



# Enhanced photocatalytic activity by bulk trapping and spatial separation of charge carriers: A case study of defect and facet mediated TiO<sub>2</sub>



Zengxia Pei<sup>a,b</sup>, Sunxian Weng<sup>b</sup>, Ping Liu<sup>b,\*</sup>

<sup>a</sup> Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong SAR, PR China

<sup>b</sup> State Key Laboratory of Photocatalysis on Energy and Environment, Research Institute of Photocatalysis, Fuzhou University, Fuzhou 350002, PR China

## ARTICLE INFO

### Article history:

Received 19 April 2015

Received in revised form 15 June 2015

Accepted 21 June 2015

Available online 30 June 2015

### Keywords:

Defect self-doping

Facet

TiO<sub>2</sub>

Water splitting

## ABSTRACT

Revealing the interplay between composition and structure of a given photocatalyst allows in-depth understanding of the photocatalytic mechanism and also presents as an effective way to optimise the photocatalytic activity. In this work, by studying the property and performance of defect and facet mediated rutile TiO<sub>2</sub> synthesized via a facile oxidation reaction, we demonstrated that the abundant self-doped defects can not only render visible response to the reduced TiO<sub>2</sub> but also suppress the prompt recombination of the charge carriers through bulk trapping, while the {111}–{110} facet couples can induce the spatial separation of the e–h pairs. A synergistic effect between the defects and the facets was observed in the co-mediated TiO<sub>2</sub>, and its performance of hydrogen liberation was enhanced by a factor of 18 under simulated solar light compared with referenced commercial rutile, consequently. The present work sheds new light on how the composition and structure of a material can be finely tuned and work synergistically to achieve a much boosted performance.

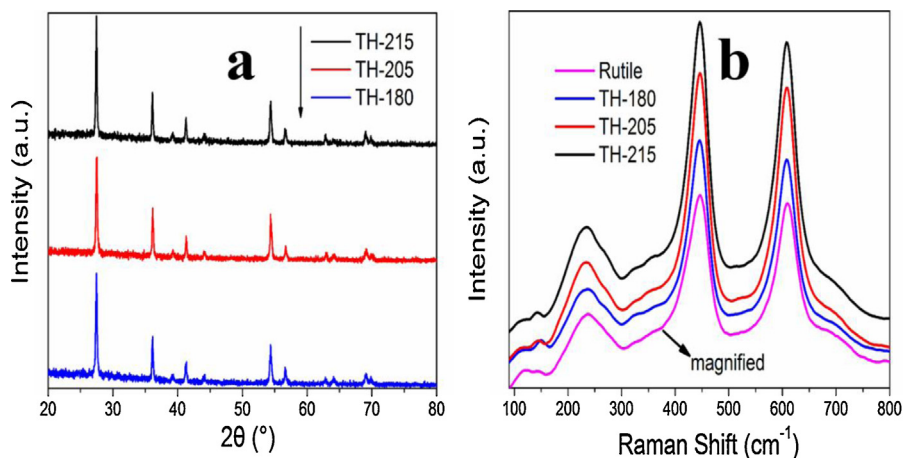
© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

The interplay between the composition and structure on the properties of a certain material has long been a significant theme of material science. While the components lay the foundation for properties, the structure of the material can always dramatically affect its performance. Conversely, rational design of the two factors is also indispensable for specific applications of a material [1,2]. Recent progress in photocatalytic materials has well witnessed this interrelationship, particularly in TiO<sub>2</sub> based photocatalyst [2,3]. In fact, among various materials that have been developed as photocatalyst, titanium dioxide is one of the most promising and popular stuffs owing to its merits like abundance, nontoxicity and high stability. Despite so, the overall efficiency of TiO<sub>2</sub> is restricted to a great extent by the light absorption limitation due to the intrinsic wide band gap and the spontaneous rapid recombination of photogenerated charge carriers within the semiconductor nature [4,5]. Therefore, further works addressing these two barriers are indeed needed for the widespread practical applications of titania.

In the perspective of composition of TiO<sub>2</sub>, Ti<sup>3+</sup> and/or oxygen vacancy (V<sub>o</sub>) self-doping, which is developed with respect to heteroatom (including metal and non-metal atoms) doping, has aroused intense research interest in the past a few years [6–12]. Just resembles that in the heteroatom doping methods, the self-doped defects can also introduce extra electronic states in the forbidden band [6–8]. The concentration of the defects, however, should theoretically be high enough to create a new band that eventually leads to the visible light absorption of the TiO<sub>2</sub> [6,7,10]. Up to now, a series of works [7–12] have reported deliberate introduction of Ti<sup>3+</sup> and/or V<sub>o</sub> defects into the bulk lattice of TiO<sub>2</sub> based on either reduction or oxidation methods, and the resulting materials exhibit good photoactivity and stability under visible light. Nevertheless, in many cases, the performance under UV light, of which the incident light possesses higher energy and is much more efficient for TiO<sub>2</sub>, is always neglected. Actually, the visible light absorption does not necessarily lead to higher overall performance as defects are sometimes reported to act as annihilation sites especially in the bulk of TiO<sub>2</sub> [13,14]. For example, Liu et al. [14] reported that their Ti<sup>3+</sup> self-doped TiO<sub>2</sub> showed negligible activity under both UV and visible light though the sample exhibited broad visible light absorption. Leshuk et al. [15] found that the performance of their hydrogenated black TiO<sub>2</sub> under simulated solar light was deteriorated by the introduction of bulk V<sub>o</sub> species. Hence, it is still

\* Corresponding author. Fax: +86 591 8377 9239.  
E-mail address: [liuping@fzu.edu.cn](mailto:liuping@fzu.edu.cn) (P. Liu).



**Fig. 1.** (a) XRD patterns of the hydrothermal products; (b) Raman spectra of different hydrothermal samples as well as commercial rutile. The spectrum intensity of the referenced rutile is magnified.

necessary to explore other facile and effective strategies to prepare defect-mediated  $\text{TiO}_2$  with wide spectral response, high activity as well as good stability.

On the other hand, the fate of the photogenerated charge carriers can be remarkably affected by the architecture of a given photocatalyst [3]. Facet, as a typical micro structure aspect of crystal, has become a research hotspot since distinct atom arrangements and electronic band structures of different facets will influence the transfer pattern of carriers [3,16–20]. Specifically, photoinduced electron and hole can be separately driven to different crystal facets due to the subtle distinction of coupled facets, which thus facilitate the charge separation [16,18]. In this regard, some recent studies have been well conducted in  $\text{BiVO}_4$  and anatase  $\text{TiO}_2$  systems [18,19]. For rutile, the presence of high energy facets like  $\{111\}$  and  $\{001\}$  can boost the photocatalytic activity, and it is demonstrated that the  $\{111\}/\{001\}$  and  $\{110\}$  facets of rutile can potentially act as oxidative and reductive sites, respectively [16,21]. Recently, Zuo et al. reported that, in comparison to irregular powder  $\text{TiO}_2$  polymorphs, the rutile with  $\{111\}$ – $\{110\}$  facet couples and bulk  $\text{Ti}^{3+}$  species showed enhanced performance in hydrogen liberation from water under visible light [10]. Notwithstanding, so far there is still the dearth of the interplay between the defect and facet, their separate and cooperative roles in boosting the photocatalytic activity of  $\text{TiO}_2$ , especially under full solar light irradiation.

In the present work, we studied the underlying interplay of the defect and facet by studying the properties of  $\text{Ti}^{3+}$  self-doped rutile which has explicit facets. A facile oxidation based synthesis process was rationally adopted in hoping of stabilizing  $\text{Ti}^{3+}$  ions by thermodynamically spontaneous oxidation of  $\text{Ti}^{2+}$  species from  $\text{TiH}_2$  in HCl solution. The products showed a distinct absorption within the whole visible light region as well as some near-infrared light. By simply varying the hydrothermal temperature,  $\text{Ti}^{3+}$  self-doped rutile with explicit  $\{111\}$  and  $\{110\}$  facets was obtained. It was demonstrated that the abundant defects can not only render visible light response to the reduced  $\text{TiO}_2$  but also suppress the prompt recombination of the charge carriers, while the  $\{111\}$ – $\{110\}$  facet couples can induce the spatial separation of the e–h pairs. A synergistic effect between the defects and the facets was observed and as a result, the performance of hydrogen liberation of the optimised sample was enhanced by a factor of 18 under simulated solar light compared with commercial rutile. The results of this work suggest that the defect composition and the facet structure of a photocatalyst can work cooperatively and be rationally tuned for a much boosted overall activity.

## 2. Experimental section

### 2.1. Synthesis of reduced $\text{TiO}_2$

Typically, 400 mg  $\text{TiH}_2$  (Alfa Aesar, 325 mesh) powders were dispersed into 25 mL 2 M HCl aqueous solution. The suspension was then transferred into a 50 mL Teflon autoclave and kept at different temperatures (180, 205 and 215 °C) for 12 h. After cooling naturally to room temperature, the precipitate was collected and washed with deionized water for several times until the ionic strength was less than 10 ppm. The clean samples were dried under vacuum overnight. The samples were denoted as TH-x, where x stands for the corresponding hydrothermal temperature.

### 2.2. Photodeposition of Pt and $\text{PbO}_2$ particles

The selective depositions of Pt and  $\text{PbO}_2$  species were carried out to determine the preferred transfer routes of the charge carriers. For Pt deposition, 100 mg of TH-215 sample was dispersed into 100 mL deionized water, and then a certain volume of  $\text{H}_2\text{PtCl}_6$  was added to ensure the nominal weight ration of Pt– $\text{TiO}_2$  being 3 wt%. The solution was irradiated by full-solar light for 1 h. The powders were then centrifuged and dried at 60 °C in vacuum. This Pt-deposited  $\text{TiO}_2$  was then dispersed into 100 mL water again, and 150 mg  $\text{Pb}(\text{NO}_3)_2$  was dissolved into the mixture followed by irradiation for another 3 h under solar simulator. The precipitate was then separated out and dried for further analyses.

### 2.3. Characterization

Crystal structure identification was performed using Bruker D8 X-ray diffractometer (XRD) with  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15418$  nm) operating at 40 kV and 40 mA. Raman scattering measurements were performed with a multichannel modular triple Raman system (Renishaw Co.) with confocal microscopy at room temperature using the 532 nm laser. A 50× microscope objective lens was used for focusing the laser beam and collection of the scattered light. Scanning electron microscope (SEM) images was obtained with an FEI Nova NanoSEM 230 field-emission scanning electron microscope. Microstructures and morphologies were investigated using TecnaiG2 F20 S-TWIN (FEI company) Transmission electron microscopy (TEM) with a field emission gun at 200 kV and the accessory Energy dispersive X-ray spectroscopy (EDS) was used to determine to composite elements. Diffuse reflection spectra (DRS) of the samples were recorded on a Varian Cary-500 spectrophotometer and  $\text{BaSO}_4$  was used as a reference. X-ray

Download English Version:

<https://daneshyari.com/en/article/45264>

Download Persian Version:

<https://daneshyari.com/article/45264>

[Daneshyari.com](https://daneshyari.com)