ELSEVIER

Materials Science and Engineering B 117 (2005) 67–75

MATERIALS SCIENCE & ENGINEERING B

www.elsevier.com/locate/mseb

Visible-light-driven nitrogen-doped TiO_2 photocatalysts: effect of nitrogen precursors on their photocatalysis for decomposition of gas-phase organic pollutants

Di Li*, Hajime Haneda, Shunichi Hishita, Naoki Ohashi

Advanced Materials Laboratory, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

Received 3 July 2004; received in revised form 18 October 2004; accepted 23 October 2004

Abstract

Yellow-colored N-doped TiO_2 (NTO) powders were synthesized by spray pyrolysis from a mixed aqueous solution containing $TiCl_4$ and an N-precursor (urea, guanidine, or ammonium fluoride). All resulting powders possessed spherical particles with an average particle diameter of 0.45 μm, however, the surface morphologies of particles significantly depended on the N-precursors. A porous surface was observed for the particles prepared by using NH_4F as N-precursor. Acetaldehyde and trichloroethylene decompositions were used as probe reactions to evaluate the photocatalytic activity of these NTO powders under visible-light (vis) irradiation. The NTO powder prepared from a mixed solution of $TiCl_4$ and NH_4F demonstrated the highest photocatalytic activity among three N-precursors, and it was much higher than that of commercial P 25. This high photocatalytic activity was ascribed to a synergetic effect of several factors: its porous and acidic surface, doped N atoms, and simultaneously codoped F atoms during nitrogen introduction. However, no correlation between N-concentration and photocatalytic activity was observed.

Keywords: Nitrogen doping; Fluorine doping; Titanium dioxide; Spray pyrolysis; Photocatalysis; Acetaldehyde; Trichloroethylene

1. Introduction

TiO_2 semiconductor is the most effective photocatalyst and has been frequently applied in the mineralization of the undesired chemical substances in air and water [1–4]. However, TiO_2 is activated only by UV light because it is a large band-gap semiconductor. It is well known that the UV light in a photocatalytic system is generated from electricity for which the conversion efficiency is usually less than 20% [5]. Furthermore, we utilize this electricity-generated light energy to decompose the pollutants in air or water, the utilization efficiency of photons is also no more than 5% [2,6–8]. Therefore, less than 1% electrical energy is virtually utilized in an UV-photocatalytic system. From energy saving point of view, a UV light source should be avoided. Solar energy is the most desired light source for a photocatalytic system due to obvious reasons. For utilizing the solar energy efficiently, development of new materials with visible-light-driven photocatalysis is a vital step [7,9–13].

Some approaches based on TiO_2 modification have been reported for achieving the visible-light-driven photocatalysis [13–18]. Among these, the simplest and most feasible approach seems to be nitrogen doping, i.e., doping nitrogen atoms into substitutional sites in the crystal structure of TiO_2 (e.g., $TiO_{2-x}N_x$) by calcination in ammonia atmosphere or by a wet chemical route [14–16]. Other approaches such as incorporating transition metal ions (e.g., V or Cr ions) by implantation and introducing oxygen vacancies by hydrogen plasma treatment need expensive special equipment [13,17]. In our previous reports, we successfully used spray pyrolysis to prepare N-doped ZnO and MO_x–ZnO (M = V, W) photocatalysts that can work efficiently under visible-light irradi-

---

* Corresponding author. Tel.: +81 298 513 354x8608; fax: +81 298 551 196.
E-mail address: li.di@nims.go.jp (D. Li).

0921-5107/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.mseb.2004.10.018

ation [7,12,19]. A distinctive feature of these sprayed powders is the homogeneous distribution of constituents throughout the entire particles because all constituents are formed from a solution [12,19–21]. Utilizing this advantage, we expected that the doped nitrogen atoms could be distributed homogeneously throughout the TiO_2 particles, as in the ZnO case.

Additionally, although the visible-light-driven photocatalysis of N-doped TiO_2 powders has been confirmed by many studies, the mechanism for demonstrating the visible-light activity on this system is still an open question [14–16]. It is quite debatable whether doped nitrogen atoms or oxygen vacancies contribute to the visible-light activity. Asahi and coworkers claimed that the doped nitrogen atoms narrow the bandgap of TiO_2 and thus make it capable for visible-light-driven photocatalysis [14,22]. However, Ihara et al. insisted that it is the oxygen vacancies that contributed to the visible-light activity, and the doped nitrogen only enhanced the stabilization of these oxygen vacancies [16]. They also confirmed this role of oxygen vacancies in the plasma-treated TiO_2 phtotocatalysts [17,23]. In addition, the structural-oxygen-vacancy-caused visible-light photocatalytic activity was also reported by Martyanov et al. [10].

This paper describes the synthesis of NTO powders by spray pyrolysis and their surface characterization by FE-SEM, XPS, NH_3-TPD, UV/vis, and elemental analysis. The effects of N-precursors on particle surface morphology, the intrinsic characteristics, and vis photocatalytic activity of TiO_2 powder were investigated in detail. The reasons invoked to demonstrate visible-light-driven photocatalysis of N-doped TiO_2 system was elucidated. This would be helpful to understand the role of doped nitrogen atoms in vis photocatalysis.

2. Experimental

2.1. Synthesis

Nitrogen-doped TiO_2 (NTO) powders were synthesized by spray pyrolysis from a mixed aqueous solution containing $TiCl_4$ (0.03 M) and an N-precursor (0.2 M) (urea, guanidine or ammonium fluoride). The starting solution was first atomized by a nebulizer; then, the formed droplets passed through a high-temperature tube under the suction of an aspirator. The pyrolysis proceeded quickly as droplets passed through the high-temperature tube. The generated powder was collected with a ceramic filter at the end of the tube. In this study, the temperature of the tube was maintained at 1173 K since we found this is the optimal temperature to prepare NTO powder with maximum photocatalytic activity. The resulting powder was designated as NTO-A for ammonium fluoride N-precursor, NTO-U for urea, and NTO-G for guanidine. For comparison, sprayed undoped TiO_2 (TO) and commercial P 25 were selected as reference samples.

2.2. Characterization

The particle morphology was observed with a JEOL S-5000 FE-SEM at an acceleration voltage of 10 kV. The XPS measurements were carried out using an ESCALAB 200-X system (VG Scientific) with monochromatic Mg Kα excitation and a charge neutralizer, and all the bonding energies were calibrated to the C 1s peak at 284.8 eV of the surface adventitious carbon. Nitrogen concentration was analyzed with a TC-436 nitrogen/oxygen determinator (LECO Corp., USA) by heating the sample in inert gas and then using a thermal conductivity detector to analyze the obtained nitrogen. The UV/vis spectra were recorded on a Jasco V-550 spectrophotometer with an integrating sphere; $BaSO_4$ was used as a reference sample. The NH_3-TPD was conducted using a TPD-1-TA instrument (BEL Japan Inc.). The sample (0.100 g) was evacuated at 673 K for 1 h, and then the sample bed temperature was cooled down to 373 K. Then ammonia (6.4×10^{-4} mol) was introduced and kept the sample for ammonia adsorption at 373 K for 0.5 h, and the gaseous ammonia was then evacuated. The bed temperature was elevated to 1173 K at a rate of 10 K min^{-1}. The desorbed ammonia was detected by a quadruple mass analyzer at $m/e = 16$ instead of 17 due to contamination from water fragmentation.

2.3. Photocatalytic activity measurements

Photocatalytic reaction was carried out in a closed circulation system (CCS) interfaced to a gas chromatograph for reactant and product analysis. Prior to the photocatalytic test, the sample (0.0500 g) was treated in a flow of oxygen gas at 673 K until we could detect no CO_2 product. The sample was then separated from the flow system and switched to the CCS by two three-way stop clocks and evacuated under a vacuum of 10^{-5} Pa at 573 K for 1.0 h. After the sample had cooled to room temperature, a gas mixture of 88.0 kPa of CH_3CHO–He (930 ppm) or $CHCl = CCl_2$–He (943 ppm) and 13.3 kPa of O_2 was introduced. The samples were irradiated from outside of the reactor. A 150 W Xe lamp (LA-254Xe, $\lambda_{max} = 470$ nm, Hayashi Watch-Works. Co., Ltd., Japan) was used as vis source. The vis wavelength was controlled through a 420 nm cut filter (L42, Kenko, Japan). The incident intensity to the sample surface was set to be 20 mW cm^{-2}.

In our study, the mass balance was checked by total carbon amount (TCA) before and after reaction. The TCA before the reaction was calculated by the introduced reactant amount. The TCA after the reaction can be specified in three parts: (1) formed CO_2, (2) undecomposed reactant, and (3) residual carbon on the surface of the photocatalyst. The amount of residual carbon was determined by the amount of CO_2 produced from its oxidation at 673 K at O_2 atmosphere. If the difference between the introduced TCA and the sum of (1), (2), and (3) is less than 2.5% of the introduced TCA, the obtained reaction data is considered to be believable; other-