

# Effects of Pre-annealing Atmosphere on Microstructure and Photocatalytic Activities of Fe-doped Titania Nanotubes



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**Abstract:** The nanotubes with an anatase structure were hydrothermally synthesized using the Fe-doped anatase nanopowder precursors that were annealed in air and reductive atmospheres. The microstructure and physicochemical properties of the nanotubes were comparably investigated. Results show that the reductive pre-annealing yields more surface-chemisorbed oxygen by introducing lower valence  $\text{Fe}^{2+}$  and  $\text{Ti}^{3+}$  ions. The specific surface area, methylene blue adsorption and photoabsorption threshold of the nanotubes are greatly enhanced by the reductive annealing when comparing with annealing in air. 1 mol% Fe doping and reductive annealing yield the highest adsorption, photocatalytic efficiency and durability for degradation of MB solution; extreme Fe doping decreases the photocatalytic efficiency. The Fe content of the nanotubes is decreased by the hydrothermal synthesis, especially in the case of annealing in air. Moreover, the action mechanism of the Fe doping and reductive annealing was discussed.

**Key words:** titania; nanotubes; reductive annealing; doping; photocatalysts; crystal defects

Nanostructured titania has been widely used in photocatalytic degradation of organic pollutants. The preparation, microstructure and photocatalytic behavior of titania nanostructures, especially the one-dimensional nanotubes, have been paid great attention to due to their superior physicochemical properties, such as large disparity, high surface activity and the fast charge transition when compared with titania nanoparticles. Hydrothermal method is generally adopted to synthesize titania nanotubes that have a diameter of 10 nm approximately and exhibit an anatase phase or anatase+rutile biphasic [1-4]. Photocatalytic activity follows the order of nanotubes > nanorods > nanobelts > P25 nanoparticles [5]. However, the titania crystals have restricted photoadsorption ability because of their larger band gap (3.2 eV for anatase and 3.0 eV for rutile). Ion-doping is frequently adopted to decrease the band-gap by generating donors or acceptors in the band that favor to separate photo-generated electrons and holes and inhibit their rapid recombination [6-9], and Fe doping is the

most attractive among them because it produces great changes in microstructure and physicochemical behaviors of the nanostructured titania [10-12]. However, the optimized Fe content varies with the applied preparation method, morphology and phase composition of titania structures and the sacrificial organics. For example, by doping with 0.5 mol% Fe, the  $\text{TiO}_2$  nanorods possessed a photocatalytic activity more than two-times of the Degussa P25 [13], the  $\text{TiO}_2$  microspheres doped with 0.5 mol% Fe had a high surface area, well-crystallized anatase phase and the best photocatalytic degradation of phenol [14]. 0.5 wt% Fe doped  $\text{TiO}_2$  hollow nanospheres show the highest photocatalytic activity that exceeds that of the undoped  $\text{TiO}_2$  for degradations of 2, 4, 6-trichlorophenol and red X-3B dye respectively [15,16]. 1.0 mol% Fe-doped dual-phase  $\text{TiO}_2$  containing 20.64 wt% of rutile phase induced a red shift of absorption edge and yielded the best degradation efficiency for methyl orange [17]. 1.5 mol% Fe doping also produced the best photocatalytic activity [18]. Moreover, Fe doping

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increased the surface area and pore volume of sol-gel derived titania nanopowders; a doping with 3.0 mol% Fe exhibited a significantly high surface area and pore volume<sup>[19]</sup>. On the contrary, the surface area of titania nanotubes was decreased while the adsorption amount for arsenic was increased by Fe-doping<sup>[20]</sup>, indicating a significant change in surface activity of the nanotubes. A substantial photodegradation efficiency of the titania thin film can also be achieved at very high doping levels, such as 20 mol% Fe<sup>3+</sup><sup>[21]</sup>. However, the studies on Fe-doped titania nanotubes have been paid less attention to.

Moreover, self-doping is a novel method that introduces low-valance Ti<sup>3+</sup> species and oxygen vacancies in bulk and surface of the TiO<sub>2</sub> structures. They decreased the band gap of the crystals, maximized the photoabsorption activity and improved the photocatalytic behavior<sup>[22-25]</sup>. Another alternative approach to promote photoabsorption and photocatalytic reactions is generation of the disorders in surface of the TiO<sub>2</sub> nanocrystals by a hydrogenation treatment, which created much narrow band gap, provided trapping sites for photogenerated carriers, promoted electron transfer and prevented their rapid recombination by yielding mid-gap (band tail) states<sup>[26]</sup>. The Ti<sup>3+</sup> sites and oxygen vacancies can be produced by high-temperature annealing, oxygen-lack annealing and the substitution of lower-valance ions such as Fe<sup>3+</sup>/Fe<sup>2+</sup> for Ti<sup>4+</sup><sup>[27-29]</sup>. For example, 15 mol% of Fe ions can be completely dissolved into titania lattices by annealing in a reductive atmosphere, which resulted in presence of the lower-valance Fe<sup>2+</sup> and Ti<sup>3+</sup> ions and much more oxygen vacancies<sup>[30]</sup>. However, the crystals containing Ti<sup>3+</sup> ions and oxygen vacancies may be unstable, especially in an oxidation environment<sup>[31, 32]</sup>. Therefore, synthesis of the stable TiO<sub>2</sub> photocatalysts with the self-dopants is significant in practice.

Based on advantages of the one-dimension, Fe-doping and self-doping, the Fe-doped titania nanotubes with an anatase phase were prepared using a reductive annealing of the precursory anatase nanopowders and a hydrothermal synthesis; the characters of microstructure and physicochemical behaviors of the nanotubes were comparatively investigated to try to find the coupling effect of Fe-doping and the reduction treatment on them.

## 1 Experiment

Analytical reagents of tetrabutyl titanate (Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>), ferric nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) and absolute alcohol (C<sub>2</sub>H<sub>5</sub>OH) were used as starting materials. 100 mL of tetrabutyl titanate was injected into 400 mL of absolute alcohol to form a base solution under stirring for 30 min, which was then divided into four equal parts. Different amounts of ferrous nitrate were individually dissolved into the solutions to form Fe-doped titania sols with different Fe/Ti ratios (mol%) (0.0, 1.0, 2.0 and 3.0). The sols were

vigorously stirred for 30 min and aged for 24 h. By heating the aged sols in stirring to 60 °C and drying at 100 °C for 24 h, the titania gels were obtained. The dried gels were annealed at 400 °C for 2 h in air atmosphere in a tube-type furnace and cooled to room temperature. To conduct a reductive annealing, CO-Ar hybrid gas was introduced to the furnace with a volume ratio of 1: 2 and a flux of 150 mL/min. Before the test started, the furnace was degassed by flowing pure Ar for 10 min. These conditions employed was due to that an anatase phase with good crystallinity and small crystals was formed under these conditions<sup>[33]</sup>. The annealed products were ground and screened into powders with a granularity of 74~63 μm (ASTM E11-58T).

The anatase powders (0.3 g) were placed into a stainless steel reaction kettle filled with a NaOH solution (10 mol/L) to 80% of the total volume. The autoclave was heated to 120 °C and kept for 16 h followed by cooling to room temperature. The obtained samples were alternatively washed in stirring with dilute HCl solution and deionized water until they were neutral. The washed samples were dried at 90 °C for 12 h to obtain the nanotubes.

The Fe doping, reductive annealing and hydrothermal reaction resulted in changes in color of the products. When annealed in air atmosphere, the powders presented yellowish (undoped), yellow and deep yellow with an increase of Fe content due to the presence of Ti<sup>4+</sup> and Fe<sup>3+</sup> ions; when annealed in reduction atmosphere, the undoped powders presented gray color and the Fe-doped powders presented black color, due to the low-valance Ti<sup>3+</sup> and Fe<sup>2+</sup> ions and the O<sup>2-</sup> vacancies<sup>[23, 29]</sup>. With the hydrothermal reaction, annealing in air made all of the nanotubes present offwhite color, which may be due to titanate inclusions remaining; the reductive annealing made the nanotubes present deep gray color, which indicates that the low-valance Ti<sup>3+</sup> and Fe<sup>2+</sup> ions still existed in the nanotubes even though they underwent a long-term of hydrothermal treatment and a repeated washing in the acid solution.

0.15 g of the nanotubes were placed in a methylene blue (MB, C<sub>16</sub>H<sub>18</sub>ClN<sub>3</sub>S<sub>2</sub>·3H<sub>2</sub>O) solution (3 mg/150 mL) with stirring. After a dark treatment of 30 min, the concentrations of the solutions were inspected as references to determine degradation ratio of the MB solutions in upcoming photocatalytic reaction. The dark-treated solutions were irradiated for 60 min by an ultraviolet lamp with a weaker power (50 W, 356 nm). The absorbance of the solutions cleaned by centrifugal separation was inspected every 10 min using UV-Vis spectrophotometry (UV-3101PC). The degradation ratio can be obtained by following calculation formulae<sup>[34]</sup>.

$$A = 0.019 + 0.197C \quad (1)$$

$$\eta = C_i / C_0 \quad (2)$$

where,  $A$  is the absorbance,  $C$  is the concentration of MB in solution,  $C_0$  is the original concentration (reference) and  $C_i$  is

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