Y, Yan S, Wu W C, Xu Q, Li C. *China Petrol Process Petrochem Technol*, 2014, 16: 42
- [26] Liu J, Yu X L, Liu Q Y, Liu R J, Shang X K, Zhang S S, Li W H, Zheng W Q, Zhang G J, Cao H B, Gu Z J. *Appl Catal B*, 2014, 158-159: 296
- [27] Pang L X, Wang X Y, Tang X D. *Solid State Sci*, 2015, 39: 29
- [28] Zhu S C, Xie S H, Liu Z P. *J Phys Chem Lett*, 2014, 18: 3162
- [29] Yang D J, Zhao J, Liu H W, Zheng Z F, Adebajo M O, Wang H X, Liu X T, Zhang H J, Zhao J C, Bell J, Zhu H Y. *Chem-Eur J*, 2013, 19: 5113
- [30] Yang D J, Liu H W, Zheng Z F, Yuan Y, Zha J C, Waclawik E R, Ke X B, Zhu H Y. *J Am Chem Soc*, 2009, 131: 17885
- [31] Li W, Liu C, Zhou Y X, Bai Y, Feng X, Yang Z H, Lu L H, Lu X H, Chan K Y. *J Phys Chem C*, 2008, 112: 20539
- [32] Lin C H, Chao J H, Liu C H, Chang J C, Wang F C. *Langmuir*, 2008, 24: 9907
- [33] Kuo H L, Kuo C Y, Liu C H, Chao J H, Lin C H. *Catal Lett*, 2007, 113: 7
- [34] Wang X, Xu Q, Li M R, Shen S, Wang X L, Wang Y C, Feng Z C, Shi J Y, Han H X, Li C. *Angew Chem Int Edit*, 2012, 51: 13089
- [35] Ma Y, Chong R F, Zhang F X, Xu Q, Shen S, Han H X, Li C. *Phys Chem Chem Phys*, 2014, 16: 17734
- [36] Bellows R J, Marucchi Soos E P, Buckley D T. *Ind Eng Chem Res*, 1996, 35: 1235
- [37] Wu G P, Chen T, Zong X, Yan H J, Ma G J, Wang X L, Xu Q, Wang D G, Lei Z B, Li C. *J Catal*, 2008, 253: 225
- [38] Wu G P, Chen T, Su W G, Zhou G H, Zong X, Lei Z B, Li C. *Int J Hydrogen Energy*, 2008, 33: 1243
- [39] Huang L, Li R G, Chong R F, Liu G, Han J F, Li C. *Catal Sci Technol*, 2014, 4: 2913
- [40] Chong R F, Li J, Zhou X, Ma Y, Yang J X, Huang L, Han H X, Zhang F X, Li C. *Chem Commun*, 2014, 50: 165
- [41] Chong R F, Li J, Ma Y, Zhang B, Han H X, Li C. *J Catal*, 2014, 314: 101
- [42] Hurum D C, Agrios A G, Gray K A, Rajh T, Thurnauer M C. *J Phys Chem B*, 2003, 107: 4545
- [43] Komaguchi K, Nakano H, Araki A, Harima Y. *Chem Phys Lett*, 2006, 428: 338
- [44] Kawahara T, Konishi Y, Tada H, Tohge N, Nishii J, Ito S. *Angew Chem Int Edit*, 2002, 41: 2811
- [45] Carneiro J T, Savenije T J, Moulijn J A, Mul G. *J Phys Chem C*, 2011, 115: 2211
- [46] Shen S, Wang X L, Chen T, Feng Z C, Li C. *J Phys Chem C*, 2014, 118: 12661
- [47] Chen T, Wu G P, Feng Z C, Hu G S, Su W G, Ying P L, Li C. *Chin J Catal* (陈涛, 吴国鹏, 冯兆池, 胡庚申, 苏伟光, 应品良, 李灿, 催化学报), 2008, 29: 105
- [48] Kang J, Wu F M, Li S S, Xia J B, Li J B. *J Phys Chem C*, 2012, 116: 20765
- [49] Scanlon D O, Dunnill C W, Buckeridge J, Shevlin S A, Logsdail A J, Woodley S M, Catlow C R A, Powell M J, Palgrave R G, Parkin I P, Watson G W, Keal T W, Sherwood P, Walsh A, Sokol A A. *Nat Mater*, 2013, 12: 798
- [50] Shen S, Wang X L, Chen T, Feng Z C, Li C. *J Phys Chem C*, 2014, 118: 12661

表面相结结构在促进光催化电荷分离中的应用

马 艺^{a,b}, 王秀丽^{a,b}, 李 灿^{a,b,*}

^a中国科学院大连化学物理研究所催化基础国家重点实验室, 辽宁大连116023

^b洁净能源国家实验室(筹), 辽宁大连116023

摘要: 二十世纪八十年代以来, 特别是近十年, 光催化研究在利用可再生能源太阳能的道路上飞速发展。越来越多的研究表明, 相

结结构的构筑是有效提高半导体光催化剂性能的重要策略。其中, TiO_2 作为重要的模型光催化剂, 其相关研究成果呈现出指数增长的趋势。本综述围绕 TiO_2 模型光催化剂, 主要介绍 TiO_2 表面相结的研究成果, 包括 TiO_2 表面相的表征、锐钛矿:金红石 TiO_2 相结用于光催化产氢研究、 TiO_2 相结在光催化中作用的最新认识等。

在表征方面, 通过表面灵敏的紫外拉曼光谱研究了 TiO_2 相变过程中表面相结构的变化, 结合可见拉曼以及XRD表征揭示了 TiO_2 独特的相变过程, 即相变始于锐钛矿粒子的界面处, 小粒子逐渐团聚为大粒子, 致其相变从大粒子体相开始最终扩展到整个粒子。使用 CO , CO_2 探针红外光谱, 根据锐钛矿和金红石表面吸附物种的差异, 进一步证实了锐钛矿:金红石表面相结结构, 为紫外拉曼光谱的表面表征特性提供坚实证据。同时, 利用发光光谱观察到锐钛矿晶相的可见发光带和金红石晶相的近红外发光带, 并基于此给出了 TiO_2 材料表面相结结构的荧光表征新方法。此外荧光光谱还提供了锐钛矿、金红石相中载流子动力学信息, 揭示了束缚态在光催化中的作用。

在光催化应用方面, 观察到混相结构 TiO_2 较单独锐钛矿及金红石相具有更高的光催化产氢活性, 通过在较大金红石颗粒上负载纳米锐钛矿粒子, 证明了相结结构在提高光催化活性中的核心作用, 并首次提出了锐钛矿:金红石表面异相结结构概念, 推断其对电荷分离的促进作用是最终提高反应活性的原因。之后将此概念应用到改善商品 TiO_2 (P25)光催化活性中, 通过可控热处理精细调控P25的表面相结构, 在光催化重整生物质衍生物产氢实验中, 成功将P25光催化产氢活性提高3–5倍。之后发展了新的 TiO_2 表面控制方法, 通过加入 Na_2SO_4 等相变控制剂, 延缓了 TiO_2 从锐钛矿向金红石的相变过程, 在较高温度下实现 TiO_2 相结结构的调控, 最终可将P25光催化重整甲醇制氢的活性提高6倍, 同时通过高分辨电镜清晰观察到锐钛矿:金红石相结的原子层生长接触。

在相结作用机理方面, 多种时间分辨光谱技术以及理论计算被用作探索锐钛矿:金红石相结处的电子转移机理。通过时间分辨红外光谱对 TiO_2 表面相结结构作用的研究, 特别是利用锐钛矿、金红石不同的瞬态吸收光谱特征, 证明了锐钛矿:金红石相结处的载流子转移过程, 存在锐钛矿向金红石的电子转移过程。模型光催化剂 TiO_2 相结的研究成果, 加深了对光催化机理的认识, 促进新型高效光催化体系的设计合成。

关键词: 光催化; 表面相结; 电荷分离; 太阳能; 二氧化钛

收稿日期: 2015-04-09. 接受日期: 2015-04-22. 出版日期: 2015-00-20.

*通讯联系人. 电话: (0411) 84379070; 传真: (0411) 84694447; 电子信箱: canli@dicp.ac.cn

基金来源: 国家自然科学基金(21203185); 国家重点基础研究发展计划(973计划, 2014CB239403).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).

For Author Index:

MA Yi, WANG Xiuli, LI Can