



# Enhancing photocatalytic activity of Sn doped TiO<sub>2</sub> dominated with {105} facets



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## ABSTRACT

Electronic structures of semiconductor photocatalysts control the light absorbance, charge-carrier separation and mobility, activation energy and consequently, photocatalytic activity. Ion doping has been widely used to modify the electronic structure of a semiconductor photocatalyst. Here, we successfully synthesized Sn doped single crystalline anatase TiO<sub>2</sub> particles dominated with {105} facets by a gas phase oxidation process, and their structure and composition were thoroughly analyzed by XRD/TEM/FESEM/XPS. The photoluminescence emission spectra measurements reveal that the small amount of doped Sn in TiO<sub>2</sub> could suppress the recombination of photogenerated electron-hole pairs. Thus, the Sn doped TiO<sub>2</sub> shows a significantly enhanced photocatalytic hydrogen evolution performance, with its hydrogen generation rate being 4.5 times higher than that of pure TiO<sub>2</sub>. First-principle simulation results suggest the doped Sn at the edge exhibit higher adsorption energy toward H, which could promote the H<sub>2</sub> generation from the splitting of water.

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## 1. Introduction

Photocatalytic water splitting using inorganic semiconductor photocatalysts has been considered as a “green” process for converting solar energy into hydrogen. Pioneering work on photoelectrochemical hydrogen production catalyzed by titanium dioxide (TiO<sub>2</sub>) was firstly reported by Fujishima and Honda in 1972 [1]. Since then, TiO<sub>2</sub> as a typical photocatalyst has been widely studied because of its low cost, nontoxicity and stability [2–11]. According to the principle of minimization of surface energy (0.90 J/m<sup>2</sup> for {001} > 0.84 J/m<sup>2</sup> for {105} > 0.53 J/m<sup>2</sup> for {100} > 0.44 J/m<sup>2</sup> for {101}) [12], specific surfaces of anatase TiO<sub>2</sub> with high reactivity usually eliminate during the crystal growth process. In recent years, intensive research attention has been

paid to the design and synthesis of anatase TiO<sub>2</sub> with exposed high-energy surfaces [13–16], which normally show excellent physicochemical properties due to their unique geometrical and electronic structures. Based on theoretical predictions, for the first time, we have successfully synthesized anatase TiO<sub>2</sub> single crystals dominated with high activity {001} facets [13]. Following these breakthroughs, TiO<sub>2</sub> crystals exposing high-index {105} facets have also been recently synthesized by a gas phase oxidation process [12].

Various cation- or anion-doping as an indispensable method in modifying the properties of anatase TiO<sub>2</sub> have been studied experimentally and theoretically to improve the photocatalytic activity of water splitting. Doping with metallic ions (e.g. W, Cu, Fe, Sn, Mo, V, Gd, Bi) [17–21] or nonmetallic ions (e.g. N, C, S, P) [22,23] has been found to be an efficient method to improve the photocatalytic activity of anatase TiO<sub>2</sub>. Moreover, C, N, F and S doped anatase TiO<sub>2</sub> with exposed high-reactive facets of {001} have been prepared and exhibited enhanced photocatalytic activities [24,25]. Herein, for the first time we report that Sn doped anatase TiO<sub>2</sub> crystals exposed by high-index {105} facets have been prepared through a high-temperature gas-phase oxidation route proposed in our previous work [12] and they exhibit more than 4.5 times of improvement in the photocatalytic water splitting. Furthermore, the PL and

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first-principle simulation illustrated the lower photogenerated charge recombination and higher adsorption energy toward H compared with pure TiO<sub>2</sub>, which result in the high photocatalytic activity.

## 2. Experimental

### 2.1. Preparation of pure and Sn doped anatase TiO<sub>2</sub>

The pure anatase TiO<sub>2</sub> particles exposed with {105} facets were produced according to our previous studies [12]. The Sn doped anatase TiO<sub>2</sub> particles dominated with high-index {105} facets were synthesized through gas-phase oxidation method by using titanium tetrachloride (TiCl<sub>4</sub>) as Ti source and tin tetrachloride (SnCl<sub>4</sub>) as Sn source. A schematic reaction apparatus is given in Fig. S1, where a straight static furnace pipe and a thin spiral tube are used as reactor and reactant feeder, respectively. In a typical experiment, the vapor phase of TiCl<sub>4</sub> (bubbling oxygen (0.2 L min<sup>-1</sup>) into TiCl<sub>4</sub> liquid at 98 °C) mixed with the vapor phase of SnCl<sub>4</sub> (bubbling oxygen (0.02 L min<sup>-1</sup>) into SnCl<sub>4</sub> liquid at 10 °C), and then passed through the furnace pipe at a temperature of 1000 °C. In our experiments, the final products were collected at the down stream by a bag filter and washed by deionized water for 3 times to remove the adsorbed chlorine on the surface.

### 2.2. Characterization of catalyst particles

The morphology and structure of the samples were characterized by field emission scanning electron microscopy (FESEM, HITACHI S4800). Transmission electron microscopy (TEM) experiments were performed by a JEOL, JEM-2100 microscope with a working voltage at 200 kV. The samples for TEM measurement were obtained by placing a drop of the dispersed solution onto a Formvar-covered copper grid and evaporating it in air at room temperature. Crystallographic information of high-index anatase TiO<sub>2</sub> single crystals was obtained with X-ray diffraction (XRD, Bruker D8 Advanced Diffractometer, Cu K $\alpha$  radiation, 40 kV). Chemical compositions as well as the bonding states of anatase TiO<sub>2</sub> single crystals were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250, Al K $\alpha$  exciting radiation). XPS spectra of Sn 3d, Ti 2p and O 1s were measured with constant analyzer-pass energy of 20.0 eV. All binding energies were referenced to the C 1s peak (284.8 eV) arising from surface hydrocarbons (or possible adventitious hydrocarbon). Prior peak deconvolution, X-ray satellites, and inelastic background (Shirley-type) were subtracted for all spectra. In order to determine the mean ratio of Sn to Ti for catalyst particles, the as-synthesized particles were completely dissolved into 96% H<sub>2</sub>SO<sub>4</sub> at 353 K, afterwards detected by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Varian 710ES). The optical absorption spectra of the samples were recorded in a UV/Vis spectrophotometer (CARY 500). The photoluminescence (PL) spectra were acquired at room temperature with a UV-VIS-NIR Fluorescence Spectrophotometer (Fluorolog-3-P) under the ultraviolet excitation of 250 nm.

### 2.3. Photoactivity assessment of the as-obtained catalyst particles

The photoactivity of Sn doped and pure TiO<sub>2</sub> particles were estimated by detecting the H<sub>2</sub> evolution from photochemical reduction of water. The as-obtained TiO<sub>2</sub> powder was loaded with 1 wt% Pt by impregnation method and calcinated at 350 °C for 2 h. 50 mg of Pt/TiO<sub>2</sub> powder was then dispersed in 100 mL aqueous solution containing 10% methanol in volume. A 300 W Xe lamp was used as

light source. The amount of H<sub>2</sub> released was determined using a gas chromatography (TECHCOMP, 7890II).

## 3. Results and discussion

### 3.1. Characterization of pure and Sn doped TiO<sub>2</sub> particles

Fig. S2 shows the X-ray diffraction (XRD) patterns of the as-synthesized Sn doped and pure TiO<sub>2</sub> particles exposed by high-index {105} facets. The main diffraction peaks of two samples can be indexed into anatase crystal phase (space group I41/amd, JCPDS No. 21-1272) and only very small amount of rutile impurities can be detected. The typical SEM image of Sn doped TiO<sub>2</sub> particles (Fig. 1a) shows that the as-synthesized anatase TiO<sub>2</sub> crystals display bipyramidal morphology with an average size of 1–10  $\mu$ m. In our previous study, we have already confirmed the exposed surfaces of the bipyramidal crystals to be the high-index {105} facets of anatase TiO<sub>2</sub> [12]. Moreover, the relative intensity of the {105} facets is much stronger than that of the standard TiO<sub>2</sub> XRD pattern, which also implies that more {105} facets are exposed. Interestingly, some TiO<sub>2</sub> crystals bounded by minority {101} facets can also be found occasionally. TEM image of a free-standing anatase TiO<sub>2</sub> bipyramidal crystal and its corresponding selected-area electron diffraction (SAED) pattern are given in Fig. 1b and c, respectively, which demonstrate the single-crystalline characteristics. The high resolution transmission electron microscopy (HRTEM) image (Fig. 1d) clearly shows the (200) and (020) atomic planes with a lattice spacing of 0.189 nm. It should be noted that both the SAED and HRTEM images were indexed along the [001] crystallographic direction of anatase TiO<sub>2</sub>. The three dimensional (3D) schematic shape of a typical Sn doped anatase TiO<sub>2</sub> bipyramidal crystal exposed by high-index {105} facets is shown in Fig. 1e. SEM images of pure TiO<sub>2</sub> with {105} facets are shown in Fig. S3, and the size and morphology of the two samples have no significant difference.

The Sn/Ti atomic ratio of 0.0021 for Sn doped particles was determined by the ICP-AES test, but the Sn/Ti atomic ratio of anatase TiO<sub>2</sub> surface was detected to be 0.015 by X-ray photoelectron spectroscopy (XPS) (see Fig. S4), which is much higher than that of ICP-AES test, indicating that the doped Sn concentrated on the {105} facets of TiO<sub>2</sub> particles. In XPS spectra of the Sn doped samples, the characteristic peaks at around 495.2 and 486.6 eV are assigned to the contribution of Sn 3d electrons (Fig. S4b). The O 1s spectrum of pure TiO<sub>2</sub> (Fig. S5) can be deconvoluted into three peaks and the peak located at 529.7 eV is attributed to lattice oxygen, while the two peaks located at 531.3 and 532.6 eV could be assigned to Ti–OH and surface adsorbed species containing oxygen only. However, the O 1s spectra of Sn doped TiO<sub>2</sub> (Fig. S4c) can be deconvoluted into four peaks and the additional peak located at 530.1 eV should be ascribed to Sn–O–Ti linkage, suggesting that the Sn and Ti ions are mixed at an atomic level [26].

### 3.2. Photoactivity assessment of the as-obtained catalyst particles

The photocatalytic activities of pure and Sn doped TiO<sub>2</sub> particles were measured by detecting the H<sub>2</sub> evolution from methanol aqueous solution and the results are shown in Fig. 2. The pure TiO<sub>2</sub> particles give rise to H<sub>2</sub> evolution rate of 0.73  $\mu$ L min<sup>-1</sup>. By contrast, the corresponding rate of the Sn doped TiO<sub>2</sub> particles is up to 3.3  $\mu$ L min<sup>-1</sup> under the same experimental conditions. The UV-visible absorption spectra and the room-temperature photoluminescence (PL) emission spectra measurements were carried out to investigate the Sn doped and pure TiO<sub>2</sub> particles. From the UV-vis spectra (Fig. 3), it can be seen that the two samples have the

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