Highly efficient visible-light driven photocatalyst with enhanced charge separation prepared by annealing continuously in ammonia and vacuum

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ABSTRACT

A highly efficient visible light driven photocatalyst was prepared by annealing samples continuously in ammonia and vacuum. The dependence of photocatalytic activity on calcination temperature was investigated. The effect of annealing temperature on crystal structure, particle size, chemical composition and optical absorbance of TiO_2 nanoparticles were characterized by X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy, photoluminescence spectroscopy and UV–visible diffuse reflectance spectroscopy, respectively. The photocatalytic degradation of benzene under visible light illumination demonstrated that the photocatalyst annealed at 600 °C (NV-TiO_2-T600) possessed the best photocatalytic property. The excellent photocatalytic activity of NV-TiO_2-T600 was attributed to the high crystallinity, strong light-harvesting and enhanced separation of photo-generated electron–hole pairs. The vacuum treatment had a positive effect on enhancing charge separation. In addition, the increased amount of surface oxygen vacancy might be the crucial factor for the improvement of photocatalytic activity.

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1. Introduction

For decades, TiO_2 has received researchers' enormous attention due to its wide applications in photocatalysis, photonics, sensors and photochromic device [1–4]. Especially for photocatalysis, TiO_2 is recognized as the best choice to purify waste water and eliminate pollutants in atmosphere, since the hydroxyl radicals with powerful oxidization produced in photocatalysis process can oxidize most of the organic pollutants. Unfortunately, the rapid recombination rate of photo-generated electron–hole pairs and the low utilization of the solar spectrum are two major blocks in the practical application of TiO_2 photocatalyst. Hence, many strategies have been developed to step over the aforementioned barriers, including doping, sensitization, coupling with the narrow bandgap semiconductors, introducing carbon nanomaterials and depositing noble metal, etc [5–10]. However, none of these strategies can overcome the two obstacles at the same time. In addition, most of these strategies are complicated and expensive. Thus, it is necessary to prepare a highly efficient photocatalyst by a simple and economical method.

In terms of indoor air pollution, benzene is one of the VOCs (Volatile organic compounds) that can be found everywhere and is carcinogen. Due to the existence of conjugated π bond, benzene is the most stable organic compound [11,12]. Hence, the tough question is how to decompose benzene completely. Among the technologies developed for treatment of benzene, the photocatalytic oxidation process is considered to be a promising technology due to the •OH radicals with strong oxidizing capability which could oxidize most of organic compounds generate in the process. A series of related studies have been carried out in the past few years. Zhong et al. have investigated the photocatalytic property of Pd/TiO_2 for the oxidation of gaseous benzene. They find the optimal ratio of Pd/Ti and the maximum conversion of benzene (initial concentration is 4.5 ppm), which is 65.3% after 6 h exposure to UV light [13]. Wang et al. have prepared novel TiO_2/Ag_3VO_4 nanocomposite photocatalyst. The photo-degradation results show that the conversion of benzene (initial concentration is 280 ppm) on 0.5% AT can reach 95% and the mineralization ratio is up to 84% under 10 h of visible light illumination [14]. However, these efforts are not sufficient to

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solve some remained problems, such as long reaction duration, low initial concentration of benzene, high dosage of photocatalyst and expensive cost of production.

Vacuum treatment is an effective and economical technology to modify the surface of materials. Xing et al. have reported a photocatalyst with high photo-activity and photosensitivity prepared by a vacuum activated procedure and suggested that the oxygen vacancy states together with the Ti^{3+} were responsible for the high yield of H_2 [15]. Luo et al. have investigated the photocatalytic activity of TiO_2 annealed in reducing atmosphere. They believe that the excellent photocatalytic activity of vacuum-activated TiO_2 may be related to subnanometer-thick disordered surface layers [16]. Therefore, we can conclude that vacuum treatment can efficiently improve the photocatalytic activity of TiO_2.

In the present work, we prepare a modified TiO_2 with high visible light photocatalytic activity by annealing continuously in ammonia and vacuum. To our surprise, this method not only makes TiO_2 respond to visible light but also enhances the separation of photo-generated electron–hole pairs. To our best knowledge, it is the first time to use an economical and simple method to achieve the two goals simultaneously. In addition, the activities of photocatalysts and their dependence on annealing temperature are also compared. It is heartening that the as-prepared photocatalyst annealed at 600 °C (NV-TiO_2-T600) can decompose high concentration of gaseous benzene (300 ppm) during 4 h of visible light illumination. The excellent photocatalytic activity may be ascribed to the high crystallinity, strong light-harvesting and fast separation of electron–hole pairs. Our findings provide an economical and convenient method to prepare highly efficient visible light driven photocatalyst.

2. Experimental

2.1. Synthesis of NV-TiO₂-Tx

The pure TiO_2 was synthesized by hydrothermal method mentioned in previous paper [17]. Then the pure TiO_2 was transferred into tube furnace and annealed in ammonia (99.9%) for 2 h. After that, ammonia stopped inletting and the vacuum pump opened immediately. The vacuum treatment lasted for 2 h, followed by naturally cooling to room temperature in vacuum (vacuum degree −0.1 atm). The heating rate was 5 °C/min. The annealing temperature ranged from 550 to 750 °C. The as-prepared sample was denoted as NV-TiO_2-Tx (x referred to the annealing temperature). The pure TiO_2 only annealed in ammonia at 600 °C for 2 h was denoted as N-TiO_2-T600.

2.2. Characterization

The crystal phases of samples were analyzed by X-ray diffraction with Cu Kα radiation (XRD: PANalytical B.V., Almelo, Netherlands). The morphology, structure and grain size of the samples were examined by transmission electron microscopy (TEM: FEI Tecnai G2 F30, Netherlands). XPS with Al Kα X-rays radiation operated at 300 W (XPS: Kratos XSAM800 spectrometer, USA) was used to analyze the surface properties. The shift of binding energy due to relative surface charging was corrected using the C 1s level at 284.6 eV as an internal standard. The spectra were fitted using a nonlinear least-squares fitting program (XPSPEAK) with a linear background and to the 80% Gausssian/20% Lorentzian peak shape. The PL spectra were gained by using a LabRAM HR spectrometer (HORIBA Jobin Yvon, France) with a laser excitation of 325 nm. The UV–vis absorbance spectra were obtained for the dry-pressed disk samples using a Scan UV–vis spectrophotometer (Perkin-Elmer, Lambda 950) equipped with an integrating sphere assembly. The spectra were recorded at room temperature in air within the range 200–900 nm.

2.3. Measurement of photocatalytic activity

Evolution of the photocatalysis was carried out in a self-designed closed aluminum alloy reactor. The volume of reactor is 2 L. The mass of photocatalyst was 0.10 g and well dispersed to form a thin layer over an aluminum slice (50 mm × 50 mm). The initial concentration of benzene was kept at 300 ppm for all experiments. The concentration of benzene was monitored every 10 min by GC 9560 gas-phase chromatogram equipped with FID detector. A 300 W Xe lamp was put over the reactor to irradiate the samples. For the visible light, an appropriate filter which cuts off the wavelength below 400 nm was placed on top of the reactor to remove the ultraviolet radiation from the lamp. The conversion was calculated by $(C_0 - C)/C_0$, where C is the concentration of the reactant after irradiation, C_0 is the concentration of the reactant after adsorption equilibrium but before the irradiation in the presence of catalyst.

3. Results and discussion

3.1. Photocatalytic activity test

The photo-degradation of benzene on surface of NV-TiO_2-Tx under visible light illumination is compared in Fig. 1. It is obvious to see that NV-TiO_2-T600 possesses the best photocatalytic activity. The conversion of benzene reaches 95.2% after 4 h of visible
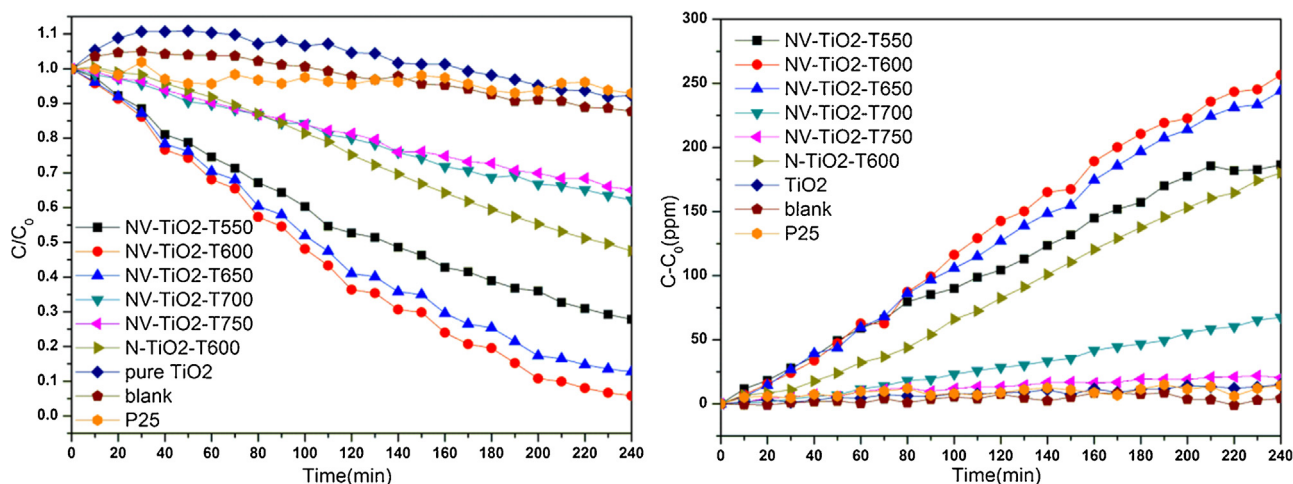

Fig. 1. Catalytic degradation of benzene (left) and CO_2 generation (right) by using all samples under visible light illumination.