Synthesis and characterization of C, N-codoped TiO2 nanotubes/nanorods with visible-light activity

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Abstract
Visible-light response C, N-codoped TiO2 nanotubes with high aspect ratios were prepared by a two-step method. First the TiO2 nanotubes were synthesized by an ion-exchange method, and then the nanotubes were calcined at different temperatures with melamine as nitrogen and carbon source. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV-vis diffusive reflectance spectroscopy (DRS), scanning electron microscopy (SEM), and N2 adsorption-desorption isotherms were employed to characterize the as-prepared samples. The results show that the nanotubular structure is destroyed when the calcination temperature is higher than 823 K. Further increase the temperature to 923 K, TiO2 is reduced to TiO. The photocatalytic activity of the codoped TiO2 nanotubes/nanorods was evaluated by degradation of Rhodamine B under visible-light irradiation (> 420 nm). Compared with N doped P25, these codoped TiO2 nanotubes/nanorods possess a superior photocatalytic acticity, owing to the synergistic effects of the nitrogen and carbon co-doping.

Keywords: titania; nitrogen; carbon; Co-doped; photocatalysis

1. Introduction
Degradation of organic pollutants with semiconductor photocatalysts is regarded as a promising way to solve the global pollution issue. Among multifarious photocatalysts, TiO2 is one of the most studied semiconductors for its non-toxic, inexpensive and high chemical stability. Various synthetic routes have done in the morphology control of TiO2 [1-6] to obtain larger specific surface area and higher photocatalysis activity. However, TiO2 has a wide band gap about 3.0 eV, means it responds merely to the ultraviolet light, and limited its further application. To obtain a more efficient utilization of visible light, many attempts, typically, either cationic or anionic impurity doping, oxygen deficiency generation, were made to expand its photocatalytic activity to the visible light.

Transition metal cations doping seldom lead to satisfactory visible light absorption [7-9], and doping TiO2 with nonmetal atoms has received a lot of attention. Since Asahi et al. first reported a photodegradation of methylene blue (MB) with a N-doped TiO2 under visible light irradiation [10], Various dopants have been extensively investigated. F-doping into TiO2 was carried out by ion implantation [11]. Jincai Zhao’s group extend the spectral response of TiO2 to the visible region and improve its catalytic efficiency by doping with boron [12]. Irie et al. [13] prepared carbon-doped anatase TiO2 nanoparticles by oxidative annealing of TiC under O2 flow at 873 K. These studies demonstrated that the doping with a nonmetal impurity can provide an effective modification of the electronic structures of TiO2.

More recently, nonmetal co-doping presents a promising strategy to further enhance the visible-light activity of TiO2. The simultaneous doping of two kinds of atoms into TiO2 attracted much interest because it can result in a more efficient visible light absorption and higher photocatalytic activity. For example, Xie et al. [14] have reported that F-N codoped samples exhibit much higher visible-light-induced catalytic activities than that of Degussa P25 and the as-prepared pure TiO2. Dong Yang synthesized a carbon and nitrogen codoped TiO2 with enhanced visible-Light photocatalytic activity by sol-gel method [15]. Such codoped TiO2 photocatalyst possess a better visible light absorption, but the specific surface area is always limited by ordinary synthesis route, and the catalysis efficiency is low. So a new approach to synthesize a visible light responded TiO2 with high specific surface area should be significative for its further application.

In this study, we synthesized C, N codoped TiO2 with nanotube structure by a heat treatment of melamine and
TiO₂ in a sealed tube furnace. And their intrinsic characteristics were analyzed using X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and UV-vis spectroscopy. The photocatalytic activity of as-synthesized TiO₂ samples was evaluated by the degradation rate of Rhodamine B (RhB) under visible light irradiation.

2. Experimental

2.1. Sample preparation

TiO₂ nanotubes were prepared as reported in literature [4]. 0.8 g TiO₂ powders and 60 ml NaOH aqueous solutions (10 M) were mixed and sonicated in a water bath for 30 min, and then sealed in a 80 ml autoclave with a polytetrafluoroethylene (PTFE) container inside. The autoclave was maintained at a temperature of 150 for 48 h, the precipitates were flitted and rinsed with deionized water for three times. After washing, the precipitates were transferred into 100 ml HCl solution (0.2 M) to form a hydrogen titanate. The obtained hydrogen titanate were filtered and washing with deionized water until pH = 7, and then dried at 40 ºC in a vacuum drying oven.

The dried hydrogen titanate was ground and transferred into a quartz boat, 5 g melamine was put into another boat, then both boats were sealed into the tube furnace which possess two heating source (as Fig. 1 shows). The boat filling with melamine was kept at 400 ºC, while another boat with the hydrogen titanate was kept at 400, 500, 600 or 650 ºC. (The obtained products named T-400, T-500, T-600 and T-650 respectively) After two hours’ heat treatment, the final products cooled down to room temperature naturally and obtained a powder with a color from light yellow to dark.

2.2. Characterization of catalysts

X-ray diffraction (XRD) patterns were recorded on a powder diffractometer (Bruker AXS D8) with a Cu Ka X-ray tube. The crystal morphology was characterized by scanning electron microscopy (SEM, Hitachi S-4800 microscope). UV-Vis diffuse reflectance spectra were recorded using Shimadzu UV 2550 spectrophotometer equipped with an integrating sphere. The surface property of TiO₂ samples was characterized by X-ray photoelectron spectroscopy (XPS) in a Thermo Fisher Scientific Escalab 250 spectrometer with monochromatized Al Ka excitation, and C1s (284.6 eV) was used to calibrate the peak positions of the elements.

2.3. Photocatalytic activity

The photocatalytic activity of prepared C, N-codoped TiO₂ was tested by decomposition of RhB. For a typical photocatalytic experiment, 0.1 g as prepared C, N codoped TiO₂ powders were added into 100 ml RhB aqueous solution (20 mg/L) under visible light irradiation. A 300 W Xe lamp (PLS-SXE300, Beijing Trusttech Co. Ltd.) with an ultraviolet cutoff filter to provide visible light (λ > 400 nm) was used as the light source. Before the lamp was turn on, the suspension was stirred in the dark for 40 min to establish adsorption/desorption equilibrium. The photocatalytic activities of the samples were evaluated by measuring the absorbance of aqueous Rhodamine B solution at 464 nm as a function of irradiation time with a UV-vis spectrophotometer (Shimadzu UV2550).

3. Results and discussion

3.1. Crystal structure and morphology characterization

XRD was used to confirm the crystal structure of the samples and the effect of calcinations temperature on it. Fig. 2 shows the XRD patterns of the samples calcining under different temperature. The samples exhibit anatase phase, when the temperature exceeded 600 ºC, TiO₂ was reduced to black TiO. Fig. 3 shows transmission electron microscopy (TEM) images of the obtained C,N-codoped TiO₂. At low calcination temperature, the C, N-codoped TiO₂ maintained the nanotube structures. The nanotubes have inner diameters of 7 nm, outside diameters of about 11 nm and lengths from 200 to 300 nm. When the calcinations temperature elevated to 500 oC, the structure of the sample transformed to nanorod. These nanorods were about 10 nm wide and 50 to 100 nm long, and with elevate calcinations temperature, the nanorods cracked and became shorter and finally covert into TiO particles with a diameter of 10~20 nm at 650 ºC. This