



# Ti<sup>3+</sup> self-doped TiO<sub>2</sub> photoelectrodes for photoelectrochemical water splitting and photoelectrocatalytic pollutant degradation<sup>☆</sup>

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## ABSTRACT

To improve the harvesting of visible light and reduce the recombination of photogenerated electrons and holes, Ti<sup>3+</sup> self-doped TiO<sub>2</sub> nanoparticles were synthesized and assembled into photoanodes with high visible light photoelectrochemical properties. X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectra, electron resonance spectroscopy and energy dispersive X-ray spectra were used to characterize the structure, crystallinity, morphology and other properties of the obtained nanoparticles. UV–visible diffuse reflectance spectra showed that the Ti<sup>3+</sup> self-doped TiO<sub>2</sub> nanoparticles had a strong absorption between 400 and 800 nm. Moreover, when hydrothermal treatment time was prolonged to 22 h, the heterogeneous junction was formed between the anatase and rutile TiO<sub>2</sub>, where the anatase particles exposed highly active {001} facets. Under visible light irradiation, the Ti<sup>3+</sup> self-doped TiO<sub>2</sub> electrode exhibited an excellent photoelectrocatalytic degradation of rhodamine B (RhB) and water splitting performance. Intriguingly, by selecting an appropriate hydrothermal time, the high photoconversion efficiency of 1.16% was achieved.

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## 1. Introduction

The photocatalytic (PC) and photoelectrocatalytic (PEC) removal of pollutants and water-splitting for hydrogen generation are environmentally significant processes for purposes of the environmental remediation and renewable energy production [1]. Titanium dioxide (TiO<sub>2</sub>) is an excellent photocatalyst because of its high photochemical stability and environmental friendliness [2,3]. However, the wide band-gap of TiO<sub>2</sub> (3.0–3.2 eV) requires UV light irradiation, and thus only a small portion of the solar spectrum can be utilized to generate electron-hole pairs. To extend the photo response of TiO<sub>2</sub> to the visible region, many modification methods, such as metal/non-metal doping [4,5] and noble metal deposition [6], have been reported. Unfortunately, these methods could cause thermal instabilities and doping impurities that would be recom-

bination centers of photo induced electron-hole pairs, which may decrease the PC and PEC efficiencies. Thus, enhancing the light harvesting and reducing the defects of the impurity doping are still worthwhile endeavors.

Instead of adding impurities, recent work reported that the Ti<sup>3+</sup> self-doping method was considered to be a new way to extend the light response of TiO<sub>2</sub> [7–9]. The oxygen vacancies (O<sub>v</sub>) will form in order to maintain charge balances of the introduction of Ti<sup>3+</sup> in TiO<sub>2</sub>. The Ti<sup>3+</sup> and O<sub>v</sub> will form a local state under the conduction band (CB) edge of TiO<sub>2</sub>, resulting in the band gap narrowing, so that the TiO<sub>2</sub> has visible even infrared light absorptions [9–11]. Compared with conventional doping methods, Ti<sup>3+</sup> is a type of self-doping that does not introduce impure elements into TiO<sub>2</sub>, which is favorable for preserving the stability of TiO<sub>2</sub> during the PC and PEC process. In addition, Ti<sup>3+</sup> can increase the electrical conductivity and accelerate the transfer of electrons and holes [8,12,13], and thus improve the photoelectric conversion efficiency [14,15].

According to electrode potentials, the generated Ti<sup>3+</sup> is very easily oxidized to Ti<sup>4+</sup> in the atmosphere. It is difficult to reduce Ti<sup>4+</sup> into Ti<sup>3+</sup> under the general conditions, and only few reduction-based methods were reported to produce Ti<sup>3+</sup> and/or O<sub>v</sub> contented TiO<sub>2</sub> [16,17]. Zhang et al. prepared a series of Ti<sup>3+</sup>

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self-doped TiO<sub>2</sub> catalysts by a solvothermal method using NaBH<sub>4</sub> or KBH<sub>4</sub> as a reductant. However, because of by-products generated in the reaction process, the subsequent treatment was inevitable to obtain pure Ti<sup>3+</sup> self-doped TiO<sub>2</sub> [18–20].

Recently, we employed an oxidation-based method to obtain Ti<sup>3+</sup> self-doped TiO<sub>2</sub> throughout the bulk and surface by a “surface oxidation-interface diffusion-redox” reaction mechanism using TiH<sub>2</sub> and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as precursors [21,22]. In contrast to reduction-based methods, the oxidation-based method has an easy reaction process because the electrode potential of Ti<sup>2+</sup>→Ti<sup>3+</sup> is much lower than that of Ti<sup>4+</sup>→Ti<sup>3+</sup>. In addition, H<sub>2</sub>O<sub>2</sub> using as an oxidation agent can significantly avoid undesired impurities in the final product.

In the PC process, the random diffusion of photo-generated charge carriers in TiO<sub>2</sub> causes the high recombination rate and low PC efficiency. Fortunately, the combination of PC and electrochemical technologies via PEC technique is an effective way to promote the separation rate of electrons-hole pairs [23,24]. It is well known that the electrical bias potential between the anode and cathode can be expected to increase charge separation, and so the recombination of photoinduced electrons-hole could be efficiently restricted [25,26]. In addition, the heterogeneous junction at the interface of anatase and rutile TiO<sub>2</sub> can also efficiently reduce the recombination and increase PC and PEC efficiencies [27,28]. Furthermore, the morphology and exposed facets of TiO<sub>2</sub> crystals are found to play a crucial role in the PC performance. The TiO<sub>2</sub> crystals with high-energy exposed facets, such as {110} and {001}, are desirable for improving photocatalysis [29–31].

In this paper, we prepared Ti<sup>3+</sup> self-doped TiO<sub>2</sub> nanoparticles, and then the photoelectrodes were prepared on FTO (F-doped SnO<sub>2</sub>) substrates from ethanol suspension by a spin-coating method. The relationship between PC and PEC performances with hydrothermal treatment time was studied. The results indicated that Ti<sup>3+</sup> self-doping enhanced the conductivity and visible-light absorption capability of TiO<sub>2</sub>. The synergistic effect between the Ti<sup>3+</sup> self-doping and applied bias is responsible for the enhanced PEC performance of these materials.

## 2. Experimental

### 2.1. Synthesis of samples

TiH<sub>2</sub> powder was purchased from Alfa Aesar. Other chemicals were purchased from Tianjin Ruijinte Chemical Reagent Co. without any further purification. Deionized water was used in all experiments. The preparation methods of Ti<sup>3+</sup> self-doped TiO<sub>2</sub> nanoparticles were similar to that of the reference, but the preparation conditions were changed slightly [21]. First, 0.40 g TiH<sub>2</sub> powders were dispersed in 10 mL of distilled water. After magnetic stirring for 10 min, the TiH<sub>2</sub> suspension was mixed with 40 mL of 30% H<sub>2</sub>O<sub>2</sub> solution under continuous stirring. When the color of the suspension changed from deep gray to yellow-green, the mixtures were transferred in a dried Teflon-lined autoclave, and then kept at 180 °C for 14 h, 18 h and 22 h, respectively. After cooled to room temperature, the blue or light-blue mixture was collected and washed by distilled water and ethanol for three times, and then dried in an oven at 60 °C for 3 h. Commercial P25 TiO<sub>2</sub> was used as a reference.

The photoelectrodes were prepared by spreading ethanol slurry of the Ti<sup>3+</sup> self-doped samples and P25 TiO<sub>2</sub> over 1.0 cm<sup>2</sup> of FTO substrates. A suspension of 2.5 g/L samples was prepared in ethanol by ultrasonication for more than 30 min. A 25 μL suspension was then spinning onto FTO substrates to form a transparent film. All samples were dried in an oven at 120 °C for 30 min.

### 2.2. Characterization of the samples

Phase compositions of the as-prepared nanoparticles were identified using X-ray diffractometer (XRD) (Rigaku D/max-2500VPC) with Ni-filtered Cu K<sub>α</sub> radiation (λ = 1.5418 Å) at a scanning rate of 0.02°/s from 10° to 80°. Transmission electron microscope (TEM, H800, Hitachi) and high-resolution transmission electron microscopy (HRTEM, JOEL-2010, JEOL Ltd.) were used for determining the size and morphologies of the nanoparticles. X-ray photoelectron spectra (XPS) measurements were carried out on an X-ray photoelectron spectrometer (ESCALAB MK II) using Mg K<sub>α</sub> (1253.6 eV) X-ray as the excitation source and C 1 s (284.6 eV) as the reference. Ultraviolet–visible (UV–Vis) diffuse reflection spectra (DRS) were recorded on a UV–Vis spectrophotometer (UV-2550, Shimadzu) in the range 200–800 nm. Electron paramagnetic resonance (EPR) measurements were carried out at 120 K without light illumination using a spectrometer (EMX 10/12 EPR, Bruker) at an X-band frequency of 9.363 GHz.

### 2.3. Measurement of PEC properties

Photocurrent was measured on a standard three-electrode cell using a CHI 660C potentiostat/galvanostat (Shanghai Chenhua Instrumental Co., Ltd., China). The as-prepared photoelectrodes were used as working electrode; a Pt wire and an Ag/AgCl electrode were used as counter and reference electrodes, respectively. A 0.2 mol/L Na<sub>2</sub>SO<sub>4</sub> aqueous solution was used as supporting electrolyte. The visible-light source was provided by a 300 W Xe lamp (PLS-SXE300, Trusttech Co., Ltd., Beijing) equipped with an ultraviolet cutoff filter.

The PEC degradation was evaluated in 100 mL 5.0 × 10<sup>-5</sup> mol/L RhB aqueous solution containing 0.2 mol/L Na<sub>2</sub>SO<sub>4</sub>. The solution was stirring in the dark for 15 min to reach the adsorption/desorption equilibrium before the irradiation started. After 10 min intervals during visible light illumination, 3 mL aliquots were taken out and centrifuged to remove the trace particles. The concentrations of RhB were analyzed at 552 nm as a function of irradiation time using UV–Vis spectroscopy (UV-7200, Unico, Shanghai). The PEC hydrogen production was evaluated in 50 mL 0.25 mol/L Na<sub>2</sub>S and 0.35 mol/L Na<sub>2</sub>SO<sub>3</sub> aqueous solution. The amount of hydrogen evolution was measured using an online gas chromatograph (Varian GC3800).

## 3. Results and discussion

### 3.1. Characterization of the as-prepared samples

XRD was used to investigate changes of the structure and phase purity of the samples obtained with different hydrothermal treatment time. Fig. 1 shows XRD patterns of the samples obtained at 180 °C for 14 h, 18 h and 22 h, respectively. It is observed that the sample is the mixture of anatase TiO<sub>2</sub> and TiH<sub>2</sub> when the reaction time is 14 h (The marked peaks with \* corresponded to TiH<sub>2</sub>). The peaks at 2θ = 25.3°, 36.9°, 37.8°, 48.0°, 53.9°, 55.1°, 62.7°, 68.8°, 70.3° and 75.0° are indexed to (101), (103), (004), (200), (105), (211), (204), (116), (220) and (215) crystal planes of anatase TiO<sub>2</sub> (JCPDF No. 21-1272), respectively. The XRD patterns exhibit weak diffraction lines at 2θ = 34.8°, 40.5°, and 58.6°, which implies the presence of TiH<sub>1.924</sub> (JCPDS Card No. 25-0982). When the hydrothermal time is prolonged to 18 h, the pattern exhibits characteristic diffraction peaks of anatase TiO<sub>2</sub> without any additional diffraction peaks, which shows the complete conversion of TiH<sub>2</sub> to anatase TiO<sub>2</sub>. When the reaction time is prolonged to 22 h, the predominant phase is still anatase TiO<sub>2</sub>, which was accompanied by a portion of rutile phase (Fig. 1(3)). This result indicated that the heterojunction is formed between anatase and rutile TiO<sub>2</sub>

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