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Minireview

Engineering vacancies for solar photocatalytic applications

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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.

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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

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photocatalysis increased dramatically in the 2000s and, accompanied by the development of visible light-driven TiO₂ catalysts [12], accelerated further after promising results were obtained from black TiO₂ 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 TiO₂ 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 TiO₂ 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 TiO₂ and CeO₂ 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 TiO₂ 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 CeO₂ 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 Bi³⁺-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 TiO₂ 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 NaBH₄ [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.,

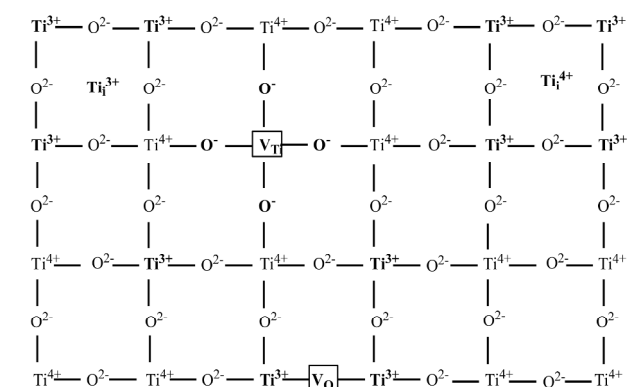


Fig. 1. Schematic representation of a defect-containing TiO₂ lattice without dopants: V_O/V_{Ti}, oxygen/titanium vacancy; Ti³⁺, Ti³⁺ ion in a titanium lattice site (quasi-free electron); O⁻, O⁻ ion in an oxygen lattice site (quasi-free hole); Ti³⁺/Ti⁴⁺, Ti³⁺/Ti⁴⁺ ion in an interstitial site (modified from Ref. [31]).

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