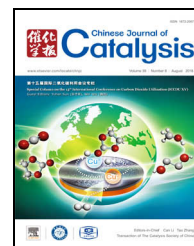


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## Article

# One-pot topotactic synthesis of $\text{Ti}^{3+}$ self-doped 3D $\text{TiO}_2$ hollow nanoboxes with enhanced visible light response

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## ABSTRACT

$\text{Ti}^{3+}$  self-doped anatase three-dimensional (3D)  $\text{TiO}_2$  hollow nanoboxes were synthesized *via* a topological transformation process involving template participation by a facile one-pot hydrothermal treatment with an ethanol solution of zinc powder and  $\text{TiOF}_2$ . It is worth noting that the 3D  $\text{TiO}_2$  hollow nanoboxes are assembled from six single-crystal nanosheets and have dominant exposure of the {001} facets. It is found from EPR spectra that adding zinc powder is an environment-friendly and effective strategy to introduce  $\text{Ti}^{3+}$  and oxygen vacancy ( $\text{O}_v$ ) into the bulk of 3D hollow nanoboxes rather than the surface, which is responsible for their enhanced visible photocatalytic properties. The photocatalytic activity was evaluated by measuring the formation rate of hydroxide free radicals using 7-hydroxycoumarin as a probe. The sample prepared with zinc/ $\text{TiOF}_2$  mass ratio of 0.25 exhibited the highest RhB photodegradation activity under visible-light irradiation with a degradation rate of 96%, which is 4.0-times higher than that of pure  $\text{TiO}_2$ . The results suggest a novel approach to construct *in-situ* 3D hierarchical  $\text{TiO}_2$  hollow nanoboxes doped with  $\text{Ti}^{3+}$  and  $\text{O}_v$  without introducing any impurity elements for superior visible-light photocatalytic activity.

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## 1. Introduction

Due to its excellent application in solving the energy crisis and environmental pollution, anatase  $\text{TiO}_2$  has attracted much attention for its chemical stability, low toxicity, photo oxidation properties, and environmental friendliness [1]. However, anatase  $\text{TiO}_2$  is not a suitable candidate for practical applications due to its large energy gap and rapid recombination of photo-generated electron-hole pairs [2–6]. Therefore, developing a simple method to overcome the 3.2-eV band gap and expand

the absorption edge of titanium dioxide to the visible light range should be studied further [7].

An effective solution to this challenge is to dope the surface or bulk of  $\text{TiO}_2$  by modifying or co-doping with different metal or non-metallic ions [8,9]. Metallic or non-metallic elements, such as  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ , N and S, act as electron acceptors or donors in the forbidden band of the photocatalyst and induce obvious absorption in the visible light range [10,11]. However, the introduction of other impurity elements may permit hazardous dopants to enter the environment. Other impurity elements

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may cause thermal instability, doping induced charge recombination, requires expensive ion implantation equipment, and generates more carrier recombination centers. Therefore, it will greatly hinder the photocatalytic activity of titanium dioxide and critically restrain its actual application [12].

Ti<sup>3+</sup> self-doping is a desirable doping modification method which does not require other metal or non-metallic ion impurities and effectively maintains the structure and morphology of TiO<sub>2</sub>. The formation of Ti<sup>3+</sup> or O<sub>v</sub> is an effective and environmental-friendly strategy for improving visible light absorption [13]. Until now, only a few methods have been capable of producing Ti<sup>3+</sup> and O<sub>v</sub>-doped TiO<sub>2</sub> nanosheets. Nonetheless, there is still no effective approach for synthesizing Ti<sup>3+</sup> self-doped three-dimensional (3D) TiO<sub>2</sub> hollow nanomaterials. For example, Si et al. [14] used a simple solution reaction to prepare reduced TiO<sub>2</sub> nanosheets with high energy facets. However, controlling the O<sub>v</sub> concentration is difficult, and Ti<sup>3+</sup> ions are introduced into the surface rather than the bulk of the catalyst. This could significantly inhibit its practical application in different visible light systems. At the same time, these methods are limited because of their high cost, complex processing techniques, and small production scale. Although the preparation and photocatalytic activity of reduced TiO<sub>2</sub> nanomaterials have aroused great interest, research on Ti<sup>3+</sup> self-doping is far from satisfactory, and there are still many problems left to be resolved in this research area, especially regarding preparation of 3D TiO<sub>2</sub> materials with hollow structure [15].

The phase structure and crystal facets play an important role in TiO<sub>2</sub> catalysts. In recent years, various 3D TiO<sub>2</sub> structures with hollow morphology have been synthesized by various methods, such as TiO<sub>2</sub> tubular structures or hollow spheres constructed from nanorods, nanowires, nanosheets or nanoparticles. However, these three-dimensional structures are primarily based on spherical morphology, which consist of randomly assembled building blocks. The preparation of non-spherical 3D TiO<sub>2</sub> hollow nanomaterials composed of an ordered superstructure or hierarchical structure, such as boxes, remains a major challenge. The relationship between the catalytic properties and high-energy {001} facets has recently attracted an explosion of interest [16]. Both theoretical and experimental analyses have demonstrated that the high energy {001} facets enable efficient separation and transfer of photo-generated electron-hole pairs, and uncoordinated Ti<sub>5c</sub> atoms in the exposed {001} facets can effectively narrow the energy gap of the catalyst [17]. 3D TiO<sub>2</sub> hollow nanoboxes were fabricated by a topotactic transformation from TiOF<sub>2</sub> precursors [18,19]. In terms of morphology and facet modification, building 3D hierarchical TiO<sub>2</sub> hollow nanoboxes enclosed by six ordered TiO<sub>2</sub> nanosheets with dominant {001} facet exposure to enhance visible light absorption, especially in the originally crystal growth process, is still a difficult problem and is restricted by the critical crystal growth environment. Thus, there is an urgent need to develop a facile and one-pot topotactic synthetic strategy to prepare Ti<sup>3+</sup> self-doped TiO<sub>2</sub> with 3D hollow structures to enhance the visible light response. To the best of our knowledge, the fabrication of Ti<sup>3+</sup>-doped 3D TiO<sub>2</sub> hollow nanoboxes with exposed {001} facets in the presence of a re-

ductant through a topotactic transformation process with a TiOF<sub>2</sub> template has not been reported.

Herein, we employ a simple one-pot topotactic hydrothermal method to introduce Ti<sup>3+</sup> and oxygen vacancies into 3D TiO<sub>2</sub> hollow nanoboxes without any other impurity elements. By using low-cost zinc powder as the reductant, TiOF<sub>2</sub> as the template, and ethanol as solution, Ti<sup>3+</sup> is successfully self-doped into the bulk of 3D hollow nanoboxes, which are assembled by six ordered arranged TiO<sub>2</sub> nanosheet arrays with dominantly exposed {001} facets. In addition, due to strong visible adsorption by Ti<sup>3+</sup> and oxygen vacancies, and charge recombination suppression, the RhB photodegradation activities were significantly enhanced under visible light irradiation.

## 2. Experimental

### 2.1. Topotactic synthesis process

TiOF<sub>2</sub> precursor was first prepared as a nanocubic template [20]. In a typical procedure, 5 mL HF was slowly added dropwise into 30 mL CH<sub>3</sub>COOH under magnetic stirring. After stirring for 30 min, the mixed solution was added to a polyvinyl fluoride beaker containing 15 g tetrabutyl titanate (TBT). A white emulsion was obtained, which was then transferred to a dried 100-mL Teflon-lined autoclave and kept at 200 °C for 12 h. After being allowed to cool to 25 °C, the product was washed several times with ethanol and distilled water. The washed product was dried at 100 °C for 4 h to obtain a white TiOF<sub>2</sub> precursor.

Using TiOF<sub>2</sub> as the precursor, ethanol as a solvent, and zinc powder as a reducing agent, Ti<sup>3+</sup> self-doped 3D hierarchical titanium dioxide hollow nanoboxes were prepared *via* a template-engaged *in-situ* topotactic transformation process. Typically, 1.0 g TiOF<sub>2</sub> and 0.05 g Zn were ground and added to 20 mL ethanol. Then the mixture was transferred to a Teflon-lined autoclave and kept in an oven at 200 °C for 24 h. After cooling, the powder was collected and washed with hydrochloric acid (38 wt%) under magnetic stirring to removal excess Zn. The washed powder was centrifuged and washed with distilled water until the pH ≈ 7. The centrifuged powder was dried overnight in a vacuum. The obtained product was marked as R0.05, where 0.05 indicates the Zn/TiOF<sub>2</sub> mass ratio. For comparison, different samples were also synthesized under identical conditions with various amounts of zinc. These samples are labeled R0, R0.2, R0.25, R0.3 and R0.4 [21–24].

### 2.2. Characterization

X-ray diffraction (XRD) measurements from the prepared powder were gathered using Cu K<sub>α</sub> radiation at a 2θ scan rate of 0.02°/s with a D8-advance X-ray diffractometer (Bruker, Germany). The phase structure and crystal facets of the product were determined with a Tecnai G220 transmission electron microscope (TEM) (USA) operated at 200 kV acceleration voltage. Scanning electron microscope (SEM) images were gathered with a field emission scanning electron microscope (Hitachi, Japan). UV-vis diffuse reflectance spectroscopy (DRS)

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