available at www.sciencedirect.com

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

Minireview

Engineering vacancies for solar photocatalytic applications

Mingce Long^{a,b,*}, Longhui Zheng^a^a School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China^b Key Laboratory for Thin Film and Microfabrication of the Ministry of Education, Shanghai Jiao Tong University, Shanghai 200240, China

ARTICLE INFO

Article history:

Received 29 October 2016

Accepted 18 November 2016

Published 5 April 2017

Keywords:

Oxygen vacancy

Hydrogenated treatment

Photocatalysis

Chemisorption

Titanium vacancy

ABSTRACT

In contrast to the exploration of novel photocatalytic materials, vacancy engineering of traditional photocatalysts comprising earth-abundant elements represents an effective method for enhancing photocatalytic performance without introducing alien elements. This minireview analyzes the latest progress in engineering vacancies in photocatalysts, remarks on state-of-the-art characterization techniques for vacancies, and reviews the formation chemistry and fundamental benefits of anion and cation vacancies in typical photocatalysts. Although knowledge of these vacancies is increasing, challenges remain in this field, and possible further research is therefore also discussed.

© 2017, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Photocatalysis represents an economical process for the conversion of solar energy for use in a broad range of applications, including environmental remediation, energy and fuel production. Intensive efforts have been undertaken to develop novel photocatalysts with improved performance in terms of broadband absorption, charge migration and reaction pathway efficiency. Strategies frequently applied in the design of photocatalysts include engineering of their nanostructures (nanoarchitectures and exposure of high energy facets [1,2]), their interfaces and surfaces (nanocomposites with matched energy band positions and Ohmic contacts [3,4]) and their band structures (doping and solid solutions [5]). Among these strategies, tailoring the vacancies in the lattices of traditional photocatalysts, such as graphitic-C₃N₄ (g-C₃N₄), titanium, tungsten or bismuth oxide-based compounds, has enormous potential for achieving high photocatalytic performance in diverse applica-

tions.

Vacancies, or point defects, are prevalent in all semiconductor materials because the conductivity of these materials originates from their inherently nonstoichiometric compositions. All chemical functions of materials, such as catalysis, adsorption or sensing behaviors, are dominated by their electronic structures and surface properties. The vacancies in a material play a critical role in the manipulation of the electronic structure, surface acidic and basic properties, dissociative adsorption, charge transportation, reactivity and other chemical properties of the material, and this has been known for a long time through both theoretical calculations and experimental observations [6–9]. However, the earliest study that directly discussed the influence of vacancies on photocatalytic performance was carried out about two decades ago by Yanagida et al. [10,11]. In their reports, sulfur vacancies on the surface of CdS were shown to promote the photocatalytic reduction of CO₂ and the selective production of CO [10,11]. Studies on oxygen vacancies (V_O) in

* Corresponding author. Tel: +86-21-54747354; Fax: +86-21-54740825; E-mail: long_mc@sjtu.edu.cn

This work was supported by the National Natural Science Foundation of China (21377084) and Special Fund for Agro-scientific Research in the Public Interest (201503107).

DOI: 10.1016/S1872-2067(17)62821-3 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 4, April 2017

photocatalysis increased dramatically in the 2000s and, accompanied by the development of visible light-driven TiO_2 catalysts [12], accelerated further after promising results were obtained from black TiO_2 and subsequent research [13–15]. Recently, vacancy-rich photocatalysts containing other vacancies besides V_O have been developed. These vacancies include anion vacancies such as sulfur [16], halogen [17–19], and nitrogen vacancies [20–23]; cation vacancies such as bismuth [24,25], titanium [26,27], and carbon vacancies [28,29]; and combinations of both anion and cation vacancies [24,30].

Vacancy engineering provides a number of notable advantages for high performance photocatalysts: (1) an approach to manipulating the compositions of catalysts without the introduction of impurities; (2) simultaneous tuning of the concentrations and types of vacancies in the bulk or surface lattice to meet requirements closely related to photocatalytic performance (e.g., narrow band gaps, enhanced optical absorption and improved charge separation); (3) a promising low-cost method using simple synthetic techniques to modify traditional photocatalysts composed of earth abundant elements, in contrast to modification using complicated procedures and rare elements; (4) a possible method to simultaneously influence thermocatalysis and photocatalysis by enabling surface chemisorption.

The critical functions of V_O on the photocatalytic performance of TiO_2 have been frequently reviewed [31–34]. In this minireview, we will introduce and discuss the latest progress regarding a broader range of anion and cation vacancies, and focus on their characterization, formation chemistry and fundamental benefits for photocatalysis.

2. Vacancy characterization

It is essential to characterize the existence, concentration and type of vacancies present in a material. The existence of vacancies can be confirmed by measuring the stoichiometric ratios of elements using elemental analysis, X-ray fluorescence (XRF), X-ray photoelectron spectroscopy (XPS) or Rietveld refinement methods. Vacancies can also be directly observed by scanning tunneling microscopy (STM) [8], or indirectly characterized by catholuminescence [35], photoluminescence [36], electron spin resonance (ESR) [12], or other techniques. ESR is a typical measurement used to confirm the existence of V_O , which exhibits a signal at $g = 2.004$. A signal at $g = 1.998$ was observed in p-type TiO_2 and attributed to titanium vacancies (V_{Ti}) [26]. However, these methods cannot distinguish among the different types of vacancies or determine their concentrations.

Positron annihilation spectroscopy is a powerful technique for investigating defects in materials, and can provide information on vacancy types and their relative concentrations [24,37,38]. Three positron lifetimes (τ_1 , τ_2 and τ_3) and their relative intensities were obtained from the positron lifetime spectra of TiO_2 and CeO_2 nanoparticles. The positron lifetimes, from shortest to longest, were attributed to small V_O in the bulk, larger clusters of V_O on the surface, and large voids in the material, respectively. The relative concentration of bulk de-

fects to surface defects can be estimated from the ratio of the intensities of the two corresponding peaks (τ_1 and τ_2). It was thus shown that a lower relative concentration of bulk vacancies in a TiO_2 crystal corresponds to a higher photocatalytic performance because of improved charge separation [37]. In contrast, there is a positive relationship between the presence of large V_O clusters on the surface of CeO_2 and the reducibility and reactivity of the photocatalyst [38]. Moreover, four positron lifetime components were observed in the spectra of ultrathin BiOCl nanosheets and nanoplates [24]. The shortest of these (~ 250 ps) was attributed to single isolated bismuth vacancies (V_{Bi}), and the second shortest (~ 325 ps) to Bi^{3+} -oxygen vacancy associates. According to their relative intensities, the associated vacancies were dominant in ultrathin BiOCl nanosheets [24]. However, despite the success of positron annihilation in defect characterization, further knowledge of the various vacancies is required, and more advanced techniques are also desirable for a better understanding of the fundamental relationships between vacancies in the lattices of photocatalysts and their photocatalytic properties.

3. Anion vacancies

The anion vacancies in photocatalytic materials are most often oxygen, nitrogen, sulfur, and halogen vacancies. Owing to the instability of sulfide photocatalysts, there are very few reports on photocatalysts containing sulfur vacancies [16]. In contrast, V_O in metal oxides have frequently been investigated because most photocatalysts are n-type metal oxide nanoparticles, in which the conductivity originates from V_O . Fig. 1 shows the oxygen and titanium vacancies in a defect-containing TiO_2 lattice without dopants.

Although V_O occur naturally in materials, higher density V_O can be generated by aliovalent ion doping (e.g., nitrogen doping) [39], formation of two-dimensional ultrathin materials [24], solid-state chemical reduction by NaBH_4 [40–42], plasma treatment [12], addition of chelation precursors with carboxylic acids [43], hydrothermal reduction with graphene oxide [44], or annealing in an inert or reducing gas atmosphere (e.g.,

Fig. 1. Schematic representation of a defect-containing TiO_2 lattice without dopants: V_O/V_{Ti} , oxygen/titanium vacancy; Ti^{3+} , Ti^{3+} ion in a titanium lattice site (quasi-free electron); O^- , O^- ion in an oxygen lattice site (quasi-free hole); $\text{Ti}^{3+}/\text{Ti}^{4+}$, $\text{Ti}^{3+}/\text{Ti}^{4+}$ ion in an interstitial site (modified from Ref. [31]).

hydrogen) [13,45]. Solid-state chemical reduction with NaBH_4 is a facile method, and the resulting colored products feature an amorphous shell with V_0 [40]. However, hydrogen treatment (HT) has also attracted considerable attention after the pioneering work by Mao's group [13]. In fact, HT has been used historically to tailor the optical and electric properties of single crystal oxide materials [46]. This method was applied to TiO_2 nanoparticles and found to be effective in improving their photooxidation performance in as early as 2003 [47]. However, it is only since the exciting results with black TiO_2 that HT has become an important area of research and been explored extensively for the treatment of TiO_2 , $\alpha\text{-Fe}_2\text{O}_3$, WO_3 , BiVO_4 , and other photocatalysts with various nanoarchitectures [48–51]. After HT, both high density V_0 and the resulting defect disorders are generated on the surface layer of the nanomaterials. Some results have indicated that the change in the properties of the materials was mainly caused by the high density of surface V_0 trap sites [36]. However, others have suggested that both V_0 and the surface structural disorder play a synergistic role, in which V_0 mainly exists in the bulk of the lattice, but the surface structural disorder is almost stoichiometric [52].

The improved photocatalytic performance after HT has been ascribed to two main effects. First, after HT, the optical absorption of the photocatalysts was greatly extended to the near infrared (NIR) range (~ 1200 nm). The visible light absorption was attributed to the localized mid-bandgap V_0 occupied by an unpaired electron in an antibonding orbital at a surface site [36]. These V_0 states are located at 0.7–1.0 eV below the conduction band (CB) (Fig. 2(A) [12,46,52]). Therefore, the electrons can be excited from the valence band (VB) and localized V_0 states to the CB or from the VB to localized V_0 states by lower energy photons, and this results in a considerably broadened absorption. Second, a high V_0 density causes an increase in the donor density in the photocatalysts because the V_0 function as electron donors. After HT, the donor density in

TiO_2 nanowires was three orders of magnitudes higher than the density before HT [14]. This increased donor density not only improves the charge transport in the lattice, but also promotes electron transfer at the interface because the upward shift of the Fermi level toward the CB as a result of the increased donor density augments the band bending. However, the considerable improvement in the photoactivity was mainly ascribed to the enhanced performance in the UV region, but not in the visible light region [14,15]. This was confirmed by time-resolved fluorescence (TRF) and femtosecond transient absorption (TA) spectroscopy, which indicated that the charge carriers slowly decayed on UV excitation, but showed considerable recombination on visible light irradiation [34]. It remains a challenge to effectively utilize the absorption in the vis-NIR range, despite the fact that the integration of photo- and thermocatalysis has great potential for maximizing the use of low energy photons [15,51,53–55]. Besides the two benefits mentioned above, HT has also been found to improve the photostability of WO_3 by V_0 production and formation of substoichiometric WO_{3-x} , which was highly resistant to reoxidation and dissolution induced by peroxy species [49].

More importantly, vacancies function as active sites and enhance the adsorption of reactants (e.g., oxygen, water, or organic molecules), promote electron migration from materials to adsorbates, and can even directly participate in specific photocatalytic or photochemical reactions. One fundamental feature of V_0 -rich oxides is their ability to chemisorb oxygen species, which also contributes to the stabilization of V_0 . Engineering of nondopant V_0 in CeO_2 is an important method for promoting the catalytic oxidation of CO by providing coordinatively unsaturated sites [56]. Interestingly, the inverse reaction, selective photochemical conversion of CO_2 to CO, was also found to be mediated by V_0 , which facilitated electron migration from CeO_2 to the chemically adsorbed and preactivated CO_2 molecules. Simultaneously, owing to the consumption of V_0

Fig. 2. (A) Schematic of the nanoparticle structure and band structure models for (a) TiO_2 and (b) black TiO_2 [52]; (B) Band structure models for defect-deficient WO_3 (D- WO_3) and defect rich WO_3 (R- WO_3) [45].

in the reaction, CO₂ photoreduction slowed down and was eventually terminated [57].

Based on their behavior in both photo- and thermocatalysis, vacancies could bridge them and enable a synergistic effect for the utilization of solar energy, even in the vis-NIR range. V_O were observed as electron-transfer mediators in the thermocatalytic decomposition of CO₂ on mesoporous WO₃, in which V_O were consumed to produce C/CO [51]. A synergistic photo/thermocatalytic process with a high selectivity for the conversion of CO₂ into CH₄ was accordingly developed using this V_O-rich WO₃ [51], which represents an important strategy for the combination of photo- and thermocatalysis to realize CO₂ reduction. However, it would be more desirable to achieve combined photo/thermocatalysis using only solar energy, thus avoiding external energy inputs. Recently, highly selective aerobic coupling of amines to the corresponding imines was achieved under NIR illumination (> 700 nm) on V_O-rich WO₃ nanosheets (Fig. 2(B)) [45]. The low energy photons were used to generate superoxide radicals (O₂^{•-}) in a chemisorbed state at V_O sites. This was achieved by electron transfer from V_O to the chemisorbed oxygen as a result of the strong electronic coupling between them. Band excitation at the reduction level for free O₂/O₂^{•-} (−0.33 V vs. NHE) is not required in this process. Surprising stability was obtained owing to the recovery of surface V_O in the reaction between O₂^{•-} and neighboring activated benzylamine. The utilization of low energy photons is thus a promising strategy for the selective conversion of substrates using V_O.

The presence of nitrogen vacancies (V_N) is an intrinsic property of nonstoichiometric nitride photocatalysts, such as Ta₃N₅ [58,59] and metal-free g-C₃N₄ [20,22]. V_N-containing g-C₃N₄ was first produced by controlling the polycondensation temperature of dicyandiamide in an open container, and promoted the photodecomposition of RhB [22]. In this material, the number of short- and long-lived charge carriers was decreased and increased, respectively. This suppressed charge-carrier recombination was attributed to the trapping of charge carriers in the localized electronic states of V_N, and the accordingly reduced spatial overlap. Thermal treatment in a hydrogen or nitrogen atmosphere, sulfur doping, and microwave synthesis have also been reported to produce g-C₃N₄ with V_N [20,21,23,60–62]. Compared with traditional modification of only the surface layer of photocatalysts, homogeneous modification features a complete change in the electronic structure of the photocatalyst, and can be realized by using layered nanostructured precursors [63]. Hydrogenation of the layered structural melon was used for the homogeneous self-modification of g-C₃N₄ with V_N, and this material had a greatly reduced band gap (2.03 eV) [20]. However, a reduced redox ability was expected owing to the band shifts in this modified g-C₃N₄. In addition to its enhanced performance in photocatalytic oxidation and water splitting, V_N-containing g-C₃N₄ also shows great potential in nitrogen fixation [23,61,62]. As well as promoting interfacial charge transfer from the catalyst to the adsorbed N₂, the V_N in g-C₃N₄ can also serve as selective chemical adsorption sites for the adsorption, activation and reduction of N₂ because of their similar proper-

ties to those of N₂-imprinted polymers [23]. The use of V_N-containing nitride photocatalysts with a negative conduction band may also be a promising strategy for the reduction of nitrogen-containing compounds.

Halogen vacancies (V_H) are easily generated in bismuth oxyhalides, which have unique layered structures consisting of positively charged [Bi₂O₂]²⁺ slabs and interleaved negative halogen slabs with nonbonding interactions along the *c*-axis [17,19]. Because of the weak van der Waals interactions, halogen ions can diffuse out of the layered structure by calcination, or be replaced by other halogen ions through ion exchange in the solution or solid state. Generally, bismuth oxyhalides possess diverse halogen-deficient crystal phases, which can be obtained simply by tuning the precursor ratios or/and calcining at relatively high temperatures. However, we recently observed that Bi₇O₉I₃ containing iodine vacancies could be obtained by calcination below the phase transition temperature [17,18]. The iodine deficiency was indicated by the decrease in the Bi/I atomic ratio from 2.36 to 2.80 after calcination at 350 °C. It was found that shallow V_H improve the carrier transport properties, whereas deep V_H have the opposite effect [64]. Homogeneous modification of the bismuth oxyiodides with iodine vacancies is expected because of their layered structure, and the whole band gap increased from 2.04 to 2.31 eV after calcination at 350 °C. Moreover, the enlargement of the band gap was confirmed by theoretical calculations, which also indicated the downward shift of the band position and the transition of the semiconductor behavior from p to n type. These changes are expected to increase the oxidation ability of the photogenerated holes, improve the electron mobility, and accordingly contribute to an enhanced photooxidation performance. However, although V_H can easily be created in layered structural bismuth oxyhalides, there are concerns about the stability of these compounds, especially in the aqueous phase, which greatly restricts their application in water purification.

4. Cation vacancies

There are very few reports on cation vacancies in the field of photocatalysis. In contrast to anion vacancies and cation interstitials, which are shallow donors, cation vacancies are shallow acceptors and always induce p-type conductivity. The benefits of V_{Ti} in TiO₂ are expected to include: (1) increase in the electrical conductivity of the ionic components; (2) increase in the mobility of electrons and interfacial transfer of charge carriers, which suppresses recombination and enhances the photocatalytic activity; (3) generation of room-temperature ferromagnetism; and (4) provision of surface active sites for water adsorption and formation of active complexes, and the corresponding enhanced photoactivity in water splitting [65–67]. Some experimental results have indicated that the band gap of TiO₂ is independent of the V_{Ti} concentration [26,65]. Theoretical calculations have also suggested that V_{Ti} would not generate new states in the band gap. However, the presence of V_{Ti} in TiO₂ nanosheets caused a slight downward shift in the VB maximum and a considerable downward shift in the CB minimum; thus resulting in a net narrowed band gap [67].

It is difficult to generate stable cation vacancies in traditional n-type oxides, for example, V_{Ti} in TiO_2 . Nowotny et al. [68] found that the transport kinetics of V_{Ti} in TiO_2 were much slower than those of V_O and titanium interstitials, and accordingly resulted in quasi-quenches of the V_{Ti} species. Therefore, V_{Ti} are expected to be restricted to the surface or near-surface regions, which could be one of the reasons for the difficulty in synthesizing V_{Ti} -containing TiO_2 . However, p-type TiO_2 containing V_{Ti} can be engineered in the following ways: (1) generation of defect disorder by calcination above 1573 K [69]; (2) prolonged oxidation ($p(O_2) = 75$ kPa) at temperatures above 1273 K [27,65,70]; (3) incorporation of aliovalent dopant ions [71,72]; and (4) controlled calcination of lamellated titanium glycerolate [26]. According to Rietveld refinement results, high concentrations of titanium defects were present in iron-doped TiO_2 [71] or TiO_2 with a particle size of several nanometers [73]. Moreover, the concentration of V_{Ti} increased with increasing iron content and decreased with increasing particle size, but remained stable when the vacancies were balanced by hydroxyl ions or protons in the lattice. Recently, Zou's group [26,74] developed stable p-type ZnO and TiO_2 with cation vacancies by calcination of the glycerolate precursors. These p-type oxides are formed through the generation of oxygen-rich structures during the decomposition of interlayer organic groups at high temperatures, which creates distortion and thus generates cation vacancies in the lattice. This method represents a promising way of producing photocatalysts with cation vacancies. However, although the generation of V_{Ti} has been greatly improved and the benefits have been theoretically discussed, the characterization of these vacancies, and their stability and effects in photocatalytic interfacial processes are far from clear.

In contrast to V_N -containing g- C_3N_4 , g- C_3N_4 containing carbon vacancies (V_C) can be developed by thermally treating bulk g- C_3N_4 in an NH_3 or Ar atmosphere [28,29]. In addition, V_C -induced room-temperature ferromagnetism of g- C_3N_4 has been confirmed [29]. The dramatically improved photocatalytic hydrogen evolution was attributed to the higher donor density and the notably longer lifetime of the charge carriers. Moreover, V_C -containing g- C_3N_4 displayed considerably higher H_2O_2 production than both pure g- C_3N_4 and V_N -containing g- C_3N_4 [28]. This was not only attributed to the enhanced optical absorption and higher donor density of V_C -containing g- C_3N_4 , but also to its improved O_2 adsorption, the promotion of electron transfer for O_2 reduction, and most importantly, the transformation of O_2 reduction into a two-electron process, in which the amino groups around the V_C had an indispensable role. This suggests that cation vacancies in g- C_3N_4 have great potential for certain photocatalytic applications.

Bismuth oxide-based photocatalysts have attracted considerable attention, owing to their narrow band gap and high activity in the visible light range, as well as the relative abundance of elemental bismuth [18,75]. Bismuth vacancies (V_{Bi}) are also ubiquitous in nonstoichiometric bismuth-oxide compounds [24,25,76,77]. Various bulk defects, including V_O and V_{Bi} , were observed in ball-milled $BiPO_4$ [76]. These defects degraded the photocatalytic performance of $BiPO_4$, but were easily removed

by reflux or calcination. Recently, a stable V_{Bi} -containing $Bi_6S_2O_{15}$ was developed by increasing the ratio of the sulfate to bismuth sources in the hydrothermal synthesis [25]. The resulting catalyst was characterized as core-shell nanowires with a disordered shell layer containing a high concentration of V_{Bi} . These vacancies contributed to the efficient separation of charge carriers, and reduced the size of the band gap by elevating the whole band and producing shallow surface states above the VB.

The components and concentration of vacancies in the surface lattice are facet-dependent; therefore, two-dimensional materials with different facets and thicknesses have different vacancy compositions. In general, V_{Bi} dominate on the surface of $BiOCl$ nanoplates. However, when the thickness of the nanoplates was reduced to 2.7 nm, Bi^{3+} -oxygen vacancy associates were observed to dominate on the surface of these ultrathin $BiOCl$ nanosheets. This resulted in a strongly negatively charged surface and a smaller band gap, and the separation of photogenerated charges was promoted [24]. Specific facets of ultrathin photocatalytic materials are exposed on light irradiation or chemical reaction; this could provide a delicate strategy for tuning the available vacancies for photocatalytic applications.

5. Conclusion and prospect

The latest progress in this field provides a greater fundamental understanding of the relationship between a diverse range of vacancies and their related photocatalytic properties, and the growing knowledge has been successfully applied to realize advanced photocatalytic processes for water splitting, N_2 fixation, H_2O_2 production, decontamination, organic synthesis, and CO_2 reduction, among others. Vacancy-rich photocatalysts display extended optical absorption, facilitate charge separation and enhance the selective chemisorption of reactants, which all result in improved photoreactivity. However, further efforts are required to deal with the following open problems or challenges. (1) More powerful characterization techniques are needed to reveal the existence, format and concentration of the vacancies. This is essential for the understanding the association between vacancies and photocatalytic performance. Currently, we cannot easily discern the different types of vacancies, let alone the format of the vacancies in the lattice surface, subsurface or bulk. (2) Current knowledge on the formation chemistry and fundamental functions of anion or cation vacancies in photocatalytic processes is insufficient and far from clear, especially for those photocatalysts containing both donor and acceptor vacancies [24,30]. (3) It is desirable that vacancies in photocatalysts retain their function and remain unchanged for long periods of time. However, although we can obtain stable vacancy-rich compounds, and we understand the dependence of stability on the vacancy format according to theoretical calculations [78], we do not yet know the exact factors that control the stability of vacancies, or how to manipulate the raw materials and synthetic methods to tune the format of the vacancies. It is expected that increasing attention on vacancies in photocatalysts and the development of vacan-

cy-engineering techniques will mean that their use in solar photocatalytic applications will be greatly accelerated in the near future.

References

- [1] G. Liu, J. C. Yu, G. Q. Lu, H. M. Cheng, *Chem. Commun.*, **2011**, 47, 6763–6783.
- [2] A. Kubacka, M. Fernandez-Garcia, G. Colon, *Chem. Rev.*, **2012**, 112, 1555–1614.
- [3] H. J. Li, Y. Zhou, W. G. Tu, J. H. Ye, Z. G. Zou, *Adv. Funct. Mater.*, **2015**, 25, 998–1013.
- [4] X. P. Chen, Z. X. Zhang, L. N. Chi, A. K. Nair, W. F. Shangguan, Z. Jiang, *Nano-Micro. Lett.*, **2016**, 8, 1–12.
- [5] A. Kudo, H. Kato, I. Tsuji, *Chem. Lett.*, **2004**, 33, 1534–1539.
- [6] U. Diebold, *Surf. Sci. Rep.*, **2003**, 48, 53–229.
- [7] G. S. Li, L. P. Li, J. Zheng, *Sci. China Chem.*, **2011**, 54, 876–886.
- [8] F. Esch, S. Fabris, L. Zhou, T. Montini, C. Africh, P. Fornasiero, G. Comelli, R. Rosei, *Science*, **2005**, 309, 752–755.
- [9] Y. Kang, Q. Leng, D. L. Guo, D. Z. Yang, Y. P. Pu, C. G. Hu, *Nano-Micro Lett.*, **2015**, 7, 2150.
- [10] H. Fujiwara, H. Hosokawa, K. Murakoshi, Y. Wada, S. Yanagida, T. Okada, H. Kobayashi, *J. Phys. Chem. B*, **1997**, 101, 8270–8278.
- [11] H. Fujiwara, H. Hosokawa, K. Murakoshi, Y. Wada, S. Yanagida, *Langmuir*, **1998**, 14, 5154–5159.
- [12] I. Nakamura, N. Negishi, S. Kutsuna, T. Ihara, S. Sugihara, E. Takeuchi, *J. Mol. Catal. A*, **2000**, 161, 205–212.
- [13] X. B. Chen, L. Liu, P. Y. Yu, S. S. Mao, *Science*, **2011**, 331, 746–750.
- [14] G. M. Wang, H. Y. Wang, Y. C. Ling, Y. C. Tang, X. Y. Yang, R. C. Fitzmorris, C. C. Wang, J. Z. Zhang, Y. Li, *Nano Lett.*, **2011**, 11, 3026–3033.
- [15] Y. H. Hu, *Angew. Chem. Int. Ed.*, **2012**, 51, 12410–12412.
- [16] X. Y. Zhang, Z. Zhao, W. W. Zhang, G. Q. Zhang, D. Qu, X. Miao, S. R. Sun, Z. C. Sun, *Small*, **2016**, 12, 793–801.
- [17] M. C. Long, P. D. Hu, H. D. Wu, Y. Y. Chen, B. H. Tan, W. M. Cai, *J. Mater. Chem. A*, **2015**, 3, 5592–5598.
- [18] M. C. Long, P. D. Hu, H. D. Wu, J. Cai, B. H. Tan, B. X. Zhou, *Appl. Catal. B*, **2016**, 184, 20–27.
- [19] J. Li, Y. Yu, L. Zhang, *Nanoscale*, **2014**, 6, 8473–8488.
- [20] P. Niu, L. C. Yin, Y. Q. Yang, G. Liu, H. M. Cheng, *Adv. Mater.*, **2014**, 26, 8046–8052.
- [21] X. L. Wang, W. Q. Fang, Y. F. Yao, P. R. Liu, Y. Wang, H. M. Zhang, H. J. Zhao, H. G. Yang, *RSC Adv.*, **2015**, 5, 21430–21433.
- [22] P. Niu, G. Liu, H. M. Cheng, *J. Phys. Chem. C*, **2012**, 116, 11013–11018.
- [23] G. H. Dong, W. K. Ho, C. Y. Wang, *J. Mater. Chem. A*, **2015**, 3, 23435–23441.
- [24] M. L. Guan, C. Xiao, J. Zhang, S. J. Fan, R. An, Q. M. Cheng, J. F. Xie, M. Zhou, B. J. Ye, Y. Xie, *J. Am. Chem. Soc.*, **2013**, 135, 10411–10417.
- [25] J. Wang, W. J. Jiang, D. Liu, Z. Wei, Y. F. Zhu, *Appl. Catal. B*, **2015**, 176, 306–314.
- [26] S. B. Wang, L. Pan, J. J. Song, W. B. Mi, J. J. Zou, L. Wang, X. W. Zhang, *J. Am. Chem. Soc.*, **2015**, 137, 2975–2983.
- [27] M. K. Nowotny, P. Bogdanoff, T. Dittrich, S. Fiechter, A. Fujishima, H. Tributsch, *Mater. Lett.*, **2010**, 64, 928–930.
- [28] S. N. Li, G. H. Dong, R. Hailili, L. P. Yang, Y. X. Li, F. Wang, Y. B. Zeng, C. Y. Wang, *Appl. Catal. B*, **2016**, 190, 26–35.
- [29] Q. H. Liang, Z. Li, Z. H. Huang, F. Y. Kang, Q. H. Yang, *Adv. Funct. Mater.*, **2015**, 25, 6885–6892.
- [30] Q. P. Wu, F. Huang, M. S. Zhao, J. Xu, J. C. Zhou, Y. S. Wang, *Nano Energy*, **2016**, 24, 63–71.
- [31] M. K. Nowotny, L. R. Sheppard, T. Bak, J. Nowotny, *J. Phys. Chem. C*, **2008**, 112, 5275–5300.
- [32] X. Y. Pan, M. Q. Yang, X. Z. Fu, N. Zhang, Y. J. Xu, *Nanoscale*, **2013**, 5, 3601–3614.
- [33] J. Nowotny, M. Abdu, T. Bak, M. A. Idris, M. Ionescu, K. Prince, M. Z. Sahdan, K. Sopian, M. A. M. Teridi, W. Sigmund, *Chem. Soc. Rev.*, **2015**, 44, 8424–8442.
- [34] H. N. Cui, H. Liu, J. Y. Shi, C. Wang, *Int. J. Photoenergy*, **2013**, 364802/1–364802/17.
- [35] L. J. Zhang, S. Wang, C. Lu, *Anal. Chem.*, **2015**, 87, 7313–7320.
- [36] D. A. Wheeler, Y. C. Ling, R. J. Dillon, R. C. Fitzmorris, C. G. Dudzik, L. Zavodivker, T. Rajh, N. M. Dimitrijevic, G. Millhauser, C. Bardeen, Y. Li, J. Z. Zhang, *J. Phys. Chem. C*, **2013**, 117, 26821–26830.
- [37] M. Kong, Y. Z. Li, X. Chen, T. T. Tian, P. F. Fang, F. Zheng, X. J. Zhao, *J. Am. Chem. Soc.*, **2011**, 133, 16414–16417.
- [38] X. W. Liu, K. B. Zhou, L. Wang, B. Y. Wang, Y. D. Li, *J. Am. Chem. Soc.*, **2009**, 131, 3140–3141.
- [39] C. Di Valentin, G. Pacchioni, A. Selloni, S. Livraghi, E. Giamello, *J. Phys. Chem. B*, **2005**, 109, 11414–11419.
- [40] H. Q. Tan, Z. Zhao, M. Niu, C. Y. Mao, D. P. Cao, D. J. Cheng, P. Y. Feng, Z. C. Sun, *Nanoscale*, **2014**, 6, 10216–10223.

Graphical Abstract

Chin. J. Catal., 2017, 38: 617–624 doi: 10.1016/S1872-2067(17)62821-3

Engineering vacancies for solar photocatalytic applications

Mingce Long *, Longhui Zheng
Shanghai Jiao Tong University

Engineering of vacancies represents an effective strategy to boost photocatalytic processes for solar energy applications. This mini-review analyzes the latest progress in the engineering of anion and cation vacancies in the field of photocatalysis.

- [41] H. Q. Tan, Z. Zhao, W. B. Zhu, E. N. Coker, B. S. Li, M. Zheng, W. X. Yu, H. Y. Fan, Z. C. Sun, *ACS Appl. Mater. Interfaces*, **2014**, 6, 19184–19190.
- [42] Z. Zhao, X. Y. Zhang, G. Q. Zhang, Z. Y. Liu, D. Qu, X. Miao, P. Y. Feng, Z. C. Sun, *Nano Res.*, **2015**, 8, 4061–4071.
- [43] X. J. Wang, Y. Zhao, F. T. Li, L. J. Dou, Y. P. Li, J. Zhao, Y. J. Hao, *Sci. Rep.*, **2016**, 6, 24918.
- [44] M. C. Long, Y. L. Qin, C. Chen, X. Y. Guo, B. H. Tan, W. M. Cai, *J. Phys. Chem. C*, **2013**, 117, 16734–16741.
- [45] N. Zhang, X. Y. Li, H. C. Ye, S. M. Chen, H. X. Ju, D. B. Liu, Y. Lin, W. Ye, C. M. Wang, Q. Xu, J. F. Zhu, L. Song, J. Jiang, Y. J. Xiong, *J. Am. Chem. Soc.*, **2016**, 138, 8928–8935.
- [46] D. C. Cronemeyer, *Phys. Rev.*, **1959**, 113, 1222–1226.
- [47] H. Liu, T. A. Ma, X. Z. Li, W. Z. Li, M. Wu, X. H. Bao, *Chemosphere*, **2003**, 50, 39–46.
- [48] A. P. Singh, N. Kodan, A. Dey, S. Krishnamurthy, B. R. Mehta, *Int. J. Hydrogen Energy*, **2015**, 40, 4311–4319.
- [49] G. M. Wang, Y. C. Ling, H. Y. Wang, X. Y. Yang, C. C. Wang, J. Z. Zhang, Y. Li, *Energy Environ. Sci.*, **2012**, 5, 6180–6187.
- [50] Z. K. Zheng, B. B. Huang, J. B. Lu, Z. Y. Wang, X. Y. Qin, X. Y. Zhang, Y. Dai, M. H. Whangbo, *Chem. Commun.*, **2012**, 48, 5733–5735.
- [51] L. C. Wang, Y. Wang, Y. Cheng, Z. F. Liu, Q. S. Guo, M. N. Ha, Z. Zhao, *J. Mater. Chem. A*, **2016**, 4, 5314–5322.
- [52] A. Naldoni, M. Allieta, S. Santangelo, M. Marelli, F. Fabbri, S. CapPELLI, C. L. Bianchi, R. Psaro, V. Dal Santo, *J. Am. Chem. Soc.*, **2012**, 134, 7600–7603.
- [53] X. Y. Pan, Y. J. Xu, *ACS Appl. Mater. Interfaces*, **2014**, 6, 1879–1886.
- [54] B. Han, W. Wei, L. Chang, P. F. Cheng, Y. H. Hu, *ACS Catal.*, **2016**, 6, 494–497.
- [55] B. Han, Y. H. Hu, *J. Phys. Chem. C*, **2015**, 119, 18927–18934.
- [56] N. J. Lawrence, J. R. Brewer, L. Wang, T. S. Wu, J. Wells-Kingsbury, M. M. Ihrig, G. H. Wang, Y. L. Soo, W. N. Mei, C. L. Cheung, *Nano Lett.*, **2011**, 11, 2666–2671.
- [57] D. Jiang, W. Z. Wang, E. P. Gao, S. M. Sun, L. Zhang, *Chem. Commun.*, **2014**, 50, 2005–2007.
- [58] J. J. Wang, J. Y. Feng, L. Zhang, Z. S. Li, Z. G. Zou, *Phys. Chem. Chem. Phys.*, **2014**, 16, 15375–15380.
- [59] A. Dabirian, R. van de Krol, *Appl. Phys. Lett.*, **2013**, 102, 033905/1–033905/4.
- [60] J. L. Chen, Z. H. Hong, Y. L. Chen, B. Z. Lin, B. F. Gao, *Mater. Lett.*, **2015**, 145, 129–132.
- [61] S. J. Li, X. Chen, S. Z. Hu, Q. Li, J. Bai, F. Wang, *RSC Adv.*, **2016**, 6, 45931–45937.
- [62] H. Q. Ma, Z. Y. Shi, S. Li, N. Liu, *Appl. Surf. Sci.*, **2016**, 379, 309–315.
- [63] G. Liu, L. Z. Wang, H. G. Yang, H. M. Cheng, G. Q. Lu, *J. Mater. Chem.*, **2010**, 20, 831–843.
- [64] H. Shi, M. H. Du, *Phys. Rev. B*, **2014**, 90, 174103/1–174103/6.
- [65] T. Bak, M. K. Nowotny, L. R. Sheppard, J. Nowotny, *J. Phys. Chem. C*, **2008**, 112, 13248–13257.
- [66] J. Nowotny, T. Bak, M. K. Nowotny, L. R. Sheppard, *J. Phys. Chem. B*, **2006**, 110, 18492–18495.
- [67] C. H. Sun, T. Liao, G. Q. Lu, S. C. Smith, *J. Phys. Chem. C*, **2012**, 116, 2477–2482.
- [68] M. K. Nowotny, T. Bak, J. Nowotny, *J. Phys. Chem. B*, **2006**, 110, 16302–16308.
- [69] M. Radecka, M. Rekas, *J. Am. Ceram. Soc.*, **2002**, 85, 346–354.
- [70] M. K. Nowotny, T. Bak, J. Nowotny, C. C. Sorrell, *Phys. Stat. Sol. (B)*, **2005**, 242, R88–R90.
- [71] J. A. Wang, R. Limas-Ballesteros, T. Lopez, A. Moreno, R. Gomez, O. Novaro, X. Bokhimi, *J. Phys. Chem. B*, **2001**, 105, 9692–9698.
- [72] J. Y. Cao, Y. J. Zhang, L. Q. Liu, J. H. Ye, *Chem. Commun.*, **2013**, 49, 3440–3442.
- [73] I. E. Grey, N. C. Wilson, *J. Solid. State. Chem.*, **2007**, 180, 670–678.
- [74] L. Pan, S. B. Wang, W. B. Mi, J. J. Song, J. J. Zou, L. Wang, X. W. Zhang, *Nano Energy*, **2014**, 9, 71–79.
- [75] R. A. He, S. W. Cao, P. Zhou, J. G. Yu, *Chin. J. Catal.*, **2014**, 35, 989–1007.
- [76] Y. Y. Zhu, Q. Ling, Y. F. Liu, H. Wang, Y. F. Zhu, *Appl. Catal. B*, **2016**, 187, 204–211.
- [77] J. Xu, Y. R. Teng, F. Teng, *Sci. Rep.*, **2016**, 6, 32457.
- [78] C. J. Zhang, A. Michaelides, D. A. King, S. J. Jenkins, *Phys. Rev. B*, **2009**, 79, 075433/1–075433/11.

用于太阳光催化反应的空位工程

龙明策^{a,b,*}, 郑龙辉^a

^a上海交通大学环境科学与工程学院, 上海200240

^b上海交通大学, 薄膜与微细技术教育部重点实验室, 上海200240

摘要: 空位是一种点缺陷, 广泛存在于非化学计量比的半导体光催化材料的晶格中。不同于其它研制复杂结构和组成的新型光催化剂的策略, 空位工程设计方法可以基于传统的, 由丰量元素组成的光催化剂进行表面或体相晶格的空位调控, 以获得宽谱响应的高效光催化材料。该方法具有不引入杂质元素、成本低廉、方法简便等优点, 且通过表面化学吸附作用可以耦合热催化和光催化过程, 以实现增强的选择性光催化反应。

空位的表征技术包括元素分析, 扫描隧道显微镜, 催化发光, 光致发光或顺磁共振等直接和间接观测技术。近期正电子湮没谱发展成为一种研究空位的重要手段。这种方法可以区分不同位置(如体相和表面)和不同形式(如单一空位或联合空位)的空位并确定其相对浓度, 从而用于探索空位影响光催化活性的规律。

氧、氮、硫和卤素原子空位均属于阴离子空位。氢化处理法可以在光催化剂晶格中形成高浓度氧空位, 并导致纳米材料表面层的晶格混乱。处理后光催化剂的光学吸收拓展到近红外区, 电子给体浓度大大提高, 促进了电子输运和界面电荷的迁移与分离; 然而, 可见光区的吸收对增强的光催化活性没有贡献。氧空位还可以作为活性位点吸附和解离反应物, 促进电子从催化剂到吸附质间的转移, 甚至直接参与到光催化和光化学反应中。富含氧空位的 WO_3 可以耦合热催化和光催化反应促进 CO_2 的选择性还原, 或者利用近红外光活化分子氧并选择性氧化胺。氮空位是含氮的n型半导体光催化材料的本质属性。石墨氮化碳中的氮空位有助于促进电荷分离, 同时可以作为化学吸附位用于选择性吸附, 活化和还原氮气, 因

此富含氮空位的光催化剂在还原含氮化合物方面具有应用潜力。由于卤素原子在层状卤氧化铋的层间以较弱的范德华力存在,该类化合物容易形成卤原子空位。通过热处理碘氧化铋可以获得活性增强的含碘空位化合物。空位的出现导致带隙变宽和价带下移,光生空穴氧化能力提高,从而获得更好的光催化活性。

传统的n型半导体光催化剂中难以形成阳离子空位。理论研究表明,含阳离子空位的 TiO_2 具有一系列优点,包括电子传输性能提高,载流子复合受到抑制等。并且钛空位可以作为表面活性位促进水的吸附和解离,从而提高光解水效率。含钛空位的p型 TiO_2 可以通过焙烧甘油化的前驱体制备,钛空位的出现使得光解水和催化降解有机物活性均大幅提高。含碳空位的石墨氮化碳不仅表现出增强的光催化活性,同时能够提高氧吸附并促进两电子还原氧气产生 H_2O_2 的反应过程。铋空位能够有效提高铋基光催化剂 BiPO_4 和 $\text{Bi}_6\text{S}_2\text{O}_{15}$ 的活性。二维纳米材料的晶面和厚度可以影响表面空位的组成和浓度。 BiOCl 纳米片的表面是以铋空位为主,而超薄的 BiOCl 纳米片则是以铋氧联合空位为主,从而表现更优异的光催化活性。

最近研究者在含空位的高性能光催化剂制备以及性能调控规律方面取得了长足进展,今后还将继续发展先进的表征技术,进一步研究空位的调控和稳定化手段,并全面理解空位对光催化反应的影响基本规律。空位工程将在半导体光催化技术中发挥更加重要的作用。

关键词: 氧空位; 氢化处理; 光催化; 化学吸附; 钛空位

收稿日期: 2016-10-29. 接受日期: 2016-11-18. 出版日期: 2017-04-05.

*通讯联系人. 电话: (021)54747354; 传真: (021)54740825; 电子邮箱: long_mc@sjtu.edu.cn

基金来源: 国家自然科学基金(21377084); 农业部公益性行业专项(201503107).

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>).

《催化学报》为被国际期刊退稿的高质量论文开辟绿色通道

我们注意到,国内一些高质量、原创性的研究工作在投稿到国际期刊上时,经常因语言和写作问题等非科学因素而被退稿和拖延发表,甚至会失去原创知识产权,这个损失是巨大的,也是非常可惜的!

众所周知,按国际学术界的共识,获得论文的首发权并保证拥有研究工作的原创性不在于论文发表在哪个刊物(只要是国际ISSN挂号的),而在于谁第一时间抢先发表了工作。

为了保护作者工作的原创性和首发知识产权,《催化学报》编委会为具有一定原创性的论文提供快速发表的绿色通道。对于投到国际著名期刊(如Science, Nature, Energy & Environmental Science, Journal of the American Chemical Society, Angewandte Chemie International Edition, ACS Catalysis和Journal of Catalysis等)上催化论文的退稿,如果其创新性较强,学术质量较高,仅仅是因为语言和文章写作原因而被退稿,《催化学报》会安排其在最近一期上抢时间发表;如果文章原创性较好,不存在学风问题,但有一些理论观点的争议、实验现象暂时无法得到完美的理论解释,或者需要进一步补充相关实验数据等,本刊主编、副主编也会协助作者尽快修改和发表相关工作。

对于国际著名相关期刊的退稿,作者需将相应的审稿意见及意见答复等材料一并提交到本刊,以加快论文的处理速度。

《催化学报》编辑部