Applied Surface Science 420 (2017) 399–406

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

# Oxygen vacancies confined in $SnO_2$ nanoparticles for desirable electronic structure and enhanced visible light photocatalytic activity

Yuanjie Yang[a,b], Yuhua Wang[a,b,*], Shu Yin[c]

[a] Director of the Key Laboratory for Special Function Materials and Structure Design of the Ministry of Education, Lanzhou University, Lanzhou 730000, PR China
[b] Department of Materials Science, School of Physical Science and Technology, Lanzhou University, Lanzhou 730000, PR China
[c] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

ARTICLE INFO

*Article history:*
Received 24 March 2017
Received in revised form 16 May 2017
Accepted 20 May 2017
Available online 22 May 2017

*Keywords:*
Tin oxide
Oxygen vacancy
Electronic structure
Photocatalytic activity

ABSTRACT

Electronic structure in principle determines the light absorbance, charge transfer and separation, and consequently, photocatalytic property of a photocatalyst. Herein, we report rutile $SnO_2$ with a desirable electronic structure that exhibits a narrowed bandgap and an increased valence band width resulted from the introduction of homogeneous oxygen vacancies. XPS, Raman, ESR and PL spectra demonstrate the homogeneous oxygen vacancies confined in $SnO_2$ nanoparticles. Moreover, the first principle calculations theoretically reveal the desirable electronic structure. The narrowed bandgap further contributes to extended light absorption range and the increased valence band width leads to efficient charge transfer and separation, hence facilitating the visible light photoreactivity. As a result, the defected $SnO_2$ exhibits a superior visible light photocatalytic activity. More strikingly, the photodegration of methyl orange (MO) is completely accomplished within only 20 min under $\lambda \geq 420$ nm. Briefly, this work both experimentally and theoretically indicates that homogeneous oxygen vacancies confined in $SnO_2$ nanoparticles lead to the optimized electronic structure and, consequently, the remarkable visible light photocatalytic activity. This could open up an innovative strategy for designing potentially efficient photocatalysts.

## 1. Introduction

Photocatalytic technology continues to be an exceedingly active approach to efficient environmental remediation and renewable production of clean energy because of its environmentally friendly nature and high-efficiency properties [1–7]. Besides seeking new highly active photocatalysts, the research and development of innovative strategies for remarkably improving photocatalytic activities of potentially known photocatalysts are still significant challenges [8]. There are two mainly limitations of photocatalytic efficiency: (1) light absorption; (2) charge transfer and separation, both of which are intrinsically controlled by the electronic structure [8–10]. Therefore, it is highly desirable to engineer appropriate electronic structure of the photocatalyst for efficient photocatalytic activity [9,11].

For the semiconductor photocatalysts, anionic p states and cationic d states contribute to valence band maxima and conduction band minima, respectively [9]. Moreover, the p states gives intrinsically smaller slope compared to d states at the extrema, hence the holes in the valence band have much smaller mobility than electrons in the conduction band, which further leads to a lower probability or a smaller population of surface reaching holes than that of electrons under light irradiation [9,12,13]. As most photocatalytic activities are controlled by holes involved in oxidizing half reactions, the photocatalytic performance is largely compromised [9,14]. Furthermore, it should be pointed out that the mobility of holes is intrinsically determined by the valence band (VB) width: the wider the VB, the higher the mobility of holes [8]. Broadening the VB width seems to be a good way to directly change the imbalanced mobility of holes and electrons, which facilitates efficient hole transfer and charge separation [15–18].

Considering the fact that these two fundamental limitations in a photocatalyst are rarely addressed simultaneously and require further promotion for high-performance photocatalytic reactivity [1,10], one possible solution is proposed to create unique electronic structures through the up-shift of valence band maximum (VBM) to narrow the band gap for extended light absorption range

---

* Corresponding author at: Director of the Key Laboratory for Special Function Materials and Structure Design of the Ministry of Education, Lanzhou University, Lanzhou 730000, PR China.

*E-mail address:* wyh@lzu.edu.cn (Y. Wang).

http://dx.doi.org/10.1016/j.apsusc.2017.05.176
0169-4332/© 2017 Published by Elsevier B.V.

and broaden the VB width for efficient charge transfer and separation. Herein, by the introduction of abundant oxygen vacancies, we demonstrate the electronic structure tune in rutile $SnO_2$ with excellent economic attraction, physical and chemical stability and material abundance [19,20]. It is noteworthy that $SnO_2$ is rarely reported as a visible-light photocatalyst because of its large band gap nature [19,21]. Notably, the effect of oxygen vacancies on the photocatalytic property of $SnO_2$ has never been investigated yet. For the doping of oxygen vacancies, the surface oxygen vacancies contribute to the formation of localized states in the bandgap, whereas the homogeneous oxygen vacancies confined in bulk material lead to a new band state above the top of original VB, which further gives rise to the narrowing of band gap and broadening of VB width [8,22,23].

Moreover, studies reveal that oxygen vacancy defects are related to the sizes and shapes of $SnO_2$ nanocrystals [24–27]. Kar et al. reported that the $SnO_2$ nanoparticles exhibit a higher concentration of oxygen vacancy and hence give a significantly higher photocatalytic activity compared to those of $SnO_2$ nanospheres and nanorods [27]. In this work, we synthesize $SnO_2$ nanoparticles with abundant oxygen vacancies via a one-pot hydrothermal process. Moreover, we experimentally confirm the homogeneous oxygen vacancies confined in $SnO_2$ nanoparticles and the corresponding electronic structure. Combining with the first principle calculation, we theoretically verify the desirable electronic structure of defected $SnO_2$. Furthermore, the photocatalytic property of $SnO_2$ with homogeneous oxygen vacancies is firstly revealed in this work. As expected, the defected $SnO_2$ shows a remarkable photocatalytic activity under visible light irradiation, indicating its considerable potential for application in solar energy conversion. Thus, this work provides an efficient approach to optimizing electronic structures and promoting visible light photoreactivitivities of wide band-gap catalysts.

## 2. Experimental

### 2.1. Preparation of defected $SnO_2$ and normal $SnO_2$

A general procedure proceeded as follows. 2 g $SnCl_2{\cdot}2H_2O$ was dissolved in a mixture of 60 ml deionized water and 2 ml hydrochloric acid (HCl, 37%) with stirring. Then, the homogeneous solution was transferred into a 100 ml Teflon-lined stainless steel autoclave, kept at 180 °C for 24 h, and allowed to cool to room temperature naturally. Afterward, the obtained precipitates were collected by centrifugation and washed several times with deionized water and ethanol. After drying at 60 °C in air for 12 h, the yellow defected $SnO_2$ nanoparticles were obtained. Normal $SnO_2$ was prepared by calcining the defected $SnO_2$ at 900 °C for 4 h in air.

### 2.2. Characterization

The crystallinity of $SnO_2$ was obtained from an X-ray diffractometer (XRD, Rigaku D/Max-2400) by using Cu-Ka radiation. The Raman spectra of $SnO_2$ nanoparticles were recorded by employing the Raman spectroscopy equipped with a 532 nm laser. High-resolution transmission electron microscopy (HRTEM, Tecnai$^{TM}$G2 F30, FEI, US) was used to investigate the morphologies. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a PHI-5702 spectrometer. The electronic structures for normal and defected $SnO_2$ were measured by the density functional theory (DFT) calculations by using the Cambridge Serial Total Energy Package (CASTEP) code [28]. An UV–vis spectrometer (PerkinElmer Lambda 950) was used to record the absorbance spectra of the $SnO_2$ nanoparticles and the photodegradation of the MO solution. The photoluminescence (PL) spectrum was obtained from a Fluorlog-3 spectrofluorometer with excitation light at 325 nm. Electron spin resonance (ESR) spectra were acquired with the use of a Bruker spectrometer (9.458 GHz, 25 °C).

### 2.3. Photocatalytic activity

The photodegradation of methyl orange (MO) was used to evaluate the photocatalytic properties of the samples. Firstly, the catalysts (50 mg)were added into the MO solution (10 mg/L, 50 ml). Afterward, the suspension was stirred for 60 min in the darkness to reach adsorption equilibrium. Reaction was conducted under a high-pressure Xe lamp (300 W) equipped with an UV-420 cut. A certain volume of MO solution was withdrawn and centrifuged at selected times. The decomposition of MO was analyzed by a PerkinElmer Lambda 950 spectrometer.

### 2.4. Photoelectrochemical measurements

The photoelectrochemical properties of normal $SnO_2$ and defected $SnO_2$ were characterized by a Wuhan Corrtest Instrument Co. Ltd CS310 electrochemical workstation. Pt foil, FTO glass coated with $SnO_2$ and Ag/AgCl (saturated KCl) electrode were used as the counter electrode, photoanode and reference electrode, respectively. The photoanode was placed into $Na_2SO_4$ (0.1 mol $L^{-1}$) electrolyte under visible light from a 300 W Xe arc lamp with an UV-420 cut. The electrochemical impedance spectra (EIS) were also conducted under the same experimental conditions (0.01–105 Hz, 5 mV).

## 3. Results and discussion

The one-step synthesis of $SnO_2$ nanoparticles with oxygen vacancies has been accomplished via the hydrolysis and oxidation of Sn(II) under simple hydrothermal conditions, following the processes shown in Eqs. (1)–(4) [29,30].

$$Sn^{2+} + 2H_2O \rightarrow Sn(OH)_2 + 2H^+ \tag{1}$$

$$Sn(OH)_2 \rightarrow SnO + H_2O \tag{2}$$

$$SnO + 1/2O_2 \rightarrow SnO_2 \tag{3}$$

$$Sn(OH)_2 + 1/2O_2 + H_2O \rightarrow Sn(OH)_4 \rightarrow SnO_2 + 2H_2O \tag{4}$$

While dissolving $SnCl_2{\cdot}2H_2O$ in only deionized water with stirring, the solution became turbid shortly resulted from the rapid hydrolysis of $Sn^{2+}$ ions. The oxidation of Sn(II) into Sn(IV) can be generally performed by dissolved oxygen in a basic aqueous solution with different pH [29–32]. Moreover, the ionic radius of hexacoordinate $Sn^{4+}$ and $Sn^{2+}$ are 0.69 Å [33] and 0.62 Å [34], which are mainly the same. Thus it is possible to introduce $Sn^{2+}$ into the lattice matrix of $SnO_2$ [35]. Furthermore, as numerous $Sn^{2+}$ existed in the reaction system, it can be doped into $SnO_2$ in principle. To preserve charge neutrality, stable accompanying oxygen vacancies can be induced [35]. Eventually, oxygen vacancies are induced into $SnO_2$ via a simple hydrothermal process.

As shown in Fig. 1, both defected $SnO_2$ and normal $SnO_2$ can be indexed to rutile $SnO_2$ (JCPDS No. 41-1445), and no any other phases or impurities are checked. Under hydrothermal conditions, the oxidation of Sn(II) into Sn(IV) was performed by dissolved oxygen, and hence we obtained $SnO_2$ rather than SnO. The normal $SnO_2$ shows an enhanced crystallinity after annealing at 900 °C in air. Broad diffraction peaks indicate that the defected $SnO_2$ nanoparticles are small, which is consistent with the TEM image shown in Fig. 2a. The grain size of the defected $SnO_2$ nanoparticles is about 7 nm, and the HRTEM image (Fig. 2b) shows the most thermodynamically stable and frequently observed rutile $SnO_2$ (110).